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# Tuning of Particle Size of Zeolitic Imidazolate Framework-7 via Rapid Synthesis Duration for CH<sub>4</sub> Adsorption

Li-Xing (Joey) Chai <sup>1</sup>, Alia Syuhada Abd Rahman <sup>1,2</sup> and Yin Fong Yeong <sup>1,2,\*</sup>

<sup>1</sup> Department of Chemical Engineering, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Perak, Malaysia; joey\_19001263@utp.edu.my (L.-X.C.); alia.rahman@utp.edu.my (A.S.A.R.)

<sup>2</sup> Centre of Carbon Capture, Utilization, and Storage (CCCUS), Institute of Sustainable Energy and Resources, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Perak, Malaysia

\* Correspondence: yinfong.yeong@utp.edu.my

**Abstract:** In this work, zeolite imidazolate framework-7 (ZIF-7) nanoparticles are synthesized via a solvothermal method and rapid synthesis durations of 1 h and 3 h. The effect of the synthesis duration on the structural properties of ZIF-7 was characterized by XRD and FESEM analyses. Subsequently, CH<sub>4</sub> single gas adsorption over ZIF-7 nanoparticles was examined using the volumetric method at room temperature and pressure ranging from 2 to 9 bar. The results showed that the synthesized ZIF-7 adsorbents were highly crystalline with a well-defined and homogeneous particle size distribution of 50–60 nm. It was found that increasing the synthesis duration from 1 h to 3 h did not amend the structure and morphology of the resultant samples significantly, mainly due to the short synthesis duration. Meanwhile, the CH<sub>4</sub> adsorbed by ZIF-7 nanoparticles increased with rising pressure for both samples, and the ZIF-7 nanoparticles synthesized at 3 h showed a greater adsorption capacity than that of 1 h, mainly due to its higher crystallinity and well-developed pore structure. The ZIF-7 synthesized at 3 h demonstrated an adsorption capacity up to 2.2 mol/kg, which was higher than those values reported in the literature for micron-sized ZIF-7 samples. The CH<sub>4</sub> gas adsorption behavior of ZIF-7 nanoparticles synthesized at 1 h and 3 h were well predicted by the Langmuir isotherm model, with coefficients of determination, R<sup>2</sup>, of 0.9994 and 0.9982, respectively.



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## 1. Introduction

Greenhouse gas (GHG) emissions are the primary contributors to climate change, trapping heat in the Earth's atmosphere and leading to global warming. Among these gasses, methane (CH<sub>4</sub>) stands out as a particularly potent GHG. Although it is present in the atmosphere in smaller quantities compared to carbon dioxide (CO<sub>2</sub>) [1], methane has a much higher global warming potential (GWP), being approximately 25 times more effective at trapping heat over a 100-year period [2]. Major sources of methane emissions include natural processes such as wetlands, as well as human activities like agriculture, waste management, and fossil fuel extraction. Due to its significant impact on climate change, reducing methane emissions has become a critical target for global environmental policies and technological innovations aimed at mitigating GHG effects [1,3].

Common methods for the removal of CH<sub>4</sub> from gas mixtures include absorption, adsorption, membrane separation, and cryogenic distillation [4,5]; amongst these, adsorption and absorption-based methods are dominant in industrial applications. Adsorption-based and membrane-based gas separations offer significant reductions in the energy consumption and costs of the separation processes [5]. Adsorption techniques utilize materials like activated carbon, zeolites, and metal–organic frameworks (MOFs), which selectively adsorb CH<sub>4</sub> from the gas stream. Membrane separation employs semi-permeable membranes to selectively allow targeted gasses to pass through while retaining other gasses. Cryogenic



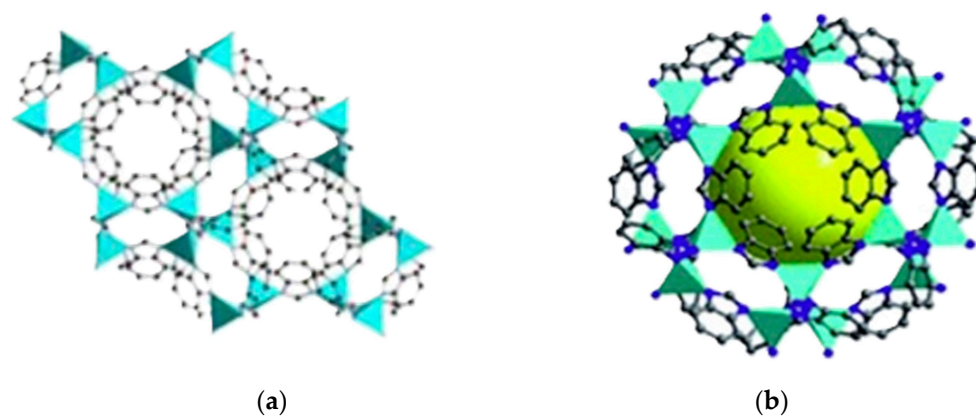
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distillation involves cooling the gas mixture to very low temperatures, where  $\text{CH}_4$  can be separated based on its boiling point. On the other hand, absorption processes use liquids that selectively dissolve  $\text{CH}_4$ , allowing for its separation from other components [6,7]. Generally, each method has its advantages and is chosen based on factors like the specific application, required purity, and economic considerations [8].

Adsorption is an equilibrium-limited technique that allows gas separation or storage due to unique physical and chemical interactions between the adsorbent and the components of the gas stream [9]. Adsorption provides a means to store and transport methane efficiently due to its desirable properties including superior adsorption kinetics and high regenerability, which are commonly linked to the specific surface area, pore size, material composition, and presence of favorable active sites for adsorption [10].  $\text{CH}_4$  can be absorbed onto a solid adsorbent material, such as activated carbon or MOFs, allowing for compact storage and easy transportation. ZIF-7, ZIF-8, ZIF-90, MOF-5, MIL-53, Fe(bdp), and Co(bdp) are common types of adsorbents used in gas methane capture, as reported in the literature [10].

The current development of adsorbents for methane capture faces significant challenges that impede their practical implementation and hinder the effective mitigation of methane emissions [11]. One of the primary challenges is the relatively low adsorption capacity of existing adsorbents for methane capture. While various materials, such as zeolites, activated carbon, and metal–organic frameworks (MOFs), have demonstrated promising adsorption capabilities, their methane uptake capacities often fall short of meeting the stringent requirements for efficient methane capture [11]. Enhancing the adsorption capacity of these materials is crucial to ensure effective and economically viable methane removal from industrial processes, agriculture, and waste management.

Among the reported literature, zeolitic imidazolate framework (ZIFs) adsorbents have gained recognition as effective materials for gas separation and storage in recent years. These frameworks are porous crystalline structures made of metal ions connected by organic linkers [12,13]. Their unique characteristics, such as high surface areas, variable pore sizes, and excellent thermal stability, make them suitable for various applications, including methane adsorption [11]. Furthermore, ZIFs have also been explored in the treatment of breast cancer recently due to their remarkable properties, including high porosity, satisfactory biocompatibility, and acidic-responsive degradation [14,15]. Among ZIFs, ZIF-7 stands out due to its remarkable ability to absorb and separate methane. ZIF-7's structure consists of zinc ions linked by 2-methylimidazole, forming a three-dimensional network of interconnected pores [12,13,16]. This design, with its high surface area and specific pore size distribution, allows for effective methane capture on ZIF-7 surfaces. The crystal and chemical structures of ZIF-7 are shown in Figure 1a,b, respectively.



**Figure 1.** (a) Crystal structure of ZIF-7 and (b) chemical structure of ZIF-7 (Zn is represented by blue tetrahedron, C by grey, N by blue, and H atom in bIm is omitted) [13].

ZIF-7 has attracted significant research interest, leading to ongoing efforts aimed at further improving its performance for CH<sub>4</sub> capture. However, ZIF-7s reported in the literature mainly synthesized at higher temperatures and longer durations, which resulted in larger particle size in microns and a relatively moderate adsorption capacity. Meanwhile, it is well known from the literature that a smaller particle size of adsorbents can enhance the gas adsorption capacity due to a higher surface area.

Thus, in this work, the particle size of ZIF-7 is tuned by rapid synthesis durations of 1 h and 3 h for CH<sub>4</sub> adsorption under room temperature, which is not commonly found in the literature. The effects of rapid synthesis duration toward the particle size, morphology, crystallinity, as well as CH<sub>4</sub> adsorption capacity of the resultant ZIF-7 samples were determined. Subsequently, different adsorption isotherm models were performed to further investigate the adsorption behavior of CH<sub>4</sub> in the ZIF-7 samples. Overall, the significance of this study is to enhance the CH<sub>4</sub> adsorption efficiency by using ZIF-7 nanoparticles produced through rapid synthesis durations of 1 h and 3 h, which are rarely found in the literature.

## 2. Materials and Methods

### 2.1. Materials

The synthesis of ZIF-7 required chemicals, such as zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%, Thermo Scientific, Monza, Italy), benzimidazole (bIm, ≥99.0%, Sigma-Aldrich, Oakville, ON, Canada), N, N-dimethylformamide (DMF, purity > 99.8%, Merck, Darmstadt, Germany), and methanol (MeOH, purity > 99.9%, Supelco, Darmstadt, Germany). Chemicals were used as received without further purification. In addition, purified methane (CH<sub>4</sub>) gas with 99.9995% purity, supplied by Air Products (M) Sdn. Bhd, Kuala Lumpur, Malaysia, was used as received for the single gas adsorption experiments.

### 2.2. Synthesis of ZIF-7

ZIF-7 was synthesized by using a solvothermal method [12]. First, 4.08 g of zinc nitrate hexahydrate was dissolved in 150 mL of DMF, and 3.6 g of benzimidazole (bIm) was dissolved in 150 mL of methanol. The zinc nitrate hexahydrate and DMF solution was promptly added into a bIm–methanol solution. The mixture gradually became turbid, and stirring continued for 1 h. A centrifuge (9000 rpm, 1 h) was used to collect the as-synthesized ZIF-7. Then, the sample was washed with methanol three times and dried at room temperature. A similar procedure was repeated to synthesize another ZIF-7 sample with stirring duration of 3 h.

### 2.3. ZIF-7 Characterization

The crystallinity of the synthesized ZIF-7 particles was analyzed using an X-ray diffraction (XRD) diffractometer (X'Pert3 Powder, Panalytical, Malvern, UK) with CuKα radiation ( $\lambda = 1.5425 \text{ \AA}$ , 45 kV, 40 mA) under ambient conditions. X-ray spectra were recorded from 2θ values of 5° to 55°. Meanwhile, the surface morphology of ZIF-7 samples was examined by using a field emission scanning electron microscope (FESEM, model Zeiss Supra 55VP, Oberkochen, Germany). The sample was prepared by fixing ZIF-7 onto the carbon conducting tape, followed by the sputtering of a gold coating to promote backscattered electrons emissions. The sample was observed at 50 kX magnification.

### 2.4. CH<sub>4</sub> Adsorption Measurement

The CH<sub>4</sub> adsorption performance of ZIF-7 samples was measured following the method reported in the literature [17], using the customized sorption cell available in our laboratory. The setup includes two chambers: a reference chamber and an adsorption chamber. It also comprises pressure and temperature transmitters, a vacuum pump, and valves. The test was performed for CH<sub>4</sub> gas over a pressure range from 2 to 9 bar using a sample weight of 0.5 g. Initially, the adsorption cell was degassed for about 1 h to eliminate any trapped gasses and impurities. Pressure transmitters were used to measure

the pressure of the chambers, which was then recorded by a data logger. CH<sub>4</sub> gas from the cylinder was first fed into the reference cell to reach the desired pressure. The gas was then transferred from the reference cell to the adsorption cell. The system was closely monitored via pressure transmitters until equilibrium was reached. The adsorption experiment was repeated by increasing the pressure in 1 bar intervals, up to 9 bar. The amount of gas remaining in both the reference and adsorption cells was measured. Finally, the amount of CH<sub>4</sub> uptake is calculated according to the following Equations (1)–(3) [17]:

$$n_1 = \left( \frac{P_{ref,1}}{Z_{ref,1}} - \frac{P_{ref,2}}{Z_{ref,2}} \right) \left( \frac{V_{ref}}{RT_{ref}} \right) \quad (1)$$

$$n_2 = \frac{P_2}{Z_{ads}} \left( \frac{V_{ads} - \frac{M_a}{ZIF-7 \text{ density}}}{RT_{ref}} \right) \quad (2)$$

$$n_3 = \frac{n_1 - n_2}{M_a} \quad (3)$$

where  $n_1$  is the amount of gas fed to the sample cell (mol/kg),  $n_2$  is the amount of gas left after adsorption in the adsorption cell (mol/kg),  $n_3$  is the amount of methane uptake (mol/kg),  $P$  is the pressure (MPa),  $V$  is the volume (cm<sup>3</sup>), “ref” is the reference cell, and “ad” is the adsorption cell. The subscripts “1” and “2” represent methane injection before and after, respectively,  $R$  is a gas constant (cm<sup>3</sup>·MPa/(mol·K)),  $M_a$  is the mass of ZIF-7 (g),  $Z$  is the compressibility factor, and  $T$  is the absolute temperature (K). Experimental data were repeated three times, and the average adsorption value was obtained.

### 2.5. CH<sub>4</sub> Adsorption Isotherm Studies

Adsorption isotherms are essential for describing the interaction of the adsorbate and adsorbent on the active sites. Langmuir, Freundlich, and Temkin models were selected to determine the adsorption isotherms of ZIF-7 samples. The Langmuir isotherm model is shown in Equation (4) as follows [17]:

$$\frac{P}{q_e} = \frac{1}{Q_{max}}P + \frac{1}{K_L Q_{max}} \quad (4)$$

where  $P$  is the equilibrium pressure (MPa),  $q_e$  is the equilibrium adsorption capacity of gas (mol/kg),  $Q_{max}$  is the maximum adsorption capacity (mol/kg), and  $K_L$  is the Langmuir constant. Then, the Freundlich isotherm model is shown in Equation (5) as follows [17]:

$$\log q_e = \frac{1}{n} \log P + \log K_F \quad (5)$$

where  $q_e$  is the equilibrium adsorption capacity of gas (mol/kg),  $P$  is the equilibrium pressure (MPa), and  $1/n$  and  $K_F$  are the Freundlich constants for sorption intensity and capacity, respectively. Meanwhile, the Temkin isotherm model is shown in Equation (6) as follows [17]:

$$q_e = \frac{RT}{b} \ln P + \frac{RT}{b} \ln K_T \quad (6)$$

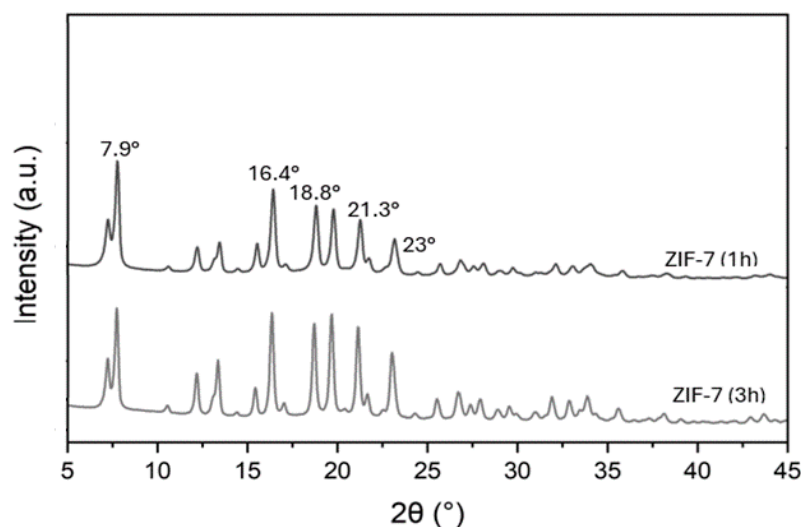
where  $K_T$  is the Temkin isotherm constant,  $q_e$  is the equilibrium amount of methane gas adsorbed per kilogram ZIF-7 (mol/kg),  $R$  is the gas constant of  $8.314 \times 10^{-3}$  kJ/(mol·K),  $P$  is the equilibrium pressure (Pa),  $T$  is the absolute temperature (K), and  $b$  is the Temkin constant related to the heat of sorption (kJ/mol).

## 3. Results and Discussion

### 3.1. X-ray Diffraction (XRD)

The XRD patterns of the synthesized ZIF-7 samples are illustrated in Figure 2. Both ZIF-7 samples showed high peak intensity, indicating the high crystallinity of the samples

obtained. From the XRD patterns, it can be confirmed that the observed peaks were identical and consistent with the relative intensities and peak positions reported in the literature for ZIF-7 samples [12,18]. The highest peak obtained for both samples was at around  $8^\circ$ , followed by several peaks ranging from  $10^\circ$  to  $25^\circ$ . It can be observed from Figure 2 that the peak intensities for the ZIF-7 sample synthesized for 3 h are slightly higher than those for the sample synthesized for 1 h. This could be mainly due to the longer synthesis duration, since the other conditions, such as the chemical concentrations used and temperature, remained unchanged during the synthesis of ZIF-7 samples. However, the lower intensities of the peak obtained for the ZIF-7 sample might also be caused by the smaller particle size, as confirmed by the SEM images presented in Section 3.2. Overall, the XRD results showed that highly crystalline ZIF-7 samples have been successfully synthesized at rapid synthesis durations.

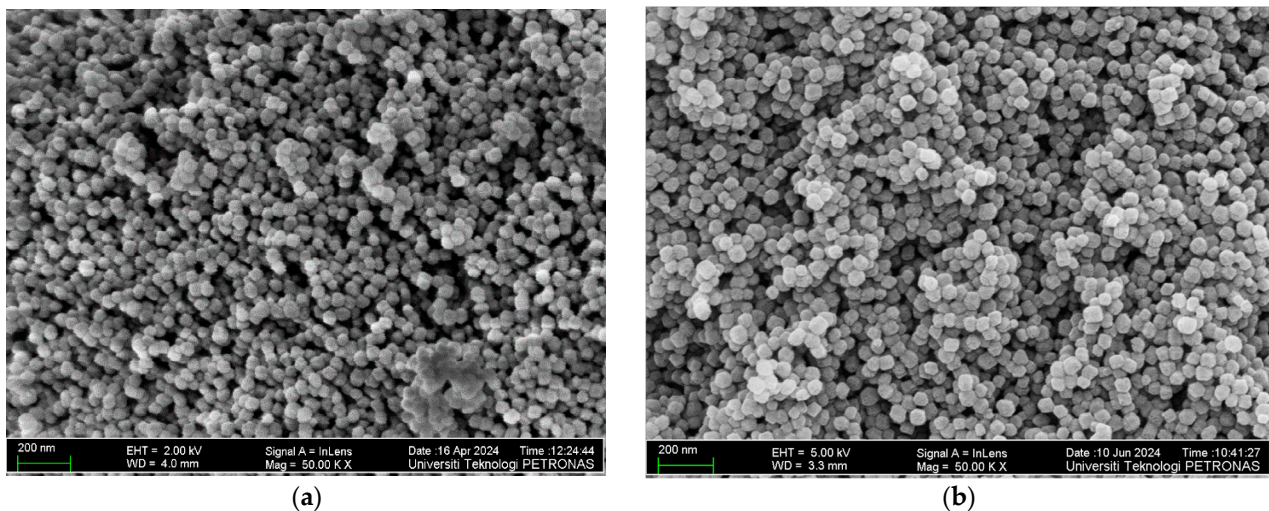


**Figure 2.** XRD patterns of the ZIF-7 samples synthesized at 1 h and 3 h.

### 3.2. Field Emission Scanning Electron Microscopy (FESEM)

Figure 3 shows the morphology of ZIF-7 samples synthesized for 1 h and 3 h. The FESEM analysis revealed a well-defined particle size distribution of ZIF-7, with an average size of  $\sim 50$  nm (s.d. = 4.7) for ZIF-7 synthesized for 1 h and  $\sim 60$  nm (s.d. = 6.2) for ZIF-7 synthesized for 3 h. The FESEM results reveal that the morphologies of both samples are uniform and homogeneous. This uniformity in size indicated that the synthesis process is controllable and consistent in producing nanoparticles of similar dimensions. Such consistency is crucial to ensure uniformity of samples during the adsorption process. Furthermore, the absence of significant surface irregularities or defects suggests a high-quality synthesis process that yields well-formed nanocrystals. Smooth surfaces can contribute to more efficient gas adsorption, as they provide an extensive and accessible area for gas molecules to interact with the adsorbents [12,18,19].

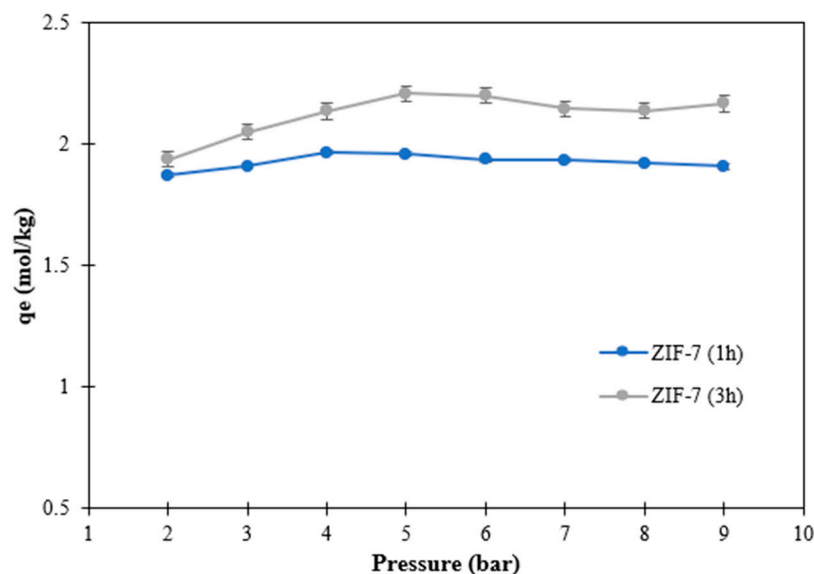
The arrangement and packing of particles within the ZIF-7 framework are clearly discernible in the FESEM images. The well-defined internal structure, characterized by the regular and orderly packing of nanocrystals, is consistent with their respective XRD results, as presented in the previous section. This well-defined structural integrity of ZIF-7 is beneficial for gas adsorption applications, as it ensures a consistent pore structure and availability, facilitating the uniform adsorption of gas molecules onto ZIF-7 surfaces [19].



**Figure 3.** FESEM images of ZIF-7 synthesized at (a) 1 h and (b) 3 h.

### 3.3. Gas Adsorption Capacities

Generally, the interaction between  $\text{CH}_4$  and the adsorbent's pore plays a significant role in the gas adsorption process [5]. The  $\text{CH}_4$  adsorption capacities of ZIF-7 obtained in this work were measured at rising pressures and ambient temperatures. The amount of  $\text{CH}_4$  adsorbed by ZIF-7 samples is shown in Figure 4. Based on Figure 4, the single component adsorption isotherms of  $\text{CH}_4$  over ZIF-7 samples show an increasing trend as the pressure increases from 2 bar to 9 bar. The  $\text{CH}_4$  adsorbed onto ZIF-7 synthesized for 1 h ranges from 1.87 to 1.97 mol/kg, while for ZIF-7 synthesized for 3 h, the amount of  $\text{CH}_4$  adsorbed is in the range of 1.94 to 2.21 mol/kg. Based on the adsorption results, ZIF-7 synthesized for 3 h showed slightly higher adsorption capacity compared to ZIF-7 synthesized for 1 h. This result could be due to the higher crystallinity of ZIF-7 (3 h), as shown in the XRD results (Figure 2). Wu et al. [18] in their study, reported that the adsorption capacity of  $\text{CH}_4$  was 0.13 mol/kg with reported particle sizes of ZIF-7 of 5–10  $\mu\text{m}$ . On the other hand, Arami et al. [19] reported the performance of ZIF-7 in  $\text{CH}_4$  adsorption and found that the highest  $\text{CH}_4$  adsorption capacity was 1.92 mol/kg. This value is slightly lower compared to the result obtained in this work, which could be mainly due to the larger particle size of ZIF-7 (~70  $\mu\text{m}$ ) obtained in their work.



**Figure 4.**  $\text{CH}_4$  gas uptake over ZIF-7 adsorbents.

3.4. Equilibrium Adsorption Isotherms

Adsorption isotherm models describe the relationship between the amount of adsorbate molecules on a solid surface and the equilibrium conditions at a constant pressure. Langmuir, Freundlich, and Temkin isotherm models were applied to study the ZIF-7 adsorption behaviors toward CH<sub>4</sub> gas at equilibrium conditions. The correlation of the experimental and predicted adsorption isotherms was examined using the coefficient of determination, R<sup>2</sup>, as shown in Table 1. Meanwhile, Figures 5 and 6 show the constructed adsorption isotherms of CH<sub>4</sub> adsorption for ZIF-7 samples obtained at 1 h and 3 h, respectively. Referring to Figures 5 and 6, experimental data for both samples are best fitted with the Langmuir isotherm model with R<sup>2</sup> of 0.9994 and 0.9982, respectively. The isotherm results obtained in this work are consistent with those results reported in the literature for CH<sub>4</sub> adsorption on ZIF-7 adsorbents [18].

Table 1. Isotherms R<sup>2</sup> of Langmuir, Freundlich, and Temkin isotherm models.

| Isotherm Model | Parameter      | ZIF-7-1 h | ZIF-7-3 h |
|----------------|----------------|-----------|-----------|
| Langmuir       | R <sup>2</sup> | 0.9994    | 0.9982    |
| Freundlich     | R <sup>2</sup> | 0.1396    | 0.6501    |
| Temkin         | R <sup>2</sup> | 0.1353    | 0.6441    |

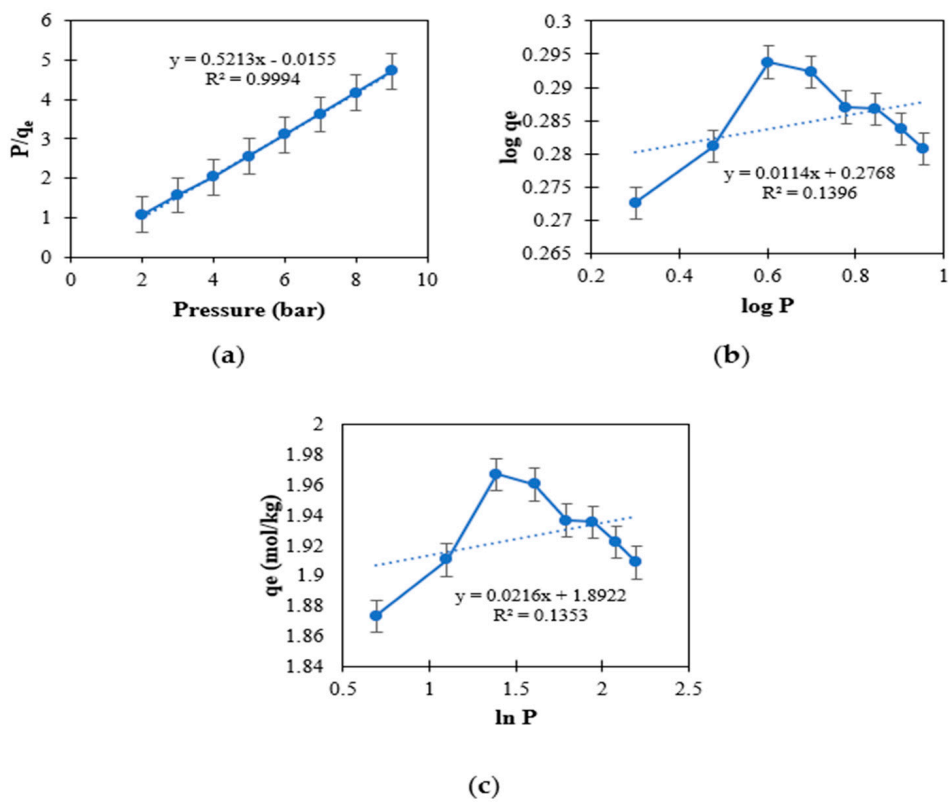
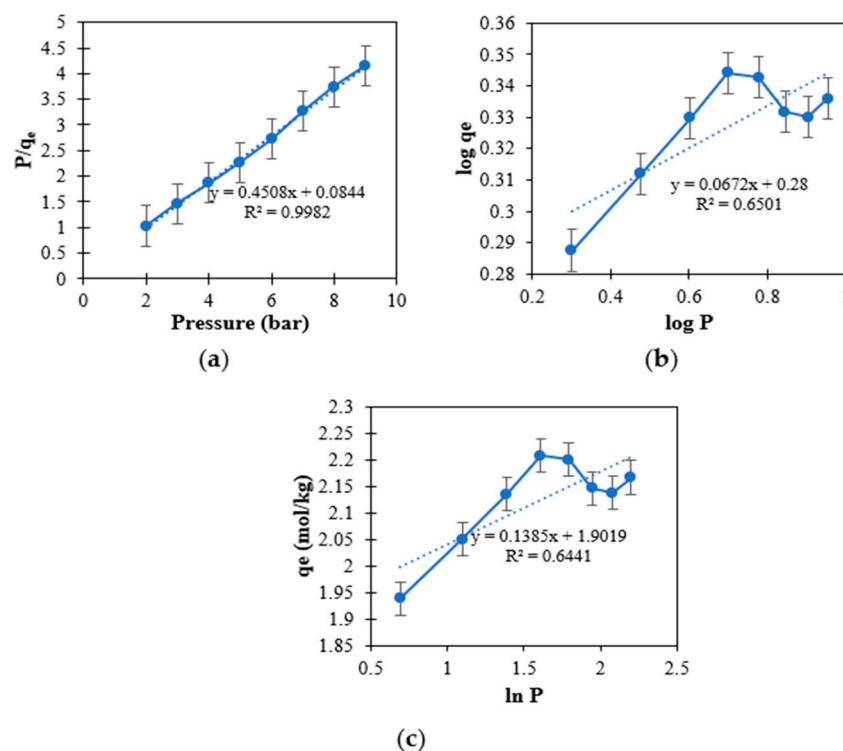


Figure 5. CH<sub>4</sub> adsorption isotherm fitting using (a) Langmuir, (b) Freundlich, and (c) Temkin models for ZIF-7 sample synthesized at 1 h. The solid lines represent the experimental data, and the dotted lines represent the model fitting.



**Figure 6.** CH<sub>4</sub> adsorption isotherm fitting using (a) Langmuir, (b) Freundlich, and (c) Temkin models for ZIF-7 sample synthesized at 3 h. The solid lines represent the experimental data, and the dotted lines represent the model fitting.

The best fitted Langmuir isotherm for both samples indicated the occurrence of the monolayer adsorption of CH<sub>4</sub> when the gas is absorbed onto the surface of ZIF-7. The Langmuir isotherm model assumes that the adsorption occurs on a homogeneous surface with a finite number of identical sites, with each site holding one adsorbate molecule [20,21]. The experimental data suggest that CH<sub>4</sub> adsorption on ZIF-7 predominantly occurs as a monolayer on a uniform surface. Furthermore, the excellent fit of the experimental data with the Langmuir isotherm implies that these sites are readily accessible and evenly distributed, facilitating a monolayer adsorption mechanism [22]. The Langmuir model also assumes that the adsorption energy is constant across all sites. The high  $R^2$  values demonstrated that the energy required for CH<sub>4</sub> molecules to adhere to the adsorption sites on ZIF-7 is relatively uniform, which is a characteristic trait of the Langmuir isotherm.

#### 4. Conclusions

The particle size of ZIF-7 was successfully tuned via a solvothermal method with rapid synthesis durations of 1 h and 3 h. The results obtained from XRD and FESEM showed that highly crystalline and homogeneous ZIF-7 particles were successfully formed, with particle sizes of ~50 nm and ~60 nm for ZIF-7 synthesized for 1 h and 3 h, respectively. The CH<sub>4</sub> adsorption capacities of ZIF-7 showed an increasing trend as the pressure increased from 2 to 9 bar, with greater CH<sub>4</sub> uptake for the ZIF-7 sample synthesized for 3 h. However, changing the synthesis duration from 1 h to 3 h only slightly affected the particles size of the ZIF-7 formed, and thus, only small differences in CH<sub>4</sub> uptake were found for both samples. Due to the samples obtained being nanosized, the ZIF-7 formed in this work showed higher CH<sub>4</sub> adsorption capacities compared to those results reported in the literature for ZIF-7 samples with greater particle sizes in micron. The adsorption behavior of CH<sub>4</sub> gas over both ZIF-7 adsorbents was best predicted by the Langmuir adsorption isotherm model, with  $R^2$  of 0.9994 and 0.9982, respectively. Overall, this study demonstrates the potential of ZIF-7 in the CH<sub>4</sub> capture process as an important approach for GHG mitigation.

**Author Contributions:** Conceptualization, Y.F.Y.; methodology, L.-X.C.; formal analysis, A.S.A.R. and Y.F.Y.; investigation, L.-X.C.; resources, L.-X.C.; data curation, L.-X.C., A.S.A.R. and Y.F.Y.; writing—original draft preparation, A.S.A.R.; writing—review and editing, A.S.A.R. and Y.F.Y.; visualization, Y.F.Y.; supervision, Y.F.Y.; project administration, Y.F.Y.; funding acquisition, Y.F.Y. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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