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Carbon Dioxide Adsorption by Metal Organic Frameworks (Synthesis, Testing and Modeling)

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Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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CARBON DIOXIDE ADSORPTION BY METAL ORGANIC FRAMEWORKS
(SYNTHESIS, TESTING AND MODELING)

(Thesis format: Integrated Article)

by

Rana Sabouni

Graduate Program
in
Chemical and Biochemical Engineering

A thesis submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

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ABSTRACT

It is essential to capture carbon dioxide from flue gas because it is considered one of the main causes of global warming. Several materials and various methods have been reported for the CO\textsubscript{2} capturing including adsorption onto zeolites, porous membranes, and absorption in amine solutions. All such methods require high energy input and high cost. New classes of porous materials called Metal Organic Frameworks (MOFs) exhibit excellent performance in capturing carbon dioxide from a gas mixture.

In the course of the current research, a novel MOF synthesis method using combined microwave and ultrasound, and microwave only was introduced and successfully applied to synthesize two different MOFs named IRMOF-1 and CPM-5. The scope of the research focuses on: 1) synthesis of two different MOFs (e.g. IRMOF-1 and CPM-5) using innovative non-traditional methods including microwave and ultrasound irradiation, and employing the optimization of three synthesis conditions: synthesis temperature, time and solvent ratio, 2) testing the MOFs for carbon dioxide adsorption to obtain the adsorption properties such as adsorption equilibrium isotherm, CO\textsubscript{2} diffusivity coefficient, adsorption kinetics and isosteric heat of adsorption, 3) testing of the best MOF for CO\textsubscript{2} adsorption using fixed bed adsorption micro-reactor column configuration at different experimental conditions such as adsorption temperature, feed concentration and feed flowrate, 4) modeling of the breakthrough curve using COMSOL simulation and comparing it with the experimental breakthrough curves.
The microwave irradiations drastically reduce the synthesis time of CPM-5 samples from 5 days using a traditional method (e.g. conventional oven) to 10 min. The outcome of the research indicated that the IRMOF-1 and CPM-5 samples synthesized using the novel synthesis methods exhibit unique properties compared to traditional synthesis method. The improved properties of the final product such as: lower particle size and narrower size distribution, more constructed crystallites, high surface area, high CO₂ adsorption isotherm capacity (e.g. 2.3 mmol CO₂/ g), high selectivity factor of CO₂ over N₂ (e.g. 16.1 at 298 K), low isosteric heat of adsorption, and a high CO₂ dynamic adsorption capacity (e.g. 11.9 wt. % at 298 K), were noted. As a result the microwave synthesized CPM-5 samples can be considered as an attractive adsorbent for the separation of CO₂ from flue gas.

**Key words:** microwave and ultrasound synthesis, IRMOF-1 and CPM-5, adsorption isotherms, breakthrough curves, fixed bed column reactor, COMSOL modeling.
DEDICATION

To:

My dear husband

*Dr. Anas Abou Shaar*

My parents

*Dr. Abdul Rahim Sabouni and Mrs. Maissaa Baroudi*

My beloved son and daughter

*Sami Abou Shaar and Judy Abou Shaar*
## CO-AUTHORSHIP

The journal articles written from the present work are listed below, and the individual contributions of all the members are indicated.

### Chapter 2

**Article Title:** Carbon Dioxide Capture Technologies: A review  
**Authors:** Rana Sabouni, Hossein Kazemian, Sohrab Rohani  
**Article Status:** Submitted for possible publication in Environmental Science and Pollution Research Journal  
This work was supervised by R. Sohrab. Various drafts of the paper were reviewed by H. Kazemian and R. Sohrab.  

### Chapter 3

**Article Title:** A novel combined manufacturing technique for rapid production of IRMOF-1 using ultrasound and microwave energies  
**Authors:** Rana Sabouni, Hossein Kazemian, Sohrab Rohani  
**Article Status:** Published, Chemical Engineering Journal  
This work was supervised by R. Sohrab. Various drafts of the paper were reviewed by H. Kazemian and R. Sohrab. All the experiments and data analysis were conducted by R. Sabouni. R. Sabouni wrote the manuscript.  

### Chapter 4

**Article Title:** Microwave Synthesis of CPM-5 Metal Organic Framework  
**Authors:** Rana Sabouni, Hossein Kazemian, Sohrab Rohani  
**Article Status:** Published, Chemical Engineering Technology Journal  
R. Sabouni conducted all the experiments, analyzed the data and wrote the manuscript for
this paper. This work was supervised by R. Sohrab. Various drafts of the paper were reviewed by H. Kazemian and R. Sohrab.


### Chapter 5

**Article Title:**
Carbon Dioxide Adsorption in Microwave- Synthesized Metal Organic Framework CPM-5: Equilibrium and Kinetics study

**Authors:**
Rana Sabouni, Hossein Kazemian, Sohrab Rohani

**Article Status:** Published, Microporous and Mesoporous Materials

R. Sabouni conducted all the experiments, analyzed the data and wrote the manuscript for this paper. This work was supervised by R. Sohrab. Various drafts of the paper were reviewed by H. Kazemian and R. Sohrab.


### Chapter 6

**Article Title:**
Mathematical Modeling and Experimental breakthrough curves of Carbon Dioxide Adsorption onto Metal Organic Framework CPM-5

**Authors:**
Rana Sabouni, Hossein Kazemian, Sohrab Rohani

**Article Status:** Just accepted for publication in Environmental Science and Technology Journal

This work was supervised by R. Sohrab. Various drafts of the paper were reviewed by H. Kazemian and R. Sohrab. All the experiments and data analysis were conducted by R. Sabouni.

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<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BTC</td>
<td>1, 2, 3-benzenetricaboxylate</td>
</tr>
<tr>
<td>$C_i$</td>
<td>the concentration of component $i$ in the solid (mol/m$^3$)</td>
</tr>
<tr>
<td>$C_o$</td>
<td>the concentration of component $i$ in the column feed (mol/m$^3$)</td>
</tr>
<tr>
<td>CPM-5</td>
<td>crystalline porous materials</td>
</tr>
<tr>
<td>$D$</td>
<td>column diameter (m)</td>
</tr>
<tr>
<td>$D_e$</td>
<td>diffusivity constant (m$^2$/s)</td>
</tr>
<tr>
<td>$D_g$</td>
<td>the distribution parameter $D_g = \left( \frac{1-\epsilon_i}{\epsilon_i} \right) \frac{Q}{C_o}$</td>
</tr>
<tr>
<td>$D_L$</td>
<td>the axial dispersion coefficient (m$^2$/s)</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>the column void fraction (-)</td>
</tr>
<tr>
<td>EIA</td>
<td>energy information administration</td>
</tr>
<tr>
<td>F value</td>
<td>F-test statistics</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>GHG</td>
<td>greenhouse gas</td>
</tr>
<tr>
<td>IPCC</td>
<td>intergovernmental panel on climate change</td>
</tr>
<tr>
<td>$k$</td>
<td>constant for a given adsorbent and adsorbate at particular temperature</td>
</tr>
<tr>
<td>$k_f$</td>
<td>film mass transfer coefficient (m/s)</td>
</tr>
<tr>
<td>$l$</td>
<td>the un-scaled vertical distance from the top of the column (m)</td>
</tr>
<tr>
<td>$L_o$</td>
<td>the length of the column (m)</td>
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MOFs metal organic frameworks

MW microwave irradiation

\( n \) constant for a given adsorbent and adsorbate at particular temperature

\( n_a \) the adsorbed amount (mmol/g)

OV conventional oven heating

\( P \) pressure (kPa)

\( P_e \) the Peclet number \( P_e = \frac{L_0 \vartheta}{D_L} \)

\( p_i \) the equilibrium pressure (kPa)

Prop value probability that variation between conditions may have occurred by chance

\( q \) the adsorbed amount (mmol/g)

\( Q \) the maximum adsorbed amount of component \( i \) (mol /m\(^3\))

\( Q_s \) isosteric heat of adsorption (kJ/mol)

\( R \) the gas constant

\( r_c \) particles radius (m)

SEM scanning electron microscope

\( T \) temperature (K)

\( t \) the scaled time (-)

\( t \) time in (s)

TGA thermal gravimmetrical analysis

\( x_i \) the concentration of component \( i \) in gas phase
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<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>$y_i$</td>
<td>the concentration component $i$ in solid phase</td>
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<tr>
<td>$\vartheta$</td>
<td>the interstitial velocity of the gas in the fixed bed column (m/s)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>the un-scaled time since the start of experiment (s)</td>
</tr>
</tbody>
</table>
Chapter 1

INTRODUCTION

1.1 Introduction:

The work presented in this thesis has been carried out to investigate the adsorption of carbon dioxide (CO$_2$) by metal organic frameworks (MOF). This thesis is structured in the “integrated article” format.

In this chapter, section 1.2 illustrates the effect of carbon dioxide on the environment. Section 1.3 presents the research motivation and objectives. Section 1.4 reviews the methodology used to address the thesis objectives. Finally, section 1.5 includes the thesis outline and organization.

1.2 Climate Change and CO$_2$ Emission:

Global warming and environmental pressures have attracted the attention of many researchers and environmental scientists in the 20th century due to the rapid increase of population, and energy consumption worldwide. It is expected that the energy consumption will increase by 57% by 2030 according to the Energy Information Administration (EIA) [1]. Although there is little agreement on the causes of global warming and environmental problems, many scientists believe that the emission of greenhouse gases contributes to the majority of environmental problems. Carbon dioxide (CO$_2$) is the most significant among all the anthropogenic greenhouse gases (GHGs). Approximately 60% of global warming effects are attributed to carbon dioxide emission [2].
There are four potential sources of carbon dioxide emission; industrial processes, fossil fueled power plants, de-carbonization (production of hydrogen from carbon rich feed stock), and transportation [3]. Among the carbon dioxide emission sources, fossil fueled power plants are ranked the number one potential source. Fossil fuels provide 81 percent of the world’s commercial energy supply [3]. Consumption of fossil fuels produces nearly 30 Pg (petagram) of carbon dioxide annually. About three-fourths of the increase in atmospheric carbon dioxide is attributed to burning of fossil fuels [4] (see Table 1-1).

In the past the total amount of carbon dioxide was relatively maintained and the atmospheric sink was considered large enough to accommodate any additional carbon dioxide until the industrial revolution. The amount of carbon dioxide has risen by more than a third since the industrial revolution from 280 parts per million (ppm) by volume to 368 ppm in 2000 [3], and 388 ppm in 2010 [3]. At present, the amount of carbon dioxide is increasing by 2 ppm per year in the atmosphere which suggests that more than a third of the carbon dioxide emitted remains in the atmosphere [3]. According to the Intergovernmental Panel on Climate Change (IPCC) [4], the atmosphere may contain up to 570 ppm of carbon dioxide in 2100 causing a rise of approximately 1.9°C in the mean global temperature, and an increase of 3.8 m in the mean sea level [5].

In general, there are several approaches that can be adopted to reduce the total carbon dioxide emission into the atmosphere such as a reduction in energy intensity by the efficient use of energy, a reduction of carbon intensity by using alternatives to fossil fuels like hydrogen and renewable energy, and enhancement of carbon dioxide sequestration by developing new carbon capture technologies [6]. From the three approaches above, the
most promising approach is carbon capture from point source emissions such as power plants. Alternatives to fossil fuels such as hydrogen, biomass, solar energy, and nuclear energy are not commercially viable as these sources cannot meet energy demands and are still at the development stage.

Table 1-1: Fossil fuel emission levels (Pounds/Billions BTU of energy input)(4).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Natural Gas</th>
<th>Coal</th>
<th>OIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>117000</td>
<td>208000</td>
<td>164000</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>40</td>
<td>208</td>
<td>33</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>92</td>
<td>457</td>
<td>448</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>1</td>
<td>2591</td>
<td>1122</td>
</tr>
<tr>
<td>Particulates</td>
<td>7</td>
<td>2744</td>
<td>84</td>
</tr>
<tr>
<td>Mercury</td>
<td>0</td>
<td>0.016</td>
<td>0.007</td>
</tr>
<tr>
<td>Total</td>
<td>117140</td>
<td>214000</td>
<td>165687</td>
</tr>
</tbody>
</table>

1.3 Research Motivation and Objective:

Reports have shown the importance of achieving a high carbon dioxide (CO$_2$) adsorption capacity at a minimum cost associated with CO$_2$ separation in the overall carbon capture and storage strategy. It has also been shown that traditional approaches, such as amine-based absorption, aqueous ammonia-based absorption, and adsorption materials such as zeolites and activated carbons have a number of shortcomings prompting a search for alternative technologies for CO$_2$ removal from flue gas.

The main objective of this thesis was the attempt to develop a transformative synthesis technology for metal organic frameworks (MOF) by using a non-traditional approach such as microwave and ultrasound irradiations, and to investigate their CO$_2$ adsorption capacities. Several tasks were addressed:
1) Develop a novel hybrid manufacturing technique using microwave and ultrasound technologies for the rapid synthesis of metal organic frameworks. The technique will take into account synthesis optimization (synthesis time, power, and reaction temperature).

2) Investigate the effect of the metal organic frameworks synthesis method on the CO$_2$ adsorption capacity by determining the adsorption equilibrium isotherms, isosteric heat of adsorption, and CO$_2$ diffusivity at three different temperatures of 273 K, 298 K, and 318 K.

3) Study the kinetic adsorption performance of metal organic frameworks using a fixed bed adsorption column under several experimental conditions by varying the flow rate of the inlet gases, adsorption temperature, and the feed concentration of CO$_2$.

4) Develop a kinetic model for the breakthrough curve of CO$_2$ on metal organic framework (CPM-5) and compare it with the experimental breakthrough curves.
1.4 Approach and Methodology:

In order to achieve the above thesis objectives, the following approaches are implemented in the course of the research project:

1) The combined energies of microwave and ultrasound irradiation are applied to the synthesis of CPM-5 and IRMOF-1 as a novel facile synthesis method which is, to the best of the author’s knowledge, has not been reported before in the literature for the synthesis of CPM-5 and IRMOF-1. Furthermore samples will be characterized using X-ray Diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) thermogravimetric analysis (TGA), and BET surface area and pore size analysis.

2) The surface area, pore volume and surface roughness of IRMOF-1 samples are optimized by investigating the effect of solvent exchange with chloroform as a sample activation method. The activated samples are then compared to the as-synthesized samples by use of X-ray Diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and BET surface area and pore size analyzer.

3) The synthesis of CPM-5 samples were optimized with experimental design approach by optimizing the synthesis conditions, such as solvent ratio, temperature, power and time of synthesis. In addition the synthesis parameters were statistically analyzed using the Design-Expert 7.1.5 program by D-optimal design of experiments, resulting in 12 experiments in total.

4) The CO₂ and N₂ adsorption equilibrium isotherm is measured volumetrically using a BET instrument (Micromeritics ASAP 2010, USA) at a CO₂ pressure of up to 105 kPa
and three temperatures of 273, 298, and 318 K. The selectivity of CO₂ over N₂ was evaluated at two different temperatures of 298 and 318 K.

5) The kinetics of CO₂ adsorption using CPM-5 samples were measured volumetrically in a pressure range of 5 to 105 kPa at three different temperatures of 273, 298, and 318 K by means of a Micrometrics BET instrument (ASAP 2010) using the ROA software. The diffusivity of CO₂ in CPM-5 was calculated experimentally by correlating the diffusion time with the fractional adsorption uptake (mₜ/m∞) based on the classical micropore diffusion model.

6) The isosteric heat of adsorption of CPM-5 samples were calculated from the Clausius-Clapeyron equation based on the experimental results obtained of the CO₂ adsorption isotherms measured at three different temperatures 273, 298, and 318 K.

7) The dynamic adsorption of CO₂ onto CPM-5 was studied experimentally in a fixed bed adsorption column. The experimental breakthrough curves obtained for the fixed bed adsorption tests were compared to the theoretical breakthrough curve generated from the axial dispersion model in a fixed bed. The COMSOL program were used to solve the mathematical model equations numerically.

1.5 Thesis Outline and Organization:

This thesis is written in an article-integrated format as specified by The School of Postgraduate Studies at the University of Western Ontario.

Pertinent literature about carbon dioxide capture technologies is reviewed and explained in chapter 2. The literature review presents general information about previous
adsorption capture technologies such as amine based absorption, aqueous ammonia based absorption, membranes, and adsorption material like zeolites, activated carbons and in detail information concerning metal organic frameworks as new emerging technologies for carbon dioxide adsorption.

Chapter 3 of this thesis is devoted to describe the synthesis method and characterization of IRMOF-1 metal organic frameworks. IRMOF-1 was successfully synthesized by applying combined ultrasonic (UTS) and microwave (MW) energy sources for rapid synthesis under various operating conditions including: sonication time and temperature as well as microwave irradiation time. The highest Langmuir surface area of the as-synthesized samples is 1315 (m$^2$/g), and the surface area of the activated sample was 2473 (m$^2$/g). The reaction products were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), solid-state Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and Micromeritics BET instrument (ASAP 2010).

Chapter 4 is dedicated to explaining the synthesis method and characterization of metal organic framework CPM-5 (Crystalline Porous Materials). In the course of the current research, CPM-5 was successfully synthesized and characterized for the first time using microwave irradiation (MW) as a rapid facile synthesis method in ca. 10 min compared to several days using the conventional solvothermal approach (e.g. 5 days). Furthermore, the microwave assisted synthesized CPM-5 samples exhibit a very high surface area of 2187 m$^2$/g compared to conventionally synthesized samples (e.g. 580 m$^2$/g).
In chapter 5 the adsorption equilibrium and diffusion of CO\textsubscript{2} in CPM-5 (Crystalline Porous Materials) were experimentally studied using a volumetric approach at three different temperatures 273, 298, and 318 K and gas pressures of up to 105 kPa. The experimental adsorption equilibrium results were fitted to the Freundlich adsorption equilibrium model, and the classical microspore diffusion model is applied to obtain the adsorption kinetic curves and the diffusivity of CO\textsubscript{2} in CPM-5. In addition, the initial isosteric heat of adsorption of CO\textsubscript{2} on the CPM-5 is calculated from the Clausius-Clapeyron equation based on the experimental results of the CO\textsubscript{2} adsorption isotherms measured at 273, 298, and 318 K. In addition the selectivity of CO\textsubscript{2} over N\textsubscript{2} was measured at 298 and 318 K. CPM-5 showed attractive adsorption properties as an adsorbent for the separation of CO\textsubscript{2} from flue gas.

In chapter 6 the dynamic adsorption of CO\textsubscript{2} using CPM-5 was studied using a fixed bed adsorption column at several experimental conditions by varying the feed flow rate, adsorption temperature and feed concentration. The experimental breakthrough curves were compared to the theoretical curves and the COMSOL simulation program was used to numerically solve the theoretical breakthrough model equations (axial dispersion model in a fixed bed). The tested CPM-5 showed an outstanding CO\textsubscript{2} adsorption capacity of 11.9 wt. % compared to other adsorbents making it an attractive adsorbent for the separation of CO\textsubscript{2} from flue gas.

Chapter 7 is devoted to presenting the general conclusions of this thesis based on the experimental results, and the carried out analyses. Major findings are summarized, followed by recommendations for future work.
1.6 References:


LITERATURE REVIEW:

CARBON DIOXIDE CAPTURE TECHNOLOGIES

2.1 Introduction:

In this chapter, the relevant literature pertaining to carbon dioxide capture technologies in general, such as amine based absorption as conventional carbon dioxide capture technology, aqueous ammonia based absorption, membranes, and adsorption material (e.g. zeolites, and activated carbons) have been reviewed. In more details, metal organic frameworks (MOFs) as new emerging technologies for carbon dioxide adsorption. The MOFs review section is intended to provide a comprehensive overview of MOFs including: material characteristics synthesis, structural features, CO$_2$ adsorption capacity, heat of adsorption and selectivity of CO$_2$.

The key challenge regarding carbon dioxide capture technologies is that the capture materials used should be regenerable. Otherwise, the chemical materials will exhaust global suppliers, if it’s used in a one-time=one-run manner. Therefore energy for the regeneration of the material is one factor considered when determining the efficiency and cost of the process. Another challenging aspect for the capture material is their ability to separate carbon dioxide from a mixture of gases. Table 2-1 summarizes the composition of gases.
(by weight) in post-combustion and pre-combustion processes [1]. According to Table 2-1 the differences in properties between the gases are relatively small which is disadvantageous in gas separation [2]. On the other hand, the electric properties of the gases such as, quadrupolar moment and polarization vary noticeably. Carbon dioxide has a quadrupole moment of $13.4 \times 10^{-40} \text{ Cm}^2$ compared to $4.7 \times 10^{-40} \text{ Cm}^2$ for N$_2$ and the non polar CH$_4$. Furthermore, CH$_4$ has a higher polarization than N$_2$. Therefore CH$_4$ adsorbs preferentially over N$_2$ based on the polarization values ($6.3 \times 10^{-25} \text{ cm}^3$ for CO$_2$, $17.6 \times 10^{-25} \text{ cm}^3$ for N$_2$ and $26.0 \times 10^{-25} \text{ cm}^3$ for CH$_4$).

Table 2-1: Composition of gases (by weight) in post-combustion and pre-combustion processes [2].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Post combustion</th>
<th>Pre-combustion</th>
<th>Kinetic diameter ($\text{Å}$)</th>
<th>Quadrupole moment ($10^{-27} \text{ esu}^{-1} \text{ cm}^4$)</th>
<th>Polarizability ($\text{cm}^{-25} \text{ cm}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>15-16%</td>
<td>35.50%</td>
<td>3.30</td>
<td>43.0</td>
<td>29.1</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>5-7%</td>
<td>0.20%</td>
<td>2.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>3-4%</td>
<td></td>
<td>3.46</td>
<td>3.9</td>
<td>15.8</td>
</tr>
<tr>
<td>H$_2$</td>
<td></td>
<td>61.50%</td>
<td>2.89</td>
<td>6.62</td>
<td>8.04</td>
</tr>
<tr>
<td>CO</td>
<td>20 ppm</td>
<td>1.10%</td>
<td>3.76</td>
<td>25.0</td>
<td>19.5</td>
</tr>
<tr>
<td>SO$_x$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_x$</td>
<td>500 ppm</td>
<td>3.49</td>
<td></td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>70-75%</td>
<td>0.25%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conditions

<table>
<thead>
<tr>
<th>Temperature</th>
<th>50-75 $^\circ$C</th>
<th>40 $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>1 bar</td>
<td>30 bar</td>
</tr>
</tbody>
</table>

There are generally three approaches to reduce the carbon dioxide emissions from power generation plants: 1) post-combustion capture by separate of carbon dioxide from the products of combustion, 2) pre-combustion capture by de-carbonation of the fuel prior to combustion, and 3) oxy-fuel combustion by reengineering the combustion process to
produce carbon dioxide as a pure combustion product [3]. These approaches are illustrated in Figure 2-1. Some of the advantages and disadvantages for each process are discussed in the following paragraphs.

Figure 2-1: CO₂ Capture from power generation [4].

2.2 Pre-Combustion Capture:

Pre-combustion capture involves de-carbonation by gasification of the primary fuel, coal or biomass. The fuel is reacted with oxygen or air to give mainly carbon monoxide and hydrogen. This method offers some potential advantages over the post-combustion capture in terms of smaller carbon dioxide capture equipment due to the higher carbon dioxide concentration and partial pressure. Moreover, different solvents can be used with lower energy for regeneration [4]. On the other hand, the total capital cost of the generating facility is very high.
2.3 Oxy-fuel Combustion Capture:

Oxy-fuel combustion requires the combustion of the fuel gases in oxygen rather than air, so that the gaseous combustion reaction product is mostly pure carbon dioxide. Oxy-fuel combustion is similar to the post combustion technique with a modified combustion process so the flue gas has higher concentration of carbon dioxide. The advantages of these techniques are that only simple carbon dioxide separation and purification is required, because the flue gas has a carbon dioxide concentration of over 80% [5], and there is no need to use any reagent and or solvents because oxy-fuel combustion depends on of physical separation processes, resulting in lower operating costs and less environmental problems. On the other hand, the disadvantage is that the need for large quantities of oxygen increases the capital cost and energy consumption.

2.4 Post-Combustion Capture:

This method involves the removal of carbon dioxide from the combustion reaction product stream, the flue gases, before emission to the atmosphere. Post-combustion capture is a downstream process and is an extension to the flue gas treatment process for NO\textsubscript{x} and SO\textsubscript{x} removal. However removal of carbon dioxide is more challenging because of its relatively higher quantities in the gas stream (typically 5-15\% v/v, depending on the fuel being used) [3], low partial pressure of carbon dioxide in the flue gas, and relatively high temperature of flue gases [4]. In addition, low carbon dioxide concentration creates additional disadvantages due to the high energy required and powerful chemical solvent used to release the carbon dioxide. Despite these challenges, post-combustion carbon capture is a promising technique because it can be retrofitted to existing units [5]. There are several technologies for post-combustion carbon dioxide capture which can be categorized
as conventional or new emerging technologies. The following paragraphs will focus on post-combustion capture technologies from fossil fuel power plants including conventional, technologies such as amine-based absorption as conventional carbon dioxide capture technology, aqueous ammonia based absorption, membranes, and new emerging technologies such as adsorption materials like zeolites, activated carbons, and metal organic frameworks.

2.4.1 Amine-based Chemical Absorption

The chemical absorption of carbon dioxide capture is based on the exothermic reaction of a sorbent with the carbon dioxide present in the gas stream usually at room temperature [3]. Then the reaction is reversed in a stripping or regeneration process at a higher temperature. The most extensively studied and used solvents are amine or carbonate solutions which are suitable for carbon dioxide capture at low partial pressures.

Amine absorbers (scrubbers) are commercially available as large scale technologies for post-combustion separation of carbon dioxide from flue gases. Amines are available in three forms primary, secondary, and tertiary. Each of them possesses advantages and disadvantages. For example, to enhance the reaction rate, primary amines are most preferable followed by secondary then tertiary. For regeneration energy and loading capacity the most preferred type would be tertiary, followed by secondary, and then primary [5].

Monoethanolamine (MEA) is an industrially important primary alkanolamine, which has been used in the natural gas industry to absorb carbon dioxide from nature gas for more than 60 years and is considered the most mature technology. Figure 2-2 illustrates the
amine-based carbon dioxide capture process from the flue gas. The flue gas entering the process at close to atmospheric pressure and required operating temperature typically 50 °C is bubbled through a packed absorber column (amine scrubber) containing 25-30% aqueous monoethanolamine (MEA) solution at high pressure (60-70 atm) [6]. Amine absorbs carbon dioxide to form a carbamate species. Flue gas exiting the top of the absorber is washed with water to reduce the entrained solvent droplets and then vented to the atmosphere. Following the absorption process, the rich solvent (high content of carbon dioxide reaction product) passes through a desorber column (stripping column) that operates at 100-140 °C and marginally at a higher pressure than the absorber in order to release the carbon dioxide with high purity (over 99%) which may be later compressed for commercial utilization or storage [2,3]. Despite the improvements to the amine-based system for post-combustion carbon dioxide chemical absorption, amine scrubbing technologies still have number of challenges and disadvantages. Some of these disadvantages include that the process in general requires large equipment size and intensive energy input, there is a low carbon dioxide loading capacity, high equipment corrosion rate, and amines are subject to degradation in the presence of oxygen, SO₂, NO₂ and HCl, which makes for additional requirements for solvent recovery and waste stream disposal [3].
2.4.2 Aqueous Ammonia-based Absorption

The aqueous ammonia-based absorption process is terms of operation to the amine systems. However, the reaction of ammonia and its derivatives with CO₂ has the advantage of having a lower heat of reaction than the equivalent amine based reactions (reaction of ammonium carbonate (AC), CO₂, and water to form ammonium bicarbonate (ABC)). This results in significant energy efficiency improvements and cost reductions compared to an amine based absorption system [5]. In addition, the aqueous ammonia process can capture all three major acidic gases (SO₂, NO₂, and CO₂) in a single process which is expected to reduce the total cost and complexity of the emission control systems. Furthermore, absorbent degradation is expected to be eliminated for the aqueous ammonia based absorption Process. One more advantage of ammonia-based absorption is the possibility of...
utilizing the major by-products including ammonium nitrate and ammonium sulfate to produces fertilizer.

This process has been developed by Alston Power Systems and the Electric Power Research Institute (EPRI, United States). The process consists mainly of a packed bed absorber (scrubber) and a solvent regeneration column. Prior to CO₂ absorption, the flue gas is cooled down using chilled water and a series of direct contact coolers. Then, the flue gas enters the absorber column at near-freezing conditions (0 - 10 °C) in which the cooled flue gas flows countercurrently to the absorbent slurry (ammonium carbonate and ammonium bicarbonate). The main reason behind the use of a low operating temperature is to allow high CO₂ loading of the solvent slurry and to reduce ammonia slip. The regenerator column operates at temperatures > 120 °C and pressures > 2 MPa which produces a high pressure CO₂ stream causing a reduction in the energy requirement for the subsequent compression and delivery of the CO₂ product stream for storage. Although the aqueous ammonia absorption process has many advantages over the conventional amine-based absorption process, it is still subject to an extensive development program including pilot testing on a 5 MW plant capturing 15 kt of CO₂ per year. The pilot study was in started operation in February 2008 by Alston power Inc in the United States

There are several drawbacks and concerns regarding aqueous ammonia chemical absorption process such as the high volatility of ammonia, cooling the flue gas to the 0-10 °C range, and loss of ammonia during the regeneration process because of the elevated temperature [7].
2.4.3 Membranes

The first implementation of membranes for gas separation technology was in the 1980s and since then membranes have been widely used in many industrial separation processes. Membranes are similar to filters, by separating specific component from a mixture of gases in a feed stream. There are various separation mechanisms: 1) solution/diffusion, 2) adsorption/diffusion, 3) molecular sieve and ionic transport [4]. In general, a flue gas stream will be passed through the membrane and the separation of CO$_2$ will be achieved due to one of the following concepts: a partial pressure difference of CO$_2$ across the membrane, a reversible chemical reaction with carriers like carbonates, amines molten salt hydrates dissolved in the membrane liquid, or porous inorganic materials including zeolites, palladium alloy tubes and ceramics [8]. Despite the promising high CO$_2$ separation efficiency, membranes technologies have some drawbacks including a lack of stability under the reforming environment and they are still in the research development phase.

2.4.4 Adsorption Materials

As discussed in the previous paragraphs there are several challenges and shortcomings in terms of the recent carbon capture technologies, where no single technology is able to meet the requirements set by the DOE/NETL: (90% CO$_2$ capture at less than a 35% increase in the cost of electricity) [9,10]. Therefore, there is a crucial need for developing an alternative capture technology that can both lower the operation cost and have a significant advantages for energy efficiency. Adsorption processes using solid physical adsorbents such as pressure, vacuum, or temperature swing adsorption cycles, possess potential advantages compared to the other capture technologies (i.e. chemical and
physical absorption processes) including less regeneration energy required, greater capacity, and selectivity and ease of handling.

There are many physical adsorbent materials that have been considered for CO₂ capture such as, activated carbon, zeolites and zeolite-like materials, and metal organic frameworks (MOF). However, suitable adsorbent for CO₂ capture from flue gas should satisfy several important criteria to compete with the present technologies, including: 1) high adsorption capacity: the CO₂ equilibrium adsorption capacity represented by its adsorption isotherm is very important criteria in order to evaluate new adsorbents in terms of the capital cost of the capture system. With the knowledge of the adsorption equilibrium capacity the amount of the adsorbent required can be obtained, and consequently the volume of the absorber vessels. The suitable adsorbent for CO₂ capture from flue gas should at least exhibit a CO₂ adsorption capacity of 2 - 4 mmol/g [11]; 2) high selectivity for CO₂: the adsorption selectivity of the adsorbent is defined as the ratio of the CO₂ capacity to other bulk gas components (i.e. N₂ and O₂). This is one of the main properties of adsorbent material, because it has a direct impact on the purity of the CO₂ captured, and consequently on the economics of the separation process [11]; 3) adequate adsorption/desorption kinetics is required a good adsorbent should exhibit fast adsorption/desorption kinetics under the operating conditions and a high rate of adsorption. In addition, adsorption kinetics primarily affect the cycle time of a fixed bed adsorption column; 4) the stability during repeated adsorption/desorption cycling it is also important it is crucial property of an adsorbent because it determines the life time of the adsorbents and the frequency of their replacement. Therefore, the stability of the adsorbents has direct impact on the economics the adsorption process; 5) it is also crucial to consider the
mechanical strength of the adsorbent: suitable adsorbents should demonstrate a stable microstructure and morphology under several operating conditions, such as high volumetric flow rate of the flue gas, vibration, and temperature. Also, a good adsorbent should tolerate the presence of moisture and other impurities in the feed (i.e. water vapor, O\textsubscript{2} and SO\textsubscript{2}). Otherwise, the CO\textsubscript{2} adsorption process will require a large sorbent recovery rate and a special strategy to accomplish this. As a result, the mechanical strength of adsorbents also has a direct impact on the overall economics of the CO\textsubscript{2} separation process; 6) low operating cost: although the cost of the adsorbent is the most important characteristic to evaluate a new adsorbent, there is limited information on adsorbent costs and other economic considerations in literature. According to a study performed by Tarka et al. [12] on the sensitivity analysis of adsorbents for economic performance, a cost of $5/kg of adsorbent results is ideal, and $15/kg of adsorbent is deemed uneconomical. Bu, $ 10/kg of adsorbent is considered economical for a CO\textsubscript{2} capture process.

Possible gas adsorptive separation is usually achieved by one or more several of the following mechanisms using adsorbent materials [13]: 1) size and/or shape exclusion of certain component of a gas mixture, which is called the molecular sieving effect; 2) the kinetic effect due to the different diffusion rates where certain components are adsorbed faster than others; 3) the thermodynamic effect, based on the surface and/or adsorbate packing interactions; 4) the quantum effect, due to the differences in the diffusion rates in the narrow micropores of some light molecules.
2.4.4.1 Activated Carbon

There is wide variety of carbon based adsorbent materials such as activated carbons, graphenes, and carbon nanotubes. However, activated carbons are the most commonly investigated materials in literature, and widely used as adsorbents in various industrial applications such as gas purification, water treatment, and monitoring air pollution [14,15]. Activated carbons are composed of carbon-containing biological materials such as coal (e.g. bituminous coal, lignite), industrial by-products (e.g. scraps of polymeric materials, petroleum, coke pitch), and wood or other biomass materials (e.g. cocoanut shells, saw dust olive stones) [16]. Therefore, activated carbons have a huge advantage over other adsorbents in terms of the low cost of raw materials. In addition, the wide variety of resources for activated carbons leads to variations in the pore size distribution, pore structures, and active surface area of the activated carbons [17]. The production of activated carbons from raw materials usually consists of two steps: carbonization, and activation [18]. The former step includes heating and thermal decomposition of the starting material at a temperature of 500-1200 °C in an inert atmosphere to make carbonaceous materials (Char) which have poor surface properties. Therefore, it is essential to follow the carbonization process with an activation step, during which the carbonaceous materials are modified to produce a suitable porosity, and active sites. The activation of the carbonaceous materials can be achieved by either physical or chemical activation. Physical activation can be carried out by the treatment of the material with water vapor and/or CO₂ at 700-100 °C [19]. On the other hand, chemical activation can be achieved by the carbonization of the starting material in the presence of dehydration agents such as KOH, ZnCl₂, or H₃PO₄ [20][17].
In literature it was found that activated carbons exhibit lower adsorption capacities than those of zeolites or molecular sieves under low pressure, and ambient temperature [21,22]. In addition, the adsorption capacity of activated carbons decreases significantly with increasing temperature [23]. For example, Na et. al. [24] measured the CO$_2$ adsorption isotherms on activated carbons at a partial pressure of 0.1 bar and two different temperatures 298 K and 328 K. They found that, activated carbons exhibits a drop in the adsorption capacity from 1.1 to 0.25 mmol/g as the temperature increases from 298 to 328 K. In addition, they found that the CO$_2$ adsorption capacity decreased from ca. 3.2 to 1.6 mmol/g, when the temperature increased from 288 to 328 K at 1 bar. In another study performed by Do et.al [23], the CO$_2$ adsorption isotherm on Ajax activated carbon was investigated at a pressure of up to 0.2 bar at three different temperatures. The results showed that the CO$_2$ adsorption capacity dropped from ca. 0.75 to 0.1 mmol/g as the temperature increased from 298 to 373 K. Chue et. al [21] investigated the heat of adsorption of activated carbon and zeolites revealing that the heat of adsorption (ΔH$_{ad}$) of activated carbon (ΔH$_{ad}$ = -30 kJ/mol) is lower than that of zeolites (ΔH$_{ad}$ = -36 kJ/mol). The CO$_2$ adsorption capacity of anthracite coal with a 2 h activation period at 890 °C was ca. 1.49 mmol /g measured using thermogravimetric analysis (TGA) [25]. Moreover, the CO$_2$ adsorption equilibrium isotherms of BPL activated carbon were performed using TGA by Kikkinides et. al [26]. Their results showed that BPL activated carbon exhibits a CO$_2$ adsorption capacity of ca. 2.1 mmol/g at 298 K and a pressure of 1 bar. Finally, activated carbons are thermally stable.
In summary, activated carbons are advantageous in that they are inexpensive and are less affected by the presence of moisture in the feed gas relative to other solid adsorbents such as zeolites, they require mild adsorption regeneration [27], and are thermally stable [28]. However, activated carbons have some limitations such as, limited CO\textsubscript{2} removal at high pressure and low temperature [29], decreased CO\textsubscript{2} adsorption capacity as the temperature increases [23], low adsorption capacity and selectivity at low partial pressures of CO\textsubscript{2}, and in general, contaminants in the flue gas have detrimental effects on the CO\textsubscript{2} adsorption capacity.

2.4.4.2 Zeolites

Zeolites are highly microporous crystalline framework materials that can be found naturally or fabricated synthetically. Zeolites are one of the most investigated adsorbent materials in literature for adsorption and separation processes [17], due to their unique properties such as pore size, ability of molecular sieving, and varied chemical compositions that affect their adsorption performance. Zeolites consists of a periodic array of TO\textsubscript{4} tetrahedrals (T=Si or Al) [30, 31]. The presence of the alumina atom in the convectional zeolites based on silicate frameworks lead to a negative charge on the framework, with exchangeable cations within the pore structure (usually Na or other alkali or alkaline earth metals). This unique structure of zeolite enables the alkali cations to generate strong electrostatic interactions with acidic molecules such as CO\textsubscript{2} [17,29]. Therefore, varying the Si/Al ratio and nature of the extra-framework cations can play a significant role in controlling the CO\textsubscript{2} adsorptive properties. Several studies in literature addressed the effect of Si/Al ratio, nature of the cations and type of zeolite on the CO\textsubscript{2} adsorption capacity. For example, Maurin et al. [32] investigated the effect of different Si/Al ratio of several
faujasite-type zeolites in sodium forms (NaY, (Si/Al=2.4), 13X, (Si/Al= 1.25) and NaY, (Si/Al= ∞)) on the CO₂ adsorption capacity. They found that, 13X was the most suitable adsorbent with favourable CO₂ adsorption isotherms. In another study, Siriwardance et al. [33] compared different commercially available zeolites including 4A, 5A, 13X, and WE-G 592. They found that zeolite 13X exhibited the highest adsorption capacity among those studied. Moreover, Walton et al. [30] studied the effect of changing the nature of the alkali cations on the CO₂ adsorption capacity with substitution on the Na cations by Rb, Cs, K and Li. Their results indicated that the natural zeolite with the highest Na cation content showed the highest CO₂ adsorption capacity compared to the other alkali cations at 0.1 bar.

The work by Tezel et al. [34] indicated that pure component CO₂ adsorption isotherms of various synthetic zeolites including, 13X, NaY, HiSiv-1000, HY-5 and ZSM-5-30 exhibited a wide range of adsorption capacities from 1.2 mmol/g (HY-5) to 4.5 mmol/g (13X) at 295 K and 1 bar and the adsorption capacities of the adsorbents followed the following order: 13X > NaY > ZSM-5-30 > HY-5. Earlier, a study of adsorption isotherms of CO₂ on various natural zeolites (erionite (ERI), mordenite (MOR), and clinoptilolite (HEU)) measured at 290 K showed a variation in the adsorption capacities according to the type of zeolite type, ranging from 1.6 to 2.7 mmol/g at a pressure of 0.1 bar [35].

Cavenati et al. [36] showed that the CO₂ adsorption capacity of zeolite NaX, (Si/Al=1) decreased drastically from 2.8 to 143 mmol/g when the temperature was increased from 298 to 323 K at 0.1 bar. In another study, similar results were obtained by Diaz et al. [37]. The CO₂ adsorption capacity of zeolite Cs-x-h decreased from 2.42 to 1.48 mmol/g at partial pressure of 1 bar when the temperature was increased from 323 to 373 K. Several studies were conducted to investigate the effect of water on CO₂ adsorption,
because water is one of the key components in the flue gas that can compete with CO\textsubscript{2} adsorption sites on zeolites [38,39]. In general, the presence of moisture in the gas has detrimental effects on CO\textsubscript{2} adsorption because it has preferential adsorption over CO\textsubscript{2} on the zeolites’ surface and blocks the access for CO\textsubscript{2} [40]. For example, Brandani \textit{et al.} [40] studied the effect of the presence of water on the CO\textsubscript{2} adsorption capacities of zeolite CaX at 0.06 bar CO\textsubscript{2} and 323 K. They found that the CO\textsubscript{2} adsorption capacity of CaX zeolite reduced drastically from 2.5 to 0.1 mmol/g when the water concentration increased from 0.8 to 16.1 wt %.

In summary, zeolites with low Si/Al ratios are one of the promising adsorbents for CO\textsubscript{2} adsorption and separation applications. However, CO\textsubscript{2} adsorption on zeolites still has some limitations since they are strongly affected by temperature pressure and the presence of water. Zeolites CO\textsubscript{2} adsorption capacities decrease as the temperature increases and increase as the gas-phase partial pressure of CO\textsubscript{2} increases. In addition, zeolites are strongly sensitive to the water content in the flue gas, and because of their highly hydrophilic character extensive drying of the flue gas is needed prior to CO\textsubscript{2} capture or a very highly regeneration temperatures is required (often in excess of 300 °C) [21,39]. This additional drying and high regeneration temperature poses an extra cost which significantly affects the adsorption applications of zeolites.

2.4.4.3 \textit{Metal Organic Frameworks (MOFs)}

2.4.4.3.1 \textit{Material Characteristics and Synthesis}

Metal organic frameworks are newly emerged class of crystalline porous materials that have attracted recent attention in the past two decades owing to their enormous
structural and chemical diversity including: robustness, high surface area (up to 5000 cm\(^2/g\)) high thermal and chemical stabilities, high void volume (55-90%), low densities (from 0.21 to 1 g/cm\(^3\)) [41], and their potential applications in gas storage, ion exchange, molecular separation, drug delivery, and heterogeneous catalysis [13,42-44].

MOF materials generally consist of three dimensional organic-inorganic hybrid networks formed by metal based nodes (e.g. Al\(^{3+}\), Cr\(^{3+}\), Cu\(^{2+}\), or Zn\(^{2+}\)) bridged by organic linking groups (e.g. carboxylate, pyridyl) principally through coordination bonds. Due to the strong coordination bonds, MOFs are geometrically and crystallographically well-defined framework structures. MOFs can be tuned and designed systematically based on changing the nature of organic linker and/or changing the connectivity of the inorganic moiety and how the building blocks come together to form a net as shown in Figure 2-3 [45]. This remarkable and easy tunability of MOFs is a key feature that distinguishes these materials from traditional porous materials, such as zeolites and activated carbon. In addition, it allows the optimization of the pore dimension and surface chemistry within metal-organic frameworks that was previously absent in zeolite materials [13].

Figure 2-3: Design and construction of MOF [Reproduced with permission from ref 45].
A large number of new MOFs have emerged in the last few years; however, their methods of preparation and synthesis are quite similar. Most are synthesized by employing a so called “modular synthesis”, wherein a mixture of metal precursors and appropriate ligands are combined under mild conditions to afford a crystalline porous network. In most of the resulting materials the solvent used during synthesis is removed by applying vacuum, heat, or exchange with volatile molecules, resulting in large pore volume and large surface area accessible to guest molecules. Synthesis approaches such as solvothermal synthesis (conventional approach), microwave synthesis [46], sonication synthesis [47], mechanochemical synthesis [48], and solid start synthesis [49] have been developed for MOFs synthesis. Despite the simplicity of the synthesis of MOFs, there are several challenges in the preparation of new materials related to the optimization of the reaction conditions that lead to the desired MOF, in high yield and crystallinity. The following parameters can play a key role in MOFs’ optimization and synthesis: temperature, solvent compositions, reaction times, reagent ratios, reagent concentrations, and pH of the co-solvent solution [45]. Accordingly, slight change in any of these parameters can result in large number of network connectivities, many of which are nonporous and have adverse effect on the gas storage and separation applications. Therefore, large number of reactions trails are required to discover the new desired MOFs in which the reaction parameters are systematically varied. As a result high throughput technologies have been employed for the synthesis of new MOFs in the recent years [50,51].
2.4.4.3.2 Structural Features

Arbitrarily, MOFs can be categorized into four following sub-sets: rigid frameworks, flexible/dynamic frameworks, surface functionalized frameworks and open metal sites. Rigid MOFs usually have stable and robust porous frameworks with permanent porosity, whereas flexible MOFs show extreme changes of shape when the guest molecules are inserted or removed, and are affected by external stimuli, such as pressure, and temperature, which is absent in the traditional adsorbent such as zeolites and activated carbons. In addition, rigid frameworks retain their porosity upon adsorption and desorption; however, flexible and dynamic frameworks exhibit framework transformation upon removal of guest solvent but restore their porous structure by adsorption of gas molecule at high pressures [52]. Such properties of flexible frameworks promote beneficial capture and release performance of gaseous molecules. Selective adsorption in rigid MOFs may occur as a result of molecular sieving, and/or preferential adsorption based on the different strengths of the adsorbent adsorbate and adsorbate-adsorbate interactions. However, selective adsorption in flexible dynamic MOFs occurs due to the flexibility and the breathing effects of the framework porous structure. Therefore, flexible MOFs are more complicated the evaluation of their performance is more complex and the selective adsorption is more difficult to study and compare to rigid frameworks. Moreover, usually rigid MOFs present a normal type-I shape adsorption isotherm. On the other hand flexible MOFs exhibit stepwise adsorption and/or show hysteretic desorption isotherms for CO$_2$ and other gases. Novel MOFs, such as MIL-53 series [53,54], MIL-88 [55] and SNU-M10 [56] provide a typical examples of breathing frameworks during adsorption and desorption of CO$_2$. 
Open metal sites enhance MOFs performance by providing a mechanism for the separation of (quadru) polar/non polar gas pairs such as CO$_2$/CH$_4$. The selective adsorption mechanism may occur due to the coordination of CO$_2$ to the metal center in an end-on fashion, i.e., O==C==O...Cu$^{2+}$ [57]. The most attractive enhancement of open metal site MOFs is that the presence of water in such frameworks possesses outstanding enhancements in their CO$_2$ capture ability. One of the most studied materials featuring open metal sites structure is Cu$_3$(btc)$_2$ (HKUST-1), which consists of paddlewheel Cu$_2$(COO$^-$) units connected through btc$^{3-}$ ligands. Recent studies showed that HKUST-1 framework containing 4 wt.% water exhibited a significant increase in CO$_2$ adsorption capacity about four times that of the benchmark material zeolite 13X [58] and enhanced CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivities [59]. In this case, the mechanism of adsorption was due to the interaction of quadrupole moment of CO$_2$ with the electric field created by the water molecules which coordinated the open Cu$^{2+}$ sites [58].

HKUST-1 contains bound solvent molecules on the axial sites of each Cu$^{2+}$ metal center; these sites can be removed in vacuo at elevated temperatures to create open binding sites for guest molecules. Consequently, these sites works as charge-dense charges attracting certain gas molecule based on their polarity and dipole or quadrupole moment [60]. In addition, HKUST-1 structure type is unique in which several new MOFs can be prepared by varying the metal ions (M= Cr, Fe, Zn, Mo) [61-63]. Accordingly, the metal type plays an important role for tuning and optimizing the adsorptive properties of the material. Dietzel et al. [64] performed a systematic study in the series of isostructural frameworks [M$_2$(dobdc)(H$_2$O)] (M= Mg, Mn, Fe, Co, Ni, Zn) to examine the influence of the identity of the metal center on the capacity and the selectivity of CO$_2$ adsorption. These
compounds exhibit honeycomb structure with hexagonal one dimensional channel of 11–12 Å diameter with high concentration of exposed M$^{2+}$ adsorption sites. The highest CO$_2$ adsorption capacity was observed for [Mg$_2$(dodbc)], which is more than double that for any other member of the series [65].

The fourth set of MOFs is surface functionalized frameworks. The surface functionalized frameworks enhanced the capacity and selectivity of MOFs for CO$_2$ adsorption by grafting a functional group with a high affinity for CO$_2$ (e.g. arylamine [66], alkylamine [67], and hydroxyl [68] groups) onto the surface of porous materials through ligand modification or coordination to unsaturated metal centers. These functional groups enhance the selective interaction between CO$_2$ and the functionalized molecule as well as the constriction in the pore space of functionalized framework compared to the parent non-functionalized material [68]. For example, amino-MIL-53 (Al) exhibited superior separation factor of 60 in the CO$_2$ uptake relative to CH$_4$ at low coverage compared with approximately 5 for the parent non-functionalized framework, in addition to increased magnitude of zero-coverage adsorption enthalpy increased from -20.1 to -38.4 kJ/mol upon functionalization [69]. Similar enhancements have been observed in the amine-functionalized frameworks USO-2-Ni and USO-3-In-A relative to their parent non-functionalized frameworks [70].

One of the most studied MOFs in literature to date is Zn$_4$O(BDC)$_3$ (MOF-5) which consist of tetrahedral [Zn4O] $^{6+}$ clusters connected by ditopic BDC $^{2-}$ ligands to form a cubic three dimensional network. Yaghi et al. [71] reported the synthesis of sixteen MOF-5 functionalized derivatives they were noted as IRMOF-1 through IRMOF-16, and they were
characterized by stable porosity upon substitution with linear dicarboxylate ligands as shown in Figure 2-4 [71]. The IRMOFs family features offer tunable pore spaces and pore functionality relative to the length of the functional group. IRMOF-16 represents the largest of the IRMOF of the IRMOFs series with crystal density of 0.21 g/mL, which was the smallest reported crystal density up to that time for any crystalline material. Following the same concept several new MOFs have been developed such as, the Zr$_6$O$_4$(OH)$_4$(BDC)$_6$ (UiO-66) [72] Al(OH)(BDC) (MIL-53) [73] and Cu$_2$(BPTC) (NOTT-100) [74].
2.4.4.3.3 CO₂ Adsorption Capacity

The evaluation of new adsorbent materials for CO₂ capture applications depends on many factors, such as the adsorption capacity, selectivity and enthalpy of adsorption. However, most of MOF literature has paid initial attention to CO₂ adsorption capacity by measuring the adsorption equilibrium rather than measuring the adsorption dynamic under fixed bed configuration. The adsorption equilibrium can be measured either gravimetrically
or volumetrically. The gravimetric CO$_2$ uptake, which refers to the quantity of CO$_2$ adsorbed within a unit of mass of the material, can provide the mass of the MOF required to form the adsorbent bed. On the other hand, the volumetric CO$_2$ uptake measures how densely the CO$_2$ can be stored within the material providing information on the volume of the adsorbent bed. In general both measuring techniques are important to determine the heat efficiency of the MOF, in terms of the energy required for regeneration and desorption of the captured CO$_2$.

Lots of MOFs have been investigated experimentally for CO$_2$ adsorption and related gas separation. The results of these experiments have been summarized in Table 2-2 which represents the adsorption capacity for MOFs collected at ambient temperatures, with pressures ranging from low pressure (<1.2 bar) to atmospheric pressure in most of the cases. The adsorption isotherms measured at ambient temperature and low pressure are mainly controlled by chemical feature of the pore surface, and most of the high capacity materials are those of highly functionalized surfaces. In addition, at these conditions the adsorption isotherms are most resembled to post combustion CO$_2$ capture application whereas, the post combustion flue gas pressure is at (~ 1 bar) and partial pressure of CO$_2$ is low (P$_{CO_2}$ ~ 0.15 bar). However, the high pressure adsorption isotherms are more relevant to the pre-combustion application (see Table 2-3). The Adsorption isotherms at high pressure are mostly influenced by the surface area of MOFs, where the greatest adsorption isotherm capacities are dictated for high surface area MOFs. The focus of this review will be on adsorptions at ambient temperature and low pressure simulating post combustion applications.
Table 2-2: Low pressure CO$_2$ adsorption capacities for different MOFs

<table>
<thead>
<tr>
<th>Material</th>
<th>Common name</th>
<th>Surface Area (m$^2$/g)</th>
<th>BET</th>
<th>Langmuir</th>
<th>Uptake Temperature (K)</th>
<th>Pressure (bar)</th>
<th>wt%</th>
<th>mmol/g</th>
<th>Ref</th>
</tr>
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<td>Zn$_4$O(BTB)$_2$</td>
<td>MOF-177</td>
<td>5400</td>
<td>4690</td>
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<td>298</td>
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<td>[75]</td>
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<tr>
<td>Zn/DOBDC</td>
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<td>816</td>
<td></td>
<td></td>
<td>296</td>
<td>1</td>
<td></td>
<td>5.8</td>
<td>[65]</td>
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<td>Mg$_2$(dobdc)</td>
<td>Mg-MOF-74, CPO-27-Mg</td>
<td>1174</td>
<td>1733</td>
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<td>298</td>
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<td>[77]</td>
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<td></td>
<td></td>
<td>298</td>
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<td>27</td>
<td>[59]</td>
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<td>303</td>
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<td>Tst</td>
<td>Pcr</td>
<td>Tc</td>
<td>Ref</td>
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<td>[84]</td>
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Table 2-3: High pressure CO$_2$ adsorption capacities for different MOFs

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<th>Material</th>
<th>Common name</th>
<th>Surface Area (m$^2$/g)</th>
<th>BET</th>
<th>Langmuir</th>
<th>Uptake Temperature (K)</th>
<th>Pressure (bar)</th>
<th>wt%</th>
<th>mmol/g</th>
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Most of the MOFs adsorption isotherms present a Langmuir shape, where at low CO\(_2\) partial pressure small changes in pressure result in large changes in capacity with a linear slope; however few MOFs exhibit other types of isotherms including: stepwise isotherms, sigmoidal isotherms, and hysteretic isotherms. There is a disagreement on the cause of the deviation of adsorption isotherms from Langmuir isotherm behavior. Some authors attributed the stepwise isotherms to the structural features of the MOFs such as MCF-19 that has biporous structure of cages and channels [115]. Others attributed the sigmoidal isotherm to the electrostatic interactions between CO\(_2\) molecules in the MOF pores such as, MOF-5, MOF-177, and MOF-210 [66,95]. Seo et al. [116] attributed the hysteretic isotherm behavior of CO\(_2\) adsorption on MOF Zn(2,7-ndc)(2,7-bdc=2,7-naphthalenedicarboxylater) to the unique arrangement of the pore channels and their narrow passages compared to the critical dimensions of the CO\(_2\) molecule.

Millward et al. [66] investigated the effect of structure, pore dimension and surface area on the CO\(_2\) adsorption capacities of nine MOF adsorbents, such as square channel (MOF-2) [117], open metal site (MOF-505 and Cu\(_3\)(BTC)\(_2\)) [118,119], hexagonally cylindrical channels (MOF-74) [120], interpenetration (IRMOF-11) [121], amino and alkyl-functionalized pore (IRMOF-3 and -6) [121]and extra high porosity frameworks IRMOF-1 and MOF-177 [71,122] (see Figure 2-5 for more details). They have found that MOF-74, MOF-505 and Cu\(_3\)(BTC)\(_2\) had the highest capacities at low pressure (ca. 1 bar) (see Figure 2-6 [66]. However, at high pressure (ca. 35 bar) MOF-177 exhibited high CO\(_2\) capacity of 33.5 mmol/g which is higher than any other reported adsorbent material at that time. As shown in Figure 2-6, MOF-177 illustrates a two-step Langmuir isotherm where at low pressure the adsorption capacity increased slowly with increasing pressure, however at
moderate pressure, there is an induction step and a sharp increase in the slope of the adsorption isotherm. This isotherm adsorption behavior was observed for other several MOFs such as MIL-53, [Cu(bpy)-(BF4)2(H2O)2](bpy) [123], Ni(bpy)3(NO3)4 [124], and IRMOF-1) [125]. More recently, the (Mg-MOF-74, Mg/DOBDC) synthesized by Caskey et al. [65] broke the CO2 adsorption record of MOF-177. The Mg-MOF-74 showed high and reversible adsorption capacity for pure CO2 (23.6 wt%, 5.36 mmol/g) at 0.1 bar and room temperature. This value is even higher than Zeolite 13X which is among the best adsorbent for CO2 separation and has been reported to provide CO2 uptake of 4.7 mmol/g (20.7 wt%) at 1 atm and 298 K [126].
Figure 2-5: list of nine MOF studied by Millward et al. [Adopted with perimission from ref 66. Copyright (2005) American Chemical society] including structures, pore dimensions, and surface area.
Yazaydin et al. [77] screened diverse collection of 14 MOFs for CO₂ capture from the flue gas combining an experimental and modeling approach. They used the experimental data to validate the generalized strategy for molecular modeling of CO₂ and other small molecules on MOFs. MOF-5 and MOF-177 exhibited high CO₂ capacity at high pressures, but did not perform well at low pressures. Adding amine functionalities to the linkers of IRMOF-1 to form IRMOF-3 had provided small improvements in CO₂ uptake. The CO₂ adsorption uptake increased dramatically with changing the metal from Zn in M/DOBDC to Mg, Co, or Ni. Finally the best performing MOFs were the ones that had open metal sites such as HKUST-1, UMCM-150 and UMCM-150(N)₂ (for more details see Figure 2-7).
In another study performed by Arstand et al. [70] the effect of adding amine functionalities into the DCB ligands of USO series MOFs was investigated. They found that the CO$_2$ adsorption capacity of USO-1-Al for the amine modified DBC ligands had increased compared to the isostructural non-functionalized MOF especially at low partial pressures as shown in Figure 2-8 [70].
Bo et al. [76] reported the adsorption equilibrium and kinetics of CO \(_2\) and CH\(_4\) on Mg-MOF-74 in volumetric adsorption unit at 278, 298, and 318 K and pressure up to 1 bar. The Mg-MOF-74 exhibited high CO \(_2\) adsorption capacity of 8.61 mmol/g (37.8 wt%), at 298 K and 1 bar, which is significantly higher than those of zeolite 13X (3.3 mmol/g; 14.5 wt. %) under the same conditions. An et al. [85] studied the CO \(_2\) adsorption in a cobalt adeninate bio-MOF-11. Bio-MOF-11 showed CO \(_2\) adsorption capacity of 4.1 mmol/g at 298 K and 1 bar compared to 0.13 mmol/g for N\(_2\). This high CO \(_2\) adsorption capacity can be attributed to the presence of the lewis basic amino and pyrimidine groups of adenine and the narrow pore dimensions of bio-MOF-11.
Llewellyn et al. [102] investigated the effect of activation conditions of MIL-101(Cr) on CO$_2$ adsorption capacity. Three samples were studied, donated MIL-101a (a: as synthesized), MIL-101b (b: activated in hot ethanol), and MIL-101c (c: activated in hot ethanol and using KF). The capacity at 5 MPa and 303 K increased from 28 mmol/g for MIL-101a and from 34 mmol/g for MIL-101b up to a record value of 40 mmol/g for MIL-101c which is above the previous record (35.5 mmol/g for MOF-177). In addition, MIL-101c exhibited a superior CO$_2$ adsorption capacity compared to zeolite NaX (7.8 mmol/g) and activated carbon –Maxsorb (25 mmol/g) [102]. Yang et al. [127] compared the CO$_2$ adsorption capacity of three MOFs (IRMOF-10, IRMOf-14 and MOF-177) with other adsorbent materials such as zeolite 13X and carbon-based material Maxsorb. They found that, the three MOFs can store much CO$_2$ than both zeolite 13X and Maxsorb. The adsorption capacities were 35.6, 34.2, and 32.7 mmol/g at 3 MPa for IRMOF-10, IRMOF-14 and MOR-177 respectively, which was approximately 4.7 times than that of zeolite 13X (7.4 mmol/g) and 1.5 times than that of Maxsorb (23.5 mmol/g). Saha et al. [128] measured the adsorption equilibrium of CO$_2$ on two newly discovered MOFs MOF-5 and MOF-177 and the traditional adsorbent zeolite 5A. Both MOF-5 and MOF-177 showed higher adsorption capacities for CO$_2$ (47.97 and 39.9 wt % at 14 bar and 298K respectively) than zeolite 5A (22 wt % at 14 bar and 298 K) at elevated pressure, suggesting that MOF-5 and MOF-177 are better adsorbents for CO$_2$ storage.

The effect of temperature on the CO$_2$ adsorption capacity of several MOFs (i.e. IRMOF-1, MOF-508b, Cu-BTC, USO-1-Al (Figure 2-8) and Ni$_2$(bpy)$_3$(NO$_3$)$_4$) was reported in literature. In general MOFs were found to exhibit lower CO$_2$ adsorption capacity upon increasing the temperature greater than room temperature. This has been
documented by Fletcher et al. [124], Bae et al. [129], Yang et al. [130], and Arstand et al. [70].

2.4.4.3.4 Heat of Adsorption

The heat of adsorption is an important parameter for CO$_2$ storage through physical adsorption. Heat of adsorption, which represents the energetic interaction strength of the adsorbent with the adsorbate molecules which plays a critical role in determining the adsorptive selectivity and the energy required to release CO$_2$ molecules during regeneration, and it could be described by different limiting properties such as isosteric heat of adsorption $Q_{st}$. If the heat of adsorption is too high the regeneration cost will increase because the material binds with CO$_2$ too strongly therefore, a large quantity of energy will be required to break the framework-CO$_2$ interaction. On the other hand, very low heat of adsorption is also not preferable although the regeneration energy will be lower however, the purity of the captured CO$_2$ will be lowered due to lower adsorption selectivity and the required volume of the adsorbent bed will be larger due to the lower density of the adsorbed CO$_2$. Table 2-4 represents the calculated isosteric heat of adsorption for CO$_2$ adsorption in different MOFs. In general, the heat of adsorption of MOFs is low ranging between 20 and 50 kJ/mol and comparable with other physical adsorbents such as zeolites.
Table 2-4: Zero-coverage heat of CO₂ adsorption in metal organic frameworks

<table>
<thead>
<tr>
<th>Material</th>
<th>Common name</th>
<th>$Q_{st}$ (kJ/mol)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₃O(H₂O)3F(BTC)₂</td>
<td>MIL-100(Cr)</td>
<td>62</td>
<td>[102]</td>
</tr>
<tr>
<td>Zn₄O(BDC)(BTB)4/3</td>
<td>UMCM-1</td>
<td>12</td>
<td>[105]</td>
</tr>
<tr>
<td>Mg₂(dobdc)</td>
<td>Mg-MOF-74, CPO-27-Mg</td>
<td>47</td>
<td>[65]</td>
</tr>
<tr>
<td>CO₂(ade)₂(CO₂CH₃)₂</td>
<td>bio-MOF-11</td>
<td>45</td>
<td>[85]</td>
</tr>
<tr>
<td>VO(BDC)₂</td>
<td>MIL-47</td>
<td>25</td>
<td>[96]</td>
</tr>
<tr>
<td>Al(OH)(abdc)</td>
<td>Amino-MIL-53(Al)</td>
<td>38.4</td>
<td>[69]</td>
</tr>
<tr>
<td>Cr₃F(H₂O)₃O(btc)</td>
<td>MIL-100</td>
<td>62</td>
<td>[109]</td>
</tr>
<tr>
<td>Zn₄O(BDC-NH₂)₃</td>
<td>IRMOF-3</td>
<td>19</td>
<td>[131]</td>
</tr>
<tr>
<td>Cr₃O(H₂O)2F(BDC)₃</td>
<td>MIL-101(Cr)</td>
<td>44</td>
<td>[74]</td>
</tr>
<tr>
<td>Ni₂(dobdc)</td>
<td>Ni-MOF-74</td>
<td>42</td>
<td>[78]</td>
</tr>
<tr>
<td>Ni/DOBDC</td>
<td></td>
<td>41</td>
<td>[65]</td>
</tr>
<tr>
<td>Al₄(OH)₈(pyromellitate)</td>
<td>MIL-120</td>
<td>38</td>
<td>[106]</td>
</tr>
<tr>
<td>Zn₂(bpdc)$_2$(bpe)</td>
<td></td>
<td>38</td>
<td>[132]</td>
</tr>
<tr>
<td>CO₂(dobdc)</td>
<td>Co-MOF-74</td>
<td>37</td>
<td>[65]</td>
</tr>
<tr>
<td>Zn₈(ade)$_4$(BPDC)$_6$O₃ 2Me₂NH₂</td>
<td>bio-MOF-1</td>
<td>35</td>
<td>[133]</td>
</tr>
<tr>
<td>Al(OH)(BDC)</td>
<td>MIL-53(Al)</td>
<td>35</td>
<td>[96]</td>
</tr>
<tr>
<td>Cu₃(BTC)₂</td>
<td>HKUST-1</td>
<td>35</td>
<td>[134]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>[131]</td>
</tr>
<tr>
<td>Cu₃(BTC)₂ 3 3H₂O</td>
<td>HKUST-1 (hydrated)</td>
<td>30</td>
<td>[135]</td>
</tr>
<tr>
<td>Al(OH)(NH₂-BDC)</td>
<td>NH2-MIL-53(Al), USO-1-Al-A</td>
<td>50</td>
<td>[70]</td>
</tr>
<tr>
<td>Zn₄O(BDC)₃</td>
<td>IRMOF-1, MOF-5</td>
<td>34</td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17</td>
<td>[136]</td>
</tr>
<tr>
<td>Al₁₂O(OH)₁₈(H₂O)₃(A₁₂(OH)₄)(BTC)$_6$</td>
<td>MIL-96</td>
<td>33</td>
<td>[77]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT@Cu₃(BTC)₂</td>
<td></td>
<td>34</td>
<td>[137]</td>
</tr>
<tr>
<td>Ni₂(pbmp)</td>
<td>Ni-STA-12</td>
<td>34</td>
<td>[93]</td>
</tr>
<tr>
<td>Cr(OH)(BDC)</td>
<td>MIL-53(Cr)</td>
<td>32</td>
<td>[96]</td>
</tr>
<tr>
<td>Zn₂(BDC)$_3$(4,40-bpy)</td>
<td></td>
<td>19</td>
<td>[138]</td>
</tr>
<tr>
<td>Al(OH)(bpydcl)</td>
<td>MOF-253</td>
<td>23</td>
<td>[81]</td>
</tr>
<tr>
<td>H₃[(Cu₄Cl)₃(BTTri)$_8$]</td>
<td>CuBTTri</td>
<td>21</td>
<td>[67]</td>
</tr>
</tbody>
</table>
Isosteric heat of adsorption at a given adsorption amount can be obtained from the Clausius-Clapeyron equation (Eq. 2-1) as follows:

\[
\frac{Q_{st}}{-RT^2} = \left( \frac{\partial \ln P}{\partial T} \right)_{n_a}
\]  
\[(\text{Eq. 2-1})\]

where \(Q_{st}\) is the isosteric heat of adsorption (kJ/mol), \(P\) is the pressure (kPa), \(T\) is the temperature (K), \(R\) is the universal gas constant, \(n_a\) is the adsorbed amount (mmol/g). Integrating Eq. 2-1 gives the following equation (Eq. 2-2):

\[
\ln P = \frac{Q_{st}}{RT} + C
\]  
\[(\text{Eq. 2-2})\]

The heat of adsorption can be calculated from the slope of linear plot of \(\ln P\) versus \(1/T\) at a given adsorption amount. Yang et al. [127] reported the isosteric heat of adsorption at infinite dilution \((q_{st}^0)\) for 9 different MOFs as shown in Table 2-5. They have concluded that, the smaller the MOFs pore size, the larger the \((q_{st}^0)\).

Table 2-5: Structural and CO₂ adsorption properties of MOFs studied by Yang et al [127].

<table>
<thead>
<tr>
<th>Material</th>
<th>Pore shape</th>
<th>(d_{\text{pore}}) (nm)</th>
<th>(\rho_{\text{cryst}}) (g/m³)</th>
<th>(S_{\text{acc}}) (m²/g)</th>
<th>(V_{\text{free}}) (cm³/g)</th>
<th>(q_{st}^0) (kJ/mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRMOF-1</td>
<td>cubic</td>
<td>1.09/1.43</td>
<td>0.59</td>
<td>3748</td>
<td>1.36</td>
<td>13.73</td>
</tr>
<tr>
<td>IRMOF-8</td>
<td>cubic</td>
<td>1.25/1.71</td>
<td>0.45</td>
<td>4360</td>
<td>1.87</td>
<td>12.67</td>
</tr>
<tr>
<td>IRMOF-10</td>
<td>cubic</td>
<td>1.67/2.02</td>
<td>0.33</td>
<td>4938</td>
<td>2.66</td>
<td>11.96</td>
</tr>
<tr>
<td>IRMOF-14</td>
<td>cubic</td>
<td>1.47/2.01</td>
<td>0.37</td>
<td>4800</td>
<td>2.30</td>
<td>13.28</td>
</tr>
<tr>
<td>IRMOF-16</td>
<td>cubic</td>
<td>2.33</td>
<td>0.21</td>
<td>5882</td>
<td>0.46</td>
<td>10.25</td>
</tr>
<tr>
<td>IRMOF-11</td>
<td>Cubic/catenation</td>
<td>0.70/1.20</td>
<td>0.76</td>
<td>2867</td>
<td>0.92</td>
<td>20.86</td>
</tr>
<tr>
<td>MOF-177</td>
<td>Pore/channel</td>
<td>1.08/1.18</td>
<td>0.43</td>
<td>4688</td>
<td>1.96</td>
<td>14.43</td>
</tr>
<tr>
<td>Cu-BTC</td>
<td>Pocket/channel</td>
<td>0.50/0.90</td>
<td>0.88</td>
<td>2368</td>
<td>0.82</td>
<td>25.60</td>
</tr>
<tr>
<td>Mn-MOF</td>
<td>Cage/channel</td>
<td>0.55/0.45</td>
<td>1.59</td>
<td>554</td>
<td>0.50</td>
<td>24.78</td>
</tr>
</tbody>
</table>
Bourrelly et al. [96] reported the heat of adsorption for MIL-53 (Al) at pressures from 1 to 4 bars in the range of 30 to 45 kJ/mol. Llewellyn et al. [102] reported 63 kJ/mol for the heat of adsorption of MIL-100. In two different studies, HKUST-1 showed two different values for the heat of adsorption values raging from 15 to 35 kJ/mol [131], which can be dictated by the variation in the synthesis and the activation procedures for the preparation of the sample and the method by which the value was calculated. Arstand et al. [70] investigated the effect of adding amine functionalities to USO-1-Al on the heat of adsorption at pressure ranging from 0 to 0.4 bar. They concluded that, amine-functionalized USO-1-Al have higher heat of adsorption (30 kJ/mol) at low CO$_2$ partial pressure (<0.15 bar) compared to the non-functionalized isostructural USO-1-Al (50 kJ/mol), because amines have been shown to have higher heats of adsorption (48 to 84 kJ/mol) [139].

2.4.4.3.5 Selectivity for CO$_2$

The third important parameter for evaluation of new adsorbent materials for CO$_2$ separation applications is selectivity for CO$_2$ over other component of the gas mixture. The selective adsorption of CO$_2$ over N$_2$ or CH$_4$ can be attributed to two main mechanisms: size exclusion (kinetic separation) and a favourable gas-pore surface interaction (thermodynamic separation). In size exclusion selectivity, the separation occurs based on the size of gas molecule where the MOF with small pore size permits molecules only up to a certain kinetic diameter to diffuse into the pores. Meanwhile, the thermodynamic separation depends on the difference between physical properties of the gas molecules such as polarizability, or the quadrupole moment. CO$_2$ has smaller kinetic diameter and its quadrupole moment (CO$_2$, 13.4 x 10$^{-40}$ C.m$^2$; N$_2$, 4.7 x 10$^{-40}$ C.m$^2$) and polarizability (CO$_2$, 29.0 x 10$^{25}$ cm$^3$; N$_2$, 17.4 x 10$^{25}$ cm$^3$) is higher compared to N$_2$ which in many cases
results in stronger interaction with pore surface of the adsorbents. The adsorption selectivity for CO$_2$ from a gas mixture can be quantitatively estimated by either single-component gas adsorption isotherms or Ideal Adsorbed Solution Theory (IAST). For the single-component isotherm method the selectivity factor defined as the molar ratio of the adsorption quantitative at relevant partial pressures of the gases as given by the following equation:

$$S = \frac{q_1/q_2}{p_1/p_2}$$  \hspace{1cm} (Eq. 2-3)

Where $S$ is the selectivity factor, $q_i$ is the quantity adsorbed of component $i$, and $p_i$ is the partial pressure of component $i$. The selectivity factor estimated by single-component isotherm method represents a simple point of comparison for evaluating the performance of different MOFs but does not represent the actual selectivity of a mixed gas. Therefore, more information is required to estimate multiple-component adsorption. The Ideal Adsorption Isotherm Theory (IAST) is used to predict multi-component adsorption isotherm and selectivity based on single-component adsorption isotherms. Table 2-6 summarizes the calculated selectivity values for CO$_2$ over N$_2$ at 298 K from the molar ratio of the CO$_2$ uptake at 0.15 bar and N$_2$ uptake at 0.75 bar. According to Table 2-6, MOFs displaying the highest selectivites are those bearing functionalized pore surface. Rallapalli et al. [94] studied the CO$_2$, CH$_4$, N$_2$, CO, O$_2$ and Ar adsorption selectivity on MIL-53(Al). The adsorption selectivities for the adsorbate gases were calculated from their adsorption isotherm. The MIL-53(Al) showed high selectivity for CO$_2$ over the rest of the studied gases. The order of adsorption selectivity towards CO$_2$ over O$_2$, Ar, N$_2$, CO and CH$_4$ was as follows: CO$_2$/O$_2$>CO$_2$/Ar>CO$_2$/N$_2$>CO$_2$/CO>CO$_2$/CH$_4$. The MIL-53(Al) exhibited high
CO$_2$/N$_2$ (10.1) selectivity compared to other carbonaceous materials such as virgin palm shell based activated carbon (7.99) [94].
Table 2-6: CO\textsubscript{2}/N\textsubscript{2} adsorption selectivity in metal organic frameworks at pressures relevant to post combustions CO\textsubscript{2} capture

<table>
<thead>
<tr>
<th>Material</th>
<th>Common name</th>
<th>CO\textsubscript{2} uptake</th>
<th>N\textsubscript{2} uptake</th>
<th>Selectivity (conditions)</th>
<th>Temp (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}(adenine)\textsubscript{2}(CO\textsubscript{2}CH\textsubscript{3})\textsubscript{2}</td>
<td>bio-MOF-11</td>
<td>5.4 wt % (1 bar)</td>
<td>0.28 wt % (0.75 bar)</td>
<td>65</td>
<td>298</td>
<td>[85]</td>
</tr>
<tr>
<td>CO\textsubscript{2}(ad)\textsubscript{2}(OA)\textsubscript{2}</td>
<td>bio-MOF-11</td>
<td>6 mmol/g (1 bar)</td>
<td>0.43 mmol/g (1 bar)</td>
<td>273</td>
<td></td>
<td>[140]</td>
</tr>
<tr>
<td>Mg\textsubscript{2}(dobdc)</td>
<td>Mg-MOF-74, Mg-CPO-27</td>
<td>20.6 wt% (0.15bar)</td>
<td>1.83 wt % (0.75 bar)</td>
<td>44</td>
<td>303</td>
<td>[140]</td>
</tr>
<tr>
<td>Zn\textsubscript{4}O(BDC-NH\textsubscript{2})\textsubscript{3}</td>
<td>IRMOF-3</td>
<td>0.6 wt% (0.15bar)</td>
<td></td>
<td></td>
<td>298</td>
<td>[66]</td>
</tr>
<tr>
<td>Ni\textsubscript{2}(dobdc)</td>
<td>Ni-MOF-74</td>
<td>16.9 wt% (0.15bar)</td>
<td>2.14 wt % (0.75 bar)</td>
<td>30</td>
<td>298</td>
<td>[64]</td>
</tr>
<tr>
<td>CO\textsubscript{2}(dobdc)</td>
<td>Co-MOF-74</td>
<td>14.2 wt% (0.15bar)</td>
<td></td>
<td></td>
<td>298</td>
<td>[77]</td>
</tr>
<tr>
<td>Cu\textsubscript{3}(BTC)\textsubscript{2}</td>
<td>HKUST-1</td>
<td>11.6 wt% (0.15bar)</td>
<td>0.41 wt % (0.75 bar)</td>
<td>101</td>
<td>293</td>
<td>[80]</td>
</tr>
<tr>
<td>Zn\textsubscript{4}O(BTB)\textsubscript{2}</td>
<td>MOF-177</td>
<td>0.6 wt% (0.15bar)</td>
<td>0.39 wt % (0.75 bar)</td>
<td>4</td>
<td>298</td>
<td>[75]</td>
</tr>
<tr>
<td>Zn\textsubscript{2}(ox)(atz)\textsubscript{2}</td>
<td></td>
<td>8.3 wt% (0.15bar)</td>
<td></td>
<td></td>
<td>293</td>
<td>[89]</td>
</tr>
<tr>
<td>Zn\textsubscript{2}(dobdc)</td>
<td>Zn-MOF-74</td>
<td>7.6 wt% (0.15bar)</td>
<td></td>
<td></td>
<td>296</td>
<td>[65]</td>
</tr>
<tr>
<td>Zn(blm)(nlm)</td>
<td>ZIF-68</td>
<td>38 (cm\textsuperscript{3}/g, 1 atm)</td>
<td>2.9 (cm\textsuperscript{3}/g, 1 atm)</td>
<td>19.5</td>
<td>298</td>
<td>[141]</td>
</tr>
<tr>
<td>Zn(MeIM)\textsubscript{2}</td>
<td>ZIF-8</td>
<td>0.6 wt% (0.15bar)</td>
<td></td>
<td></td>
<td>298</td>
<td>[77]</td>
</tr>
<tr>
<td>Cu\textsubscript{3}(TATB)\textsubscript{2}</td>
<td>CuTATB-60</td>
<td>5.8 wt% (0.15bar)</td>
<td>0.82 wt % (0.75 bar)</td>
<td>24</td>
<td>298</td>
<td>[87]</td>
</tr>
<tr>
<td>Zn(cblm)(nlm)</td>
<td>ZIF-69</td>
<td>41 (cm\textsuperscript{3}/g, 1 atm)</td>
<td>3.4 (cm\textsuperscript{3}/g, 1 atm)</td>
<td>20</td>
<td>298</td>
<td>[141]</td>
</tr>
<tr>
<td>Fe\textsubscript{3}[(Fe\textsubscript{4}Cl\textsubscript{3})(BTT)\textsubscript{8}(MeOH)\textsubscript{4}]\textsubscript{2}</td>
<td>Fe-BTT</td>
<td>5.3 wt% (0.15bar)</td>
<td>0.95 wt %</td>
<td>18</td>
<td>298</td>
<td>[142]</td>
</tr>
<tr>
<td>Zn(mblm)(nlm)</td>
<td>ZIF-79</td>
<td>34 (cm^3/g, 1 atm)</td>
<td>2.9 (cm^3/g, 1 atm)</td>
<td>22.5</td>
<td>298</td>
<td>[141]</td>
</tr>
<tr>
<td>-----------------------</td>
<td>------------</td>
<td>--------------------</td>
<td>---------------------</td>
<td>------</td>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>Zn(nblm)(nlm)</td>
<td>ZIF-78</td>
<td>3.3 wt% (0.15bar)</td>
<td>0.36 wt% (0.75 bar)</td>
<td>30</td>
<td>298</td>
<td>[143]</td>
</tr>
<tr>
<td>Al(OH)(2-amino-BDC)</td>
<td>NH2-MIL-53(Al), USO-1-Al-A</td>
<td>3.1 wt% (0.15bar)</td>
<td>298</td>
<td>[70]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H3[(Cu4Cl)3(BTTri)8]</td>
<td>Cu-BTTrI</td>
<td>2.9 wt% (0.15bar)</td>
<td>0.49 wt% (0.75 bar)</td>
<td>19</td>
<td>298</td>
<td>[67]</td>
</tr>
<tr>
<td>Zn(cnlm)(nlm)</td>
<td>ZIF-82</td>
<td>54 (cm^3/g, 1 atm)</td>
<td>3.9 (cm^3/g, 1 atm)</td>
<td>25.5</td>
<td>298</td>
<td>[141]</td>
</tr>
<tr>
<td>Cu₃(BPT(N₂))₂</td>
<td>UMC-150(N)2</td>
<td>1.9 wt% (0.15bar)</td>
<td>298</td>
<td>[77]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(OH)(BDC)</td>
<td>MIL-53(Al), USO-1-A</td>
<td>1.7wt% (0.15bar)</td>
<td>298</td>
<td>[70]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₂(2-amino-BDC)₂(DABCO)</td>
<td>USO-2-Ni-A</td>
<td>2.1 wt% (0.15bar)</td>
<td>298</td>
<td>[70]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V(IV)O(BDC)</td>
<td>MIL-47</td>
<td>1.1 wt% (0.15bar)</td>
<td>298</td>
<td>[77]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn₂(BTetB)</td>
<td>1.8 wt% (0.15bar)</td>
<td>0.31 wt % (0.75 bar)</td>
<td>19</td>
<td>298</td>
<td>[144]</td>
<td></td>
</tr>
<tr>
<td>Zn(bdc)(4,4'-bipy)₀.₅</td>
<td>MOF-508b</td>
<td>26 wt% (4.5bar)</td>
<td>1.90 wt % (4.5bar)</td>
<td>3</td>
<td>303</td>
<td>[114]</td>
</tr>
<tr>
<td>Zn₂(bmbdc)₂(4,40-bpy)</td>
<td>1.4 wt% (0.15bar)</td>
<td>0.01 wt % (0.75 bar)</td>
<td>298</td>
<td>298</td>
<td>[145]</td>
<td></td>
</tr>
<tr>
<td>Cu₃(BPT)₂</td>
<td>UMCM-150</td>
<td>1.8 wt% (0.15bar)</td>
<td>298</td>
<td>[77]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(OH)(bpydc)</td>
<td>MOF-253</td>
<td>1 wt% (0.15bar)</td>
<td>0.37 wt% (0.75 bar)</td>
<td>9</td>
<td>298</td>
<td>[81]</td>
</tr>
<tr>
<td>Zn₂0(cbIm)₃9(OH)</td>
<td>ZIF-100</td>
<td>1 wt% (0.15bar)</td>
<td>0.15 wt% (0.75 bar)</td>
<td>22</td>
<td>298</td>
<td>[146]</td>
</tr>
<tr>
<td>Zn(nblm)(nlm)</td>
<td>ZIF-78</td>
<td>51 (cm^3/g, 1 atm)</td>
<td>4.2 (cm^3/g, 1 atm)</td>
<td>50</td>
<td>298</td>
<td>[77]</td>
</tr>
<tr>
<td>Zn₂(BTetB)(py-CF₃)₂</td>
<td>0.9 wt% (0.15bar)</td>
<td>0.06 wt %</td>
<td>50</td>
<td>298</td>
<td>[144]</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Framework</td>
<td>Concentration</td>
<td>Temperature (°C)</td>
<td>Ref.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------</td>
<td>---------------</td>
<td>------------------</td>
<td>------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$_2$(bdcppi)(DMF)$_2$</td>
<td>SNU-50</td>
<td>2.9 wt% (0.15 bar)</td>
<td>298</td>
<td>[90]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn$<em>4$O(BDC)(BTB)$</em>{4/3}$</td>
<td>UMCM-1</td>
<td>0.5 wt% (0.15 bar)</td>
<td>298</td>
<td>[77]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn$_4$O(BDC)$_3$</td>
<td>MOF-5, IRMOF-1</td>
<td>0.5 wt% (0.15 bar)</td>
<td>298</td>
<td>[77]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
An et al. [85] reported the CO\textsubscript{2}/N\textsubscript{2} adsorption selectivity in a cobalt adeninate MOF (Bio-MOF-11). The adsorption selectivity was estimated from the ratio of the initial slopes of CO\textsubscript{2} and N\textsubscript{2} adsorption isotherms. Bio-MOF-11 showed CO\textsubscript{2}/N\textsubscript{2} selectivity of 81:1 at 273 K and 75:1 at 298 K, which are the best reported selectivity values for MOF materials. Saha et al. [128] studied the adsorption equilibrium selectivity of CO\textsubscript{2} over N\textsubscript{2} in MOF-5, MOF-177 and zeolite 5A. They found that, both MOFs showed lower CO\textsubscript{2}/N\textsubscript{2} selectivity (17.73 and 17.48 for MOF-177 and MOF-5, respectively) compared to zeolite 5A. Bae et al. [144] compared the adsorption selectivity of CO\textsubscript{2} over N\textsubscript{2} in several modified MOFs based on Zn(bttb)(X\textsubscript{2}) (x=pyridine substitutes) parent framework. Single component adsorption isotherms for CO\textsubscript{2} and N\textsubscript{2} were measured experimentally, and then from the pure component isotherm the selectivity for CO\textsubscript{2}/N\textsubscript{2} was calculated using ideal adsorbed solution theory (IAST). The results showed that, Zn\textsubscript{2}(bttb)(CF\textsubscript{3}-py)\textsubscript{2} (py=pyridine) exhibited the highest CO\textsubscript{2}/N\textsubscript{2} selectivity (~42) of 5 at low pressure compared to other samples, because of the high polar –CF\textsubscript{3} group which attracts CO\textsubscript{2} more than N\textsubscript{2} and their more constricted pores. Also they found that, the selectivity increased with decreasing the pressure of CO\textsubscript{2}, and surpassed the selectivities reported for zeolite and carbon adsorbents at the same conditions. In addition, they showed that the selectivity increases as y\textsubscript{N2} approaches unit, but at zero, where coverage does not depend on the gas composition, the selectivity was in the range of 25-45.

One simple way to evaluate the performance of MOFs experimentally is by performing breakthrough experiments. The process consists of column filled with the sample particles in form of powder or pellets and the inlet gas mixtures pass through the column and the composition of the outgoing stream is monitored usually by
chromatography or mass spectrometry. The results of the breakthrough laboratory experiments are very useful as they demonstrate the separation performance of a material prior to scale-up applications. Bastin et al. [114] examined the MOFs Zn(BDC)(4,4’-Bipy)_{0.5} (MOF-508b, BDC=1,4 benzenedicarboxylate, 4,4’-Bipy=4,4’– bipyridine) for the separation and removal of CO₂ from binary CO₂/N₂ and CO₂/CH₄ ternary CO₂/N₂/CH₄ mixture by fixed bed adsorption. They found that MOF-508b showed highly selective adsorption to CO₂ with adsorption capacity of 26.0 wt % at 303 K and 4.5 bar. Liu et al. [147] investigated the water effect on CO₂ adsorption and CO₂/N₂ selectivity of Ni/DOBDC (Ni-MOF-74) in a fixed bed breakthrough study. The Ni-MOF-74 pellets showed high CO₂ capacity of 3.74 mol/kg at 0.15 bar and high CO₂/N₂ selectivity of 38 which is higher than those of the reported zeolites such as 13X at dry conditions. Below 3% RH water Ni-MOF-74 exhibited significant CO₂ capacity of 2.2 mol/kg and CO₂/N₂ selectivity of 22 at 0.15 bar. These results indicate that, Ni-MOF-74 is a promising material for capturing CO₂ from flue gas. Hamon et al. [148] measured the adsorption selectivity of CO₂ over CH₄ of MIL-100 (Cr) in fixed bed breakthrough experiment at different mole fractions of CO₂-CH₄ mixture 25:75, 50:50, and 75:25 at 3 pressures (1, 5, and 10 bar). They showed that, the selectivity decreases from 1 to 5 bar and then increases again for the higher pressures. The selectivity of CO₂/CH₄ for equimolar bulk mixture at 303 K ranges from 8-12, which is comparable to the experimental values in Cu-BTC (5-10) [111] and flexible MIL-53-(Al) (4-7) [53].
In summary, CO\textsubscript{2} capture is attracting the board attention of both science and technology, because of the large anthropogenic CO\textsubscript{2} emission in the last few decades as a potential way to reduce greenhouse gas emissions. Among the highlighted separation technologies in this review are amine-based absorption, aqueous ammonia-based absorption, and membrane Adsorption with metal organic frameworks seems to be the most promising CO\textsubscript{2} capture technologies. Metal organic frameworks represent a new class of crystalline porous material with advantages such as ease of design and synthesis high porosity and tunable pore properties. In addition, metal organic frameworks possess a great advantage over other capture technologies, due to the reduced heat capacity which reflects the quantity of energy required for heating of the sorbent material to the desorption (regeneration) temperature. MOFs hold several records between porous materials such as the highest surface area, the highest hydrogen uptake based on physical adsorption, and the highest methane, and CO\textsubscript{2} storage. Therefore, MOFs are promising candidates as separation materials for CO\textsubscript{2} capture; however, further investigation and research is needed in several aspects to make metal organic frameworks suitable for real-world applications. For example, controlling the structure of metal organic frameworks such as increasing the strength of the metal-ligand bonds through the incorporation of high-valent metal cations (e.g. Al\textsuperscript{3+} and Ti\textsuperscript{4+}) or more strongly binding ligands (e.g. pyrazolates and triazolate) that can improve the chemical and thermal stability of MOFs and make them more capable of withstanding the high level of water present in the flue gas steam in post-combustion CO\textsubscript{2} capture application.
2.5 References


[139] Chen S, Chen M, Takamizawa S, Chen M, Su Z, Sun W. Temperature dependent selective gas sorption of the microporous metal-imidazolate framework [Cu(L)] [H 2L = 1,4-di(1H-imidazol-4-yl) benzene]. Chemical Communications 2011;47:752-4.


**Chapter 3**

A NOVEL COMBINED MANUFACTURING TECHNIQUE FOR RAPID PRODUCTION OF IRMOF-1 USING ULTRASOUND AND MICROWAVE ENERGIES

### 3.1 Introduction

In the last 10 years metal organic frameworks materials (MOFs) have attracted tremendous interest amongst researchers in diverse science and technology areas, due to their outstanding properties including very large surface areas, which is leading to wide varieties of potential industrial applications such as hydrogen storage technology [1]. MOFs are a new class of crystalline porous material [2,3] composed of metal ions (or metal clusters) connected by means of multi-functional organic ligands (e.g. carboxylates, tetrazolate, sulfonates, etc.) in order to form a three-dimensional structure [4]. Remarkable improvements of MOFs have been reported regarding their extremely high surface area and pore volume as well as high structural and chemical diversity, which can be achieved by changing the nature of the organic linker and/or changing the connectivity of the inorganic moiety. For instances, MOF-177 with surface area of 5640 m$^2$/g [5], MIL-101 with 5900 m$^2$/g [6], and UMCM-2 with 6000 m$^2$/g [7] are landmarks in this regard. The pore size of MOF materials is tuneable from microporous (i.e. Angstrom) to mesoporous (i.e. nanometer) scale [8–10].
There are hundreds of articles reporting new types of MOF materials; however IRMOF-1 is amongst the most well studied MOF with promising industrialization potential. IRMOF-1 consists of Zn₄O as metal clusters connected by 1, 4-benzenedicaboxylate (BDC) as a linear linkers to form a cubic network. Li et al. [2] were the first group who reported IRMOF-1 in 1999. Later on, many studies were carried out on the synthesis of this MOF using different carboxylate linkers by means of classical solvothermal method [3], microwave radiation [11] and ultrasonic irradiation [12]. Furthermore, IRMOF-1 capability toward gas adsorption and storage including hydrogen storage [13], carbon dioxide adsorption (21.7 mmol CO₂/g or 290 cm³ (STP)/cm³) [14] were also investigated.

Potentially, MOF materials can be applied to numerous industrial applications including gas separation, adsorption and storage process [15,16], heterogeneous catalysis [7], pharmaceutical manufacturing processes and drug delivery [10]. Carbon dioxide (CO₂) is one of the main green-house gases, which is known for its harmful effects on global warming and climate change. Consequently, tremendous efforts have been intensified to reduce CO₂ emissions into the atmosphere. At the present, removal of CO₂ from exhaust flues of power plants is primarily accomplished by means of solvent absorption using aqueous alkanolamine solvents or by cooling and pressurizing the exhaust gasses [17], which are costly and inefficient techniques having several other environmental issues including the alkanolamines volatility [18]. In this regards, MOF materials, which have shown remarkable adsorption selectivity and capacity for CO₂ capturing offer unique opportunities for CO₂ removal. According to the literature, one of the most effective MOF types for CO₂ adsorption is MIL-101 with a capacity of 40 mmol CO₂/g or 390 cm³
followed by MOF-177 with an adsorption capacity of 33.5 mmol CO$_2$/g or 320 cm$^3$ (STP)/cm$^3$ [19].

Although there are a large number of articles reporting the synthesis of new types of MOFs, but few of them focused on optimizing the synthesis procedures in order to develop higher yield manufacturing techniques. Most MOFs are synthesised using classical solvothermal methods [20,21]. These methods require very long time of reaction (e.g. up to several days). However, because of the large potential for industrial application of MOFs [1,22], it is important to develop novel and more efficient alternative synthesis techniques, which are techno-economically viable and capable for scaling up to larger industrial production scales. It is desirable to reduce costs of the final product by reducing synthesis time and increasing energy efficiency. In this respect, several alternative synthesis techniques such as solvent free method, microwave irradiation [11,23–25], electrochemical methods [26] and ultrasonic irradiation [10,12,27] have been reported. Interests toward the new techniques are attributed to their higher efficiency in terms of synthesis time and production yield as well as to their environmental friendly nature [28].

Although the ultrasonic method has been widely employed in several research areas including biological cell-disruption, medical imaging, thermoplastic welding, waste treatment, food processing and pharmaceutical industries, so far, only a few articles have reported the utilization of ultrasonic energy to synthesize MOF materials. The ultrasonic synthesis of IRMOF-1 (MOF-5) was first reported in 2008 [12]. The ultrasonic irradiation accelerates the chemical reactions and initiates new reactions that are difficult to achieve under normal conditions [29,30]. In addition, ultrasound can lead to homogenous
nucleation [31,32]. The main effect of ultrasound energy on the chemical synthesis arises from the acoustic cavitation phenomenon, which includes: creation, growth and collapse of bubbles in a liquid medium [33–35]. The collapse of the bubbles during cavitation phenomenon leads to very unique conditions such an extremely high local temperatures (i.e. local hot spots; 2500–5000 K), high pressures (i.e. >20 MPa), and very high cooling rates (i.e. >10⁷ Ks⁻¹) [23–25,36]. In addition, shock waves created by homogenous cavitation causes particle collisions in high velocities generating dramatic changes in their surface morphology, composition and reactivity [35].

Nowadays, microwave irradiation is known as a promising energy source for large scale production of materials. Microwave generates direct and uniform energy which can be absorbed throughout the entire volume of an object causing even and rapid heating. Furthermore, microwave leads to homogeneous nucleation, fast crystallization [37], diverse morphology/size [38], phase selectivity and reduction in particle size [24]. Choi et al. synthesized IRMOF-1 by means of microwave irradiation in 2008 [25]. Later in 2009, Lu et al. [11] demonstrated an improved microwave synthesis technique for synthesizing IRMOF-1 [25] and investigated its capability to capture CO₂.

The main objective of this work was to develop a novel hybrid manufacturing technique by applying a combination of both ultrasonic (UTS) and microwave (MW) irradiation to develop a rapid and more efficient procedure for synthesis of IRMOF-1. To the best of the authors’ knowledge, this is the first time that a combination of UTS and MW energies is used for the synthesis of IRMOF-1 (MOF-5). The experimental parameters were optimized by means of statistical methods using a 3² factorial design with center
points per block (i.e. 9 experiments in total). The synthesized samples were then characterized by means of different instrumental techniques including XRD, FTIR, TGA, and BET.

### 3.2 Materials and Methods

Zinc (II) nitrate hexahydrate (Zn (NO$_3$)$_2$·6H$_2$O, 99.5%) was purchased from J.T Baker, Phillipsburg, U.S.A), Benzene-1,4-dicarboxylic acid (H$_2$BDC, 98%) and N,N-diethylformamide (DEF, 99%) were purchased from Alfa-Aesar (Jobson Matthey Company, WardHill, U.S.A). N, N-dimethylformamide (DMF, 99.9%) was purchased from Caledon Libratory Chemicals (Georgetown, Ontario, Canada). Chloroform 99% was purchased from OmniSolv EMD Chemicals (Gibbstown, New Jersey, U.S.A). The instruments used in the study are as follows: ultrasonic bath (240 W, 50/60 Hz, Crest Ultrasonics, Malaysia, microwave system (Daytron), BET surface area and pore size analyzer (Micromeritics ASAP 2010). The IRMOF-1 products were characterized by X-ray Diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The XRD data was performed on a Rigaku – MiniFlex powder diffractometer (woodlands, U.S.A), using CuK$_\alpha$ (\( \lambda = 1.54059 \text{Å} \)) the radiation was over the range of 5°<2θ<40° with step width of 0.02 °, counting time of 1 s for each step and obtained at 30 kV and 15 mA. Data was processed using MDI-Jade version 7.5 software. The SEM images were taken by JSM 600 F model, Joel, Japan operating at 10 keV of acceleration voltage. The FTIR spectra were recorded on solid state by (Bruker Vector 22, Milton, Ontario, Canada) running by OPUS v 3.1. The transmission mode was implemented in order to analyze the samples though a diamond window. The sample scan time was 32s over the 400 – 4000 cm$^{-1}$ spectral region with
resolution of 4 cm$^{-1}$. Air was selected to run a background sample in the same range. The thermal analyses were performed using a Mettler Toledo TGA/SDTA 851© model (Mississauga, Canada) with version 6.1 Star© software. Aluminum crucibles with lids were used to hold samples of known weight (3 – 15 mg) for TG analysis. The samples were heated from 25 $^\circ$C to 600 $^\circ$C at heating rate of 10$^\circ$ C/min under nitrogen purge (50 mL/min). Surface area and pore size of the samples were measure by means of a BET analyzer (Micrometrics ASAP 2010). Known amounts of samples (e.g. 50–80 mg) were loaded into the BET sample tube and degassed under vacuum (10$^{-5}$ Torr) at 125 $^\circ$C for 6 h. The Langmuir model was applied to measure the specific surface area of the prepared samples.

3.2.1 Synthesis

The IRMOF-1 samples were synthesized with the same batch composition reported by Millward and Yaghi [14], while some minor modifications were also applied. In the first stage for evaluation of the classical solvothermal synthesis by means of a electrical oven (OV), a IRMOF-1 sample was synthesized as following: in a 100 mL beaker, 0.947 g of Zn(NO$_3$)$_2$·6 H$_2$O and 0.176 g of H$_2$BDC were dissolved in 10mL of DEF.

Then the resultant solution was transferred into a 25mL Teflon reactor with a tight cap and kept at 100 $^\circ$C for 20 h. The product crystallites were then washed four times with fresh DMF (40 ml). For two step synthesis (UTS and MW), the same batch composition as of the classical synthesis was used, however, the energies sources for heating were UTS and MW irradiations instead of electrical oven. After mixing and dissolving the reactants, the clear solution was transferred into a 25 mL Teflon reactor and irradiated in the
ultrasonic bath for specific sonication times at the predetermined temperature according to the experimental design (see Table 3-1). The sonified samples were then irradiated in a microwave oven for various irradiation times depending on the sonication conditions (see Table 3-1). The produced solid phase was then filtered and washed four times with fresh DMF (40 mL) and dried at room temperature. The investigated parameters for ultrasonic energy were sonication time (i.e. 15 min, 1 h and 3.5 h) and ultrasonic bath temperature (i.e. 25 °C, 52 °C and 80 °C).

Sample activation was investigated to improve surface area and pore volume of the synthesized IRMOF-1 samples. Solvent exchange was employed as activation method. Solvent exchange techniques are often used to remove guest molecules (i.e. DEF in our study). It is noteworthy to mention that boiling point and polarity of the solvent must be considered in order not to damage the original framework. Some of the synthesized samples were exposed to fresh chloroform for three times in 72 h. The solvent exchanged IRMOF-1 samples were dried in an electrical oven at 70 °C for 1 h. The activated products were then immediately transferred into desiccators in order to minimize exposure to humidity and other contaminants from air.
Studies have shown that various parameters including synthesis condition (i.e. linker and metal centers, solvent, source of heating, time and temperature, pressure, etc.), activation procedure, type of solvent used for sample activation (solvent exchange), as well as storage condition can remarkably affect the surface area of MOFs materials [39]. For instance, using DMF as an alternative cheaper solvent to DEF, has resulted in MOF products with lower surface areas [13]. Moreover, increasing the temperature and extending the synthesis reaction time caused yellow crystals to be produced with lower surface areas [13]. Literature data for the surface area of IRMOF-1 (MOF-5) along with data obtained in this research are compared in Table 3-2. It is obvious that preparation methods can remarkably influence the MOF surface area. According to the literatures data, the reported Langmuir surface areas for IRMOF-1 are in the range of 1014 – 4400 m²/g, where the Langmuir surface area we achieved in this work (i.e. 2473 m²/g) is in that range.

### Table 3-1: Experimental design for as synthesized samples, effect of ultrasonic bath temperature and time.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>UTS time (h)</th>
<th>UTS Temperature (°C)</th>
<th>MW time (s)</th>
<th>Langmuir surface area (m²/g)</th>
<th>Particles size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRMOF-1(S1)</td>
<td>0.25</td>
<td>RT</td>
<td>120</td>
<td>79</td>
<td>11</td>
</tr>
<tr>
<td>IRMOF-1(S2)</td>
<td>0.25</td>
<td>52</td>
<td>90</td>
<td>903</td>
<td>9</td>
</tr>
<tr>
<td>IRMOF-1(S3)</td>
<td>0.25</td>
<td>80</td>
<td>85</td>
<td>549</td>
<td>12</td>
</tr>
<tr>
<td>IRMOF-1(S4)</td>
<td>1.8</td>
<td>RT</td>
<td>190</td>
<td>780</td>
<td>12</td>
</tr>
<tr>
<td>IRMOF-1(S5)</td>
<td>1.8</td>
<td>52</td>
<td>93</td>
<td>420</td>
<td>8</td>
</tr>
<tr>
<td>IRMOF-1(S6)</td>
<td>1.8</td>
<td>80</td>
<td>73</td>
<td>954</td>
<td>7</td>
</tr>
<tr>
<td>IRMOF-1(S7)</td>
<td>3.5</td>
<td>RT</td>
<td>150</td>
<td>162</td>
<td>8</td>
</tr>
<tr>
<td>IRMOF-1(S8)</td>
<td>3.5</td>
<td>52</td>
<td>100</td>
<td>289</td>
<td>6</td>
</tr>
<tr>
<td>IRMOF-1(S9)</td>
<td>3.5</td>
<td>80</td>
<td>83</td>
<td>1315</td>
<td>5</td>
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</tbody>
</table>
Table 3-2: Comparison of various preparation methods of IRMOF-1.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Nitrogen uptake (mmol/g)</th>
<th>BET surface Area (m²/g)</th>
<th>Langmuir Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>23.3</td>
<td>1810</td>
<td>2160</td>
</tr>
<tr>
<td>10</td>
<td>11.8</td>
<td>572</td>
<td>1014</td>
</tr>
<tr>
<td>46</td>
<td></td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td></td>
<td>773</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>29.7</td>
<td></td>
<td>2900</td>
</tr>
<tr>
<td>49</td>
<td></td>
<td></td>
<td>3080</td>
</tr>
<tr>
<td>10</td>
<td>44.5</td>
<td>3800</td>
<td>4400</td>
</tr>
<tr>
<td>S2 (this study)</td>
<td></td>
<td>1874</td>
<td>2473</td>
</tr>
</tbody>
</table>

3.2.2 Experimental Design

In order to optimize the IRMOF-1 production condition by means of the novel combined UTS +MW technique, a statistical approach using a 3² factorial design with center points per block we considered. Design-Expert 7.1.5 software (StatEase, Minneapolis, USA) was employed to investigate the effect that ultrasonic bath temperature and sonication time had on the microwave irradiation time and consequently on the morphology, surface area and particle size and distribution of the synthesized IRMOF-1 samples. The details of the factor levels employed for the experimental design and the responses examined in the study are summarized in Table 3-1.

The analysis of variance (ANOVA) was used to investigate which factors significantly influenced the microwave irradiation time and consequently the Langmuir surface area, and particle size. It was found that both investigated factors (i.e. UTS time and UTS temperature) strongly influence the final product microwave irradiation as well as particle size. However, these two factors were shown less effects on Langmuir surface area.
Therefore, both particle size and microwave irradiation time were statistically analyzed using Design Expert 7.1.5 software by carrying data transformation (inverse transformation) to create strong model with a probability greater than $F$-value less than 0.05. The $F$-value was 19.38 for the inverse transformation of particle size data compared to an $F$-value of 5.69 for data without any transformation. An $F$-value of 10.99 was obtained when applying inverse transformation of the microwave data, and an $F$-value equal to 4.34 for the data without any transformation. The input factors were coded alphabetically (i.e. A for UTS time and B for UTS bath temperature). The two input factor interaction terms were coded by combining the main factors; AB for UTS time and UTS temperature interaction. The model was constructed by step-wise backward elimination of the statistically insignificant factorial terms and non-hierarchical terms. The final model for the particle size data is presented in Tables 3-3 and 3-5. In addition, final model of the microwave time data are summarized in Tables 3-4 and 3-5.

Table 3-3: Summary of the analysis of variance of the model equation of the particles size as function of synthesis variable.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Degree of freedom</th>
<th>Mean Square</th>
<th>$F$-Value</th>
<th>Prob &gt; $F$-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.011515602</td>
<td>3</td>
<td>0.003838534</td>
<td>19.3756842</td>
<td>0.0035</td>
</tr>
<tr>
<td>A-UTS time</td>
<td>0.007231561</td>
<td>1</td>
<td>0.007231561</td>
<td>36.5025891</td>
<td>0.0018</td>
</tr>
<tr>
<td>B-UTS Temp</td>
<td>0.00274901</td>
<td>1</td>
<td>0.00274901</td>
<td>13.8761169</td>
<td>0.0136</td>
</tr>
<tr>
<td>AB</td>
<td>0.001687709</td>
<td>1</td>
<td>0.001687709</td>
<td>8.51901176</td>
<td>0.0331</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.014075187</td>
<td></td>
<td>R²</td>
<td></td>
<td>0.92079465</td>
</tr>
<tr>
<td>Mean</td>
<td>0.125356742</td>
<td></td>
<td>Adj-R²</td>
<td></td>
<td>0.87327144</td>
</tr>
<tr>
<td>Pred-R²</td>
<td>0.763095814</td>
<td></td>
<td>Adeq Precision</td>
<td></td>
<td>11.9523914</td>
</tr>
</tbody>
</table>
Table 3-4: Summary of the analysis of variance of the model equation of the microwave time as function of synthesis variable.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Degree of freedom</th>
<th>Mean Square</th>
<th>F-Value</th>
<th>Prob &gt; F-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>5.13169E-05</td>
<td>3</td>
<td>1.71056E-05</td>
<td>10.9856493</td>
<td>0.0122</td>
</tr>
<tr>
<td>A-UTS time</td>
<td>1.01017E-06</td>
<td>1</td>
<td>1.01017E-06</td>
<td>0.64875478</td>
<td>0.4571</td>
</tr>
<tr>
<td>B-UTS Temp</td>
<td>4.96501E-05</td>
<td>1</td>
<td>4.96501E-05</td>
<td>31.8865078</td>
<td>0.0024</td>
</tr>
<tr>
<td>AB</td>
<td>8.32585E-07</td>
<td>1</td>
<td>8.32585E-07</td>
<td>0.53470637</td>
<td>0.4974</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.001247833</td>
<td>R²</td>
<td></td>
<td>0.86827181</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.009959832</td>
<td>Adj- R²</td>
<td></td>
<td>0.78923489</td>
<td></td>
</tr>
<tr>
<td>Pred-R²</td>
<td>0.43504233</td>
<td>Adeq Precision</td>
<td></td>
<td>8.01779884</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-5: Final model equations for particles size and microwave time parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles size</td>
<td>( \frac{1}{PS} = 0.13 + 0.035A + 0.021B + 0.021AB )</td>
</tr>
<tr>
<td>Microwave time</td>
<td>( \frac{1}{MW(time)} = 9.9966 \times 10^{-3} - 4.098 \times 10^{-4}A + 2.877 \times 10^{-3}B + 4.553 \times 10^{-4}AB )</td>
</tr>
</tbody>
</table>

A, sonication time; B, ultrasonic temperature; PS, particles size; MW (time), microwave irradiation time.

According to the data in Table 3-3, it can be concluded that IRMOF-1 particle size is affected by both ultrasonic temperature and time. The higher \( F \)-value (36.2) of the sonication time indicates that particle size is strongly affected by sonication time rather than ultrasonic temperature with an \( F \)-value of 13.87. Therefore, as sonication time increases, particle size decreases. In addition, particle size decreases as ultrasonic temperature increases. On the other hand, microwave irradiation time is strongly affected by ultrasonic temperature (\( F \)-value = 31.88). Increasing ultrasonic temperature reduces the microwave irradiation time during synthesis of IRMOF-1 crystallites as is shown in Table 3-4.
3.3 Result and Discussion

3.3.1 As-synthesized samples

The IRMOF-1 crystallites synthesized by means of the novel hybrid two steps technique using UTS followed by MW irradiation sources were compared with those of synthesized by means of the conventional solvothermal method using an electrical oven (OV) to confirm the existence of IRMOF-1 crystalline phase. The XRD patterns of some of the samples synthesized under the hybrid technique at different experimental conditions are illustrated in Figure 3-1. According to the XRD patterns, most of the peaks match well with those for IRMOF-1 [10,12,13,29]. The main peak at $2\theta = 9.88^\circ$ ascertain the formation of IRMOF-1 crystalline phase which appears in all samples. In addition, two other peaks at $2\theta = 7.30^\circ$ and $14.02^\circ$ appear in all samples because of microwave heating process which is consistent with other literatures [48,49]. Moreover, sample 4 and 6 shows an extra peak at $2\theta = 8.8^\circ$ in addition to the three characteristic peaks, which indicates that these two samples are a mixture of IRMOF-1 and an unidentified crystalline phase [11]. However, it can be seen that the XRD pattern of OV sample is slightly different.
In this study, several trials were performed to synthesize IRMOF-1 using the classical oven technique, but none of them were successful (3 trials) even though the same procedure as Millward et al. [14] was followed. This phenomenon has been reported previously [10]. Figure 3-2 illustrates the SEM images of IRMOF-1 samples synthesized.
by means of the hybrid technique of UTS and MW. The IRMOF-1 morphology is characterized by typical cubic shaped crystals with approximate dimensions of 5–15µm. It can be observed that the IRMOF-1 crystallites synthesized under UTS and MW method (see Figure 3-2(a)) are more regulated cubic shaped comparing to those synthesized with OV (see Figure 3-1(b)). In addition, the IRMOF-1 synthesized by UTS and MW produced particles with a size reduction by a magnitude of approximately 10 comparing to those produced by oven. This reduction in particle size is common among crystals prepared using microwave or ultrasonic irradiations [32,46]. Moreover, particles size decreased with increasing ultrasonic bath temperature and sonication time (see Section 3.2.2). This can be attributed to the combination effects of ultrasonic and microwave irradiation as discussed earlier, where UTS and MW irradiations promote uniform and fast nucleation [47,48]. As a result, it can be concluded that using the two step synthesis method (UTS and MW) has produced IRMOF-1 with a higher quality than those synthesized by OV method [11]. It can be concluded that combination of ultrasonic and microwave irradiation provides a unique and promising method for the synthesis of MOFs. Figure 3-3 illustrates the FTIR spectra of IRMOF-1 samples synthesized at different experimental conditions using the two step technique.
The FTIR spectrums are in good agreement with the literature [49]. The vibration bands at 1700-1400 cm\(^{-1}\) represent the carboxylic functional group (COO). The vibration bands at 1608–1540 cm\(^{-1}\) and 1410–1340 cm\(^{-1}\) can be assigned to the symmetric and asymmetric vibrations of BDC [50]. The two absorptions bands located at 1572 cm\(^{-1}\) and 1506 cm\(^{-1}\) belong to the carboxylic (COO) asymmetric stretching, whereas the band at 1391 cm\(^{-1}\) can be assigned to the corresponding symmetric stretching vibration. The vibration bands at 1200-700 cm\(^{-1}\) can be considered as the fingerprint of terephthalate compounds. The absorption peak at 530 cm\(^{-1}\) is relevant to the secondary building unit (SBU) of IRMOF 1, which represents the (Zn–O) vibration of tetrahedral coordinated Zn\(_4\)O cluster. The vibration peaks of at 3500–3200 cm\(^{-1}\) correspond to the OH group of the adsorbed water molecules [50].
Figure 3-3: FTIR spectra of IRMOF-1 samples.

Figure 3-4 illustrates the TGA curves of the IRMOF-1 samples synthesized in this study by means of the hybrid technique. Thermal analysis results revealed that the overall thermal stability of the samples is similar to those reported in the literatures [14,44,25]. TGA curves show two distinguished weight loses. The first gentle slope of weight loss occurs between 100–250º C (ca. 20%) and corresponds to the evaporation of trapped DEF and DMF and adsorbed water molecules [51]. This amount of non-volatile DEF and DMF is trapped inside the IRMOF-1 samples during the crystallization period and washing.
process. The second sharp weight loss occurs between 420 and 500 °C (ca. 38%), which is attributed to decomposition of IRMOF-1 structure [14].

![Thermogravimetric analysis results for IRMOF-1 samples, the heating rate of all samples was 10 °C/min and the atmosphere was N₂.](image)

In this study, the Langmuir surface area of IRMOF-1 as-synthesized (i.e. without any activation) for the two steps synthesis (UTS +MW) technique, was between 79 and 1315 m²/g. The lower surface area of the sample in the present work can be attributed not only to
the presence of Zn species in the pores [39,40], but also to the different condition applied for synthesis. However, the Langmuir surface area of the IRMOF-1 synthesized in the two steps (UTS +MW) technique, was increased radically for the activated samples (three times solvent exchange with chloroform in 72 h) (see Section 3.3.2)

### 3.3.2 Sample Activation (solvent exchange)

The XRD patterns of the as-synthesized IRMOF-1 samples (i.e. S2, S9 and S10) and their corresponding activated samples are compared in Figure 3-5(a). The XRD patterns have the same patterns; however, they show a slight difference in the peak intensity of both samples. The peaks at \(2\theta = 7.9^{\circ}\) increased significantly and peaks at \(2\theta = 9.89^{\circ}\) decreased for the samples that had undergone solvent exchange with chloroform [11]. The difference in peaks intensity can be attributed to the removal of guest molecules during solvent exchange [11]. Moreover the SEM images illustrate changes in the surface roughness for the activated samples (as shown in Figure 3-6). However, thermal analysis results show the changes between the as-synthesized and the modified samples. TGA curves in Figure 3-5(b) show different thermal pattern between the as-synthesized and activated samples. The TGA curves corresponding to the as-synthesized samples show two distinct weight losses stages at 100–250\(^{\circ}\) C and 420–500\(^{\circ}\) C, however, in the activated sample the first gentle weight loss almost disappears and the samples show a steady continuous weight loss up to ca. 420\(^{\circ}\) C followed by a sharp weight loss at 430–500\(^{\circ}\) C. The disappearing of first small drop in weight loss can be related to the solvent exchange with chloroform and the way the samples were stored inside desiccators to minimize exposure to air and humidity.
Figure 3-5: (a) XRD comparison between as-synthesized samples and activated samples, (b) TGA comparison between as-synthesized samples and activated samples.
The highest Langmuir surface area achieved in this study for the activated sample was 2473 m$^2$/g, which is in the range of the previously reported values using the conventional oven method (see Tables 3-2 and 3-6). On the other hand, to the best of the authors’ knowledge, 2473 m$^2$/g can be considered as the highest Langmuir surface area reported for alternative synthesis methods such as microwave irradiation. Lu et al. [11] have reported a successful synthesis of IRMOF-1 with 1263 m$^2$/g Langmuir surface area using microwave irradiation only. This improvement in the surface area can be attributed to the removal of guest molecules (e.g. DEF and DMF), which can be achieved by means of solvent exchange with fresh chloroform [11].
Table 3-6: Effect of activation (solvent exchange).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>UTS (h)</th>
<th>UTS (°C)</th>
<th>MW (s)</th>
<th>Post synthesis</th>
<th>Langmuir surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10 as</td>
<td>0.5</td>
<td>80</td>
<td>85</td>
<td>None</td>
<td>1370</td>
</tr>
<tr>
<td>S10 Post</td>
<td>0.5</td>
<td>80</td>
<td>85</td>
<td>Solvent exchange (chloroform thrice for 3 days and later dry in oven at 70 °Cfor 1 h)</td>
<td>1723</td>
</tr>
<tr>
<td>S9 As</td>
<td>3.5</td>
<td>80</td>
<td>83</td>
<td>None</td>
<td>1315</td>
</tr>
<tr>
<td>S9 Post</td>
<td>3.5</td>
<td>80</td>
<td>83</td>
<td>Solvent exchange (chloroform thrice for 3 days and later dry in oven at 70 °Cfor 1 h)</td>
<td>1786</td>
</tr>
<tr>
<td>S2 As</td>
<td>0.25</td>
<td>52</td>
<td>90</td>
<td>None</td>
<td>903</td>
</tr>
<tr>
<td>S2 Post</td>
<td>0.25</td>
<td>52</td>
<td>90</td>
<td>Solvent exchange (chloroform thrice for 3 days and later dry in oven at 70 °Cfor 1 h)</td>
<td>2473</td>
</tr>
</tbody>
</table>

3.4 Conclusions

A novel hybrid synthesis technique based on a combined application of ultrasound and microwave energies was developed for rapid synthesis of IRMOF-1. The metal organic framework of IRMOF-1 (Zn₄O(BDC)₃) was successfully synthesized by means of the developed two step combined technique. This rapid manufacturing method showed promising results in terms of particles size distribution (lower particles size (5µm, and narrower size distribution), morphology (more constructed crystallites) and surface area (higher surface area 2473 m²/g) of the synthesized IRMOF-1 crystallites. Particle size of the samples synthesized by means of this novel hybrid technique was smaller in order of 10µm in comparison to the classical solvothermal synthesis method (e.g. solvothermal oven synthesis). Furthermore, it can be concluded that the solvent exchange activation of IRMOF-1 synthesized by means of the combined techniques plays a very essential role to improve surface area of the MOF final product.
3.5 References


Chapter 4

MICROWAVE SYNTHESIS OF THE CPM-5 METAL ORGANIC FRAMEWORKS

4.1 Introduction

Global warming and environmental issues have attracted the attention of many researchers in the 21st century, due to the rapid population increase and expansion of energy consumption world-wide. According to the Energy Information Administration (EIA), it is expected that the energy consumption will increase by 57% from 2004 to 2030 [1]. Although there is no agreement on the causes of the global warming and environmental problems, many scientists believe that the emission of greenhouse gases (GHG) contributes to the majority of the environmental problems. Carbon dioxide (CO$_2$) is the most significant anthropogenic GHG. About 60% of the global warming effects are attributed to carbon dioxide emissions [2].

According to the Intergovernmental Panel on Climate Change (IPCC) [3], the atmosphere may contain up to 570 ppm of carbon dioxide in 2100, causing a rise in the mean global temperature of around 1.9 °C and an increase in the mean sea level of 3.8m [4]. As a result, tremendous efforts have been invested to reduce CO$_2$ emission into the atmosphere. At present, removal of CO$_2$ from exhaust flues of power plants is primarily accomplished by means of solvent absorption using aqueous alkanolamine solvents or by cooling and pressurizing the exhaust gasses [5], which are costly and inefficient techniques having several other environmental issues including the volatility of the alkanolamines [6].
In recent years, crystalline porous materials (CPM) have emerged as an important class of material in many industrial applications including gas separation, adsorption and storage processes [7], heterogeneous catalysis [8], pharmaceutical manufacturing processes and drug delivery [9]. Consequently, new generations of CPM that can be used for carbon dioxide adsorption with high capacity at atmospheric pressure are intensively investigated [10, 11]. In this regard, metal organic frameworks (MOFs) are one of the most promising porous materials due to their outstanding properties, including extremely their high surface area and pore volume as well as their high structural and chemical diversity, which can be achieved by changing the nature of the organic linkers and/or changing the connectivity of the inorganic moieties. In addition, the pore size of the MOF materials is tunable from the microporous, i.e., Angstrom, to the mesoporous (i.e., nanometer) scale [9, 12, 13]. MOFs are a new class of CPM composed of metal ions (or metal clusters) connected by means of multi-functional organic ligands, e.g., carboxylates, tetrazolate, sulfonates, etc., in order to form a three-dimensional structure [14]. Several MOFs have shown remarkable surface area, adsorption, selectivity and capacity for CO\textsubscript{2} capturing. According to the literature, one of the most effective MOF types for CO\textsubscript{2} adsorption is MIL-101 with a surface area of 5900 m\textsuperscript{2}g\textsuperscript{-1} [15] and a CO\textsubscript{2} adsorption capacity of 40 mmol CO\textsubscript{2}/g or 390 cm\textsuperscript{3} (STP)/cm\textsuperscript{3} (STP = standard temperature and pressure) [16]. Next is MOF-177 with a surface area of 5640 m\textsuperscript{2}g\textsuperscript{-1} [17] and an adsorption capacity of 33.5 mmol CO\textsubscript{2}/g or 320 cm\textsuperscript{3} (STP)/ cm\textsuperscript{3} [15]. For example, if MOF-177 with the chemical formula Zn\textsubscript{4}O(BTB)\textsubscript{2} is added to a pressurized container at 35 bar, it can store nine times more CO\textsubscript{2} than a container without adsorbent material [18].
MOFs are classically synthesized by hydrothermal and solvothermal methods based on mass transfer techniques using conventional thermal sources [19, 20]; however, these methods require very long crystallization times that can be up to several days. Hence, it is essential to improve the conventional synthesis protocols and develop facile and more efficient alternative synthesis techniques for large industrial-scale production that can be techno-economically viable [21]. Among many alternative synthesis techniques such as microwave irradiation [22, 23], ultrasonic irradiation, combined microwave and ultrasonic irradiations [21], and electrochemical methods [24], microwave irradiation has emerged as one of the favorites. Interest towards new synthesis techniques is attributed to their higher efficiency in terms of synthesis time and production yield as well as their environment-friendly nature.

Despite all the advantages of microwave irradiation such as homogeneous nucleation, fast crystallization [20], diverse morphology and size [25], phase selectivity and reduction in particle size leading to higher surface area [21], this method has rarely been applied to the synthesis of organic-inorganic materials [26]. In the literature, few MOFs have been synthesized under microwave radiation; the list includes MOF-5 [10], MIL-101, MIL-100 [15], and MIL-77 [17]. The localized superheating effect of microwave irradiation increases the reaction rate by an order of magnitude compared to conventional heating, due to the following mechanism: (1) dipolar polarization, (2) enhanced refluxing within the sealed vessel, (3) electrically conducting materials, and (4) accelerated condensation of the metal oxide [10]. CPM-5 is a highly porous indium based MOF with a surface area of 580 m$^2$g$^{-1}$ [11]. CPM-5 consists of In-O clusters as metal centers connected by 1,3 ,5 benzenetricaboxylate (BTC) as a linear linker. Zheng et al. [11] were the first
group who reported in 2010 the synthesis of CPM-5 by autoclaving at 120 °C for 5 days. CPM-5 exhibits high hydrothermal, thermal, and photochemical stability. In addition, CPM-5 has three unique cage-within-cage-based porous structures that contribute to its high CO$_2$ uptake capacity. Although, CPM-5 can be considered as a promising candidate for CO$_2$ adsorption, the long time and high energy consumption of the conventional synthesis method can be considered as a barrier for its industrial application and large-scale production. Therefore, in the course of the current research, a new alternative synthesis method using microwave irradiation is proposed, which is believed to be more time and energy efficient compared to the conventional synthesis method using an autoclave. To the best of our knowledge, the microwave synthesis method for indium MOF has not been reported before in the literature.

There is a dearth of reported data on the synthesis, characteristics and applications of indium MOFs. This study intends to report a newly developed rapid synthesis method of CPM-5 MOF by applying microwave irradiation. The synthesis parameters, such as solvent ratio, temperature, power and time of synthesis, were optimized by means of an experimental design approach, and the carbon dioxide adsorption of the synthesized CPM-5 samples was studied under controlled temperature and atmospheric pressure by means of thermogravimetric analysis (TGA). The synthesis parameters were statistically analyzed using the Design-Expert 7.1.5 program by D-optimal design of experiments, resulting in 12 experiments in total.
4.2 Materials and Methods

Indium (II) nitrate hydrate [In(NO$_3$)$_3$·xH$_2$O; 99.5%] was purchased from J.T Baker (Phillipsburg, USA), 1, 3, 5 benzenetricaboxylate (BTC) and N,N-dimethylformamide (DMF, 99.9%) were purchased from Caledon Laboratory Chemicals (Georgetown, Ontario, Canada). All of the chemicals were used as purchased without further purification.

The CPM-5 samples were synthesized with the same batch composition reported by Zheng et al. [11] using microwave irradiation as the heating source (Discovery system model of CEM Laboratory Microwave, USA) and conventional oven for comparison purposes. For microwave synthesis: a mixture of In(NO$_3$)$_3$·xH$_2$O (0.2 g), and 1,2,3-benzenetricaboxylate (BTC) (0.17 g) were dissolved in a solution of H$_2$O/DMF. After mixing and dissolving the reactants, the clear solution was transferred into a 40 mL glass pressurized tube and irradiated in the microwave. For conventional oven synthesis CPM-5(OV) (OV: Oven), batch composition was the same as microwave synthesis. The reactants were transferred into a Teflon lined stainless steel reactor and crystallized at 120 °C for 5 days. Experimental design was used to optimize the synthesis conditions. Detailed information of the selected parameters including solvent ratio, temperature, time and power of synthesis are summarized in Table 4-1. After cooling to room temperature the product crystallites were separated by means of centrifugation at 20,000 rpm for 20 min. Using fresh 1:1 solution of ethanol/DMF, the sample was washed three times by repeated dispersing and centrifuging to remove all of the un-reacted chemicals. Subsequently, the clear crystals were dried in an electrical oven at 100 °C for 1 hr. To check the effect of optimal condition, an additional sample (CPM-5M (1) CPM-5M (2), where M stands for microwave synthesis; 1 stands for the first trial, and 2 stands for the second trial as
replicate) was synthesized at the optimal synthesis conditions (i.e. T= 150 °C, t= 10 min, power = 300 W, H₂O/DMF v/v ratio of 1/4.2). In order to consider the reproducibility of the developed manufacturing method, CPM-5M, S12 and S7 were repeated twice at the same synthesis conditions.

All samples were characterized by means of X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), Thermalgravimetric Analysis (TGA), and Brunauer-Emmett-Teller (BET). The XRD data were obtained using a Rigaku – MiniFlex powder diffractometer (Japan), using CuKα (λ for Kα = 1.54059 Å) over 2θ range of 5° to 40° with step width of 0.02°. The SEM images were taken by Joel instrument (JSM 600F model, Japan) operating at 10 keV of acceleration voltage. A Burker Vector 22 instrument (Milton, Ontario, Canada) was employed to record the FTIR spectra of CPM-5 samples. The sample scan time was 32 s over the wave number of 400 – 4000 cm⁻¹ with resolution of 4cm⁻¹. The thermal analyses were performed using a Mettler Toledo TGA/SDTA 851e model (Switzerland) with a 6.1 Stare software version. The samples were heated from 25 °C to 600 °C at a heating rate of 10 °C/min under nitrogen purge (50 mL/min). Micromeritics ASAP 2010, (USA) was used to measure surface area of the samples using nitrogen adsorption/desorption isotherms. Known amounts of samples (e.g. 70 to 90 mg) were loaded into the BET sample tube and degassed under vacuum (10⁻⁵ Torr) at 150 °C for 12 h. The Langmuir model and BET model were applied to measure the specific surface area of the prepared samples. CO₂ adsorption measurements were performed by means of a thermogravimetical analyzer (TGA, Mettler Toledo TGA/SDTA 851e model) according to the following procedure reported elsewhere [10]. First, the sample was degassed at 150 °C (10⁻⁵ torr) for 12 h. Next, sufficient amount of degassed
sample (i.e. in the range of 3-5mg) was transferred into an aluminum crucible and purged under N₂ and heated from room temperature to 300 °C at heating rate of 10 °C/min and kept at this temperature for 30 min to make sure all the water and solvent molecules are evaporated. Then, sample was cooled to 30 °C at cooling rate of -10 °C/min. At this temperature, purge gas (i.e. N₂) was switched to CO₂. Weight change was recorded until the weight gain was reached to a steady state (i.e. plateau) indicating the maximum CO₂ adsorption capacity. Figure 8 shows the detailed desorption/adsorption curve for CO₂ using TGA method.

Table 4-1: Experimental design of CPM-5 using microwave irradiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>Power (W)</th>
<th>Solvent Ratio (v/v)</th>
<th>BET (m²/g)*</th>
<th>Langmuir (m²/g)*</th>
<th>CO₂ ads. (mmolCO₂/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>112.5</td>
<td>6.25</td>
<td>150</td>
<td>2.5H₂O/2.5DMF</td>
<td>1140</td>
<td>1577</td>
<td>0.98</td>
</tr>
<tr>
<td>S2</td>
<td>150</td>
<td>10</td>
<td>100</td>
<td>1H₂O/4.2DMF</td>
<td>1365</td>
<td>1888</td>
<td>N/A</td>
</tr>
<tr>
<td>S3</td>
<td>150</td>
<td>5</td>
<td>100</td>
<td>4.2H₂O/1DMF</td>
<td>1371</td>
<td>1887</td>
<td>N/A</td>
</tr>
<tr>
<td>S4</td>
<td>100</td>
<td>5</td>
<td>100</td>
<td>1H₂O/4.2DMF</td>
<td>1155</td>
<td>1596</td>
<td>N/A</td>
</tr>
<tr>
<td>S5</td>
<td>100</td>
<td>5</td>
<td>300</td>
<td>1H₂O/4.2DMF</td>
<td>1028</td>
<td>1411</td>
<td>N/A</td>
</tr>
<tr>
<td>S6</td>
<td>125</td>
<td>7.5</td>
<td>200</td>
<td>4.2H₂O/1DMF</td>
<td>135</td>
<td>180</td>
<td>N/A</td>
</tr>
<tr>
<td>S7</td>
<td>100</td>
<td>10</td>
<td>300</td>
<td>4.2H₂O/1DMF</td>
<td>101</td>
<td>135</td>
<td>N/A</td>
</tr>
<tr>
<td>S8</td>
<td>100</td>
<td>10</td>
<td>100</td>
<td>2.5H₂O/2.5DMF</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S9</td>
<td>137.5</td>
<td>6.25</td>
<td>150</td>
<td>1H₂O/4.2DMF</td>
<td>1074</td>
<td>1480</td>
<td>N/A</td>
</tr>
<tr>
<td>S10</td>
<td>150</td>
<td>5</td>
<td>300</td>
<td>2.5H₂O/2.5DMF</td>
<td>1736</td>
<td>2394</td>
<td>1.60</td>
</tr>
<tr>
<td>S11</td>
<td>100</td>
<td>10</td>
<td>300</td>
<td>4.2H₂O/1DMF</td>
<td>91</td>
<td>128</td>
<td>N/A</td>
</tr>
<tr>
<td>S12</td>
<td>150</td>
<td>10</td>
<td>300</td>
<td>2.5H₂O/2.5DMF</td>
<td>1273</td>
<td>1757</td>
<td>1.17</td>
</tr>
<tr>
<td>S13 (replicate of S12)</td>
<td>150</td>
<td>10</td>
<td>300</td>
<td>2.5H₂O/2.5DMF</td>
<td>1282</td>
<td>1762</td>
<td>N/A</td>
</tr>
<tr>
<td>CPM-5M(1)</td>
<td>150</td>
<td>10</td>
<td>300</td>
<td>1H₂O/4.2DMF</td>
<td>2187</td>
<td>3003</td>
<td>2.55</td>
</tr>
<tr>
<td>CPM-5M(2)</td>
<td>150</td>
<td>10</td>
<td>300</td>
<td>1H₂O/4.2DMF</td>
<td>2086</td>
<td>2842</td>
<td>N/A</td>
</tr>
<tr>
<td>CPM-5(OV)</td>
<td>120</td>
<td>5 days</td>
<td></td>
<td>1/H₂O/4.2DMF</td>
<td>686</td>
<td>922</td>
<td>0.80</td>
</tr>
</tbody>
</table>
4.2.1 Experimental Design

Design-Expert 7.1.5 software (StatEase, Minneapolis, USA) was employed to investigate the effect of microwave irradiation power, synthesis time, and solvent ratio on the Langmuir and BET surface area of the synthesized CPM-5 samples. The D-optimal approach was considered to optimize the CPM-5 production conditions. Table 4-2 summarizes the experimental design equations. It was found that BET surface area was strongly influenced by reactor temperature, solvent ratio and interaction between them with the following model equations (the most significant model according to Design Expert program with Prop value less than F value = 0.0023) (F value stands for F-test statistics, Prop value stands for probability that variation between conditions may have occurred by chance), where square root transformation is applied to create a model with an F-value less than 0.0500:

\[
(BET)^{1/2} = 37.52 + 2.54 A -4.17 D + 2.84 AD
\]  
(Eq. 4-1)

Where BET is the BET surface area (m²/g), A is the microwave temperature (°C), D is the solvent ratio (v/v), AD the interaction between microwave temperature (A) and solvent ratio (D) as shown in Figure 4-1.
Figure 4-1: Result of DOE model: the effect of solvent ratio (v/v) and reactor temperature on BET surface area at reaction time of 10min and microwave power of 300W.

Table 4-2: Experimental design models. This table represents only the significant models.

<table>
<thead>
<tr>
<th>Source</th>
<th>Prop value &gt;F value</th>
<th>Model equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-Temperature</td>
<td>0.0262</td>
<td>(BET)(^{1/2}) = 28.92+9.14A</td>
</tr>
<tr>
<td>B-Time</td>
<td>0.0811</td>
<td>(BET)(^{1/2}) = 28.17-8.25B</td>
</tr>
<tr>
<td>C-Power</td>
<td>Not significant</td>
<td></td>
</tr>
<tr>
<td>D-solvent ratio</td>
<td>0.0145</td>
<td>(BET)(^{1/2})= 38.86-5.27D</td>
</tr>
<tr>
<td>A, B, C, D</td>
<td>0.0041</td>
<td>(BET)(^{1/2})=35.38+8.09A-6.17B+0.84C-3.76D</td>
</tr>
<tr>
<td>A, B, and AB</td>
<td>0.0114</td>
<td>(BET)(^{1/2})= 28.17+9.29A-8.25B+4.91AB</td>
</tr>
<tr>
<td>A, B, C, D and AC</td>
<td>0.0165</td>
<td>(BET)(^{1/2})=35.33+8A-6.07B+0.74C-3.68D+0.47AC</td>
</tr>
<tr>
<td>A, D and AD</td>
<td>0.0023</td>
<td>(BET)(^{1/2})= 37.52+2.54A-4.17D+2.8AD</td>
</tr>
<tr>
<td>A, D, B and AD</td>
<td>0.0042</td>
<td>(BET)(^{1/2})=35.7+6.85A-5.10B-3.76D+0.57AD</td>
</tr>
<tr>
<td>A, C, B, D and AD</td>
<td>0.0152</td>
<td>(BET)=35.87+6.29A-4.81B+1.28C-3.84D+1.02A</td>
</tr>
<tr>
<td>A, C, B, D, Ad and AB</td>
<td>0.0246</td>
<td>(BET)(^{1/2})=45.07-4.47A+4.65B+1.49C-7.58D-8.9AB+6.08AD</td>
</tr>
<tr>
<td>A, B, C, D and BC</td>
<td>0.0153</td>
<td>(BET)(^{1/2})=35.53+8.37A-6.4B+1.15C-4.02D+1.23BC</td>
</tr>
<tr>
<td>A, D, and BD</td>
<td>0.0049</td>
<td>(BET)(^{1/2})=38.48+1.99B-4.33D-3.98BD</td>
</tr>
<tr>
<td>A, B and BD</td>
<td>0.0043</td>
<td>(BET)(^{1/2})=35.78+7.18A-4.86B-3.78D-0.55BD</td>
</tr>
</tbody>
</table>

A: temperature (°C); B: Time (min); C: Power (W); D: Solvent ratio (v/v); AB: interaction between temperature and time of microwave irradiation; AC: interaction between temperature and power of microwave irradiation; AD: interaction between temperature and solvent ratio. Note this table represents the significant models only.
4.3 Result and Discussion

Figure 4-2 demonstrates the XRD patterns for CPM-5 samples. By comparing the XRD patterns of the synthesized samples and the literature data on CPM-5 [11], it was found that the XRD patterns are in good agreement with the reported XRD data for CPM-5. The main peaks at $2\theta = 6.2^\circ$, 10.9° and 19.7° confirm that the CPM-5 crystals were successfully synthesized under microwave irradiation. While samples S7 and S11 show small shifts in the place of the main peaks, the XRD patterns of the samples S1 to S5, S10, S9 and S12 are very similar. Moreover, the XRD pattern of sample S8 was not compatible with the reference pattern, meaning that it was not successfully synthesized. This can be explained based on the synthesis conditions, i.e., the minimum temperature and the irradiation power applied were not sufficient to start the crystallization reaction. In addition, the XRD patterns of samples S6, S7 and S11 showed CPM-5 as major crystalline phase with lower crystallinity compared to the other successful samples. This observation can be considered as a result of the higher water-to-DMF ratio and the lower synthesis temperature, i.e., 100 °C. Considering the reproducibility of the developed method for microwave synthesis of CPM-5, several replicate samples were synthesized under various conditions, which are summarized in Table 4-1.
Figure 4-2: XRD patterns of the as-synthesized CPM-5 Samples at different condition under microwave irradiation in comparison to the reference CPM-5(OV) synthesized in electrical oven.

Figure 4-3 represents the SEM micrographs of the CPM-5M (1) and CPM-5(OV) samples. Comparing these images, it can be clearly seen that CPM-5M, i.e., microwave synthesis, has a much more homogeneous morphology and particle sizes that are remarkably smaller than those of CPM-5(OV) with a magnitude of 10. In conventional hydrothermal synthesis, usually an electrothermal energy source in the walls of the reactor is used for heating; then, the reactants will be heated by means of a convection or conduction mechanism. As a result of these slow heat transfer mechanisms, it might take a much longer time for the core of the sample to achieve the target temperature (particularly for larger reactors), causing an inhomogeneous heat profile resulting in uneven particle sizes and morphology. In contrast, microwave heating is a more efficient approach because of the capability to heat the target compounds in a more selective and uniform manner. Fast
and homogeneous heating of the reactants leads to an accelerated reaction rate, high-purity products, a narrower particle size distribution and smaller particle size.

Figure 4-3: SEM micrographs of (a) CPM-5M and (b) CPM-5(OV) at two different magnifications.

Figure 4-4 shows the TGA curves for some of the CPM-5 samples, which are in good agreement with those reported in the literature [11]. The TGA curves show two distinct stages of weight loss. The first two gentle slopes of weight loss occur between 100 and 250 °C, e.g., up to 20 %, which corresponds to the evaporation of trapped solvent molecules, in which the first step shows evaporation of water molecules and the second step exhibits evaporation of DMF molecules. The observed difference in the first two steps can be attributed to the H₂O/DMF ratio of the used solvent for each synthesis. The second sharp weight loss, which occurs between 360 and 450 °C, e.g., up to 30 %, is attributed to the decomposition of the CPM-5 structure. This means that the CPM-5 synthesized by the microwave-assisted method is stable at up to 360 °C. Furthermore, the thermal stabilities of the two samples S6 and S7 are slightly higher than those of the other samples, which might
be attributed to their different crystalline structures, as can be seen from their XRD patterns and also their very low BET surface areas (see Figure 4-2 and Table 4-1).

Figure 4-4: TGA curves of some of the as-synthesized CPM-5 sample under microwave irradiation (Heating rate: 10°C/min, Atmosphere: nitrogen).

Figure 4-5 represents typical FTIR spectra of some of the as-synthesized CPM-5 samples. The FTIR spectra of the samples are in good agreement with the literature [11]. The vibration bands at 1400–1700 cm\(^{-1}\) represent the different carboxylate group (\(\nu\)(C-O) and c(C-OH)) vibration modes. The benzene ring vibrates between the 1500 and 1330 cm\(^{-1}\) bands.
Figure 4-5: FTIR spectra of some of the typical as-synthesized CPM-5 samples in comparison to the CPM-5(OV) spectrum as the reference [11].

Figure 4-6 represents the nitrogen adsorption isotherms of some of the as-synthesized CPM-5 samples. Overall, the CPM-5 samples exhibit a type-I adsorption isotherm, which is the characteristic behavior of materials of permanent microporosity. The isotherms are in good agreement with those reported in [11]. All CPM-5 samples synthesized using microwave irradiation exhibited an outstanding specific surface area, ranging from 1028 to 1736 m²g⁻¹, compared to the surface area of the oven-synthesized sample, which was 686 m²g⁻¹, i.e., in the same range as the previously reported sample [11]. This can be related to the nature of the microwave irradiation energy, as the microwave energy promotes homogenous nucleation in supersaturated mixture solutions as a result of direct and
uniform energy absorption throughout the entire volume of the solution. In addition, microwave energy leads to local superheating of the solvent, creating hot spots that nucleate crystal growth all at once, in contrast to the convectional heating method (oven) where nucleation takes place near the walls of the reactor or near dust particles. Therefore, smaller particles and a narrower size distribution can be generated, which results in a remarkably higher surface area. However, the optimal BET surface area for CPM-5M synthesized under microwave irradiation was 2187 m$^2$g$^{-1}$, which is much larger than the reported BET surface area for CPM-5 synthesized under conventional oven conditions, i.e., 686 m$^2$g$^{-1}$. Taking into account this outstandingly large surface area, the CPM-5 synthesized by the microwave-assisted method can be considered as a promising candidate for CO$_2$ adsorption as well as other gas separation applications and catalytic studies.
Figure 4-6: Nitrogen adsorption isotherms of typical activated CPM-5 samples at 77 K. The samples were activated by evacuation at 150 °C for 12 h.
Figure 4-7 demonstrates the CO$_2$ adsorption results for typical CPM-5 samples. In this study, the CO$_2$ adsorption tests were performed using the TGA technique [10], as described in the Materials and Methods section. Figure 4-8 represents the complete desorption/adsorption process for the sample CPM-5M synthesized under optimal conditions. As shown in Figure 4-8, the desorption part (steps 2 and 3) occurs in a nitrogen atmosphere and at high temperature of up to 300 °C, to make sure that all the water moisture and organic solvent is removed from the pores of the adsorbent. However, the adsorption part occurs at the desired adsorption temperature (30 °C). The CMP-5M sample showed a CO$_2$ adsorption capacity of 2.55 mmol CO$_2$/g at 1 atm and 30 °C, which represents the maximum adsorption for the CPM-5 samples prepared in this work. This high adsorption capacity of CPM-5M can be attributed to the synthesis conditions that resulted in CPM-5 samples with remarkably larger surface area. The CO$_2$ uptake of the CPM-5 samples synthesized by the microwave-assisted method in this work was in the range of 0.96–2.55 mmol CO$_2$/g, depending on the synthesis conditions, which is in the same range as for other high-surface area MOFs previously reported in the literatures (Table 4-3). It is noteworthy that CPM-5(OV) showed a lower adsorption capacity, i.e., 0.8 mmol CO$_2$/g at 30 °C and 1 atm, than any other CPM-5 sample prepared under microwave irradiation, i.e., 2.55 mmol CO$_2$/g at 30 °C and 1 atm. This large difference in adsorption capacity of the conventionally synthesized and the microwave irradiated CPM-5 samples can be attributed to the remarkably smaller particle size and the narrower size distribution of the microwave samples, resulting in a much larger surface area. Therefore, more adsorption sites are easily accessible for CO$_2$ molecules.
Figure 4-7: CO₂ adsorption of some typical activated CPM-5 samples at 30°C and atmospheric pressure.
115

Figure 4-8: Complete desorption/adsorption cycle applied to a typical sample in the TGA adsorption test (i.e. CPM-5M (1) synthesized under optimal conditions).

Table 4-3: Comparison of CO$_2$ adsorption capacity on different reported adsorbents in literature.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mmol CO$_2$/g)</th>
<th>Pressure (atm)</th>
<th>Temperature (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRMOF-1 (UTS+MW)</td>
<td>2.23</td>
<td>1</td>
<td>303</td>
<td>27</td>
</tr>
<tr>
<td>IRMOF-1 (solvothermal)</td>
<td>1.92</td>
<td>1</td>
<td>298</td>
<td>28</td>
</tr>
<tr>
<td>MOF-5 (sonochemical)</td>
<td>1.13</td>
<td>1</td>
<td>296</td>
<td>22</td>
</tr>
<tr>
<td>MOF-5 (MW)</td>
<td>1.12</td>
<td>1</td>
<td>298</td>
<td>29</td>
</tr>
<tr>
<td>CPM-5 (MW)</td>
<td>2.55</td>
<td>1</td>
<td>303</td>
<td>this study</td>
</tr>
</tbody>
</table>
4.4 Conclusions

A facile microwave-assisted synthesis method was successfully developed for the rapid and efficient manufacturing of indium-based MOFs of CPM-5 within several minutes, and its physiochemical and texture properties are very similar to those synthesized by conventional hydrothermal methods. The microwave-assisted synthesis approach resulted in a dramatic improvement by increasing the surface area of the product, increasing the CO₂ adsorption capacity and decreasing the synthesis time of the CPM-5 MOF. Microwave synthesis of CPM-5 has many benefits in comparison with conventional synthesis methods, including lower energy consumption and a very short synthesis time for larger-scale production. All these factors can play an important role to facilitate the commercialization of MOF materials.
4.5 References


5.1 Introduction

Carbon dioxide (CO\textsubscript{2}) is one of the major greenhouse gases responsible for global warming. As the excessive discharge of CO\textsubscript{2} in the atmosphere keeps increasing, mainly due to the combustion of huge amounts of fossil fuels, more serious concerns are raised with respect to its impact on the global warming and environmental damages. Carbon dioxide has risen by more than a third since the industrial revolution from (ppm) by volume to 368 ppm in 2000 [1], and 388 ppm in 2010 [1]. According to the Intergovernmental Panel on Climate Change (IPCC) [2], the atmosphere may contain up to 570 ppm of carbon dioxide in 2100 causing a rise in the mean global temperature of around 1.9 °C and an increase in the mean sea level of 3.8 m [3]. Accordingly, tremendous efforts have been invested to develop effective methods for capturing CO\textsubscript{2} from post-combustion flue gas. Aqueous alkanolamine absorbents is the most studied method to date and have been known for several decades, however it is still considered as state-of-the-art [4]. The most well known alkanolamine for CO\textsubscript{2} capture is monoethanolamine (MEA). However this technique has several significant drawbacks: The process in general requires large equipment size and intensive energy input, low carbon dioxide loading capacity, high equipment corrosion rate, and amines are subject to degradation in the presence of O\textsubscript{2}, SO\textsubscript{2}, NO\textsubscript{2} and HCl which adds additional requirements for solvent make-up and waste steam.
disposal. In addition, the main disadvantage of alkanolamines solutions is the high heat capacity which can reach the heat capacity of pure water for low concentration of the alkanolamine (e.g. 20 and 40 mol\% MEA solutions) [4,5]. According to Li et al. [6] no single technology has been identified to meet the requirements set by the DOE/NEXTL: 90% CO\(_2\) capture at less than a 35% increase in the cost electricity. Therefore, there is a crucial need for developing an alternative capture technology that can lower the operation cost and have significant advantages for energy efficiency. Accordingly, adsorption processes using solid physical adsorbents possess many potential advantages compared to the other capture technologies (i.e. chemical and physical absorption processes). These include less regeneration energy requirement, greater capacity, higher selectivity, ease of handling, minimal environmental impact and low costs. Adsorption and storage of CO\(_2\) in nanoporous adsorbents is a viable route compared to other technologies, because of their high CO\(_2\) adsorption capacities, low energy requirement [7,8], low heat capacities which present a promising way to reduce the regeneration energy penalty [4]. Recently, metal organic frameworks (MOFs) have emerged as a new class of zeolitic like porous materials that have potential industrial applications including gas separation, adsorption and storage processes [9], heterogeneous catalysis [10], and pharmaceutical manufacturing processes and drug delivery carriers [11]. Metal organic frameworks have gained significant interests as promising adsorbents, due to their outstanding properties including high specific surface areas and pore volume as well as highly diverse structural chemistry [12], and tuneable pore size from microporous (i.e. <2 nm) to mesoporous (i.e. 2–50 nm) scale [11]. According to the literature, MOF-210 and MOF-200 are the most effective MOFs for CO\(_2\) adsorption exhibiting CO\(_2\) adsorption capacity of 54.5 mmol/g (74.2 wt.\%) at 298 K and
5000 kPa [13] with extremely high BET (and Langmuir) surface areas of 4530 (10400), 6240 (10400) m²/g for MOF-200 and MOF-210, respectively. Both MOF-200 and MOF-210 exceed the CO₂ uptake of the top previously reported MOFs such as MOF-177 and MIL-101 (Cr) (33.5 mmol/g (60.8 wt.%) and 40 mmol/g (56.9, wt.%), respectively) [14,15]. NU-100 is another example of high CO₂ uptake MOFs which showed a CO₂ adsorption capacity of 52.6 mmol/g (69.8 wt.%) at 298 K and 4000 kPa and BET surface area of 6143 m²/g [16]. In addition to the high CO₂ adsorption uptake of the previous top MOFs, suitable adsorbents for CO₂ capture from flue gas should satisfy several other important criteria to compete with the present technologies, including: (1) high adsorption capacity: the CO₂ equilibrium adsorption capacity represented by its adsorption isotherm is the most important criterion to evaluate new adsorbents in terms of the capital cost of the capture system. With the knowledge of the adsorption equilibrium capacity, the amount of the adsorbent required can be calculated, consequently the volume of the adsorber vessel. The suitable adsorbent for CO₂ capture from flue gas should exhibit a minimum CO₂ adsorption capacity of 2–4 mmol/g [17]; (2) high selectivity for CO₂: the adsorption selectivity is defined as the ratio of CO₂ capacity to other bulk gas components (i.e. N₂ and O₂). The selectivity is one of the main properties of the adsorbent materials, because it has a direct impact on the purity of the CO₂ captured and consequently on the economics of the separation process [17]; (3) adequate adsorption/desorption kinetics: good adsorbent should exhibit fast adsorption/desorption kinetics under the operating conditions and high rate of adsorption; (4) stability during repeated adsorption/desorption cycling: Stability is a crucial property of an adsorbent, because it determines the lifetime of the adsorbents and the frequency of their replacement; (5) mechanical strength: suitable adsorbents should
demonstrate stable microstructure and morphology under several operating conditions, such as high volumetric flow rate of flue gas, vibration, and temperature. In addition, good adsorbents should tolerate presence of moisture and other impurities in the feed (i.e. water vapor, O\textsubscript{2} and SO\textsubscript{2}). Otherwise, the CO\textsubscript{2} adsorption process will require large sorbent makeup rate. As a result, mechanical strength of adsorbents has direct impact on the overall economics of the CO\textsubscript{2} separation process; (6) low cost: the cost of an adsorbent is one of the most important characteristics. According to a study performed by Tarka et al. [18] on the sensitivity analysis of adsorbents for economic performance, a cost of $5/kg of adsorbent offers a very good picture and $15/kg of adsorbent is not economical. Thus, $10/kg of adsorbent is considered economical for CO\textsubscript{2} capture process. Finally, a key challenge in the CO\textsubscript{2} adsorption process is to develop adsorbents with high adsorption capacity for CO\textsubscript{2} at lower partial pressures. Zongbi Bao et al. [19] have reported the CO\textsubscript{2} adsorption capacity of 8.61 mmol/g (27.5 wt.%) at 298 K and low pressure of 100 kPa on Mg-MOF-74. Furthermore, at room temperature and pressure of 100 kPa, MOF-5 and MOF-177 have exhibited CO\textsubscript{2} adsorption capacity of 1.2 mmol/g (4.5 wt.%) and 1.7 mmol/g (7 wt.%), respectively [20,21]. Recently, CPM-5 synthesized under microwave irradiation has proven to be a promising candidate for CO\textsubscript{2} adsorption due to its high CO\textsubscript{2} adsorption capacity of 2.55 mmol/g at room temperature and low pressure of 100 kPa [22].

The objective of the present work is to determine the adsorption equilibrium isotherms, kinetic and diffusion mechanisms, isosteric heat of adsorption and diffusivity of CO\textsubscript{2} in CPM-5 at three different temperatures of 273 K, 298 K, and 318 K. All the CO\textsubscript{2} adsorption experiments in this work were carried out at low pressures (i.e. up to 105 kPa) to
evaluate the potential of CPM-5 for application as adsorbent for CO₂ capturing from flue gas at low pressure.

5.2 Experimental

5.2.1 Synthesis of CPM-5

All chemicals including indium (II) nitrate hydrate (In(NO₃)₃·xH₂O; 99.5%, J.T Baker; USA), 1,3,5 benzenetricaboxylic acid (H₃BTC; 99%, Aldrich, USA), and N-dimethylformamide (DMF; 99.9%, Aldrich, USA), were used as purchased without further purification. The CPM-5 was synthesized following our previously reported procedure [22] using microwave irradiation as heating source (Discovery system model of CEM Laboratory Microwave, USA). The detailed synthesis procedure can be found elsewhere in [22]. The purity of the sample was confirmed by the powder X-ray diffraction.

5.2.2 Characterization of CPM-5

Crystallinity of the products was examined by X-ray powder diffraction (XRPD) technique using a Rigaku–MiniFlex powder diffractometer (Japan; CuKα = 1.54059 Å) over 2θ range of 5°–40° with step width of 0.02°. Surface area of the adsorbents was measured by BET technique (Micromeritics ASAP 2010, USA). Further characterization of the produced CPM-5 sample including, morphology thermogravimetric analysis (TGA) curve, N₂ adsorption/desorption isotherms, and Fourier Transform Infrared (FTIR) spectra can be found in the authors’ previous article [22].

5.2.3 CO₂ Adsorption Study

Adsorption equilibrium of CO₂ and N₂ in CPM-5 was measured volumetrically using a BET instrument (Micromeritics ASAP 2010, USA) at CO₂ pressure up to 105 kPa and three temperatures of 273, 298, and 318 K for CO₂ and 273, 298 K for N₂. Ultra high pure
CO₂ and N₂ (Praxair Canada Inc.) were used as received for the adsorption measurements and backfill gas, respectively. The temperature was controlled using a circulating jacket (ThermoNeslab; Newington, NH, USA). The rate of adsorption (ROA) of CO₂ on CPM-5 was also measured using the ASAP 2010 system equipped with the “Rate of Adsorption” software at the same time when the adsorption equilibrium data were collected. All the diffusion data were measured at stepped pressure increments, from 0 to 105 kPa. For each increment pressure the ROA software reports the amount adsorbed as a function of time. The amount adsorbed is converted into transient adsorption uptakes to generate the adsorption kinetics. The adsorption equilibrium amount is considered as the final adsorption amount at the terminal pressure and temperature. To do the measurement, known amounts of samples (e.g. 90–100 mg) were loaded into the BET sample tube and degassed under vacuum (10⁻⁶ kPa) at 423 K overnight. Ultra pure helium gas (Praxair Canada Inc.) was used to measure the free space. To study the effect of re-generation on the used adsorbent, the spent sample was degassed again for the second cycle at 423 K under vacuum (10⁻⁶ kPa) for 5 h.

The Freundlich isotherm model was used to correlate the adsorption isotherms at different tested temperatures. The Freundlich isotherm equation fitted well the experimental data with regression coefficients greater than 0.99. The Freundlich isotherm can be written as following:

\[ q = K p_i^{1/n} \]  

(Eq. 5-1)

where \( q \) is the adsorbed amount (mmol/g), \( p_i \) is the equilibrium pressure (kPa), and \( K \) ((mmol/g) (kPa⁻¹/\( n \))), \( n \) are constants for a given adsorbent and adsorbate at particular
temperature. Estimates of $K$ and $n$ can be obtained from the experimental data of CO$_2$ adsorption isotherms using the intercept and slope of a linear Freundlich plot of $\ln(q)$ versus $\ln(p_i)$. The adsorption isotherm parameters for Freundlich equation are listed in Table 5-1.

Table 5-1: Freundlich Isotherm Equation Parameters for CO$_2$ adsorption on CPM-5

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K$ ((mmol/g) (kPa$^{-1/n}$)),</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>0.143</td>
<td>1.552</td>
<td>0.9986</td>
</tr>
<tr>
<td>298</td>
<td>0.049</td>
<td>1.214</td>
<td>0.9992</td>
</tr>
<tr>
<td>318</td>
<td>0.008</td>
<td>0.984</td>
<td>0.9982</td>
</tr>
</tbody>
</table>

Working capacity or delta loading, $\Delta q$ is an important parameter that determines the economics of Pressure Swing Adsorption process (PSA). To increase the CO$_2$ working capacity the adsorber volume must be smaller. Therefore, the capital and capture cost will decrease. Working capacity is defined as the difference in the amount of component (CO$_2$) that needs to be adsorbed in moles per kilogram of adsorbent material, at the adsorption pressure ($q_{\text{CO}_2\text{ adsorption}}$) and the amount adsorbed at the desorption/evacuation pressure ($q_{\text{CO}_2\text{ desorption}}$) (Eq. 5-2) [17]. The adsorption pressure could range between 0.1 and 10 MPa, and the desorption pressure could range from 0.01–0.1 MPa [23],

$$\Delta q_{\text{CO}_2} = \Delta q_{\text{CO}_2\text{ adsorption}} - \Delta q_{\text{CO}_2\text{ desorption}}$$

(Eq. 5-2)

5.3 Results and Discussion

5.3.1 Characterization of synthesized CPM-5

CPM-5 is a highly porous indium based metal organic framework with a surface area of 2187 m$^2$/g [22]. CPM-5 consists of In$_3$O clusters as metal centres connected by 1, 2, 3-benzenetricarboxylic acid (H$_3$BTC) as a linear organic linker. In addition, CPM-5 has three
unique cage-within-cage based porous structures which contribute to a high CO₂ uptake capacity. Figure 5-1 presents the structure of the CPM-5 particles [24]. To the best of the authors’ knowledge, CPM-5 has not been studied in details for CO₂ adsorption including adsorption equilibrium isotherm at different temperatures (i.e. 273 K, 298 K and 318K), adsorption kinetics, isosteric heat of adsorption, and diffusivity of CO₂ in CPM-5.
Figure 5-1: Structures of $\text{In}_{12}@\text{In}_{24}$ cage CPM-5. The green solid lines represent BTCs. [24]
One of the main drawbacks for industrial scale applications of most of MOF compounds is low physico-chemical stability of these materials when exposed to air and water vapour. Thus this instability may limit their industrial applications. Many zinc-based MOFs such as MOF-5 and MOF-177 decompose very easily upon exposure to air and moisture; therefore they have to be stored under vacuum or controlled atmosphere. The stability of MOF-5 upon exposure to air was studied by Yang et al. [25] and Kaye et al. [26]. It was shown that decomposition of MOF-5 structure was complete after one week of exposure and qualitatively a different XRD pattern was obtained. Figure 5-2 demonstrates the XRPD patterns of the CPM-5 samples over 4 weeks of exposure to the environment humidity at room temperature. According to the XRPD pattern, however, the synthesized CPM-5 was shown to have a very stable structure after exposure to ambient conditions for several weeks.

It can be seen that the main peaks of the samples well matched with previously published XRPD pattern for CPM-5 prepared under microwave irradiation [22] (Figure 5-2). It is found that the XRPD pattern remains unchanged for the aged samples. This reveals that the CPM-5 structure is stable under laboratory condition (296 K and relative humidity of 62%) for several weeks. Furthermore, shelf life of the CPM-5 aged for several weeks was studied by measuring the effective surface area by BET. The surface area of the fresh CPM-5, 2 weeks old and 4 weeks old samples were 2187 cm$^2$/g, 2085 cm$^2$/g and 2050 cm$^2$/g, respectively, confirming the durability of samples in the normal lab environment. Accordingly, CPM-5 can be considered as a durable and attractive MOF candidate with long shelf life for practical industrial application.
Figure 5-2: XRD patterns of the microwave-synthesized CPM-5 prepared in this study.

5.3.2 CO$_2$ Adsorption Equilibrium

Experimental and modelled CO$_2$ adsorption isotherms at three different temperatures of 273 K, 298 K, and 318 K under CO$_2$ pressure of 0–105 kPa are plotted in Figure 5-3a. The experimental N$_2$ adsorption isotherms are plotted in Figure 5-3b at 273 and 298 K under N$_2$ pressure of 0–105 kPa. In general, it was observed that the amount of adsorbed gases decrease with increasing temperature for both gases as a result of higher thermal energy of the molecules at higher temperatures. Moreover, the CO$_2$ adsorption capacity is
higher than that for N₂ at all temperatures due to the greater quadrupole moment and polarization of CO₂ (13.4 × 10⁻⁴⁰ cm² and 26.3 × 10⁻²⁵ cm³, respectively) compared to N₂ (4.7 × 10⁻⁴⁰ cm² and 17.7 × 10⁻²⁵ cm³, respectively) [27] result in higher affinity of the surface of the material for CO₂. According to the isothermal data, CO₂ uptake at 273 K, 298 K and 318 K under 105 kPa of feed pressure were 3 mmol/g (13.2 wt.%), 2.3 mmol/g (10.1 wt.%), and 1 mmol/g (4.3 wt.%), respectively. However the N₂ uptake at 273 K and 298 K and pressure of 105 kPa were 0.86 and 0.4 mmol/g, respectively.
Figure 5-3: CO$_2$ adsorption isotherms at different adsorption temperatures, 273 K, 298 K and 318 K Experimental data; (open symbols). Frenundlich isotherm model data (solid line), desorption isotherm data (filled symbols), (b) N$_2$ adsorption isotherms at different adsorption temperatures, 273 K, and 298 K Experimental data; (open symbols), desorption isotherm data (filled symbols), and pressures up to 105 kPa.

The CO$_2$ adsorption uptake of CPM-5 at 298 K under 105 kPa is 2.3 mmol/g (10.1 wt.%) higher than those of the published results at similar conditions of MOF-5 (i.e. 1.2 mmol/g (4.5 wt.%) and MOF-177 (i.e. 1.7 mmol/g (7 wt.%)), respectively, [20,21] and
in the same range of MIL-53(Al) (i.e. 10.6 wt.%), UMCM-150 (i.e. 10.2 wt.%), and Ni-STA-12 (i.e. 9.9 wt.%) [28–30]. However, CPM-5 showed a CO₂ adsorption capacity lower than functionalized and open metal sites MOFs such as Mg-MOF-74 8.61 mmol/g (i.e. 27.5 wt.%) [19], HKUST-1 6.8 mmol/g (i.e. 27 wt.%) [31], NH₂ MIL-53(Al) (i.e. 12 wt.%) [28]. This comparison can be explained in more detail based on the framework structure of the CPM-5, the CPM-5 material composed of negatively charged single metal binding blocks \{\text{In(CO}_2\}_4\} and positively charged trimeric clusters \{\text{In}_3\text{O}\} lead to three unique cage within cage based porous materials in which a large Archimedean cage donated as the \text{In}_{24} encapsulates a small Archimedean cage donated as the \text{In}_{12} cage (see Figure 5-1(a,b)). The overall 3D structure shown in Figure 5-1b can be explained as centered cubic packing of the larger \text{In}_{24} cages each of which contains one \text{In}_{12} at the center. This unique core–shell type \text{In}_{12}@\text{In}_{24} 3D structure partition the pore size into small charge separated domains that can enhance the adsorption of small gas molecules such as CO₂ through better size match and stronger charged induced forces. Therefore CPM-5 shows a higher CO₂ adsorption than MOF-5 and MOF-177. However, still some functionalized MOFs as mentioned before show higher CO₂ adsorption. For example: Mg-MOF-74 features high density of exposed Mg²⁺ cation sites. Those strong adsorption sites have a high affinity to CO₂ uptake at low pressures [32]. Mason et al. [32] showed that Mg-MOF-74 CO₂ adsorption isotherm exhibited steep increase in the CO₂ uptake at low pressures due to the presence of coordinatively unsaturated Mg²⁺ sites on the surface of the metal. As temperature increased the isotherm data become nearly linear beyond 120 °C. The amine functional group in NH₂ MIL-53(Al) exhibits strong CO₂ binding sites especially at low pressure relevant to flue gas separation. As a result, the open metal sites
and functionalized frameworks show enhanced CO$_2$ adsorption selectivity compared to CPM-5 (see section Section 5.3.3).

The working capacity of CPM-5 at pressure range from adsorption pressure of 100 kPa and desorption pressure of 10 kPa is 2.4, 2 and 0.91 mmol/g at 273, 298, and 318 K, respectively.

Figure 5-3 shows a gradual increase in the adsorbed amount of CO$_2$ with increasing the CO$_2$ pressure without reaching a plateau in the adsorption isotherm. Therefore, CPM-5 can adsorb more CO$_2$ at higher pressures. In addition, it is observed that the adsorption and desorption isotherms match each other, indicating that the adsorption process is reversible [21] as shown in Figure 5-3.

5.3.2.1 Adsorption Cycles

In order to investigate the regeneration process of the CPM-5 adsorbents and its efficiency, the CPM-5 was tested under four repeated adsorption-desorption cycles at 273 K and 298 K as indicated in Figure 5-4. The CPM-5 samples were degassed overnight under vacuum (10$^{-6}$ kPa) at 423 K after each adsorption test to regenerate the CPM-5 for the next CO$_2$ adsorption cycle. The decrease in the CO$_2$ adsorption capacity is negligible even after four repeated adsorption cycles at both tested temperatures of 273 and 298 K revealing that CPM-5 can be considered as a promising candidate for CO$_2$ adsorption. The reduction in the maximum CO$_2$ adsorption capacity from first cycle to the fourth cycle ranges from 0.36 wt% to 1.6 wt% at 273 K and from 0.31 wt% to 0.62 wt % at 298 K.
5.3.3 Selectivity

The selectivity factor, $S_{ads}$ was evaluated using the most basic method based on the experimental single component gas adsorption isotherms [4]. The selectivity factor is defined as the molar ratio of the adsorbed amount at the relevant partial pressure of the gases for post combustion CO$_2$ capture (i.e. 0.15 bar $P_{CO2}$ and 0.75 bar $N_2$). The selectivity should be normalized to the composition of the gas mixture as given by the following equation:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$  \hspace{1cm} (Eq. 5-3)

where $S_{ads}$ is the selectivity factor, $q_i$ (mmkol/g) represents the quantity adsorbed of component $i$, and $p_i$ (kPa) represents the partial pressure of component $i$. 

Figure 5-4: CO$_2$ adsorption isotherms on CPM-5 using multiple cycles at (a, b) 273 K, (b) represents the adsorbed amount of CO$_2$ as a function of number of cycles at 273 K and (c, d) 298 K, (d) represents the adsorbed amount of CO$_2$ as a function of number of cycles, error bar presented by 5% error for three repeated runs.
The CPM-5 has a selectivity factor of 14.2 and 16.1 at 273 and 298 K, respectively. Comparing the CPM-5 selectivity factor value with the literature, it was found that CPM-5 exhibited higher selectivity factor than MOF-177 (i.e. $S_{ads} = 4$) and MOF-253 (i.e. $S_{ads} = 9$) [4] at the same conditions. On the other hand CPM-5 showed lower selectivity compared to the top Mg-MOF-74 featuring open metal sites in literature (i.e. $S_{ads} = 44$) [4]. The better selectivity of Mg-MOF-74 compare to CPM-5 can be related to the presence of Mg$^{2+}$ sites which exhibits a high affinity to CO$_2$ as discussed in details previously (see Section 5.3.2).

5.3.4 CO$_2$ Adsorption Kinetics

Kinetics of CO$_2$ adsorption on the CPM-5 samples were studied volumetrically in the pressure range of 5 to 105 kPa at three different temperatures of 273, 298, and 318 K by means of a Micrometrics BET instrument (ASAP 2010) using the ROA software. The diffusivity of CO$_2$ in CPM-5 was calculated experimentally by correlating the diffusion time with the fractional adsorption uptake ($m_t/m_\infty$) based on the classical micropore diffusion model as shown in Eq. 5-2 with only 99% > ($m_t/m_\infty$) > 70% [33].

\[
1 - \frac{m_t}{m_\infty} = \frac{6}{\pi^2} \exp \left[ -\frac{\pi^2 D_c t}{r_c^2} \right]
\]

(Eq. 5-4)

$r_c$ is the particle radius (m), the diffusivity (D$_c$, m$^2$/s) can be calculated from the slope of linear plot of ln (1- $m_t/m_\infty$) versus time ($t$) at a given pressure.

The adsorption kinetics is one important factor in evaluating the suitability of the adsorbent for gas adsorption applications, because it controls the cycle time of a fixed bed adsorption system and has an impact on the amount of adsorbent required and the size of the adsorber column. Figure 5-5 shows the fractional CO$_2$ adsorption curves on CPM-5 at 273 K and
298 K and pressure of 105 kPa. The kinetic plots at other pressures have similar shape. From Figure 5-5 it can be found that the CPM-5 reaches the CO₂ saturation capacity within 3–10 s depending on the applied temperatures and pressures. CO₂ diffusivity in CPM-5 obtained by regressing the uptake curves with Eq. 5-4 at three temperatures and pressure of 105 kPa are summarized in Table 5-2. According to the data, the CO₂ diffusivity in CPM-5 increases with increasing temperature and it ranges from 1.86 × 10⁻¹² to 7.87 × 10⁻¹² (m²/s). In Table 5-3, CO₂ diffusion data in CPM-5 are compared with those of other adsorbents reported in literature under similar adsorption conditions. As it is shown in Table 5-3, the CPM-5 sample developed in this work exhibits a modest adsorption for CO₂ compared to other adsorbents. While the CO₂ diffusivity in CPM-5 is higher than MOF-5; however, MOF-177 exhibited higher diffusivity for CO₂. This difference can be related to the differences in the particle size distributions of the compared adsorbents.
Figure 5-5: CO$_2$ adsorption kinetics at (a) 298 K and (b) 273 K on CPM-5(1); solid line, (modeling data) filled squared, (experimental data) and pressure up to 105 kPa.

Table 5-2: CO$_2$ diffusivity in CPM-5 at three different temperatures and pressures up to 105 kPa.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>D$_{CO2}(10^{12}$ m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>1.86</td>
</tr>
<tr>
<td>298</td>
<td>7.04</td>
</tr>
<tr>
<td>318</td>
<td>7.87</td>
</tr>
</tbody>
</table>
Table 5-3: Comparison of experimental CO$_2$ diffusivity with the previously reported diffusivity Data in literature.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature (K)</th>
<th>$D_{CO2}$ (m$^2$/s)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPM-5</td>
<td>298</td>
<td>7.04 x 10$^{-12}$</td>
<td>This work</td>
</tr>
<tr>
<td>MOF-5</td>
<td>296</td>
<td>7.9 x 10$^{-13}$</td>
<td>[36]</td>
</tr>
<tr>
<td>MOF-177</td>
<td>298</td>
<td>2.3 x 10$^{-9}$</td>
<td>[21]</td>
</tr>
</tbody>
</table>

**5.3.5 Isosteric Heat of Adsorption**

Isosteric heat of adsorption is an important parameter for the design of practical gas separation processes such as pressure swing and thermal swing adsorption. It determines the extent of adsorbent temperature during the adsorption (exothermic) process. The isosteric heat of adsorption at a given adsorption amount can be obtained from the Clausius-Clapeyron equation (Eq. 5-5) as follows:

$$\frac{Q_{st}}{-RT^2} = \left(\frac{\partial \ln P}{\partial T}\right)_{n_a}$$

(Eq. 5-5)

where $Q_{st}$ is isosteric heat of adsorption (kJ/mol), $P$ is the pressure (kPa), $T$ is the temperature (K), $R$ is the universal gas constant, $n_a$ is the adsorbed amount (mmol/g).

Integrating Eq. 5-5 gives the following equation (Eq. 5-6):

$$\ln P = \frac{Q_{st}}{RT} + C$$

(Eq. 5-6)

The heat of adsorption can be calculated from the slope of linear plot of $\ln P$ versus $1/T$ at a given adsorption amount [32]. The CO$_2$ adsorption isotherm at 273, 298, and 318 K were used to measure the heat of adsorption. Figure 5-6 illustrates the variation of $Q_{st}$ on CPM-5 as a function of adsorbed amount of CO$_2$. It is observed from Figure 5-6 that,
isosteric heat of adsorption decreases with loading indicating strong interaction between the quadrupole momentums of carbon dioxide with the adsorbent surface. The initial $Q_{st}$ of CO$_2$ for CPM-5 is 36.1 kJ/mol, which is higher than HKUST-1 metal organic framework (24.2 kJ/mol) [34] and in the same range of 13X zeolite and MOF-5 (33–34.1 kJ/mol), however it is lower than other MOFs materials featuring amine functionality or open metal organic frameworks such as MIL-100(Cr) (i.e. 62 kJ/mol) [35], NH$_2$-MIL-53(Al) (i.e. 50 kJ/mol) [28].

Figure 5-6: Heat of adsorption of CO$_2$ on CPM-5 at three different temperatures 273, 298 and 318 K.
5.4 Conclusions:

This study has revealed that CPM-5 synthesized under microwave irradiation is an attractive candidate for CO$_2$ adsorption due to its high CO$_2$ adsorption capacity of 3 mmol/g (or 13 wt.%) at 273 K and pressure of 105 kPa, stability under ambient conditions for several weeks, and high surface area of 2187 m$^2$/g. The initial heat of adsorption was estimated to be 36.1 kJ/mol from the corresponding isotherms at 273 K, 298 K, and 318 K. The Freundlich adsorption equation fits well the isotherm data. The adsorption kinetics curves were obtained experimentally. The CO$_2$ diffusivity in CPM-5 estimated from the adsorption kinetic data at CO$_2$ pressures up to 105 kPa are $1.86 \times 10^{-12}$, $7.04 \times 10^{-12}$, and $7.86 \times 10^{-12}$ m$^2$/s at 273 K, 298 K and 318 K.
5.5 References


Chapter 6

MATHEMATICAL MODELING AND EXPERIMENTAL BREAKTHROUGH CURVES OF CARBON DIOXIDE ADSORPTION ON METAL ORGANIC FRAMEWORK CMP-5

6.1 Introduction

The release of harmful greenhouse gases such as CO₂, CH₄, and N₂O into the environment is a growing concern for the world’s climate change. Carbon dioxide is the paramount contributor to the global warming phenomenon. About 60% of global warming attributed to CO₂ emissions [1]. More than 22 billion tons of the annual emission of CO₂ gas is resulted from the excessive human activities such as fossil fuel combustion, industrial processes and transportations [2]. Fossil fueled power plants are the largest potential source of CO₂ emission. Fossil fuels provide 81 percent of the world’s commercial energy supply [3]. Fossil fuels produce nearly 3x10¹⁰ metric tons (30 petagram) of carbon dioxide annually. About three-quarters of the increase in atmospheric carbon dioxide is attributed to burning fossil fuels [4]. The current levels of CO₂ concentration in the atmosphere have increased by more than 35% since the industrial revolution, i.e. from 280 ppm by volume in pre-industrial times to 368 ppm in 2000 [3], and 388 ppm in 2010 [3]. According to the Intergovernmental Panel on Climate Change (IPCC) [4], the atmosphere may contain up to 570 ppm of carbon dioxide in 2100 causing a rise in the mean global temperature of around 1.9 °C and an increase in the mean sea level of 3.8 m [5]. Therefore, effective capture and sequestration of CO₂ from post-combustion
effluent such as flue gas is of immense importance to allow humankind to continue burning fossil fuels for years to come until substituting of alternative renewable energies are feasible at competitive and reasonable costs [6].

In this regards, scientists are trying to develop effective systems for CO$_2$ removal from post-combustion flue gas by combining the high capacity and selectivity, fast kinetics, mild conditions for regeneration, and tolerance to moisture with minimal cost [7]. Liquid-phase gas absorption using alkanolamine solution (e.g. mono and tri-ethanolamine), is one of the most developed and applied technology for CO$_2$ capturing in industrial scales for decades [6]. Some of the drawbacks of this process can be expressed as the high energy required for the regeneration of the degraded amines under the high temperature treatments, severe corrosion of the equipment, and environmental issues related to the alkanolamine volatility [9, 10]. Porous membrane is another technology that is recently emerged for CO$_2$ capturing. The first implementation of membranes technology for gas separation was reported in the 1980s and since then membranes have been widely used in many industrial separation processes. Membrane based technologies have some disadvantages such as low stability under the reforming environment and low separation factor. Since membranes cannot achieve high degree of separation, multiple stages are required. Nevertheless, membrane technologies are still under development phase [11]. In order to overcome the techno economical restrictions of the above-mentioned technologies, search for alternative technologies have been prompted. Adsorption in porous adsorbents is considered as an alternative viable approach for CO$_2$ capturing. Adsorption into solid porous adsorbents is an attractive technology to improve or substitute the current CO$_2$ absorption technologies due to their high CO$_2$ adsorption capacities, simple and easy to control process, low energy
consumption, and superior energy efficiency [7, 9, 12]. Many adsorbents have been
developed and studied for CO₂ capturing such as zeolites [13], activated carbons [14],
modified mesoporous silica [15]; however the common drawbacks of these conventional
adsorbents are: high energy consumption for regeneration, low productivity [16] and low
CO₂ capacities.

New porous materials with higher adsorption capacity and selectivity are needed to
improve the CO₂ separation and storage process. Metal organic frameworks (MOFs) have
emerged as a new class of crystalline porous materials composed of self-assembled
metallic species and organic linkers to form three dimensional network structure [16,17].
MOFs are renowned materials having remarkable high specific surface area, highly divers
structural chemistry [16], and controlled pore size and shape from microporous (i.e.
Angstrom) to mesoporous (i.e. nanometers) scale [20]. MOFs are under extensive studies
for potential divers industrial applications from gas separation, adsorption and storage
processes [18], to heterogeneous catalysis [19], pharmaceutical manufacturing processes
and drug carriers [20].

Review of the literature shows that most studies on the MOFs as adsorbents for CO₂
adsorption are performed using pure CO₂ under high pressure and often at room or sub-
ambient temperature. It has been reported that MOF-117, MIL-101 and IRMOF-1 exhibit
exceptional CO₂ storage capacity at high pressure e.g. 33.5 mmol/g at 40 bar, 40 mmol/g at
5 bar, and 21.7 mmol/g at 3 bar, respectively [21, 22]. However, their capacities are
dramatically reduced under dynamic conditions and sub-atmospheric pressure. More
recently, Zongbi Bao et al. [23] and Sabouni et al.[24] have reported the CO₂ adsorption
capacity of 8.61 mmol/g at 298 K and low pressure of 1 bar on Mg-MOF-47 and 3 mmol/g at room temperature and low pressure of 1 bar, respectively. To the best of our knowledge, virtually no research work has been conducted to examine the dynamic gas adsorption and kinetic properties of MOFs when exposed to a mixture of gases as would be the actual case of power plant flue gas streams [25]. In addition, the number of studies that have examined the experimental operating conditions of the breakthrough data compared with mathematical modeling of CO$_2$ capturing onto the MOFs is limited [26-28]. Accordingly, it is essential to know the dynamic adsorption capacity of CO$_2$ onto MOFs, which can be measured by exposing the MOF materials to a gas mixture and detect the appearance of an arbitrary “breakthrough” value, which is 10% of the feed concentration in this study.

The metal organic framework that is studied in the present work is CPM-5, which is a highly porous indium based metal organic framework with a surface area of 2187 m$^2$/g [29]. CPM-5 consists of In$_3$O clusters as metal centres connected by 1, 3, 5 benzenetricaboxylic acid (H$_3$BTC) as a linear organic linker. In addition, CPM-5 has three unique cage-within-cage based porous structures which contribute to a high CO$_2$ uptake capacity. In our previous work, it has been shown that CPM-5 exhibits a high CO$_2$ adsorption of 2.55 mmol/g, at 298K and 1 bar with an isosteric heat of adsorption of 36.1 kJ/mol according to the isothermal adsorption experimental data [24].

To the best of our knowledge, no literature has reported the dynamic adsorption capacity of CO$_2$ onto CPM-5 from experimental breakthrough data coupled with the mathematical modeling.
The main objective of the present work is to measure the dynamic adsorption of CO$_2$ onto CPM-5 and compare the experimental results with the mathematical modeling of the breakthrough curve using COMSOL program. Furthermore, the effect of several experimental operating conditions on the breakthrough value are studied. The experimental breakthrough curves are obtained under different operational conditions including: a) the various flow rates of the gaseous mixture of CO$_2$ and N$_2$ (i.e. 8 mL/min and 32 mL/min), b) feed concentration of CO$_2$ (i.e. 12.5 % and 25 % by volume), and c) adsorption temperature (i.e., 298 K and 318 K).

6.2 Experimental

6.2.1 Synthesis of CPM-5

The CPM-5 was synthesized and activated according to the procedure reported previously [29] using microwave irradiation as heating source (Discovery system model of CEM Laboratory Microwave, USA). A mixture of In(NO$_3$)$_3$.xH$_2$O (0.2 g), and 1, 3, 5 benzenetricaboxylate (0.17 g) was dissolved in H$_2$O/DMF (1/4.2 v/v) solvent. After mixing and dissolving the reactants using a magnetic stirrer, the clear solution was transferred into a 40 mL glass reactor and irradiated at 300 W microwave for 10 min at 423 K. After cooling to room temperature the produced crystallites were separated by means of centrifugation at 20,000 rpm for 20 min. CPM-5 washed with fresh 1:1 solution of H$_2$O/DMF for three times by repeated dispersing and centrifuging to remove all of the un-reacted chemicals. Subsequently, the CPM-5 powders were dried at 373 K for 1 h in an electrical oven and then characterized.
6.2.2 Characterization of CPM-5

The CPM-5 structure was confirmed by powder X-ray diffraction (XRPD) analysis using a Rigaku – MiniFlex powder diffractometer (Japan; CuK$_\alpha$ = 1.54059 Å) over 2θ range of 5° to 40° with step width of 0.02°. Adsorption equilibrium of CO$_2$ on CPM-5 was measured volumetrically using a BET instrument (Micromeritics ASAP 2010, USA) at CO$_2$ pressure up to 1 bar and two temperatures of 298, and 318 K. Ultra high pure CO$_2$ and N$_2$ (Praxair Canada Inc.) were used as received for the adsorption measurements and backfill gas, respectively. Further characteristic data of the as-synthesized CPM-5 including the crystallites morphology, shape and size as well as its FTIR spectrum were reported in the author’s previous work (24).

6.2.3 CO$_2$ Adsorption Apparatus and Breakthrough Measurements

A simplified scheme of the system (BTRS-Jr-PC; Autoclave engineers, Division of Sap-tite, Inc., Erie, PA, USA) used to conduct the breakthrough experiments is shown in Figure 6-1, Supportive Information. The experimental setup consisted of: 1) a steel fixed bed adsorbent reactor with internal diameter of 0.00792 m and length of 0.153 m that was equipped with an inlet filter, an outlet filter and a full-length internal thermo-well; 2) a bypass line for measuring the feed concentration; 3) flow-meters/controllers to control the flow-rates of the inlet gases; 4) a gas mixture; the inlet gases mix thoroughly before flowing through the adsorbent bed, 5) and an on-line gas chromatograph (CP-3800, Varian Inc., Lake Forest, CA) equipped with a TCD detector, and a CP7429 capillary column to measure the CO$_2$ concentration. CO$_2$ (99.995%) and N$_2$ (99.995 %) were used as feed gas mixture (Praxair Canada Inc., Sarnia, ON, Canada). The experiments were conducted as follows: 100 mg of CPM-5 were fixed between glass wool plugs in the reactor. The CPM-5
adsorbent was activated in the N$_2$ flow of 100 mL/min at 298 K until no other gases were detected in the reactor outlet. The N$_2$ flow was set to the desired flow according to the experimental conditions (e.g., 7 mL/min in the case of 12.5 wt. % CO$_2$). The CO$_2$ was introduced at a flow rate of 1 mL/min resulting in a gas mixture with CO$_2$ content of 12.5 % by volume. The other CO$_2$ feed concentration (i.e., 25% mixture) was obtained in the same manner. The breakthrough value was defined to be at 10% of the CO$_2$ feed concentration. In order to fully regenerate the saturated adsorbent for the next experiment the column temperature was raised to 373 K and N$_2$ flow of 100 mL/min was purged for 1 h. The experimental conditions for the breakthrough curve are summarized in Table 6-1.

![Figure 6-1: Schematic diagram of the system used for breakthrough experiments](image-url)
Table 6-1: Breakthrough Experimental conditions

<table>
<thead>
<tr>
<th>Run</th>
<th>Total flow rate (mL/min)</th>
<th>Adsorption Temperature (K)</th>
<th>CO₂ Feed Concentration % (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.00</td>
<td>298</td>
<td>25.00</td>
</tr>
<tr>
<td>2</td>
<td>8.00</td>
<td>318</td>
<td>25.00</td>
</tr>
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<td>3</td>
<td>8.00</td>
<td>318</td>
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<tr>
<td>8</td>
<td>32.00</td>
<td>318</td>
<td>12.50</td>
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</table>

6.3 Breakthrough Curve Model

The fixed bed adsorber packed with porous spherical particles of CPM-5 was subjected to an inert gas flows in a steady-state. To formulate breakthrough curves for this system, the following mathematical model was developed based on the following assumptions: 1) the flow pattern is described by the axially dispersed plug flow model. 2) The system operates under isothermal conditions. 3) the frictional pressure drop through the column is negligible. 4) the adsorption equilibrium isotherm is described by Freundlich isotherm. 5) the adsorbent particles are spherical and homogenous in size and density. 6) The velocity of the gas is constant. The driving force is the concentration gradient of the adsorbed phase and the diffusion coefficient is constant. Under the above assumptions, a set of governing scaled equations and appropriate scaled initial and boundary conditions can be established as follows:
Assuming radial effects are negligible, an unsteady state material balance on the gas phase:

\[
QC|_z - QC|_{z+dz} + A \left[ -D_L \frac{\partial C}{\partial z} \right]_z - A \left[ -D_L \frac{\partial C}{\partial z} \right]_{z+dz} = \varepsilon \frac{\partial C}{\partial t} Adz + \left( \frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial q}{\partial t} Adz \quad \text{(Eq. 6-1)}
\]

Divide by \(Adz\) and taking limits \(\vartheta = \frac{q}{A}\) and multiply by (-):

\[
\vartheta \frac{\partial C}{\partial \tau} - D_L \frac{\partial^2 C}{\partial \tau^2} + \frac{\partial C}{\partial \tau} + \left( \frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial q}{\partial \tau} = 0 \quad \text{(Eq. 6-2)}
\]

Solid phase:

\[
\frac{\partial q}{\partial \tau} = \frac{3k_c}{r_c} (q^* - q) \quad \text{(Eq. 6-3)}
\]

Dimensionless:

\[
y_i = \frac{q_i}{Q}; \quad x_i = \frac{C_i}{C_o}; \quad z = \frac{l}{L_o}; \quad t = \frac{\tau v}{L_o}
\]

Dimensionless material balance:

\[
\frac{\partial x_i}{\partial z} - \frac{1}{Pe} \frac{\partial^2 x_i}{\partial z^2} + \frac{\partial x_i}{\partial t} + D_g \frac{\partial y_i}{\partial t} = 0 \quad \text{(Eq. 6-4)}
\]

\[
\frac{\partial y_i}{\partial t} = \frac{3}{r_c} Sh_m (y_i^* - y_i) \quad \text{(Eq. 6-5)}
\]

where:

\[
D_g = \left( \frac{1-\varepsilon_i}{\varepsilon_i} \right)
\]
Thermodynamic equilibrium:

\[ y_i^* = \frac{k_i x_i^{1/n} C_i^{1/n}}{Q} \quad \text{(Eq. 6-6)} \]

The initial and boundary conditions:

- \( t=0 \), \( 0<z<1 \), \( x_i = 0 \), \( y_i = 0 \)
- \( z=0 \), \( t>0 \), \( x_i = 1 + \frac{1}{Pe} \frac{\partial x_i}{\partial z} \)
- \( z=1 \), \( t>0 \), \( \frac{\partial x_i}{\partial z} = 0 \)

where; \( x_i \) is the concentration of component \( i \) in gas phase, \( y_i \) is the concentration component \( i \) in solid phase, \( C_i \) is the concentration of component \( i \) in the solid (mol /m\(^3\)), \( C_o \) is the concentration of component \( i \) in the column feed (mol /m\(^3\)), \( k_i \) is film mass transfer coefficient (m/s), \( l \) is the un-scaled vertical distance from the top of the column (m), \( L_o \) is the length of the column (m), \( Q \) is the maximum adsorbed amount of component \( i \) (mol /m\(^3\)). The left hand side of Eq. 6-1 represent the concentration of component \( i \) in the gas due to convection, the axial dispersion, the accumulation in the packing, and sorption onto the solid sorbent. The right hand side of Eq. 6-3 represents the rate of diffusion of the component, is expressed using mass transfer coefficient \( k_i \) and corresponding driving force, where the \( Sh_m \) depends on the value of \( k_i \).
The above set of equations was solved numerically with the aid of COMSOL Multiphysics program, Version 4.2 (USA) equipped with chemical reaction engineering module. The model was developed using the Coefficient Form PDE model. The numerical values of the parameters employed in the calculations are listed in Table 6-2. The axial dispersion coefficient is calculated from the correlation of Edwards and Richardson [30, 31]. The isothermal equilibrium constants $K$ and $n$ were estimated from the experimental data of CO$_2$ adsorption isotherms using the intercept and slope of a linear Freundlich plot of $\ln(q)$ versus $\ln(C_i)$ as shown in the following equation:

$$q = KC^{1/n}$$  \hspace{1cm} (Eq. 6-7)

where; $q$ is the adsorbed amount (mol/g), $C$ is the equilibrium concentration (mol/m$^3$), and $K ((\text{mol/g}).(\text{mol/m}^3)^{-1/n})$, $n$ are constants for a given adsorbent and adsorbate at a particular temperature. The adsorption isotherm parameters for Freundlich equation are listed in Table 6-2.

Table 6-2: Input parameter for the model at 298 K

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>0.406</td>
<td></td>
</tr>
<tr>
<td>$C_o$</td>
<td>5.9</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$D_L$</td>
<td>1.85 x10$^{-5}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$r_c$</td>
<td>1.25 x10$^{-6}$</td>
<td>m</td>
</tr>
<tr>
<td>$k_t$</td>
<td>2.44 x10$^{-5}$</td>
<td>m/s</td>
</tr>
<tr>
<td>$\theta_o$</td>
<td>1.34 x10$^{-3}$</td>
<td>m/s</td>
</tr>
<tr>
<td>$L_o$</td>
<td>0.15</td>
<td>m</td>
</tr>
<tr>
<td>$D$</td>
<td>7.92 x10$^{-2}$</td>
<td>m</td>
</tr>
<tr>
<td>$K$</td>
<td>1.1x10$^{-4}$</td>
<td>(mol/g).((mol/m$^3$)$^{-1/n}$)</td>
</tr>
<tr>
<td>$n$</td>
<td>1.2</td>
<td>-</td>
</tr>
</tbody>
</table>
6.4 Results and Discussion

6.4.1 Characterization and isotherm equilibrium data

The XRD pattern of the CPM-5 sample presented in Figure 6-2 is identical to the reference pattern [29]. The TGA results showed that the sample was stable up to 633 K as reported previously [29]. The BET surface area was 2187 m$^2$/g. Further characteristic data for the CPM-5 sample including the thermo-gravimetric analysis (TGA) curve, N$_2$ adsorption/desorption isotherms, and Fourier Transform Infrared (FTIR) spectra can be found in the authors’ previous article [29].

![XRD pattern of the microwave-synthesized CPM-5](image)

Figure 6-2: XRD pattern of the microwave-synthesized CPM-5
Figure 6-3 demonstrates the adsorption of pure CO$_2$ at two different temperatures (i.e. 298 and 318 K). The maximum amount of the adsorbed CO$_2$ is 0.0029 mol/g and 0.00096 mol/g at 298K and 318 K, respectively. The CO$_2$ isotherms are similar to those reported previously [24].

![CO$_2$ adsorption equilibrium at different temperatures, 298 K and 318 K.](image)

Figure 6-3: CO$_2$ adsorption equilibrium at different temperatures, 298 K and 318 K.

### 6.4.2 Breakthrough curve results

The accuracy of the modelling was evaluated by comparing the model predictions with the experimental results. The model results match well with the experimental data. Figure 6-4, 5 and 6 compare the experimental breakthrough curves with the theoretical ones using the equilibrium model, where lines indicate the modelled curves and the points are the experimental results. A good match of the modelled data with the experimental results reveals with root mean square error (RMSE) ranges from 1.5% to 9.5%. Run #8 shows best match between experimental and modelling data with RMSE of 1.5%. On the other hand run #1 shows the highest RMSE value of 9.5%.
6.4.2.1 Parametric of the breakthrough experiments

To investigate the effect of experimental parameters on the adsorption kinetics of CO$_2$ on CPM-5, the breakthrough curves of CO$_2$ were measured at different flow rates (i.e. 8 and 32 mL/min), adsorption temperatures (i.e. 298, and 318K), and CO$_2$ concentrations (i.e. 12.5% and 25% v/v).

Effect of feed flow rate

The effect of CO$_2$ flow rate on the breakthrough curve on CPM-5 is shown in Figure 6-4. It can be seen that increasing the flow rate of the feed decreases breakthrough time and therefore the amount of CO$_2$ that can be adsorbed (the breakthrough value was calculated at the time that CO$_2$ concentration in the reactor outlet was 10% of the feed concentration). Table 6-3 shows the breakthrough times for values of the experimental conditions given in Table 6-1. The largest breakthrough value was found to be 27 wt % according to the experimental conditions of run# 5 and the lowest value was for the run # 7 (i.e. 3.2 wt %). This result can be related to the experimental conditions, where run # 5 represents the optimal conditions of all the experimental parameters (i.e. 8 mL/min, 298 K, and 12.5% v/v).

As illustrated in Figure 6-5a; by increasing the feed flow rate from 8 mL/min to 32 mL/min at 298K, the breakthrough time was reduced from 25 min to 11.7 min, in which the breakthrough value was reduced from 10.6 wt % to 4.7 wt % of CO$_2$, respectively. Working at a faster flow rate reduces the retention time of the gas molecules in the fixed bed resulting in a decrease in adsorption, which leads to earlier breakthrough times. These observations are in agreement with those reported elsewhere [26, 32]. In addition longer
breakthrough times are desired, because this required less frequent need for regeneration of the adsorbent particles which in terms affect the amount of energy and cost of process operation.

Figure 6-4: The effect of feed flow rate on the CO₂ breakthrough time for, a) 12.5 % CO₂ at 298 K, b) 12.5 % CO₂ at 318 K, c) 25 % CO₂ at 298 K, and d) 25 % CO₂ at 318 K.

Table 6-3: Breakthrough times and values at different experimental conditions (refer to table 6.1 for details of each run)

<table>
<thead>
<tr>
<th>Run</th>
<th>Breakthrough time (min)</th>
<th>Breakthrough value wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run#1</td>
<td>6.0</td>
<td>11.9</td>
</tr>
<tr>
<td>Run#2</td>
<td>3.3</td>
<td>6.5</td>
</tr>
<tr>
<td>Run#3</td>
<td>12</td>
<td>13.9</td>
</tr>
<tr>
<td>Run#4</td>
<td>1.3</td>
<td>10.6</td>
</tr>
<tr>
<td>Run#5</td>
<td>25</td>
<td>27.0</td>
</tr>
<tr>
<td>Run#6</td>
<td>11.7</td>
<td>4.7</td>
</tr>
<tr>
<td>Run#7</td>
<td>0.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Run#8</td>
<td>3.1</td>
<td>12.5</td>
</tr>
</tbody>
</table>
Effect of adsorption temperature

Figure 6-5 illustrates the effect of temperature (e.g. 298 K and 318 K) on the adsorption kinetics of CO$_2$ onto CPM-5. Under the experimental conditions, the breakthrough points were shifted to longer times as the adsorption temperature decreases. Shorter breakthrough times and consequently lower breakthrough values at higher adsorption temperatures may be attributed to the fact that the adsorption capacity of the CPM-5 adsorbent is reduced at elevated temperatures [26, 33]. The results of the breakthrough curves reveal that the influence of temperature are more prominent at lower concentrations (Figure 6-5 (a) and (c)) compared to the higher concentrations (Figure 6-5 (b) and (d)). Nevertheless, the effect of temperature (in the examined range) on the breakthrough point is minimal when the CO$_2$ concentration and the gas flow rate are at maximum.
Figure 6-5: The effect of temperature on the CO$_2$ breakthrough time for, a) 12.5 % CO$_2$ and $F_t=8$ mL/min, b) 25 % CO$_2$ and $F_t=8$ mL/min, c) 12.5 % CO$_2$ and $F_t=32$ mL/min, and d) 25 % CO$_2$ and $F_t=32$ mL/min.

**Effect of feed concentration**

The influence of the CO$_2$ concentration on the CPM-5 adsorption kinetics was studied at two different CO$_2$ concentrations of 12.5% and 25%. The results are illustrated in Figure 6-6 Increasing the feed concentration accelerates the CO$_2$ breakthrough point, because the adsorbent gets saturated much faster due to the larger concentration gradient. As it is shown in Figure 6-6a., at a CO$_2$ feed concentration of 12.5 wt%, the breakthrough point appears after 25 min (i.e. breakthrough value of 27%), however, for the CO$_2$ feed concentration of 25%, the breakthrough point happens after 6.0 min (i.e. breakthrough value of 11.9 wt%) at 298 K. This phenomenon was observed previously according to Kyu-Suk et al. [26].
Figure 6-6: The effect of CO\textsubscript{2} feed concentration on the CO\textsubscript{2} breakthrough time for, a) T= 298 K and F\textsubscript{t}= 8 mL/min, b) T= 298 K and F\textsubscript{t}= 32 mL/min, c) T= 318 K and F\textsubscript{t}= 8 mL/min, and d) T= 318 K and F\textsubscript{t}= 32 mL/min.

The possibility of regeneration of the saturated CPM-5 adsorbent as well as the efficiency of the regenerated adsorbent was also studied. To do this, the spent adsorbent was regenerated by heating the reactor at 373 K for 1 h under N\textsubscript{2} gas purge of a flow rate of 100 mL/min. The regenerated CMP-5 sample was subjected to another CO\textsubscript{2} adsorption cycle to evaluate its efficiency. Figure 6-7 compares the adsorption breakthrough curves of a fresh sample and its regenerated counterpart at the same adsorption condition. According to the experimental data presented in Figure 6-7, it can be seen that the adsorption behaviour of the regenerated sample is the same as the fresh sample. This means the CPM-5 is fully recovered at the applied regeneration conditions. While several reaction
parameters such as flow rate, pressure and temperature are considered as influential factors that affect the regeneration process, it is noteworthy that the developed CPM-5 adsorbent can be regenerated to almost 100% of its adsorption capacity under very mild regeneration conditions.

![Graph showing CO₂ breakthrough curves](image)

Figure 6-7: Comparing of CO₂ breakthrough curves on the regenerated CPM-5 and its fresh counterpart at the same adsorption condition (CPM-5 is fully regenerated after subjecting to N₂ flow of 100 mL/min at 373 K for 1 h) (error bar represented by the standard deviation of the three repeated regenerated runs).

To evaluate the efficiency of the developed CPM-5 adsorbents for CO₂ capturing, the results obtained in this work are compared with those reported for other standard adsorbents in the literature. CO₂ adsorption data of different adsorbents including CMP-5 of this work are summarized in Table 6-4 [27, 34-38]. According to the data, the developed CPM-5 adsorbent shows a high breakthrough storage capacity for CO₂ (i.e.11.9 wt. %) with moderate regeneration conditions compared with other reported materials at the similar experimental conditions. The mono-ethanol-amine (MEA) liquid absorbent is
shown to have higher CO$_2$ capacity compared to CPM-5 and more widely used industrially than porous adsorbents [34]. However, the nature of process with MEA is chemisorptions that has several drawbacks such as: requiring high regeneration energy, high toxicity and huge equipment corrosion, and many other environmental challenges. Therefore, it can be concluded that the tested CPM-5 adsorbent represents a very promising candidate for energy efficient CO$_2$ capturing compared to other solid porous adsorbents including NaX, MOF-74, MIL-53 and ZIF-78.

Table 6-4: Comparison of adsorption capacity of CPM-5 and previously reported CO$_2$ separation materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Separation capacity (wt. %)</th>
<th>Initial Heat of adsorption (kJ/mol)</th>
<th>Regeneration conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPM-5 (Run #1)</td>
<td>11.9</td>
<td>36.1</td>
<td>373 K, purge flow</td>
<td>This study</td>
</tr>
<tr>
<td>Mg-MOF-74</td>
<td>8.9</td>
<td>39</td>
<td>353 K, purge flow</td>
<td>[27]</td>
</tr>
<tr>
<td>NaX</td>
<td>8.5</td>
<td>43</td>
<td>391 K, purge flow</td>
<td>[35]</td>
</tr>
<tr>
<td>30% monoethanol-amine (MEA)</td>
<td>13.4</td>
<td>84</td>
<td>393 K, recirculation</td>
<td>[34, 36]</td>
</tr>
<tr>
<td>Amine-MIL-53</td>
<td>3.7</td>
<td>-</td>
<td>432 K, purge flow</td>
<td>[37]</td>
</tr>
<tr>
<td>ZIF-78</td>
<td>1.4</td>
<td>29</td>
<td>-</td>
<td>[38]</td>
</tr>
</tbody>
</table>
6.5 Conclusions

The CPM-5 was synthesized under microwave irradiation and studied for CO$_2$ adsorption in a fixed bed at different experimental conditions including flow rate, adsorption temperature and feed concentration. The experimental breakthrough curves were fitted well to the theoretical breakthrough curve with correlation coefficient of 0.997 (i.e. for run # 3). Experimentally, under the conditions of run #1 the CPM-5 sample had a high breakthrough CO$_2$ capacity of 11.9 wt. % which is higher than other adsorbents tested at almost similar conditions. Furthermore, the CPM-5 can be regenerated completely under a very moderate condition (i.e. 1 hour at 373 K under N$_2$ purge of the flow rate of 100 mL/min). Accordingly, CPM-5 offers outstanding properties in terms of high CO$_2$ capacity and regeneration properties making it a very promising candidate for efficient CO$_2$ separation and storage.
6.6 References


[34] Khol Al and Nielsen RB (2997) Gas Purification Gulf Publishing Companu, Houston 5th Ed,


Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes the main conclusions of this thesis, and presents some recommendations for future research.

7.1 Conclusions:

The research of this thesis is focused on the synthesis of two types of metal organic frameworks (MOFs) named IRMOF-1 and CPM-5 using non-traditional synthesis techniques such as, microwave and ultrasound irradiations. The synthesized samples of IRMOF-1 and CPM-5 were characterized using XRD, FTIR, TGA and BET and tested for CO₂ adsorption. The CPM-5 was tested for dynamic CO₂ adsorption using a laboratory scale reactor column scale. The CO₂ adsorption breakthrough curves were obtained experimentally and verified theoretically through numerical modeling using several operating conditions such as feed concentration, adsorption temperature and feed flow rate.

The following are the main conclusions of the research:

1) The metal organic framework IRMOF-1 was successfully synthesized using novel synthesis procedure of combined ultrasonic (UTS) and microwave (MW) energy sources for rapid synthesis under various operating conditions including: sonication time and temperature as well as microwave irradiation time. This novel synthesis technique showed promising results in terms of particles size distribution (lower particles size by magnitude of 10, and narrower size distribution), morphology (more
constructed crystallites, a surface area of 2473 m$^2$/g, higher in comparison to the classical solvothermal synthesis method. Moreover sample activation was employed to improve surface area of the synthesized IRMOF-1. The activated samples exhibited improved surface area compared to as synthesized samples.

2) The metal organic framework CPM-5 (Crystalline Porous Materials) was successfully synthesized and characterized for the first time, to the best of the author’s knowledge, using microwave irradiation (MW) as a rapid facile synthesis method in ca. 10 min compared to several days crystallization time required for the conventional solvothermal approaches (e.g. 5 days) [1]. The microwave synthesis resulted in an improved CPM-5 samples in terms of surface area (e.g. 2187 m$^2$/g), and higher carbon dioxide adsorption capacity to conventionally synthesized samples.

3) The adsorption equilibrium and diffusion of CO$_2$ in CPM-5 were experimentally studied using a volumetric approach at three different temperatures 273, 298, and 318 K and gas pressures up to 105 kPa. The Freundlich adsorption equilibrium model was applied to correlate the adsorption isotherms, and the classical microspore diffusion model was applied to obtain the adsorption kinetic curves and diffusivity of CO$_2$ in CPM-5. The Freundlich adsorption equation fit well the isotherm data. The selectivity of CO$_2$ over N$_2$ was estimated from the single component isotherms at conditions relevant to post combustion applications (0.15 bar $p_{CO_2}$ and 0.75 bar $p_{N_2}$). It was found that at pressures up to 105 kPa, the CPM-5 adsorbent has CO$_2$ adsorption capacity of 3 mmol/g, 2.3 mmol/g, at 273 K and 298 K, respectively, which is significantly higher than those of MOF-5 under the same conditions. The selectivity factor was 14.2 and 16.1 at 273 and 298 K, respectively. The CO$_2$ diffusivity in CPM-5, estimated from the
adsorption kinetic data measured at low pressures, were $1.86 \times 10^{-12}$ m$^2$/s, $7.04 \times 10^{-12}$ m$^2$/s, and $7.87 \times 10^{-12}$ m$^2$/s at 273 K, 298 K and 318 K, respectively. The initial isosteric heat of adsorption of CO$_2$ on the CPM-5 was 36.1 kJ/mol. CPM-5 shows attractive adsorption properties as an adsorbent for separation of CO$_2$ from flue gas.

4) The breakthrough curves for the adsorption of carbon dioxide on CPM-5 were obtained experimentally and verified theoretically through numerical modeling using a laboratory scale fixed bed column at different experimental conditions such as feed flow rate, adsorption temperature and feed concentration. The experimental breakthrough curves were in good agreement with the theoretical ones with a root mean square error (RMSE) ranging from 1.5% - 9.5%. It was found that the CPM-5 had a dynamic CO$_2$ adsorption capacity of 11.9 wt. % (corresponding to 8 mL/min, 298 K and 25% v/v CO$_2$) which is higher than other adsorbents tested at almost similar conditions. Furthermore, the CPM-5 can be regenerated completely under a very moderate condition (i.e. 1 hour at 373 K under N$_2$ purge of the flow rate of 100 mL/min). Finally CPM-5 showed unique adsorption properties, therefore, it can be considered as an attractive adsorbent for separation of CO$_2$ from flue gas.

7.2 Recommendations for further research:

Based on the course of the current research and its findings, it is recommended that further research be conducted to include: application to other MOFs, adsorption tests under real flue gas composition, extension to bench scale, multi-cycle adsorption columns and adsorption test at elevated pressures.
7.2.1 Application to other MOFs

In this study, the ultrasound and microwave irradiation were applied for the synthesis of CMP-5 and IRMOF-1. This technique can be applied to other MOFs for rapid synthesis for industrial applications, and include a comparison among various microwave and ultrasound MOFs synthesized samples for CO₂ adsorption.

7.2.2 Flue gas composition

In this study, the adsorption tests were conducted for the single component adsorption isotherm (i.e. CO₂ and N₂), however it is recommended to conduct adsorption tests for multi-component adsorption isotherm simulating real flue gas composition.

7.2.3 Extension to Bench Scale:

The scope of the current research focused on the micro scale adsorption test, and it is recommended a similar test is devised for a bench scale apparatus. This may require design and model of the adsorption column apparatus, and shall include testing of CO₂ adsorption at different operating conditions such as temperature of adsorption, concentration of feed gases, composition of feed, and adsorption pressure. It is expected that such a scale up apparatus tests support the possibility of using CPM-5 for industrial scale applications.

7.2.4 Multi-Cycle adsorption columns:

The CO₂ adsorption tests on CPM-5 sample have been conducted in a laboratory scale fixed bed column reactor under different operating conditions such as adsorption temperature, feed concentration and flowrate of gases. The regeneration of CPM-5 sample was performed by heating the adsorption column to 373 K under N₂ purging for 1 h. However, it is necessary to check the multi cycle adsorption/desorption using bench scale
apparatus of multi adsorption/desorption columns in order to verify the efficiency of MOFs samples for CO$_2$ adsorption after multi adsorption cycles.

7.2.5 Adsorption test at elevated pressures

In the current research the CO$_2$ adoption tests were performed under atmospheric pressure (e.g. 1 kPa) and conditions similar to post-combustions conditions. It is recommended to extend this work to cover other industrial applications at elevated pressures such as pre-combustion conditions.
7.3 References:

A.1 Heat of adsorption data

Figure A-1: $\ln(p)$ vs. $1/T$ at 0.3 mmol/g

Figure A-2: $\ln(p)$ vs. $1/T$ at 0.4 mmol/g.
Figure A-3: $\ln(p)$ vs. $1/T$ at 0.5 mmol/g.

Figure A-4: $\ln(p)$ vs. $1/T$ at 0.6 mmol/g.
Figure A-5: \( \ln(p) \) vs. \( 1/T \) at 0.7 mmol/g.

Figure A-6: \( \ln(p) \) vs. \( 1/T \) at 0.8 mmol/g.
Figure A-7: $\ln(p)$ vs. $1/T$ at 0.9 mmol/g.

Figure A-8: $\ln(p)$ vs. $1/T$ at 0.95 mmol/g.
A.2 Freundlich data

Figure A-9: Freundlich isotherm constant parameters $K$ and $n$ at 273 K

\[ \ln(p) = 0.644 \ln(q) - 1.9387 \]
\[ R^2 = 0.9986 \]

Figure A-10: Freundlich isotherm constant parameters $K$ and $n$ at 298 K

\[ \ln(q) = 0.8235 \ln(p) - 2.9988 \]
\[ R^2 = 0.9992 \]
Figure A-11: Freundlich isotherm constant parameters $K$ and $n$ at 318 K

$$\ln(q) = 1.0153 \ln(p) - 4.7667$$

$R^2 = 0.9982$
CURRICULUM VITA

Education
- PhD-Candidate, University of Western Ontario, Canada, 2009 to present, Thesis Topic: *Carbon Dioxide Adsorption by Metal Organic Frameworks (Synthesis, Testing, and Modeling)*, Scheduled to finish in May 2013.
- MESc, University of Western Ontario, Canada, 2009, Thesis Topic: *Pulse Sprays for Better Contact Between Liquid and Fluidized Solids*.
- BESc, United Arab Emirates University, 2006

Teaching/Research Experience
- Teaching Assistant, University of Western Ontario, Chemical and Biochemical Engineering Department, Canada, 2007- Present.
- Teaching Assistant, ALHOSN University, Industrial Engineering Department, United Arab Emirates, 2006-2007
- Presented numerous oral presentations (monthly) to the researchers in Syncrude Canada Ltd. Company during my master’s study. In addition, gained good experience in preparing technical reports most of which have been submitted to supervisors during the MESc and the PhD work.
- Gained supervisory, teaching and project management experience as a teaching assistant at University of Western Ontario for the following courses: Transport phenomena, Chemical process calculations, Mass transfer operations, and particulate operations.
- Chosen to give an oral presentation to freshman students to promote engineering among female students. Also I have been awarded “The Best Student Presentation Award” in the “7th research conference, 2006, Al Ain, UAE” for presenting research paper related to my graduation project.
- Gained good research experience through the preparation of my Master’s thesis. Conducted extensive literature survey and explored various alternatives for the solution of the problem. Also, I did some research during my co-op with Syncrude Canada (Master’s work).

Selected Honors and Awards
- Ontario Graduate Scholarship (OGS), 2012-2013
- Queen Elizabeth II Graduate Scholarships in Science and Technology (QEII GSST), 2011-2012
- MITACS Accelerated graduate scholarship, 2011
- Ivan Malek Scholarship, 2011
- On the honors student list throughout my undergraduate study, and ranked first in the UAE University, Class of 2006.
Contributions to research and development

Refereed contributions:


Non-refereed contributions: