

**Structural Evaluation of Zeolite Imidazolate Framework 8 (ZIF-8)  
Nanoparticles as Adsorbent for Carbon Dioxide Removal**

by

Noraishah Binti Che Ani

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

Chemical Engineering

MAY 2013

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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(CHEMICAL ENGINEERING)

Approved by,

---

(Dr. Yeong Yin Fong)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2013

## CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NORAISHAH BINTI CHE ANI

## **ABSTRACT**

Zeolitic imidazole frameworks-8 (ZIF-8) is a class of metal-organic frameworks (MOFs) which is linked by imidazolate anion into tetrahedral frameworks, zeolite-like topologies. This material has been discovered as a promising candidate for carbon dioxide (CO<sub>2</sub>) capture due to its excellent properties including large intracrystallite surface area and chemical and thermal stabilities. Hence, this research project is focuses on the synthesis of ZIF-8 with varies particles size by monitoring synthesis duration, concentration (molar ratios) and pH of the synthesis solution. The resulting particles were characterized using variety of analytical tools such as X-ray diffraction (XRD), scanning electron microscope (SEM), and Brunauer–Emmett–Teller (BET) surface area analyzer. The samples were further tested for CO<sub>2</sub> adsorptionc by using BELSORP physisorption analyzer.

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# CHAPTER 1

## PROJECT BACKGROUND

In 2005, Department of Environment (2005) stated that the world CO<sub>2</sub> emission were estimated at 28, 051 million metric tons (MMT) and projected to 42,325 MMT for 2030. IEA statis

tic stated that two sectors produced nearly two-thirds of global CO<sub>2</sub> emissions in 2010: electricity and heat generation accounted for 41% while transport produced 22% (Figure 1). According to United States Environment Protection Agency (EPA) in 2010, human activities contribute for about 84% for CO<sub>2</sub> greenhouse gas emission in U.S. Attempt to solve the greenhouse problem have led to increasing interest in removing CO<sub>2</sub>. So, capture of CO<sub>2</sub> before emission to the environment may always the best solution to reduce the greenhouse problem [1].

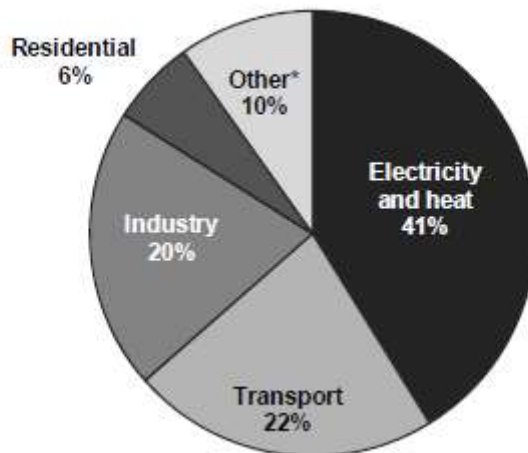


Figure 1: World Emission by Sector in 2010

In industry, gas sweetening purification processes of natural gas by removing the acidic contaminant are important prior to sale. Carbon dioxide (CO<sub>2</sub>) removal is an essential process in sweetening of natural gas. Natural gas generally contains a large quantity of methane (CH<sub>4</sub>) along with heavier hydrocarbons such as ethane, propane, isobutene, normal butane and CO<sub>2</sub> as shown in Table 1 [2]. CO<sub>2</sub> must be removed from natural gas to protect pipelines and equipment from corrosion. This is because CO<sub>2</sub> with the presence of water is highly corrosive [3]. In addition, when cooling the natural gas to a very low temperature in LNG processing plant, transportation drawback may occur as CO<sub>2</sub> can be frozen and block the pipeline systems. It also reduces the heating value of a natural gas stream [4]. Thus, removal of CO<sub>2</sub> from the natural gas through the purification processes is vital for an improvement in the quality of the product [2].

Table 1: Typical Natural Gas composition[2]

Component	Chemical Formula	Percentage (%)
Methane	CH <sub>4</sub>	70-90
Ethane	C <sub>2</sub> H <sub>6</sub>	0-20
Propane	C <sub>3</sub> H <sub>8</sub>	
Butane	C <sub>4</sub> H <sub>10</sub>	
<b>Carbon Dioxide</b>	<b>CO<sub>2</sub></b>	<b>0-8</b>
Oxygen	O <sub>2</sub>	0-0.2
Nitrogen	N <sub>2</sub>	0-5
Hydrogen sulphide	H <sub>2</sub> S	0-5
Rare gases	A,HE,NE,XE	Trace

Zeolitic Imidazole Framework-8 (ZIF-8) is a class of metal-organic frameworks (MOF) that are topologically isomorphic with zeolites [5]. ZIF-8 is the promising materials for gas storage. It was reported that the adsorption and desorption process for ZIF-8 was completely reversible with no hysteresis, indicating a fast adsorption and desorption process. ZIF-8 was observed in porous materials with large surface area. This characteristic is very useful for a material in practical gas storage applications [6](See Table 2).[7] reported that the application of ZIF-8 in gas separation has been increased rapidly due to their promising molecular sieve

properties. In term of its excellent characteristic including large surface area, good water solubility, and high chemical and thermal stabilities ,ZIF-8 is the promising candidate as compared to other ZIF family based on the economic consideration and the capacity of the CO<sub>2</sub> adsorption, [8]. The properties of ZIF-8 are rarely to be found among other type of MOF materials.

Table 2: Physical data of ZIFs Single Crystal [9]

<b>ZIF-n</b>	<b>Physical Density g/cm<sup>3</sup></b>	<b>Porosity, P %</b>
ZIF-zni	1.56	36.9
ZIF-4	1.22	50.9
ZIF-7	1.24	26.57
<b>ZIF-8</b>	<b>0.95</b>	<b>50.38</b>
ZIF-9	1.23	26.78
ZIF-20	1.04	57.3

ZIF-8 crystals were synthesized with varying particle sizes. For controlling the size of the crystals, by changing of synthesis time, the concentration (molar ratios) and as well as pH synthesis solution were reported [10]. The main idea was by controlling the balance of kinetics of nucleation and growth [11]. For synthesis of ZIF-8, the rate of nucleation was higher than the growth rate in highly concentrated solutions and thereby, high concentrated solution medium results in smaller particle size and thus, could affect the CO<sub>2</sub> adsorption characteristic. The reason was because of when the particle size is smaller, it will produce a larger surface area of the particle and thus, enhance the CO<sub>2</sub> uptake rate [12].

So, this research project is focuses on the synthesis of nanoparticles ZIF-8 by monitoring synthesis time, concentration (molar ratios) and pH of synthesis solution. The resulting particles were characterized using variety of analytical tools such as X-ray diffraction (XRD), scanning electron microscope (SEM) and Brunauer–Emmett–Teller (BET) surface area analyzer.

Development of right kind of absorbent is believed to enhance CO<sub>2</sub> removal. In the present project, ZIF-8 with different particle sizes will be synthesized by varying the aforementioned synthesis parameters. The structural evaluation and the CO<sub>2</sub> adsorption characteristics of the resulting ZIF-8 synthesized using different conditions will be studied.

### **1.1 Objectives**

The objectives of the present project are:

1. To synthesis ZIF-8 particles by varying the synthesis time, concentration (molar ratios) and pH of the synthesis solution.
2. To characterize the resultant materials using X-ray diffraction (XRD), scanning electron microscope (SEM), and Brunauer–Emmett–Teller (BET) surface area analyzer.
3. To test the CO<sub>2</sub> adsorption characteristic of ZIF-8 using CO<sub>2</sub> physisorption analyzer, BELSORP

### **1.2 Relevancy and Feasibility of Project**

Development of right kind of absorbent is believed to enhance CO<sub>2</sub> removal. The relevancy of this project is to synthesis ZIF-8 by varying the aforementioned synthesis parameters in order to study the structural evaluation of the resulting ZIF-8 and their CO<sub>2</sub> adsorption characteristics.

### **1.3 Scope of Study**

This research is targeting to increase the rate of CO<sub>2</sub> uptake of ZIF-8 by reducing its particles size ZIF-8 will be synthesized by varying three parameters: synthesis time, concentration (molar ratios) and pH of the synthesis solution. The properties of the resulting particles will be characterized using different analytical tools such as X-ray diffraction (XRD), scanning electron microscope (SEM), and Brunauer–Emmett–Teller (BET) Surface Area Analyzer. The CO<sub>2</sub> adsorption characteristic of the resulting ZIF-8 will be study using CO<sub>2</sub> physisorption analyzer, BELSORP

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2. Carbon Dioxide Removal**

The burning of fossil fuels releases large amounts of CO<sub>2</sub> into the atmosphere. This has disturbed the carbon balance of the planet which has been steady over hundreds of millions of years. According to United States Energy Information Administration, U.S. (U.S. Department of Energy, 2012) CO<sub>2</sub> emissions from energy consumption totaled 1,340 million metric tons during the first quarter of 2012. So, reducing CO<sub>2</sub> emission and lowering the concentration of greenhouse gases in the atmosphere has quickly become one of the most urgent environmental issues of this age.

A natural gas reserve with low CO<sub>2</sub> content has gradually depleted. Most of the remaining natural gas fields have high CO<sub>2</sub> content mostly within 20% to 60 % and few are as high as 80% [4]. Removal of CO<sub>2</sub> in natural gas is crucial in order to achieve sweet gas in ppm levels.[3]. In addition, CO<sub>2</sub> concentration is around 13 % with the maximum specification limit is 100 ppm. This very rigorous CO<sub>2</sub> specification in treated gas is required for liquefaction process as gas must have all impurities removed prior to cooling [3]. The CO<sub>2</sub> specification for the liquefaction process would be around 50 to 100 ppm. More specifically, carbon dioxide and water must be extracted upstream of liquefaction or they would cause damage to liquefaction facilities by freezing.

LEOL et al (2007) reported that contaminants such as water, hydrogen sulfide (H<sub>2</sub>S), carbon dioxide, helium, nitrogen, and other compounds found in raw natural gas can generate several problems. CO<sub>2</sub> when combined with water creates carbonic acid which is corrosive. CO<sub>2</sub> also reduces the BTU value (heat capacity) of gas and in concentrations of more than 2% or 3 % and thus makes it not economic viable.



## **2.1 Existing Technologies for CO<sub>2</sub> Removal**

A variety of CO<sub>2</sub> removal technologies exist such as

- i) Chemical and physical adsorption
- ii) Pressure swing adsorption
- iii) Membrane technology.

An ease of operation, quick start up and high on stream factors are needed for CO<sub>2</sub> removal technologies [12].

### **2.1.1 Chemical and Physical Adsorption**

Chemical absorption mostly using amine with solvents have been proposed to sequester CO<sub>2</sub> from flue gases from combustion of fossil fuels [13]. CO<sub>2</sub> was separated from the flue gas by passing the flue gas through a continuous scrubbing system. The system consists of an absorber and a desorber. Absorption processes utilize the reversible chemical reaction of CO<sub>2</sub> with amine. In the desorber, the absorbed CO<sub>2</sub> is stripped from the solution and a pure stream of CO<sub>2</sub> is sent for compression while the regenerated solvent is sent back to the absorber [14].

If it is advantageous to use a physical solvent that combines less strongly with CO<sub>2</sub> than do chemical solvents when there is highly concentrated stream of CO<sub>2</sub> at high pressures[15]. Hence, CO<sub>2</sub> can be separated from such solvents mainly by reducing the pressure in the desorber, significantly reducing the energy requirements in the desorption process[16].

### **2.1.2 Pressure Swing Adsorption (PSA)**

PSA is an adsorption method utilizing change of the adsorption amount according to the pressure[17]. Despite PSA's widespread use in industry, the drawbacks of conventional valves as the complex piping network required to link the array of valves adds dead volume to the overall PSA process, reducing product yield and overall process efficiency.

### **2.1.3 Membrane Technology**

Efforts to reduce the membrane thickness in order to increase the membrane permeability are still yet to achieve. The chemical absorption process exhibited low carbon dioxide loading capacity, high equipment corrosion rate and high energy consumption during absorbent regeneration[18].

Adsorption is considered as one of cost advantage and ease of application over a relatively wide range of temperature and pressure as well as viable technologies in commercial and industrial application. Furthermore, the main advantage of physical adsorption methods is its low energy requirement for the regeneration of the sorbent material with short period of time associated with the change in pressure [19]. But all this technologies depend on the development of a low cost adsorbent with high CO<sub>2</sub> selectivity and CO<sub>2</sub> adsorption capacity. Recent years, ZIF-8 have become prominent due to larger pore size, surface area, and possession of inorganic-organic properties that make them more versatile for certain industrial application in comparison to others porous materials such as Zeolite [20].

### **2.2 Zeolitic Imidazolate Frameworks (ZIFs) as adsorbent**

A new class of porous materials known as metal organic frameworks (MOFs) has been reported due to its well-defined pores, high surface areas and desired chemical functionalities [21, 22]. Zeolitic imidazolate frameworks (ZIFs), which have topologies analogous to zeolite structures, are particularly interesting members of the MOF family. In ZIFs, Zn, Co and Cu are linked through N atoms by diprotic Imidazole or functionalised Im links to form neutral framework and tuneable nanosized pores. It formed by four ring and six ring ZnN<sub>4</sub>, CoN<sub>4</sub>, and CuN<sub>4</sub> cluster. Their bond angles in both structures are 145° as shown in Figure 2.

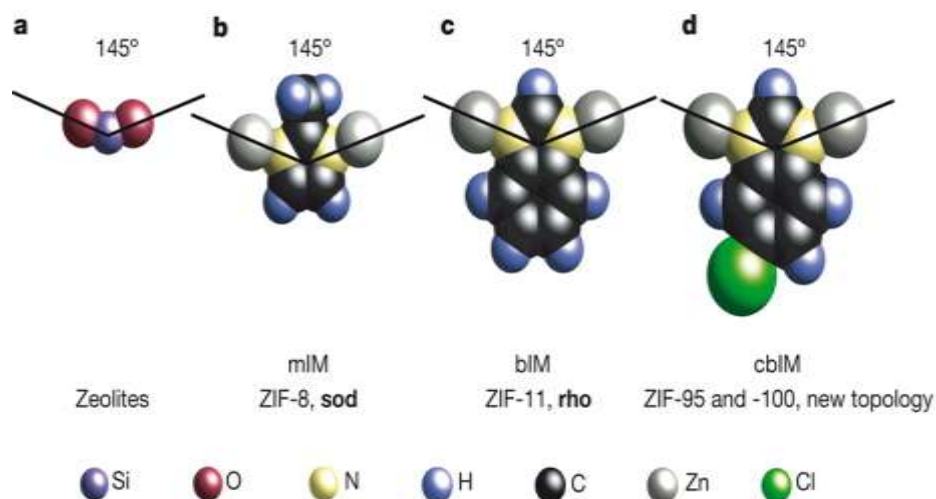


Figure 2: Bond angles of ZIFs structure at 145°

Over 100 ZIFs have been synthesized and 105 different crystals have been characterized extensively in which 49 have structures based on a zeotype topology (ana, crb, gis, gme, lta, mer, rho and sod)[23]. Table 3 shows first 10 ZIFs structures based on a zeotype topology.

Table 3: Composition, and topological information of ZIFs.[23]

Name	Composition	Framework Type		T/V <sup>§</sup>	Dp <sup>#</sup>	Df <sup>¶</sup>
		RCSR* Code	IZA	Nm <sup>-3</sup>	Å	Å
ZIF 1	Zn(Im) <sub>2</sub>	Crb	BCT	3.64	6.3	6.94
ZIF 2	Zn <sub>2</sub> (Im) <sub>4</sub>	Crb	BCT	2.8	6.4	6.9
ZIF 3	Zn <sub>2</sub> (Im) <sub>4</sub>	Dft	n.a <sup>§§</sup>	2.66	4.6	6
ZIF 4	Zn(Im) <sub>2</sub>	Cag	n.a <sup>§§</sup>	3.68	2.0	2.1
ZIF 5	Zn <sub>3</sub> In <sub>2</sub> (Im) <sub>12</sub>	Grr	n.a <sup>§§</sup>	1.51	1.7	1.31
ZIF6	Zn(Im) <sub>2</sub>	Grr	n.a <sup>§§</sup>	2.31	1.5	3.03
ZIF 7	Zn(bIm) <sub>2</sub>	Sod	SOD	2.49	2.9	4.31
<b>ZIF8</b>	<b>Zn(mIm)<sub>2</sub></b>	<b>Sod</b>	<b>SOD</b>	<b>2.45</b>	<b>3.4</b>	<b>11.6</b>
ZIF 9	Co(bIm) <sub>2</sub>	Sod	SOD	2.51	2.9	4.31
ZIF 10	Zn(Im) <sub>2</sub>	Mer	MER	2.25	8.2	12.2

RCSR stand for Reticular Chemistry Structure Resource.[24].  $T/V^s$  is the density of metal atoms per unit volume.  $dp^{\#}$  is the diameter of the largest sphere that will pass through the pore.  $df^{!!}$  is the diameter of the largest sphere that will fit into the cages without contacting the framework atoms. Pore metrics measurements exclude guests. §§ The name, RCSR symbols, and zeolite symbols not applicable or that the structure, CCDC code, and deposition number are not yet available.[25]

The adjustable pore sizes and group functionalities, low densities and unusually high surface areas of the ZIF-8 make them attractive materials for many applications [26]. The pores are accessible through small channels (3.4Å)[27, 28].The structure of ZIF-8 can be seen in Figure 3.

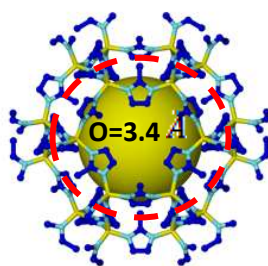


Figure 3: Structure of ZIF-8

ZIF-8 is its apparent thermal stability up to nearly 400 °C and has a high surface area of 1300–1600 m<sup>2</sup>/g [27]. Due to their large surface area, it is expected that ZIF-8 nanoparticles yield better contact with polymer matrix and reduction in interfacial voids [27]. ZIF-8 have a great potential for usage in different application areas such as gas storage and separation, catalysis, chemical sensing, construction of advanced nanotechnology devices as they have exceptional chemical and thermal stabilities [29]. Furthermore, reducing the ZIF-8 size to nanoscale might facilitate large surface area with increased uptake and selectivity of CO<sub>2</sub>.

### 2.3 Synthesis of ZIF-8

Identification and modification of synthesis conditions are important to allow the assembly of the building units in the desirable composite pattern. Therefore, proper selection of inorganic salt, organic ligands and solvents, monitoring of reaction conditions in ZIF-8 synthesis for example synthesis time, concentration (molar ratios) and pH synthesis solution can produce ZIF-8 with high crystallinity and porosity as well as desirable shape and functionality[23, 27, 30].

Some degree of size and shape control can be achieved through various method have been reported to synthesize ZIF-8 particles such rapid room temperature synthesis, direct mixing, microwave, ultrasound and micro emulsion methods whereby [31]. In comparison with all these methods, rapid room temperature method is selected in this project as it does not need any auxillary stabilizing agent or activation[32, 33]. Rapid room temperature synthesis method also yields well shaped ZIF-8 nanoparticles in the form of powders or stable colloidal dispersions. This method was carried out by pouring at room temperature a methanol solution of Zinc hexahydrate into a methanol solution of excess 2-methylimidazole. Excess 2-methylimidazole is required to produce large particles [5]

Synthesis of ZIF-8 in the presence of excess solvent at room temperature has been carried out by Venna et al (2009). For 1 hour synthesis period, 230 nm of ZIF-8 crystals were obtained with a BET surface area of  $744\text{m}^2/\text{g}$  [11].

## **CHAPTER 3**

### **METHODOLOGY**

#### **3 Research Methodology and Project Activities**

The project activities in this research are mainly experimental work. The results obtained from this research can be used to compare with literature results. The results can hence further enhance the research and development of the synthesis nanoparticles. After thorough literature review is done, experimental works were conducted under rapid room temperature to investigate the three factors: synthesis time of ZIF-8, concentration (molar ratios) and pH of synthesis solution. The results obtained were compared with the results reported in the literature. The effect of particle size on CO<sub>2</sub> adsorption will be analyzed.

### 3.1 Experimental Procedures/Approach

Figure 4 shows the overview experimental procedures in this research project.

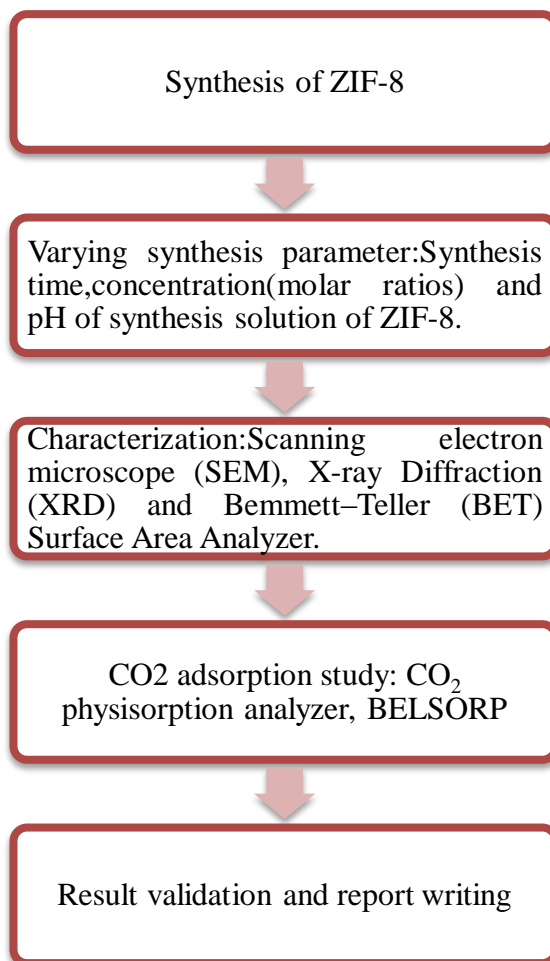


Figure 4: Overview of experimental procedures

### 3.2 Experimental Procedure

#### 3.2.1 Synthesis of ZIF-8 particles by varying synthesis time.

1. 4.606 g of zinc nitrate hexahydrate, 2.11g of 2-methylimidazole was diluted in 100ml of methanol to give a molar ratio of 1:7.9:695. Molar ratio of 1:7.9:698 synthesized solutions were fixed for all three samples.
2. These two solutions were and stirred for 5 min at room temperature.
3. The resulting nanoparticle was separated from milky dispersion by centrifugation at 7000 rpm for 5min.
4. The precipitate was washed with fresh methanol, and repeated for three times.
5. The resulting nanoparticles are dried in oven overnight at 353 K and store in desiccator prior to use.

- Steps 1-4 were repeated for synthesis of ZIF-8 by varying stirring time of 60 minutes and 1440 minutes at room temperature.

### 3.2.2 Synthesis of ZIF-8 particles by varying concentration (molar ratios)

Figure 5 shows the schematic flow diagram for ZIF-8 synthesizing.

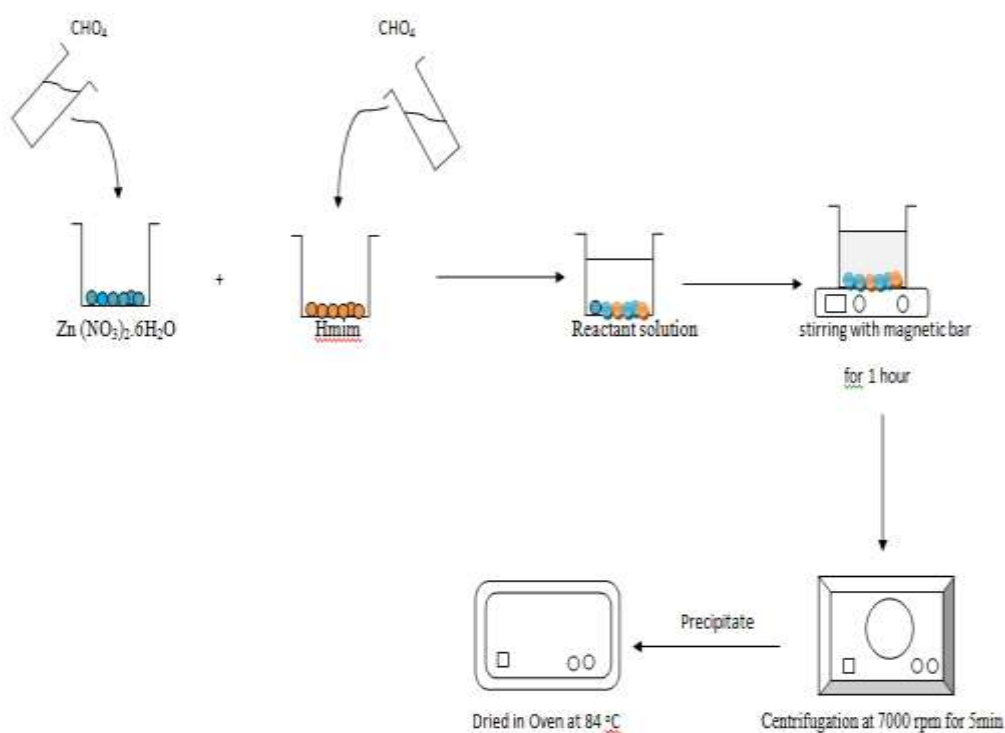


Figure 5: Schematic flow diagram for ZIF 8 synthesizing

The experimental procedure for ZIF-8 synthesis is outlined as follows:

- 2.933 g of,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 200 mL methanol and 6.489g of 2-methylimidazole, Hmim in 200 mL of methanol was prepared under stirring with magnetic bar for 1 hour as shown in Figure 5.
- The resulting nanoparticle was separated from milky dispersion by centrifugation at 7000 rpm for 5min.
- The precipitate was washed with fresh methanol, and repeated for three times.



4. The resulting nanoparticles were dried in oven overnight at 353 K and store in desiccator prior to use.
5. Steps 1-4 were repeated for synthesis of ZIF-8 by varying the methanol concentration. Figure 6 shows ZIF-8 solution is prepared under stirring with magnetic bar 1 hour respectively.



Figure 6: ZIF-8 solution with magnetic stirrer

### 3.2.3 Synthesis of ZIF-8 particles by varying pH of reactant solution

1. 4.606 g of zinc nitrate hexahydrate, 2.11g of 2-methylimidazole is diluted in 100ml of methanol to give a molar ratio of 1:7.9:695. Molar ratio of 1:7.9:698 synthesized solutions were fixed for all three samples.
2. These two solutions are and stirred for 1 hour at room temperature.
3. For pH range between pH 8 until 8.8, sodium formate, 2 Mol of HCl was added dropwise until the solution pH reaches the desired pH value. For pH range between 6.7 to pH 7, hydrochloric acid, 2 M was added into the synthesis solution during stirring.
4. The resulting nanoparticle was separated from milky dispersion by centrifugation at 7000 rpm for 5min.
5. The precipitate was washed with fresh methanol, and repeated for three times.
6. The resulting nanoparticles were dried in oven overnight at 353 K and store in desiccator prior to use. Figure 7 shows the pH meter used to measure ZIF-8 solution. Figure 8 shows the centrifuge used in the experiment to separate the milky solution of ZIF-8.

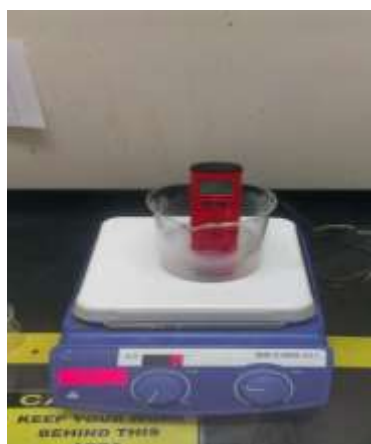


Figure 7: pH meter used to measure pH of ZIF-8 solution

The crystal growth of ZIF-8 is studied by varying the synthesis parameters including synthesis time, concentration (molar ratios) and pH of synthesis solution to provide information on the crystal morphology, crystal size and the effects on the CO<sub>2</sub> uptake.

### 3.3 Characterization Method

Methods used to characterize the resulting ZIF-8 particles are listed in Table 4:

Table 4: Characterization of ZIF-8

Characterization Method	Properties
X-ray diffraction (XRD)	Crystallinity of the particles
Scanning Electron Microscope (SEM)	Microstructure and size of the particles
Brunauer–Emmett–Teller (BET) Surface Area Analyzer	Surface area of crystal

### 3.4 CO<sub>2</sub> Adsorption Study

Equipment used to study the CO<sub>2</sub> adsorption characteristic of the resulting ZIF-8.

CO<sub>2</sub> adsorption characterization can be determined by using CO<sub>2</sub> physisorption analyzer BELSORP.

Chemicals and apparatus used in the current research work are listed in the following section.

#### 3.4.1 Chemicals

- i. Zinc nitrate hexahydrate , Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O
- ii. 2-methylimidazole , (Hmim) C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>
- iii. Methanol , MeOH
- iv. Hydrochloric Acid, HCl
- v. Sodium Formate, NaCOOH

#### 3.4.2 Apparatus/equipment

- i. Electronic weighting balance
- ii. pH meter
- iii. Magnetic stirrer
- iv. Centrifuge
- v. Oven
- vi. X-ray diffraction (XRD)
- vii. Scanning Electron Microscope (SEM)
- viii. Brunauer–Emmett–Teller (BET) Surface Area Analyzer
- ix. CO<sub>2</sub> physisorption analyzer, BELSORP



Figure 8: Centrifuge used in the experiment to separate the milky solution of ZIF-8.

### 3.5 Project Activities

Table 5 lists the activities that have been completed so far in FYP 1.

Table 5: List of Project Activities for FYP I until week 13

Week	Project Activities
3	1 <sup>st</sup> Meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Discussed on the Final Year Project topic: Structural Evaluation of ZIF-8 nanoparticles as adsorbent for CO<sub>2</sub> Removal.</li> <li>• Find relevant info and literature review regarding the topic proposed.</li> </ul>
4	2 <sup>nd</sup> meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Discussed on the finding for the FYP topic based on literature review.</li> <li>• Proposed ammonia impregnation method to modified ZIF-8 structure.</li> <li>• Clarify on the synthesized method, characterization technique and chemical used.</li> <li>• Was introduced to Ms. Lai Li Sze, postgraduate student that will work together on this project.</li> </ul>
5	<ul style="list-style-type: none"> <li>• Ms. Lai showed how to centrifuge synthesized sample.</li> </ul>
6	3 <sup>rd</sup> meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Update progress extended proposal</li> </ul>

	<ul style="list-style-type: none"> <li>• Submission of extended proposal</li> </ul>
<b>7</b>	<p>4<sup>th</sup> meeting with Dr. Yeong</p> <ul style="list-style-type: none"> <li>• Slides review for oral presentation</li> <li>• Discussed on synthesizing ZIF-8 and equipment used to modified ZIF-8 structure.</li> </ul>
<b>8</b>	<p>5<sup>th</sup> meeting with Dr. Yeong</p> <ul style="list-style-type: none"> <li>• Slides review on oral presentation</li> <li>• Mock oral presentation</li> </ul>
<b>9</b>	<ul style="list-style-type: none"> <li>• Proposal defense Oral Presentation</li> </ul>
<b>10</b>	<p>6<sup>th</sup> meeting with Dr. Yeong</p> <ul style="list-style-type: none"> <li>• Discussed on the feedback after oral presentation</li> <li>• Start to synthesized ZIF-8 as per literature review methodology</li> <li>• Prepare 1:7.9:86.5 and 1:7.9:698 molar ratio of <math>Zn(NO_3)_2 \cdot 6H_2O</math>, Hmim and MEOH</li> </ul>
<b>11</b>	<p>7<sup>th</sup> meeting with Dr. Yeong</p> <ul style="list-style-type: none"> <li>• Discussed on the synthesized ZIF-8 crystal.</li> <li>• Synthesized ZIF-8 crystal with pH 8.8</li> <li>• Synthesized ZIF-8 with pH 5</li> <li>• Characterization study and equipment booking.</li> </ul>
<b>12</b>	<p>8<sup>th</sup> meeting with Dr. Yeong</p> <ul style="list-style-type: none"> <li>• Update all the lab progress.</li> <li>• Discussed on the unreacted ZIF-8 in acidic condition</li> <li>• Lab safety briefing with Dr. Yeong and Ms. Lai</li> <li>• Synthesized ZIF-8 for pH 8.0</li> <li>• Synthesized ZIF-8 molar ration of 1:7.9:698 with stirring time 24 hours</li> </ul>
<b>13</b>	<p>9<sup>th</sup> meeting with Dr. Yeong</p> <ul style="list-style-type: none"> <li>• Discussed XRD result for tested sample</li> <li>• Synthesized ZIF-8 with pH 7 and pH 6.7</li> <li>• First draft interim report submission</li> </ul>
<b>14</b>	<ul style="list-style-type: none"> <li>• Micromeristics ASAP 2000 characterization using nitrogen</li> </ul>

The project activities which have been conducted during semester II is listed in Table 6.

Table 6: The list of Project Activities for FYP II until Week 8

<b>Week</b>	<b>Project Activities</b>
<b>1</b>	1 <sup>st</sup> meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Update on progress work.</li> <li>• Equipment Booking for FESEM, BET and XRD</li> </ul>
<b>2</b>	2 <sup>nd</sup> meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Update on work progress, result and discuss on problem faced.</li> <li>• Sample synthesis for molar ratio 86.7 and 1002</li> <li>• Sample synthesis for ph varying parameter: with NaCOOH, HCl and normal.</li> <li>• Sample synthesis for time varying parameter: 60 minutes and 1440 minutes synthesis time.</li> </ul>
<b>3</b>	3 <sup>rd</sup> meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Send in 2 samples for BET surface area analyse.</li> </ul>
<b>4</b>	4 <sup>th</sup> meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Journal Paper task distribution with Ms. Lai</li> <li>• Send in 3 samples for XRD characterization.</li> <li>• Send in 5 samples for FESEM.</li> </ul>
<b>5</b>	5 <sup>th</sup> meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Send in 3 sample for FESEM</li> <li>• Prepare journal paper</li> </ul>
<b>6</b>	6 <sup>th</sup> meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Discuss on relevancy of XRD, FESEM and BET result.</li> <li>• Prepare journal paper</li> </ul>
<b>7</b>	7 <sup>th</sup> meeting with Dr. Yeong <ul style="list-style-type: none"> <li>• Discuss XRD , FESEM, BET result.</li> <li>• Journal paper 1<sup>st</sup> draft submission</li> </ul>

	<ul style="list-style-type: none"> <li>• Prepare 695 molar ratio with 5minute synthesis time</li> </ul>
<b>8</b>	<ul style="list-style-type: none"> <li>• Progress report submission</li> </ul>

### 3.6 Key Milestones

The key milestones for this research project for FYP I & FYP II are listed in Table 7.

Table 7: Suggested milestone

<b>No.</b>	<b>Milestones (FYP I)</b>	<b>Week</b>
1	Completion of literature review on ZIF-8 studies	Week 4
2	Completion of extended proposal	Week 6
3	Completion of interim draft report	Week 13
4	Completion of interim report	Week 14
<b>No</b>	<b>Milestones (FYP II)</b>	<b>Week</b>
1	Completion of Progress report	Week 8
2	Completion of draft report	Week 12
3	Completion of Dissertation (Soft copy)	Week 13
4	Completion of Technical paper	Week 13
5	Completion of Final Dissertation (Hard bound)	Week 15

### 3.7 Gantt Chart and Research Activities

Table 8 shows the activity Gantt chart of current research project

Table 8: Activity Gantt for FYP I and FYP II

Semester	FYP I (Semester May 2013)														FYP II (Semester September 2013)														
Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Selection of project title	█	█																											
Preliminary Research Work and Literature Review -Laboratory & Apparatus Requisition	█	█	█																										
Experiment Design and Run: Synthesis of ZIF-8				█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█						
Characterization of sample & study															█	█	█	█	█	█	█	█	█	█					
Submission of						█																							







## CHAPTER 4

### RESULTS AND DISCUSSION

The framework structure of the synthesized crystals were confirmed by X-ray Diffraction (XRD) where their diffraction patterns were compared with the standard pattern for ZIF-8 reported in the literature, followed by observation of crystal morphology and size using Scanning Electron Microscopy (SEM). The surface area of the resulting particles was tested using Brunauer–Emmett–Teller (BET) Surface Area Analyzer. Finally, the CO<sub>2</sub> adsorption capability of the resultant particles was tested using CO<sub>2</sub> physisorption analyzer, BELSORP.

Table 9 shows the samples synthesized with the present work. All the samples were synthesized at room temperature.

Table 9: Samples synthesized in the present work.

Sample Code	Zn <sup>2+</sup> :Hmim:MeOH	Synthesized time (minutes)	pH
A	1:7.9:695	5	pH 7.2
B	1:7.9:695	60	pH 7.2
C	1:7.9:695	1440	pH 7.2
D	1:7.9:86.5	60	pH 7.2
E	1:7.9:1002	60	pH 7.2
F	1:7.9:695	60	pH 6.7
G	1:7.9:695	60	pH 8.3

## 4 Characterization

### 4.1 Crystallinity Evaluation of ZIF-8 Particles using X-ray Diffraction (XRD)

The crystallinity of the resulting particles (XRD) obtained were compared with the reported XRD patterns of ZIF-8 sample. The XRD patterns for all samples synthesized in the present works show ZIF-8 topology without presence of any others phases. The area under the curve of the highest peaks corresponding to the planes (011) was used to determine the relative crystallinity of ZIF-8 crystals formed.

The ZIF-8 relative crystallinity was calculated using equation 1 as follows:[11]

$$\text{ZIF-8} = \frac{\text{Area under the curve (011) plane for each sample}}{\text{Area under the curve (011)plane at highest peak}} \dots\dots\dots (1)$$

#### 4.1.1 Effect of Synthesis time

Figure 9 shows the XRD patterns for ZIF-8 as a function of synthesis time. Referring to Figure 9, rapid increase in the relative crystallinity is observed in when the synthesis duration increase from 5 minutes to 60 minutes. Since longer stirring duration of 1440 minutes did not affect the crystallinity of the resulting ZIF-8, it is assumed that ZIF-8 achieves its optimum crystallinity at 60 minutes. Therefore, in the remaining experiments, all the samples were synthesized at 60 minutes. Table 10 shows the relative crystallinity of the samples synthesized at 5, 60 and 1440 minutes, respectively.

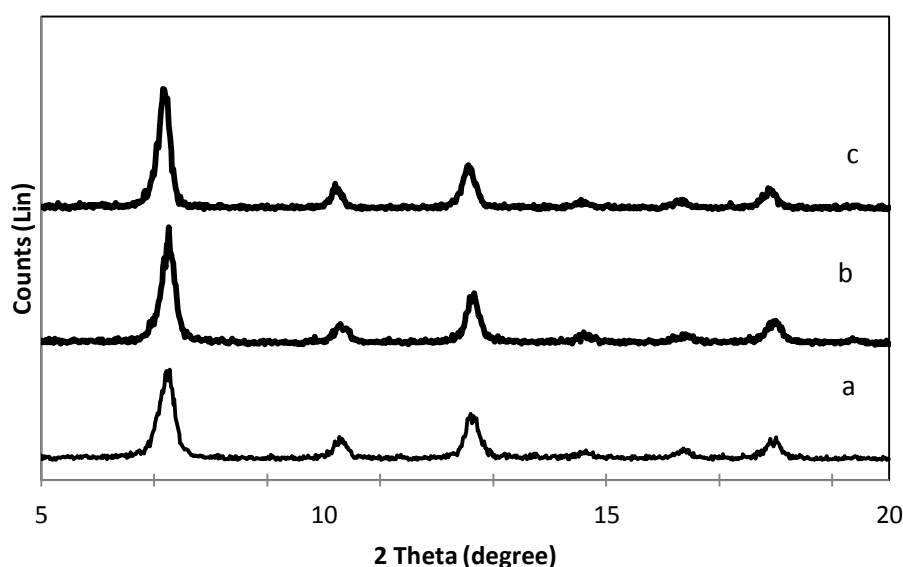


Figure 9: XRD patterns of ZIF-8 as a function of synthesis time. a) Sample A (5 minutes); b) Sample B (60 minutes); c) Sample C (1440 minutes). Molar ratio  $Zn^{2+}:Hmim:MeOH = 1:7.9:695$ , pH = 7

Table 10: Relative crystallinity of Samples ZIF-8 synthesized at different duration Molar ratio  $Zn^{2+}:Hmim:MeOH = 1:7.9:695$ , pH = 7)

Samples	Area under the curve	Relative crystallinity, %
A	93	40
B	315	100*
C	305	97

Note: The \* asterisk is referred to as the base

#### 4.1.2 Effect of Molar ratio

The XRD patterns of ZIF-8 synthesized at different  $Zn^{2+}$ :Hmim: MeOH molar ratios are shown in Figure 10. When molar ratio of  $Zn^{2+}$ :Hmim:MeOH changed from 1:7.9:86.7 to 1:7.9:1002, the relative crystallinity of the resulting ZIF-8 decreases. Table 11 shows the summary of relative crystallinity as a function of molar ratios. In order to study the effect of the solution pH on the formation of ZIF-8, the molar ratio of  $Zn^{2+}$ :Hmim:MeOH used to synthesize Samples F and G was maintained at 1:7.9:695

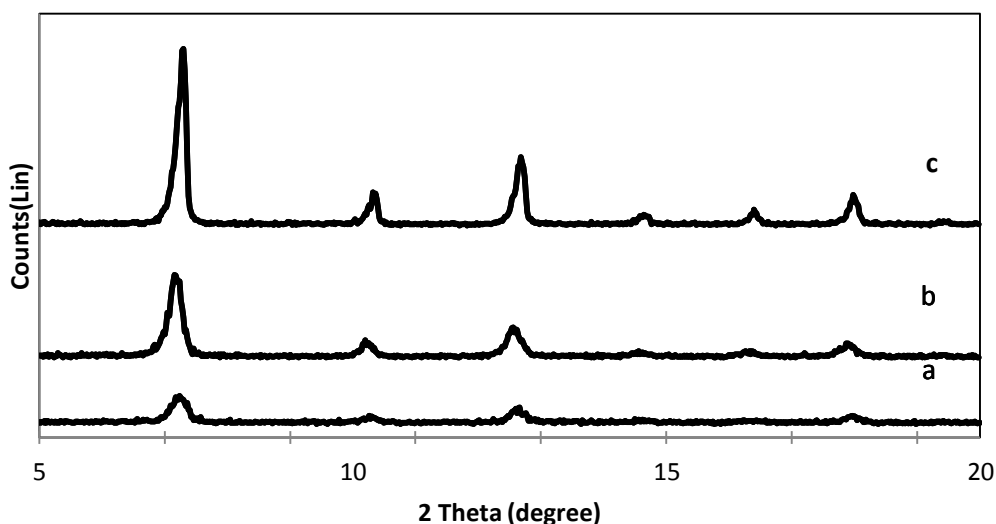


Figure 10: XRD pattern of ZIF-8 as a function of molar ratios: a) Sample E(1:7.9:1002); b) Sample B (1:7.9:695); c) Sample D (1:7.9:86.5) .60 minutes, pH=7.2

Table 11: Relative crystallinity as a function of molar ratios. 60 minutes, pH=7.2

Molar ratio	Area under the curve	Relative crystallinity, %
B	315	47
E	106	16
D	660	100*

Note: The \* asterisk is referred to as the base

### 4.1.3 Effect of pH

Figure 11 shows the XRD patterns of ZIF-8 synthesized at normal condition (pH=7.2 without present of hydrochloric acid and sodium formate), with present of hydrochloric acid (pH=6.7) and with present of sodium formate (pH=8.3). At pH 7.2, 2-methylimidazole linkers at ZIF-8 crystal are likely to be fully deprotonated and thus resulted in higher crystallinity. From these results, it was found that formation of ZIF-8 particles did not favour by an acidic or alkali solution. Table 12 shows the summary of relative crystallinity as a function of pH.

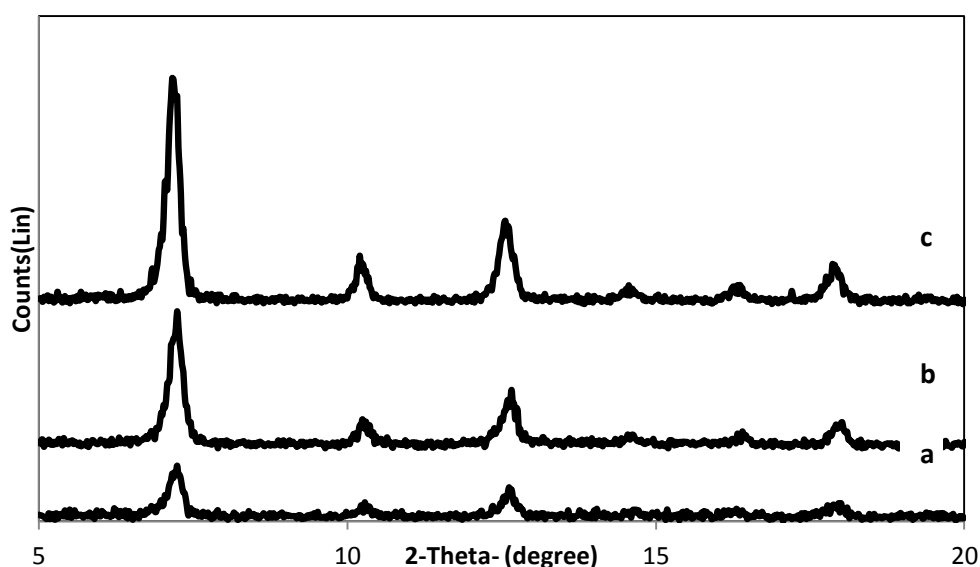


Figure 11: XRD pattern of ZIF-8 as a function of pH: a) Sample G (pH=8.3); b) Sample F (pH=6.7); c) Sample B (pH=7.2) .1:7.9:695, 60 minutes.

Table 12: Relative crystallinity as a function of pH.  $Zn^{2+}$ :Hmim:MeOH =1:7.9:695, 60 minutes .

Sample Code	Area under the curve	Relative crystallinity, %
B	315	100*
F	190	62
G	76	25

Note: The \* asterisk is referred to as the base

As a conclusion from results obtained from X-ray Diffraction (XRD) characterization, all the major peaks obtained for all the samples were matched well with the reported XRD pattern for ZIF-8 [27]. The well resolved peaks indicate the high crystallinity of the ZIF-8 samples obtained. These results show that particles with ZIF-8 structure were formed by using both reactant solutions with different synthesis duration, concentration (molar ratios) and pH of the synthesis solution.

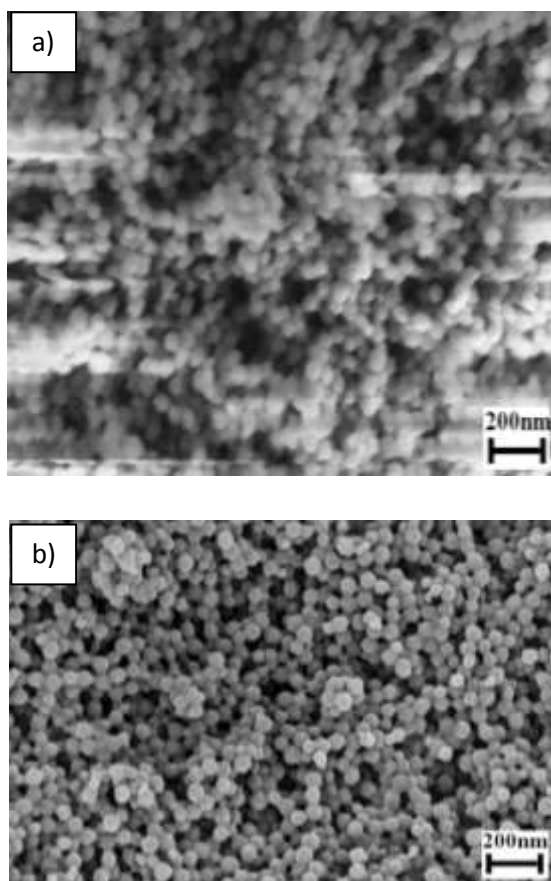


## 4.2 Morphology Evaluation of ZIF-8 particles using Scanning Electron Microscope (SEM)

The morphology and crystal sizes of the resulting ZIF-8 synthesized using different synthesis duration, concentration (molar ratios) and pH of the solution were confirmed by using SEM and the images are shown in the following section.

### 4.2.1 Effect of synthesis time

Figure 12 illustrates the SEM morphology of ZIF-8 synthesized at different synthesis duration. It was found that the average particles size of ZIF-8 did not change much when the synthesis time increases from 5 minutes to 1440 minutes. Referring to Figure 12, average particle size of ~80 nm was obtained for all three samples, sample A, sample B and sample C. These results revealed that the synthesis time did not affect the particles size of the resultant ZIF-8. Table 13 shows the average particle size (nm) of the resultant ZIF-8 as a function of synthesis time (min). These results were consistent with XRD results (Figure 9) whereas the changes of synthesis time did not affect the crystallinity and the crystal size of the resulting ZIF-8 particles.



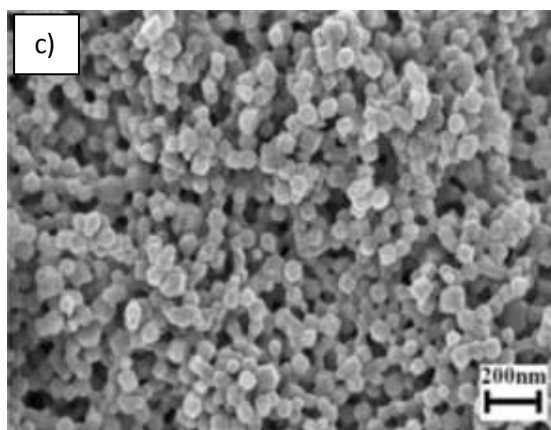


Figure 12: SEM image of ZIF-8 particles synthesized at different synthesis time (a) Sample A (5 min) (b) Sample B (60 min) and (c) Sample C (1440 min).  $Zn^{2+} :Hmim:MeOH = 1:7.9:695$ ,  $pH = 7.2$

Table 13: Particle size (nm) as a function of synthesise time (min).  $Zn^{2+} :Hmim:MeOH = 1:7.9:695$ ,  $pH=7.2$

Sample Code	Synthesis Time (min)	Average Particle size (nm)
<b>A</b>	<b>5</b>	<b>~77</b>
<b>B</b>	<b>60</b>	<b>~80</b>
<b>C</b>	<b>1440</b>	<b>~80</b>

#### 4.2.2 Effect of Molar Ratios

Figure 13 shows the SEM pictures of ZIF-8 samples synthesized using different molar ratio of  $\text{Zn}^{2+}$ :Hmim:MeOH. The average particle sizes increase from ~40 to ~380 nm when the ratio of  $\text{Zn}^{2+}$ :Hmim:MeOH changed from 1:7.9:1002 to 1:7.9:86.7. Referring to Figure 13 (a),(b) and (c), ZIF-8 particles synthesized using lower amount of methanol ( $\text{Zn}^{2+}$ :Hmim:MeOH = 1: 7.9:86.7 ) showed largest average particle size (~380 nm) as compared to ZIF-8 particle synthesized using higher amount of methanol ,which were about ~80 nm ( $\text{Zn}^{2+}$ :Hmim:MeOH=1:7.9:695) and ~40 nm ( $\text{Zn}^{2+}$ :Hmim:MeOH=1.7.9:1002). These results are consistent with the earlier reported results for the synthesis of ZIF-8 [10].This was due to the low amount of methanol reduced the number of nuclei formed and stimulates the formation of larger crystal which caused by higher  $\text{Zn}^{2+}$  and Hmim concentration. But, high amount of methanol present in the synthesis solution resulted in the formation of smaller crystals. This was due to that at lower concentration of  $\text{Zn}^{2+}$  and Hmim, nucleation rate was relatively larger than the crystal growth rate. Table 14 shows the summary of the average particle size (nm) as a function of molar ratios  $\text{Zn}^{2+}$ :Hmim:MeOH

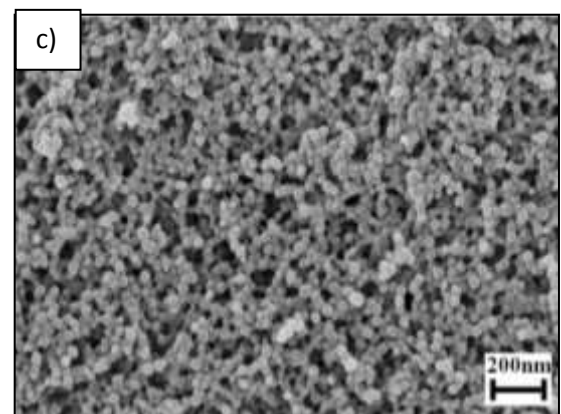
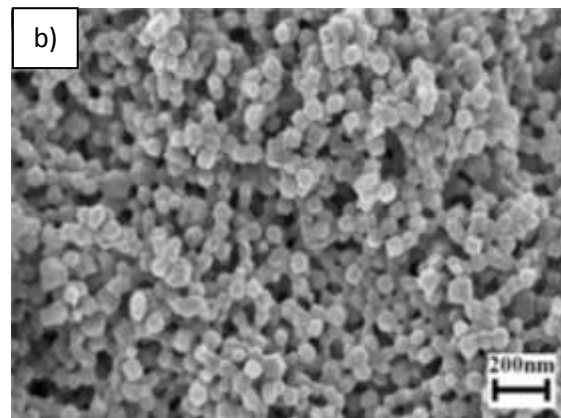
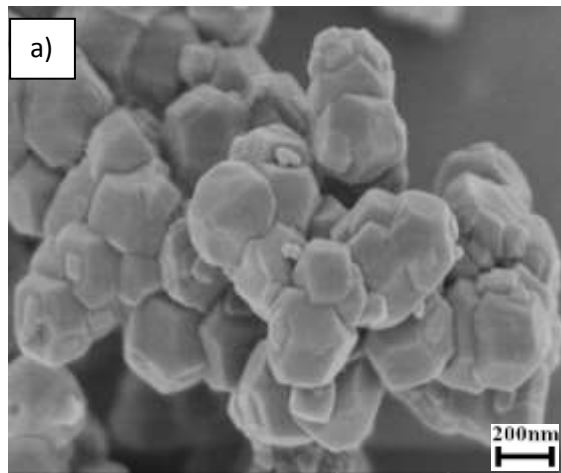


Figure 13: SEM image of ZIF-8 particles synthesized at different molar ratio (a) Sample D (1:7.9:86.7); (b) Sample B (1:7.9:695); (c) Sample E (1:7.9:1002) in 60 minutes, pH=7.2

Table 14: Particle size (nm) as a function of molar ratios  $Zn^{2+}$  :Hmim:MeOH. 60 minutes, pH =7.2

Sample	$Zn^{2+}$ :Hmim MeOH:	Average Particle size (nm)
<b>D</b>	<b>1:7.9:86.7</b>	<b>~380</b>
<b>B</b>	<b>1:7.9:695</b>	<b>~80</b>
<b>E</b>	<b>1:7.9:1002</b>	<b>~40</b>

#### 4.2.3 Effect of pH

Figure 14 shows the ZIF-8 particles synthesis with and without adding acidic and alkali solution. From Figure 14, it is observed that the particles formed well intergrown particles.

Figure 14 (b) shows the SEM morphology of ZIF-8 particles formed from the synthesis solution with pH 6.7 after the addition of hydrochloric acid (HCl). The resulting particles show smaller size of ~70 nm as compared to those particles formed from the synthesis solution with pH 7.2 (80 nm, Figure 14a). Referring to Figure 14, the distribution of the particles was uniform. This result shows that acidic condition is preferable for ZIF-8 formation than alkaline condition. This was mainly due to the concentration of deprotonated linkers is decreased as pH decreasing.

On the other hand, Figure 13 (c) shows the ZIF-8 synthesized from the solution containing sodium formate (NaCOOH) and the pH of the synthesis solution was 8.3. It was observed that the particle was poorly intergrown and agglomerate which resulted in the difficulties for the size measurement. These results show that pH of 8.3 which was higher than the normal pH condition of 7.2 was not favorable for crystal growth of ZIF-8 at room temperature. According to Cravillon et al (2009), NaCOOH acted as the deprotonator only at high temperature, but as the competitor at room temperature. Hence, in the experiment, NaCOOH competed with the organic ligands for the  $Zn^{2+}$  reaction site. ZIF-8 particles could hardly be formed uniformly. In addition, the Hmim linkers may not deprotonated due to the present of optimum protonate in the reactant solutions and thus, an increase in pH did not result in the well intergrown crystal. Table 15 shows Particle size (nm) as a function of pH.

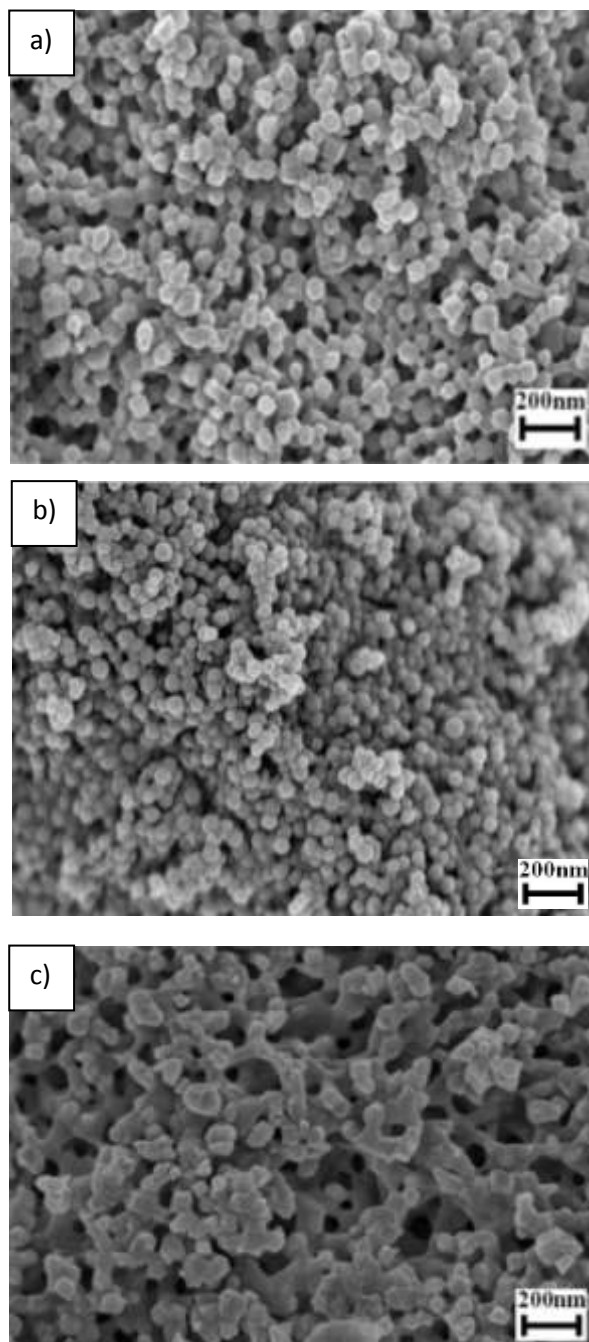


Figure 14: SEM image of ZIF-8 particles synthesized with and without the addition of hydrochloric acid and sodium formate a) B (pH=7.2); b) F (pH 6.7); c) G (pH 8.3) .Molar ratio  $Zn^{2+}$  :Hmim:MeOH=1:7.9:695, 60 minutes.

Table 15: Particle size (nm) as a function of pH. Molar ratio  $Zn^{2+}$ :Hmim:MeOH=1:7.9:695, 60 minutes.

<b>Sample Code</b>	<b>pH</b>	<b>Average Particle size (nm)</b>
<b>B</b>	<b>7.2</b>	<b>~80</b>
<b>F</b>	<b>6.7</b>	<b>~70</b>
<b>G</b>	<b>8.3</b>	<b>NA</b>

As a conclusion from the characterization results, the SEM images show that ZIF-8 growth most preferable at normal condition (pH=7.2), preferable at acidic condition (pH=6.7) and least preferable at alkali condition (pH=8.3).

### 4.3 BET Surface Area

#### 4.3.1 Effect of molar ratio of the synthesis solution (amount of methanol) on the BET surface area of ZIF-8

ZIF-8 synthesized by Park et.al (2006) [27] showed BET surface area of 1630 m<sup>2</sup>/g, which was the highest surface area reported in the literature for ZIF-8. Table 16 shows the effect of molar ratio of the synthesis solution on the BET surface area of the resulting ZIF-8 samples. ZIF-8 obtained shows BET surface area up 1386 m<sup>2</sup>/g, 1344 m<sup>2</sup>/g and 1262 m<sup>2</sup>/g for ZIF-8 synthesized using Zn<sup>2+</sup> :Hmim:MeOH = 1: 7.9:86.7 (Sample D), 1:7.9:695 (sample B), and 1:7.9:1002 (sample E) respectively. The relatively similar BET surface area was observed for all ZIF-8 samples synthesized regardless to their different in particle size which had led to similar N<sub>2</sub> adsorption. This result show that high BET surface areas of ZIF-8 samples can be obtained even the ZIF-8 samples have yet to achieve full crystallinity (Figure 10,XRD pattern).

Table 16: Effect of molar ratio on the average particle size and BET surface area of ZIF-8.samples synthesized at 60 minutes, pH=7.2

Sample Code	Average Particles Size(nm)	BET Surface Area m <sup>2</sup> /g
B	~80	1386
D	~380	1344
E	~40	1262



#### 4.4 CO<sub>2</sub> adsorption testing

##### 4.4.1 Effect of molar ratio of the synthesis solution (amount of methanol) on the CO<sub>2</sub> adsorption and desorption

The CO<sub>2</sub> adsorptions characteristic of the ZIF-8 samples were tested using CO<sub>2</sub> physisorption analyzer, BELSORP. Figure 15 shows adsorption and desorption isotherm for samples B, sample D and sample E. Referring to Figure 15, all the samples exhibits the uniform trending of adsorption/desorption isotherm. The CO<sub>2</sub> adsorption capacity of 0.00055 mol<sup>-1</sup>/g, 0.00053 mol<sup>-1</sup>/g and 0.00047 mol<sup>-1</sup>/g were obtained for sample B,D and E respectively as the reported CO<sub>2</sub> adsorption is 0.00102 mol<sup>-1</sup>/g [34]. These results indicate that all the three samples show relatively same amount of CO<sub>2</sub> adsorbed/desorbed regardless to their different in particles size. These results consistent with results obtained in BET surface area whereas all the samples show similar BET surface areas.

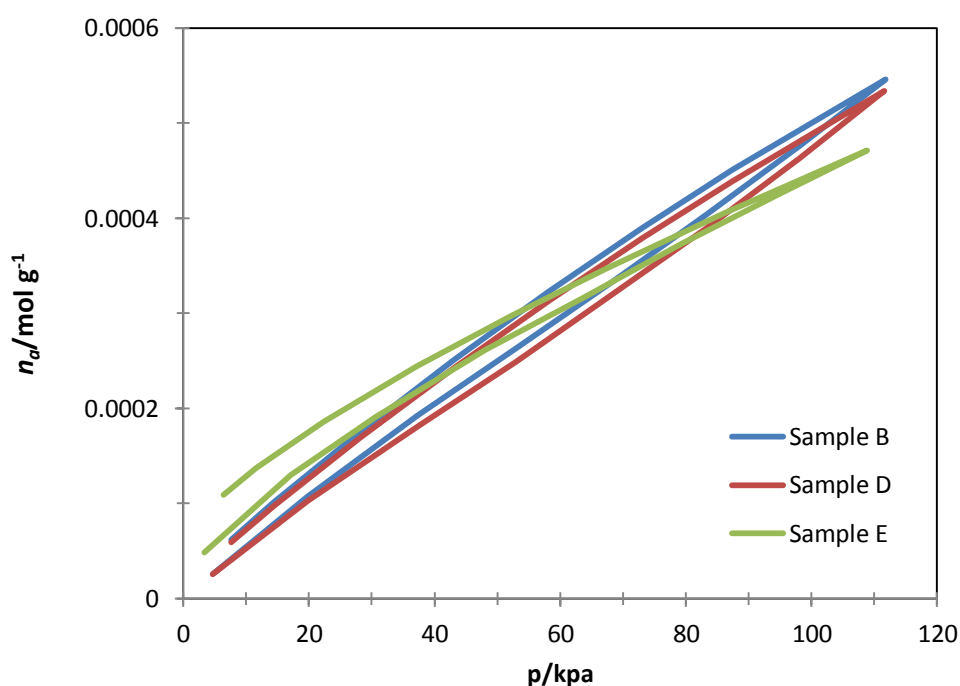


Figure 15: CO<sub>2</sub> adsorption/desorption isotherm for Sample B, Sample D and Sample E.

The reduction in size could increase the surface area of the particles and thus increase their CO<sub>2</sub> adsorption capability. However, the results obtained in the present research work shows that the reduction of particle size did not increase both the surface area and CO<sub>2</sub> adsorption capability. Referring to XRD patterns, these results could be mainly due to the crystallinity of the samples formed. Although the particle sizes reduced, the crystallinity of the resultant ZIF-8 was also reduced. The surface areas might be off-set by the decrease in the crystallinity of the sample and thus, reduction in particle size could not increase the surface area of the resultant particles. Therefore, the CO<sub>2</sub> adsorption for the samples did not change much although the particle size reduced.

## CHAPTER 5

### CONCLUSION & RECOMMENDATION

#### 5. Conclusion

This project is focuses on the synthesis and characterization of ZIF-8 particles as adsorbent for CO<sub>2</sub> removal. Based on the results,

- 1) The experimental XRD pattern showed that all the samples synthesized in the present work demonstrated ZIF-8 structure regardless to the synthesis duration, molar ratio of Zn<sup>2+</sup>:MeOH in the synthesis solution and pH of the synthesis duration .Referring to XRD patterns, all major peaks obtained were matching well with the reported XRD patterns of ZIF-8 [27].
  
- 2) The SEM image showed that ZIF-8 particles synthesized using lower amount of methanol (Zn<sup>2+</sup>:Hmim :MeOH = 1:7.9:86.7) produced larger particle size of ZIF-8. Besides, ZIF-8 particles synthesized at longer duration (60 minutes and 1440 minutes) exhibit higher crystallinity with rhombic dodecahedron structure as compared while particles synthesized at very short duration (5 minutes) which showed spherical features. Presence of NaCOOH in the synthesis solution caused the particles to agglomerate and resulted in difficulty in particle size measurement. Addition of HCl in the synthesis solution resulted in smaller particles size which is particularly interesting for further investigation.

- 3) Varying the  $\text{Zn}^{2+}$ :Hmim:MeOH molar ratios in the synthesis solution resulted in different particle size of ZIF-8 produced .Higher amount of methanol presence in the synthesis solution produced smaller particle size of ZIF-8. On the other hand, formation of larger particles size of ZIF-8 was observed for the sample synthesized using lower amount of methanol.
  
- 4)  $\text{CO}_2$  adsorption results showed that particles with varies particle sizes do not have significant effect on the  $\text{CO}_2$  adsorption and this result was consistent with the BET surface area results. This was mainly attributed to the crystallinity of the samples obtained. Although the particle sizes reduced, the crystallinity of the resultant ZIF-8 was also reduced. The surface areas might be off-set by the decrease in the crystallinity of the sample and thus, reduction in particle size could not increase the surface area of the resultant particles. Therefore, the  $\text{CO}_2$  adsorption for the samples did not change much although the particle size reduced.

### **5.1 Recommendation**

For further expansion of this work, the samples should be synthesized using different temperature in order to study the effect of synthesis temperature on the characteristic of the resulting ZIF-8 particles.

## CHAPTER 6

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# APPENDIX

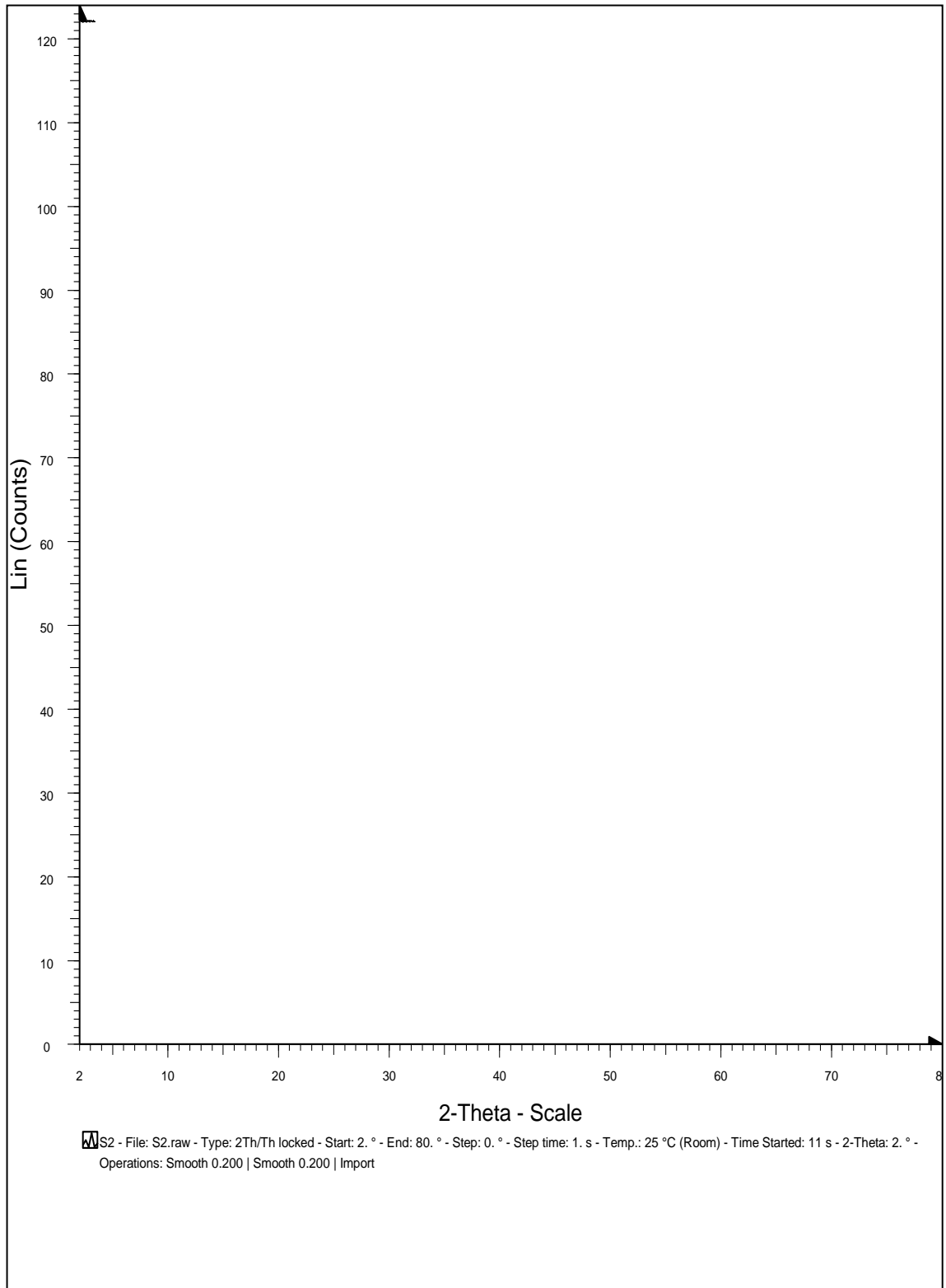


Figure 16: XRD pattern of ZIF-8 (Sample A)



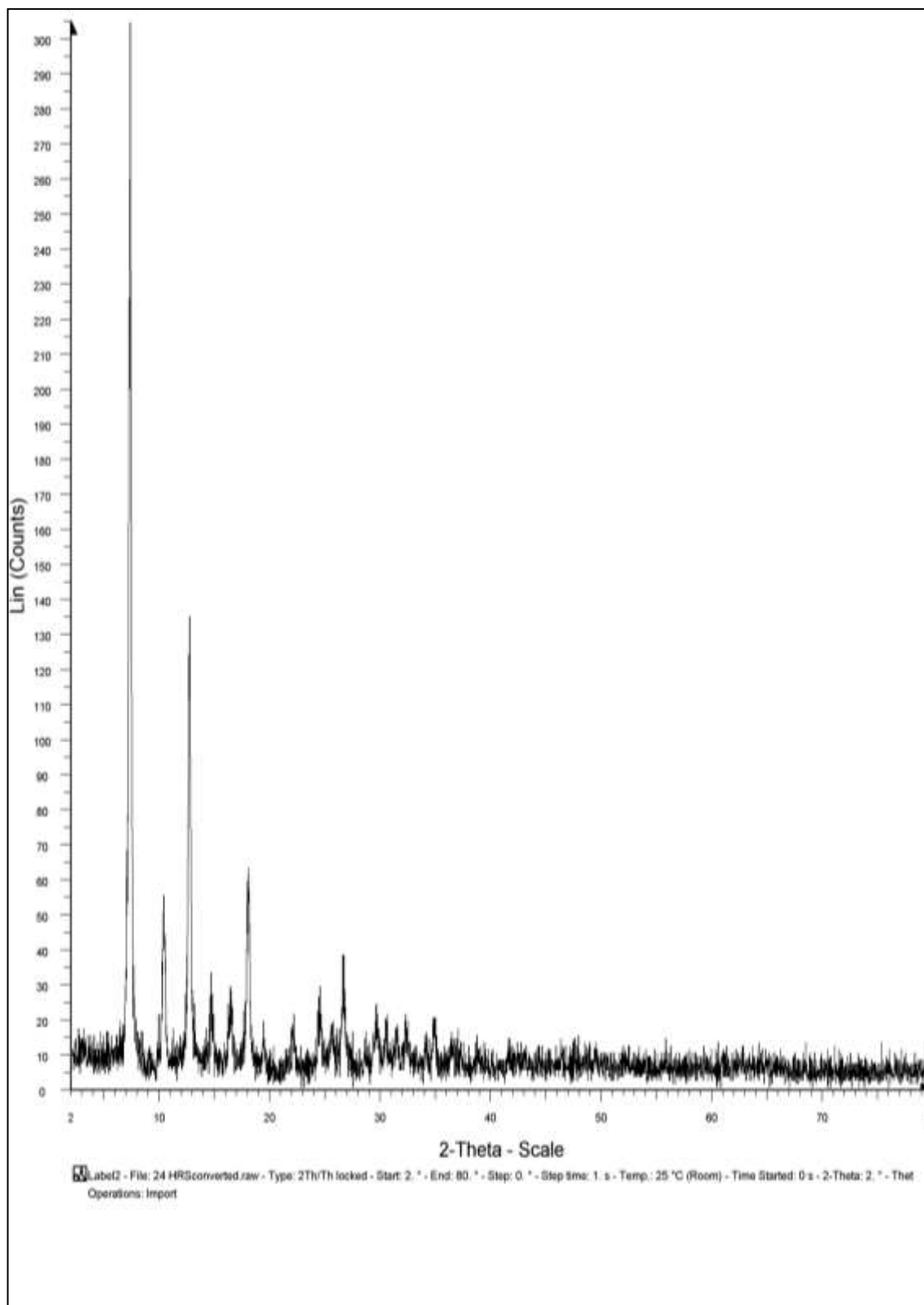


Figure 18: XRD pattern of ZIF-8 (Sample C)

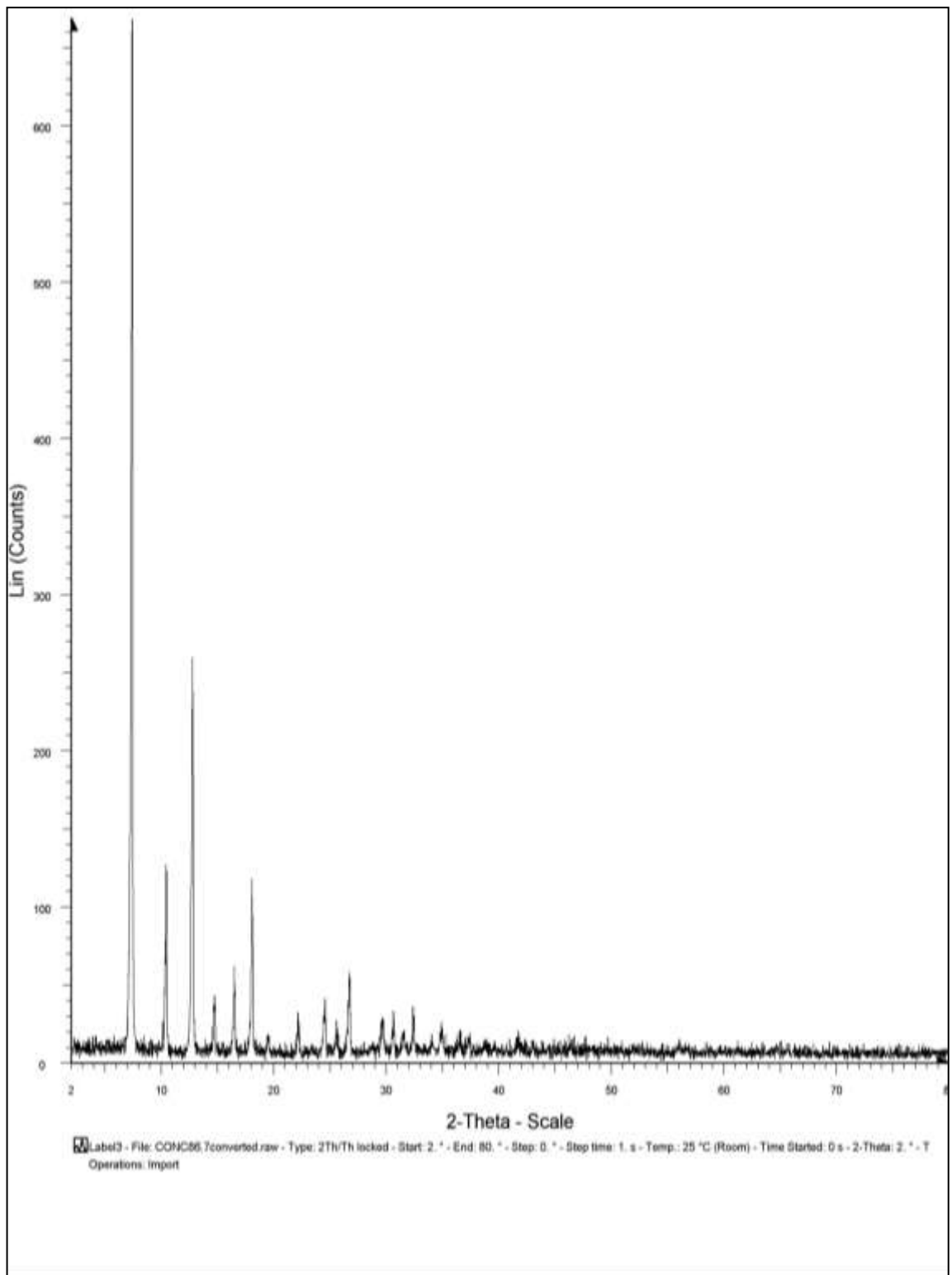


Figure 19: XRD pattern of ZIF-8 (Sample D)

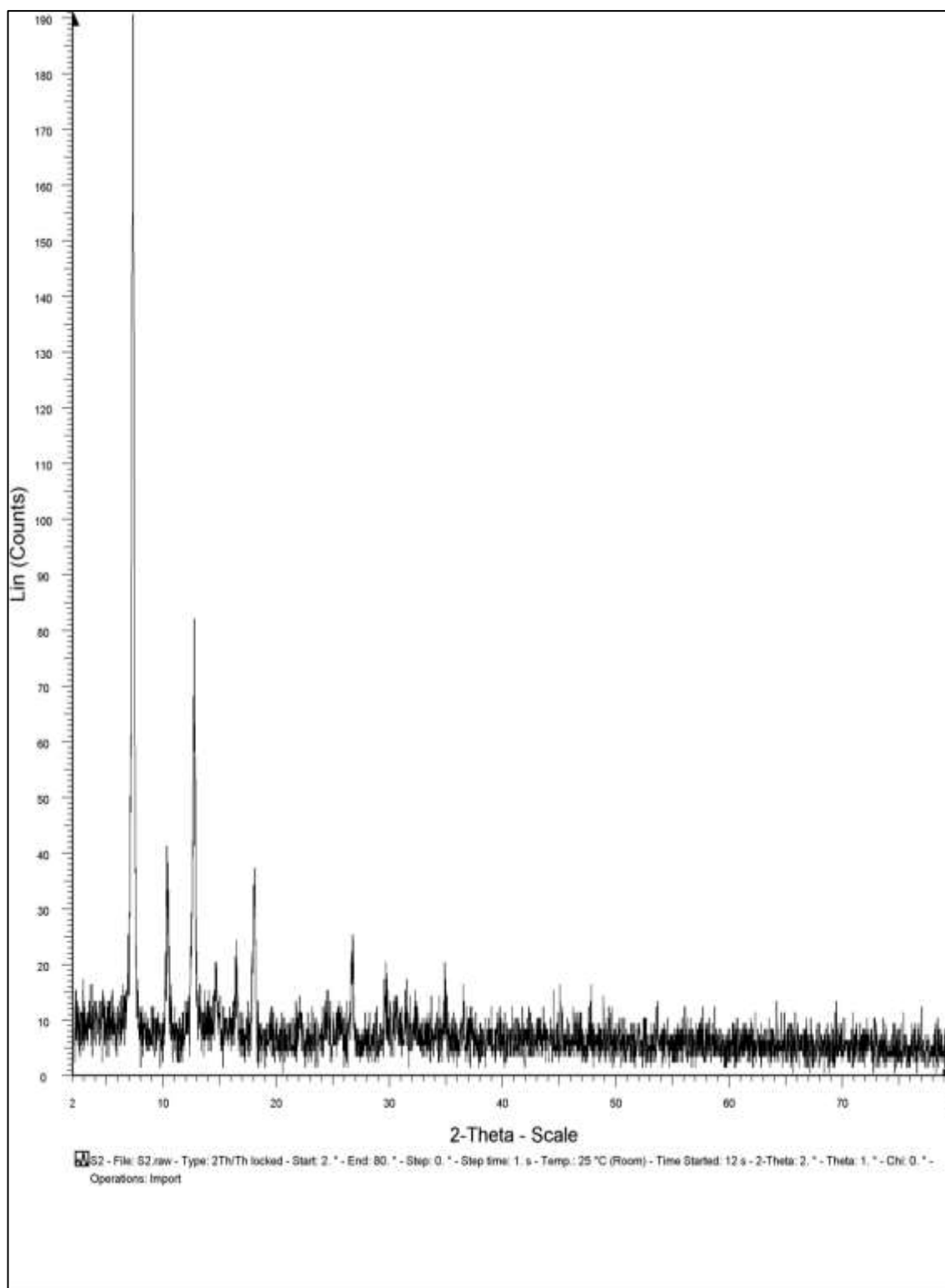


Figure 20: XRD pattern of ZIF-8 (Sample F)



Full Report Set

Port 3

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Page 1

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Equilibration Interval: 10 s  
Sample Density: 1.000 g/cm<sup>3</sup>

Analysis Adsorptive: N<sub>2</sub>  
Analysis Bath Temp.: -195.800 °C  
Sample Mass: 0.1912 g  
Cold Free Space: 60.0197 cm<sup>3</sup> Measured  
Low Pressure Dose: None  
Automatic Degas: Yes

Sample Prep. Stage	Temperature (°C)	Ramp Rate (°C/min)	Time (min)
1	90	10	30
2	150	10	240

Summary Report

Surface Area

Single point surface area at  $p/p^* = 0.293798787$ : 1346.1739 m<sup>2</sup>/g

BET Surface Area: 1385.9322 m<sup>2</sup>/g

Langmuir Surface Area: 1926.3612 m<sup>2</sup>/g

t-Plot Micropore Area: 1257.3914 m<sup>2</sup>/g

t-Plot External Surface Area: 128.5408 m<sup>2</sup>/g

BJH Adsorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 68.116 m<sup>2</sup>/g

BJH Desorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 103.5588 m<sup>2</sup>/g

D-H Adsorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 98.369 m<sup>2</sup>/g

D-H Desorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 87.8230 m<sup>2</sup>/g

Pore Volume

Single point adsorption total pore volume of pores  
less than 1453.900 Å diameter at  $p/p^* = 0.988509159$ : 1.071553 cm<sup>3</sup>/g

t-Plot micropore volume: 0.614292 cm<sup>3</sup>/g

BJH Adsorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.500559 cm<sup>3</sup>/g

BJH Desorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.695006 cm<sup>3</sup>/g

D-H Adsorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.527126 cm<sup>3</sup>/g

D-H Desorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.681001 cm<sup>3</sup>/g

Figure 21: BET surface analyzer report summary (Sample B)



Full Report Set

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Page 7

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Equilibration Interval: 10 s  
Sample Density: 1.000 g/cm<sup>3</sup>

Analysis Adsorptive: N<sub>2</sub>  
Analysis Bath Temp.: -195.800 °C  
Sample Mass: 0.1912 g  
Cold Free Space: 60.0197 cm<sup>3</sup> Measured  
Low Pressure Dose: None  
Automatic Degas: Yes

Sample Prep: Stage	Temperature (°C)	Ramp Rate (°C/min)	Time (min)
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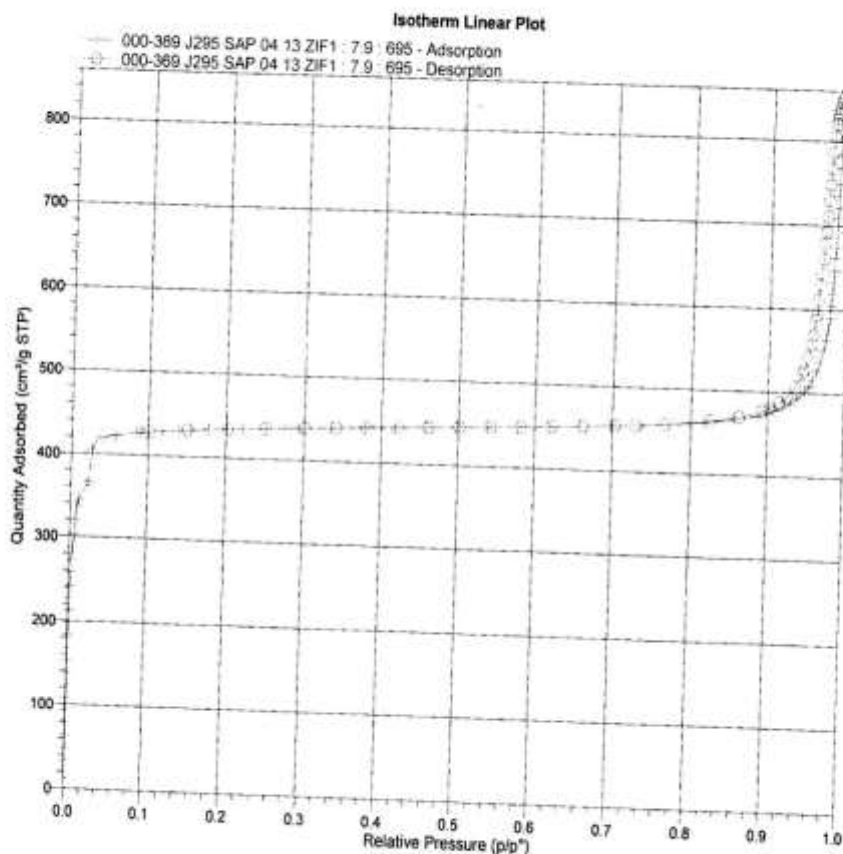


Figure 22: BET surface analyzer isotherm linear plot (Sample B)



Full Report Set

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Equilibration Interval: 10 s  
Sample Density: 1.000 g/cm<sup>3</sup>

Analysis Adsorptive: N<sub>2</sub>  
Analysis Bath Temp.: -195.800 °C  
Sample Mass: 0.1999 g  
Cold Free Space: 58.5433 cm<sup>3</sup> Measured  
Low Pressure Dose: None  
Automatic Degas: Yes

Sample Prep:	Stage	Temperature (°C)	Ramp Rate (°C/min)	Time (min)
	1	90	10	30
	2	150	10	240

#### Summary Report

##### Surface Area

Single point surface area at  $p/p^* = 0.294783818$ : 1295.3778 m<sup>2</sup>/g

BET Surface Area: 1344.0225 m<sup>2</sup>/g

Langmuir Surface Area: 1842.7176 m<sup>2</sup>/g

t-Plot Micropore Area: 1308.5917 m<sup>2</sup>/g

t-Plot External Surface Area: 35.4308 m<sup>2</sup>/g

BJH Adsorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 12.959 m<sup>2</sup>/g

BJH Desorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 23.6861 m<sup>2</sup>/g

D-H Adsorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 24.943 m<sup>2</sup>/g

D-H Desorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 20.1852 m<sup>2</sup>/g

##### Pore Volume

Single point adsorption total pore volume of pores  
less than 3126.863 Å diameter at  $p/p^* = 0.993793030$ : 0.679181 cm<sup>3</sup>/g

t-Plot micropore volume: 0.635316 cm<sup>3</sup>/g

BJH Adsorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.030530 cm<sup>3</sup>/g

BJH Desorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.043740 cm<sup>3</sup>/g

D-H Adsorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.038221 cm<sup>3</sup>/g

D-H Desorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.040767 cm<sup>3</sup>/g

Figure 23: BET surface analyzer report summary (Sample D)







Full Report Set

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Equilibration Interval: 10 s  
Sample Density: 1.000 g/cm<sup>3</sup>

Analysis Adsorptive: N<sub>2</sub>  
Analysis Bath Temp.: -195.800 °C  
Sample Mass: 0.1999 g  
Cold Free Space: 58.5433 cm<sup>3</sup> Measured  
Low Pressure Dose: None  
Automatic Degas: Yes

Sample Prep: Stage	Temperature (°C)	Ramp Rate (°C/min)	Time (min)
1	90	10	30
2	150	10	240

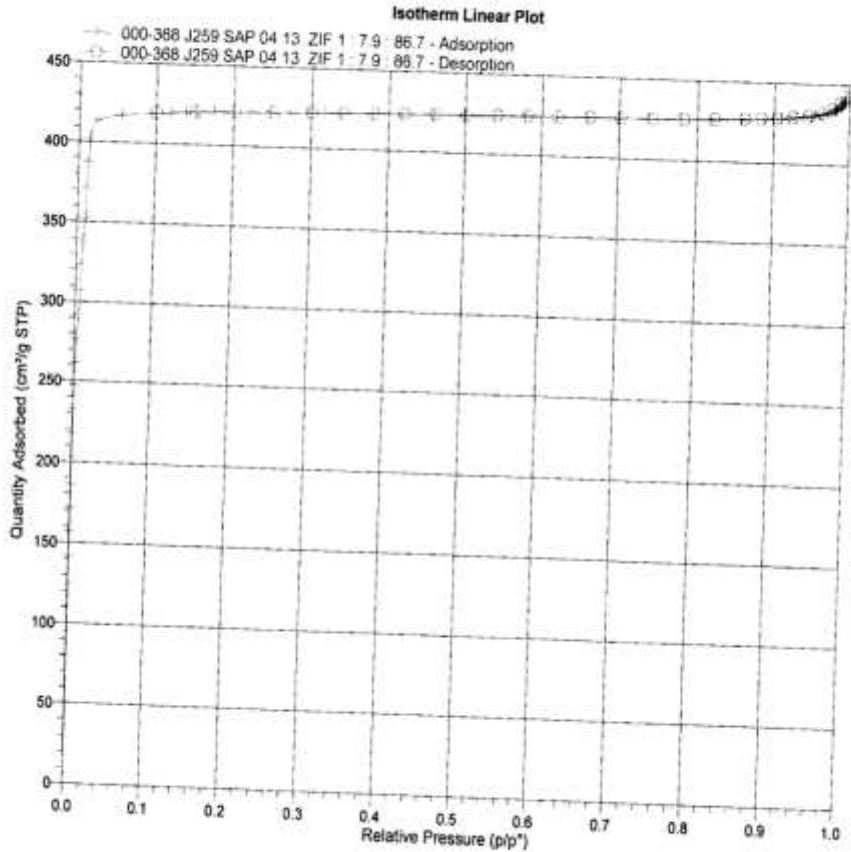


Figure 24: BET surface analyzer isotherm linear plot (Sample D)



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08 13 S1

File: C:\WIN3020\DATA\000-437.SMP

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Completed: 21/6/2013 4:08:44AM	Analysis Bath Temp.: -195.800 °C
Report Time: 28/6/2013 12:03:13PM	Sample Mass: 0.1992 g
Warm Free Space: 20.5754 cm <sup>3</sup> Measured	Cold Free Space: 61.7723 cm <sup>3</sup> Measured
Equilibration Interval: 10 s	Low Pressure Dose: None
Sample Density: 1.000 g/cm <sup>3</sup>	Automatic Degas: Yes

Sample Prep: Stage	Temperature (°C)	Ramp Rate (°C/min)	Time (min)
1	90	10	30
2	150	10	240

Summary Report

Surface Area

Single point surface area at  $p/p^* = 0.297222064$ : 1218.1866 m<sup>2</sup>/g

BET Surface Area: 1262.2549 m<sup>2</sup>/g

Langmuir Surface Area: 1750.8438 m<sup>2</sup>/g

t-Plot Micropore Area: 1192.6528 m<sup>2</sup>/g

t-Plot External Surface Area: 69.6021 m<sup>2</sup>/g

BJH Adsorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 39.002 m<sup>2</sup>/g

BJH Desorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 71.7817 m<sup>2</sup>/g

D-H Adsorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 53.859 m<sup>2</sup>/g

D-H Desorption cumulative surface area of pores  
between 17.000 Å and 3000.000 Å diameter: 69.4338 m<sup>2</sup>/g

Pore Volume

Single point adsorption total pore volume of pores  
less than 0.000 Å diameter at  $p/p^* = 1.000959646$ : 0.921281 cm<sup>3</sup>/g

t-Plot micropore volume: 0.582274 cm<sup>3</sup>/g

BJH Adsorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.309027 cm<sup>3</sup>/g

BJH Desorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.334427 cm<sup>3</sup>/g

D-H Adsorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.326849 cm<sup>3</sup>/g

D-H Desorption cumulative volume of pores  
between 17.000 Å and 3000.000 Å diameter: 0.340629 cm<sup>3</sup>/g

Figure 25: BET surface analyzer report summary (Sample E)



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Equilibration Interval: 10 s  
Sample Density: 1.000 g/cm<sup>3</sup>

Analysis Adsorptive: N2  
Analysis Bath Temp: -195.800 °C  
Sample Mass: 0.1992 g  
Cold Free Space: 61.7723 cm<sup>3</sup> Measured  
Low Pressure Dose: None  
Automatic Degas: Yes

Sample Prep: Stage	Temperature (°C)	Ramp Rate (°C/min)	Time (min)
1	90	10	30
2	150	10	240

Isotherm Linear Plot

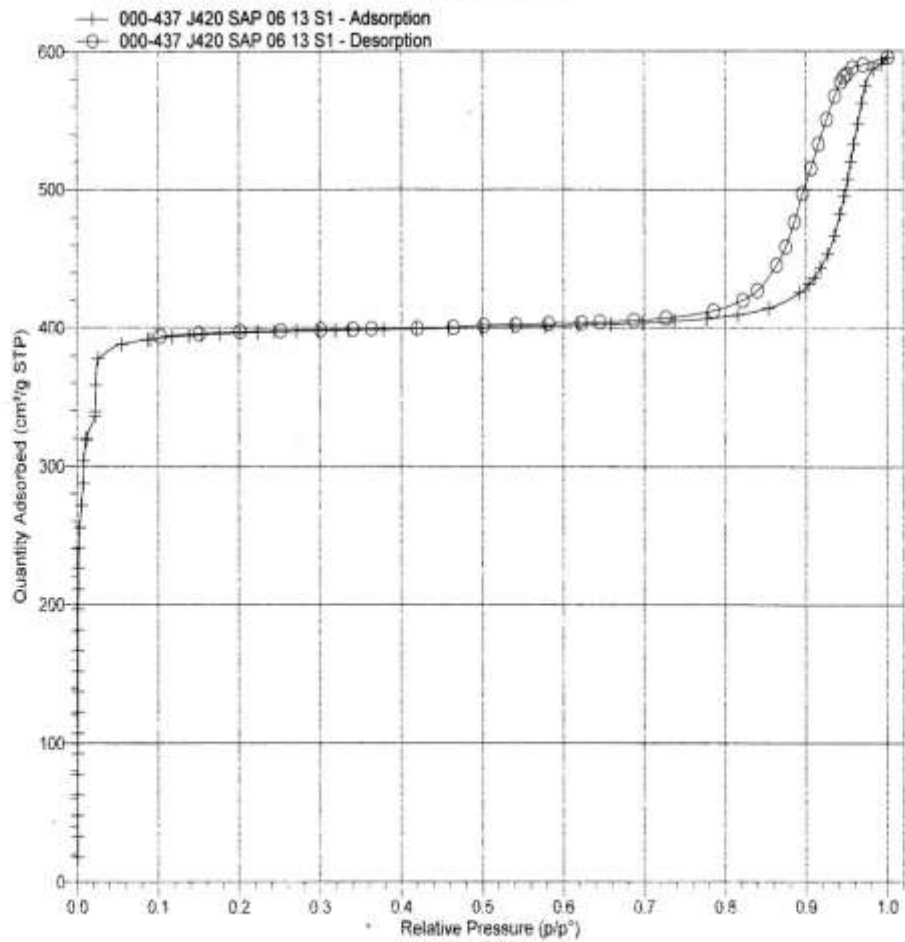


Figure 26: BET surface analyzer isotherm linear plot (Sample E)