Static and Dynamic Simulation of Single and Binary Component Adsorption of CO₂ and CH₄ on Fixed Bed Using Molecular Sieve of Zeolite 4A

Supatsorn Parinyakit and Patcharin Worathanakul

Abstract: The simulation of carbon dioxide (CO₂)-methane (CH₄) mixed gas adsorption and the selectivity on zeolite 4A using Aspen Adsorption were studied. The influence of temperature ranging from 273 to 343 K, pressure up to 10 bar and various compositions of CO₂ in the binary system were simulated. The findings of the study demonstrate that the models are accurate. In addition, the effects of various key parameters such as temperature, pressure, and various compositions of binary gases were investigated. The highest CO₂ and CH₄ adsorption are found at 273 K and 10 bar in the Langmuir isotherm model with 5.86 and 2.88 mmol/g, respectively. The amount of CO₂ adsorbed and the selectivity of the binary mixture gas depends on the composition of CO₂. The kinetics of adsorption for pure components of CO₂ at high temperatures can reach saturation faster than CH₄. The influence of the physical properties of zeolite 4A on kinetic adsorption were also studied, and it was observed that small adsorbent particles, large pore diameter, and large pore volume would enter saturation quickly. The prediction of CO₂-CH₄ mixed gas adsorption and selectivity on zeolite 4A were developed for further use for commercial gas separation.

Keywords: adsorption; simulation; carbon dioxide; methane; Aspen Adsorption

1. Introduction

Carbon dioxide (CO₂) and methane (CH₄) are the main components of greenhouse gases that affect global warming. CO₂ emissions primarily involve the burning of fossil fuels [1]. Therefore, carbon dioxide trapping and storage also reduces CO₂ emissions into the atmosphere, and the stored CO₂ can be used for various benefits. The purity of CO₂ is often used directly in the food industry and enhanced oil recovery. There are new chemical and biological transformations of CO₂ into a feedstock for the manufacturing of chemicals and materials such as organic chemistry, minerals, and polymers. Conversion of CO₂ into polymers is one of the added value methods for CO₂ [2]. Therefore, improving the purity of CO₂ from the burning of fossil fuels through various processes is important. Improving of CH₄ purity produced from natural gas, fermenting organic matter, and coal and natural gas refining by removing contaminant gases such as CO₂, O₂, N₂, H₂S, and H₂O is also important. Pure CH₄ is important for industries such as pulp and paper manufacturing, food processes, and petroleum refineries. In addition, CH₄ is an ingredient in various materials such as fabric, antifreeze, and fertilizer [3]. The purity of CO₂ and CH₄ can be accomplished effectively through pressure swing adsorption (PSA) or temperature swing adsorption (TSA).

The CO₂ and CH₄ gas separation process can be performed through various methods, including distillation, extraction, membrane separation, and adsorption [4–7]. The chemical
industry realized the sustainable development of new innovative processes that use energy and materials more efficiently, since separation processes are of great economic importance accounting for 40–60% of operating costs in the industry. Therefore, a separation process must be developed to save energy consumption and costs. Gas separation by adsorption technology with effective adsorbents is the most common method in the chemical industry [8]. The adsorption process of the components of a fluid mixture flowing through the packed bed of an adsorbent porous material with a large surface area must be considered for proper separation. Different characteristics of the adsorbent influence their applications and these characteristics are influenced by the preparation methods. The most common adsorbents used for the purification of CO$_2$/CH$_4$ purposes are activated carbon, alumina, silica gel, and zeolites [9–12]. This research chose the adsorbent zeolite because of its high surface area and high adsorption capacity.

Zeolites are crystalline aluminosilicates of alkaline metals, alkaline earth metals, or other cations with various porous characteristics [13]. Zeolites can be used for a variety of applications depending on the pore structure and the properties of each type of zeolite. They can be used for separation or purification gas processes because of their molecular sieve property. Zeolite has a specific cation for the ion exchange process. Therefore, zeolite is an important adsorbent with specific properties for CO$_2$ adsorption because of the high adsorbent surface area and the medium and small pores such as synthesized zeolite A, zeolite X, and zeolite Y [14,15].

Moreover, the development in the simulation process is important to help save cost, energy, and time. In addition, it can help to reduce environmental pollution due to the suitable conditions found in the simulation models. Aspen Adsorption is a simulator developed for the design of the adsorption process simulation, covering a wide range of adsorption conditions. Therefore, this research chose Aspen Adsorption for the simulation of the adsorption processes. The molecular simulation of the adsorption processes can also be simulated using GCMC simulation. Chong and Myshakin [16] studied the molecular simulations of the competitive adsorption of the CO$_2$-CH$_4$ mixture on illitic clay surfaces under dry conditions, which showed that CO$_2$ was specially adsorbed on illitic surfaces and possessed the ability to promote methane desorption. The gas mixture adsorption isotherms of CO$_2$:CH$_4$ indicated that the CO$_2$ concentration increase, caused consistent suppression of CH$_4$ adsorption [16]. However, the adsorption simulation can use mathematical models for prediction breakthrough curves for adsorption. Al Mesfer [17] studied the simulation for CO$_2$ adsorption from CO$_2$-N$_2$ mixture using a packed column on activated carbon, which illustrated that breakthrough time decreased with increasing temperature, feed rate, and increased CO$_2$ concentration [17]. The experimental results were compared to simulate mathematical models of breakthrough curves with high accuracy [18]. Until now, there were no studies for CO$_2$ adsorption from CO$_2$-CH$_4$ mixed gas using zeolite 4A, which were reviewed.

This computer simulation research through Aspen Adsorption aimed for CO$_2$ adsorption from CO$_2$-CH$_4$ mixed gas using zeolite 4A and the optimum conditions for adsorption. Therefore, the main objectives of this research were to study the factors affecting CO$_2$ and CH$_4$ adsorption and the selectivity of binary gas mixtures on zeolite 4A at temperatures ranging from 273 to 343 K, a pressure range of 0–10 bar, and the compositions of CO$_2$ in the binary system were 10:90, 30:70, 40:60, 50:50, 60:40, and 80:20.

2. Materials and Methods
2.1. Simulation Setting

Data for program modeling included the physical properties of the adsorbent tower, the adsorbent and the conditions of operation. For this research, the adsorbent material was zeolite 4A and CO$_2$ and CH$_4$ were adsorbates. The physical properties of the adsorbents and the column for the packing tower are shown in Table 1. The characterization of zeolite 4A and experimental data are from Seabra and coworkers [19]. This research used the results from the experiment of adsorption of pure CO$_2$ and CH$_4$ on zeolite 4A at
303 and 343 K to predict the adsorption at 273, 283, and 323 K with the program Aspen Adsorption V11.

**Table 1.** Physical properties of the zeolite 4A adsorbent and column used in simulation of adsorption.

| Parameters                          | Value  |
|-------------------------------------|--------|
| Packing length (mm)                 | 97.5   |
| Internal bed diameter (mm)          | 9.1    |
| Particle size (cm)                  | 0.2 (average diameter) |
| Pellet density (kg/m³)              | 1109   |
| Solid density of adsorbent (kg/m³)  | 2429   |
| Total intrusion volume (cm³/g)      | 0.3147 |
| BET surface area (m²/g)             | 501.4  |

The zeolite 4A diameter was in the range of 0.16–0.25 cm in granular form as shown in Table 1. The pellet density and total intrusion volume were obtained by mercury intrusion and the solid density was obtained by helium picnometry. The BET surface area was measured from the N₂ adsorption at 77 K in granule form [19].

Dynamic Simulation of Adsorption Experiments

Dynamic adsorption experiments were simulated by the Aspen Adsorption V11 program. The flow sheet including adsorbent characteristics (gas bed), feed gas, and product streams is shown in Figure 1. The internal diameter bed was 9.1 mm and the packing length was 97.5 mm in the column. The gas bed model configuration allowed for specifying the number of layers, labels for each component and setting the geometry of the bed. There were a set of assumptions for all layers, constant variables, and initial conditions. General assumptions of Aspen Adsorption including partial differential equation (PDE) discretization method were used to approximate spatial derivatives and number PDE nodes with 20 nodes. Material balance was assumed with convection only, momentum balance was laminar, and turbulent flow conditions during operation used the Ergun equation. The kinetic model was set as linear lumped resistance (LDF) and the mass transfer coefficient was constant. The isotherm for the pure components was determined using the Langmuir isotherm. The simulation model was calculated in the multicomponent with an extended Langmuir model based on partial pressure. Energy balance for this research was defined for non-isothermal conditions with no conduction. The heat transfer to the environment was set as adiabatic (no external heat transfer) [20,21].

![Flowsheet configuration used to run the simulation of adsorption using Aspen Adsorption V11 simulation.](image)

**Figure 1.** Flowsheet configuration used to run the simulation of adsorption using Aspen Adsorption V11 simulation.

2.2. Adsorption Isotherm Model

2.2.1. Pure Component Adsorption Isotherm

Isotherms of pure CO₂ and CH₄ at 273, 283, 303, 323 and 343 K and pressure ranging from 1 to 10 bar were studied using the Langmuir isotherm model. This simulation was compared to the results of Seabra and coworkers [19].
The Langmuir isotherm model is a replica of the easiest and most popular isotherm model as shown in Equation (1). This model was used for monolayer adsorption and physical adsorption [22].

\[ q = \frac{q_m b P}{1 + b P} \tag{1} \]

where \( q \) (mmol/g) is the amount adsorbed, \( q_m \) (mmol/g) is the maximum adsorption capacity of the adsorbent, \( P \) (bar) is the pressure and \( b \) (bar\(^{-1}\)) is the Langmuir constant. The Langmuir constant depends on the temperature of the system, represented by Equation (2).

\[ b = b_0 e^{-\frac{-\Delta H}{RT}} \tag{2} \]

where \( b_0 \) (bar\(^{-1}\)) is the adsorption constant at an infinite temperature, \( -\Delta H \) (J/mmol) is the heat of adsorption, \( R \) (J·K\(^{-1}\)·mol\(^{-1}\)) is the universal gas constant, and \( T \) (K) is the temperature of the system.

2.2.2. Binary Component Adsorption Isotherm

Adsorption equilibrium for the binary gas mixture between CO\(_2\) and CH\(_4\) was predicted. The temperatures were at 273, 283, 303, 323, and 343 K with pressure ranging from 1 to 10 bars. The compositions of CO\(_2\) to CH\(_4\) were 10:90, 30:70, 40:60, 50:50, 60:40, and 80:20 using an extended Langmuir (EL) isotherm model and the ideal adsorbed solution theory (IAST). The extended Langmuir isotherm model for a binary component or multi-component adsorption was developed from the Langmuir model. In pure components, EL used the information of adsorption from Equation (3) [23].

\[ q_i = \frac{q_m b_i P_i}{1 + \sum b_i P_i} \tag{3} \]

where \( q_i \) (mmol/g) is the amount adsorbed of component \( i \), \( q_m \) (mmol/g) is the maximum adsorption capacity of the adsorbent of component \( i \), \( P_i \) (bar) is the partial pressure of component \( i \) and \( b \) (bar\(^{-1}\)) is the Langmuir constant of component \( i \). Therefore, the EL model for binary components is shown in Equations (4) and (5).

For binary component:

\[ q_1 = \frac{q_m b_1 P_1}{1 + b_1 P_1 + b_2 P_2} \tag{4} \]

\[ q_2 = \frac{q_m b_2 P_2}{1 + b_1 P_1 + b_2 P_2} \tag{5} \]

IAST is used to predict the adsorption capacity of binary mixed gas using pure component data. IAST is a thermodynamic method based on the adsorption equilibrium with Raoult’s law for vapor-liquid equilibrium. The equilibrium between adsorbed phase and ideal gas phase can be specified by Equation (6) [24–26].

\[ P y_i = P_i^0 (\pi^*) x_i \tag{6} \]

where \( y_i \) and \( x_i \) are the molar fractions of component \( i \) in the gas phase and adsorbed phase, respectively. \( P \) (bar) is the total pressure of the mixture, and \( P_i^0 (\pi^*) \) (bar) is the equilibrium gas phase pressure of pure component \( i \) corresponding to solution temperature and solution spreading pressure, \( \pi^* \).

For a pure component \( i \), the spreading pressure using Equations (7) and (8) was followed:

\[ \pi^* = \frac{\pi_i A}{RT} = \int_0^{p_i^0} \frac{q_i}{P_i} dP_i \tag{7} \]

where \( \pi_i^* \) is the reduced spreading pressure of component \( i \) in the adsorbed phase, \( \pi_i \) is the spreading pressure of component \( i \) in the adsorbed phase, \( A \) is the specific surface area of the adsorbent, \( \bar{q}_i \) is the pure component adsorption isotherm equation, and \( P_i^0 \) is
the standard state pressure of pure component \(i\) corresponding to spreading pressure of the mixture.

At the standard state, reduced spreading pressure of the mixture (\(\pi^*\)) is the same as the reduced spreading pressure of a single component according to Equation (8).

\[
\pi^*_1 = \pi^*_2 = \ldots = \pi^*
\]  \hspace{1cm} (8)

For binary mixtures, Equations (6)–(8) were solved numerically and the total adsorbed amount was calculated by Equations (9)–(11).

\[
\frac{1}{q_T} = \frac{x_1}{q_1(p_1^0)} + \frac{x_2}{q_2(p_2^0)} \hspace{1cm} (9)
\]

\[
x_1 + x_2 = 1 \hspace{1cm} (10)
\]

\[
q_i = x_iq_T \hspace{1cm} (11)
\]

where \(q_T\) (mmol/g) is the total amount adsorbed.

### 2.3. Modeling of Mass Transfer Coefficient

Mass transfer coefficients (MTC) were shown in Equation (12) which was assumed to be constant. MTC included the effects of micropore, macropore and film resistances [27]. The effect of macropore was considered using the following equation.

\[
k_i = \frac{15\varepsilon_p D_{pi}}{R_p^2} \hspace{1cm} (12)
\]

where \(k_i\) (s\(^{-1}\)) is the overall mass transfer coefficient of species \(i\), \(D_{pi}\) (cm\(^2\)/s) is the macropore diffusivity of species \(i\), and \(R_p\) (cm) is the particle radius and \(\varepsilon_p\) is the porosity of adsorbent particle or intraparticle.

The effective macropore diffusivity can be determined using the Bosanquet equation [28]:

\[
\frac{1}{D_{pi}} = \tau \left( \frac{1}{D_{ki}} + \frac{1}{D_{mi}} \right) \hspace{1cm} (13)
\]

where \(\tau\) is the pore tortuosity factor, \(D_{ki}\) (cm\(^2\)/s) is the Knudsen diffusivity and \(D_{mi}\) (cm\(^2\)/s) is the molecular diffusivity.

Estimation of the molecular diffusivity of binary gas mixtures with the best method calculated from the Lennard-Jones equation represented using Equation (14) [28]. The molecular diffusivity was determined using the following equation.

\[
D_m = \frac{0.001858T^\frac{3}{2}}{P\sigma_{12}^2\Omega_D} \left\{ \frac{1}{M_1} + \frac{1}{M_2} \right\} \hspace{1cm} (14)
\]

where \(M_i\) (g/mol) is the molecular weight of species \(i\), \(\Omega_D\) is the collision integral and \(\sigma_{12}\) (Å) is the collision diameter of the binary pair of species A and B.

Knudsen diffusion is gas diffusion through small pores, which can be calculated using Equation (15).

\[
D_{ki} = 9700R_p\sqrt{\frac{T}{m_i}} \hspace{1cm} (15)
\]

where \(R_p\) (cm) is pore radius.

### 2.4. Selectivity of CO\(_2\) over CH\(_4\) in Binary Mixture Gas

Selectivity represents the ratio of the amount of adsorption of the two gases. It can also be called separation coefficient. If the selectivity of CO\(_2\)/CH\(_4\) is high, it means that the adsorption amount of CO\(_2\) is greater than CH\(_4\) [10].
The adsorption selectivity of CO$_2$ over CH$_4$ in binary mixtures was defined in Equation (16).

\[ S_{\text{CO}_2/\text{CH}_4} = \frac{q_{\text{CO}_2}}{q_{\text{CH}_4}} \]  

\[ \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} \]  

(16)

where $q_{\text{CO}_2}$ and $q_{\text{CH}_4}$ (mmol/g) are the amount adsorbed of CO$_2$ and CH$_4$, and $P_{\text{CO}_2}$ and $P_{\text{CH}_4}$ (bar) are the partial pressures of CO$_2$ and CH$_4$, respectively.

2.5. Breakthrough Curves Modeling

To assess the performance of the fixed-bed adsorption column and measure the breakthrough curves, it is necessary to design and utilize the lab-scale experimental setup. By optimizing the mathematical models to the measured experimental data, the useful information can be used to design large-scale industrial columns and to predict the practical conditions. The model used in this work are the Thomas model and the Yoon–Nelson model.

2.5.1. Thomas Model

The Thomas model [29] is one of the most commonly used in the prediction of the breakthrough curve and the describing of the column performance. This model was developed based on the Langmuir kinetics of adsorption that assumed negligible axial dispersion in the column adsorption. The rate of the driving force carries out the second-order reversible reaction kinetics [30]. The Thomas model is shown in Equation (17):

\[ \frac{C}{C_0} = \frac{1}{1 + \exp \left( \frac{k_{\text{Th}} q_0 M}{Q} - k_{\text{Th}} C_0 t \right)} \]  

(17)

where $q_0$ is the equilibrium adsorbate uptake in adsorbent (mg/g), $Q$ is the flow rate (mL/min), $M$ is the mass of the adsorbent (g), $C$ is effluent concentration (mg/L), $C_0$ is influent concentration (mg/L), $t$ is time (min), and $k_{\text{Th}}$ is the Thomas model constant (mL/min mg).

2.5.2. Yoon-Nelson Model

The Yoon-Nelson model [31] is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate is proportional to the probability of adsorbate breakthrough on the adsorbent [32]. The Yoon-Nelson model was used for the following equation.

\[ \frac{C}{C_0} = \frac{\exp(k_{\text{YN}} t - \tau k_{\text{YN}})}{1 + \exp(k_{\text{YN}} t - \tau k_{\text{YN}})} \]  

(18)

where $k_{\text{YN}}$ is the Yoon-Nelson constant (min$^{-1}$) and $\tau$ is the time required to reach the effluent concentration to 50% of the influent concentration (min).

3. Results and Discussion

3.1. Pure Component Adsorption Isotherm

Adsorption isotherm of pure CO$_2$ and pure CH$_4$ at different temperatures and pressures are shown in Figure 2. The experimental data for pure CO$_2$ and CH$_4$ adsorption at 303 and 343 K were from Seabra [19]. The experimental results are fitted with the Langmuir isotherm model in Equations (1) and (2).

The adsorption capacity of CO$_2$ and CH$_4$ decreased with the rising temperature, indicating the adsorption of CO$_2$ and CH$_4$ are exothermic physical. The type of physical and chemical adsorption depends on the amount of heat in the adsorption. For heat of adsorption with 80 kJ mol$^{-1}$ or more, the adsorption process indicates chemisorption, while lower values represent a physical adsorption [33]. Values of the isosteric heat of adsorption in zeolite 4A of 47.8 kJ mol$^{-1}$ for the adsorption of CO$_2$ [34] and 16.72 kJ mol$^{-1}$ for CH$_4$ [35] were found. Thus, the adsorption of CO$_2$ and CH$_4$ on zeolite 4A was physical adsorption;
it could adsorb well when the temperature is decreased. In fact, as temperature decreases, gas molecules have less kinetic energy because the bond between gas and adsorbent is increased [36,37]. Moreover, the effect of pressure on the adsorption capacity is shown in Figure 2. The adsorption capacity increased rapidly as the pressure increased due to an increase in the gas molecules hitting the surface. Therefore, the increase in pressure caused the adsorption rate to increase linearly. However, when the pressure became high and almost the entire surface of the adsorbent received saturated gas, the pressure had little effect on the adsorption capacity. Ultimately, it could reach a point where the pressure did not affect the adsorption capacity because the number of adsorption sites was fixed, and no more adsorption occurred in those sites. At the same pressure and temperature conditions, the adsorption capacity of CO\(_2\) is much higher than CH\(_4\) because CO\(_2\) has a quadrupole moment and polarizability greater than CH\(_4\), and it also has a high critical temperature as shown in Table 2 [38,39].

![Adsorption isotherm on zeolite 4A at different temperatures and pressures: (a) pure CO\(_2\); (b) pure CH\(_4\).](image)

Figure 2. Adsorption isotherm on zeolite 4A at different temperatures and pressures: (a) pure CO\(_2\); (b) pure CH\(_4\).

| Table 2. Properties of carbon dioxide and methane. |
|--------------------------------------------------|
| Properties                                      | CO\(_2\) | CH\(_4\) |
| Kinetic diameter (Å)                            | 3.3      | 3.8      |
| Critical temperature (K)                        | 304.12   | 190.56   |
| Quadrupole moment (\(\times 10^{26}\) esu cm\(^2\)) | 4.30    | 0        |
| Polarizability (\(\times 10^{-25}\) cm\(^3\))   | 29.11    | 25.93    |

Table 3 shows the parameters of the Langmuir isotherm model for CO\(_2\) and CH\(_4\) adsorption on zeolite 4A. Where \(q_{m,0}\) is maximum adsorption capacity, \(b_0\) is Henry law constant, \(Q/R\) is adsorption heat and \(X\) is empirical constant. The constant values in Table 3 were used in the Langmuir isotherm model in Equations (1) and (2).

| Table 3. Parameters of the Langmuir isotherm model for CO\(_2\) and CH\(_4\) adsorption on zeolite 4A. |
|---------------------------------------------------|
| Equation                                          | Parameters     | CO\(_2\)  | CH\(_4\)  |
| \( q = \frac{q_{m,0} b P}{1 + b P} \)            | \( q_{m,0} \) (mmol/g) | 3.7881    | 3.4698    |
| \( b = b_0 \exp \left( \frac{Q}{R T} \right) \) | \( b_0 \) (bar\(^{-1}\)) | 0.7078    | 5.88 \(\times 10^{-5}\) |
| \( q_m = q_{m,0} \exp \left( X \left( 1 - \frac{T}{T_m} \right) \right) \) | \( Q/R \) (K) | 470.91    | 2465.8    |
|                                                   | \( X \) (dimensionless) | 1.7188    | 0.003     |
|                                                   | RMS (dimensionless)   | 0.0915    | 0.0236    |
Parameters of the previously mentioned equations were determined by minimizing the root-mean-square (RMS) in Equation (19):

\[
\text{RMS} = \left( \frac{\sum_{i=1}^{N} (q_{i}^{\text{cal}} - q_{i}^{\text{exp}})^2}{N} \right)^{0.5}
\]  

(19)

where \(N\) is the number of data points and \(q_{i}^{\text{cal}}\) and \(q_{i}^{\text{exp}}\) are calculated and experimental adsorbed amounts, respectively. Low RMS value indicates that the Langmuir isotherm model is suitable.

The Langmuir isotherm model depends on pressure, maximum adsorption capacity of the adsorbent, and the Langmuir constant. Maximum adsorption capacity and the Langmuir constant depend on temperature. Therefore, the amount of adsorption for each pressure and temperature could be determined [22].

The crystal structure of zeolite 4A with sodium cation distribution as shown in Figure 3. There are three sites for sodium cation distribution including site I (S1) at the center of the 6-rings of sodalite cages, site II (S2) at the center of the 8-ring window of \(\alpha\) cages and site III (S3) at opposite the 4-rings on the interior of \(\alpha\) cages. Sodium ions in zeolite 4A contain 12 ions per unit cell (S1:S2:S3 = 8:3:1) [40,41].

![Figure 3. The crystal structure of zeolite 4A.](image)

The adsorption mechanism of the CO\(_2\) molecule on zeolite 4A showed that CO\(_2\) interacts with the sodium cations in the adsorption site. Interaction between the CO\(_2\) quadrupole and sodium cations was electrostatic interaction. Sites of CO\(_2\) adsorption interaction with the sodium cation were shown in a single cation site. CO\(_2\) interacted with two sodium cations at dual cation sites. Moreover, CO\(_2\) could interact with more than two sodium cations and was denoted as multiple cation sites [42,43]. For instance, interaction between CO\(_2\) and zeolite 4A was shown in Figure 4. The CO\(_2\) molecule interacted with the sodium cation in S1 perpendicular to the plane of the 6-rings of sodalite cages along the body diagonal. If the distance between the CO\(_2\) molecule and sodium cation is long distance, it indicates a weak interaction.
Like wise, CH\textsubscript{4} interacted with sodium cation the same as CO\textsubscript{2}. However, the distance or molecular arrangement may differ due to the different properties of CO\textsubscript{2} and CH\textsubscript{4} as shown in Table 2. The CH\textsubscript{4} has zero quadrupole moment and polarizability less than CO\textsubscript{2}. Therefore, the electrostatic affinity and adsorption capacity for CH\textsubscript{4} were less than CO\textsubscript{2}. For the distance between the gas molecule and the cation, the longer distance indicated a weak interaction. In addition, CO\textsubscript{2} and CH\textsubscript{4} molecules could interact with oxygen atoms of the framework as well.

### 3.2. Binary Component Adsorption Isotherm

The simulation was predicted for a binary gas mixture using extended Langmuir Equations (4) and (5) and the ideal adsorbed solution theory models used in Equations (9)–(11). The composition of CO\textsubscript{2} and CH\textsubscript{4} in the gas mixture affected the amount of adsorption. The predictions of the adsorption of the binary gas mixture between CO\textsubscript{2} and CH\textsubscript{4} on zeolite 4A with the EL isotherm model were shown in Figure 5a,b.

The results showed that the total amount of adsorbed gas mixture increased with the amount of CO\textsubscript{2} adsorption. In other words, the higher the composition of CO\textsubscript{2} received the greater the amount of total gas adsorption. Thus, the adsorption capacity of the mixed gas was between the two pure gases due to gas mixture had competition and was a hinderance between CO\textsubscript{2} and CH\textsubscript{4} molecules in the adsorption. It was indicated that the quadrupole
moment of CO$_2$ could result in strong interactions between CO$_2$ molecules and the surface of zeolite 4A. The effect of pressure and temperature on the adsorption of the binary gas mixture showed the same tendency as the pure component [44–46]. Therefore, the adsorption of the mixed gas was also a physical adsorption because the total amount adsorbed decreased with the rising temperature.

Zeolite 4A has a cubic structure as shown in Figure 3. The effective size of its windows depends on the sodium cation of zeolite 4A, which has a pore window size of approximately 0.38 nm. The kinetic diameter affected the separation of CO$_2$ from CH$_4$ as observed in theory. These pores of zeolite have dimensions very close to the kinetic diameters of CO$_2$ and CH$_4$, allowing CO$_2$ to diffuse through the adsorbent faster than CH$_4$. Therefore, CO$_2$ can be separated from CH$_4$ while CO$_2$ diffuses more quickly in narrow pores than CH$_4$ with a kinetic diameter effect. For the molecular sieve effect, both CO$_2$ and CH$_4$ have different kinetic diameters inside a zeolite as shown in Table 2. CO$_2$ has the smallest kinetic diameter at 0.33 nm, and CH$_4$ at 0.38 nm. Zeolite 4A showed pore window apertures that are similar to the kinetic diameter of CH$_4$. Therefore, CO$_2$ could enter the zeolite 4A freely, but CH$_4$ was blocked [47].

Figure 6 showed the comparison between the EL and IAST models of the CO$_2$-CH$_4$ mixture in different CO$_2$ and CH$_4$ ratios. The total adsorption of IAST is a little higher than the EL model. The total adsorption between IAST and EL models was approximately the same. The IAST model showed better adsorption of the CO$_2$-CH$_4$ gas mixture than the EL model compared to the experimental results according to the study of Rios [48]. In Wu’s research [39], IAST could be used to predict the behavior of a binary mixture with very high accuracy. The IAST model was able to work very well when the adsorbates were similar sizes. On the other hand, the EL model was able to predict sorption behavior with acceptable precision.

![Figure 6](image_url). Adsorption isotherm of CO$_2$-CH$_4$ mixture on zeolite 4A at 303 K with different models for EL (dash line) and IAST (solid line).

### 3.3. Selectivity for Separating of CO$_2$-CH$_4$ Mixture

The selectivity of binary gas mixtures can be calculated from Equation (16). The selectivity at different compositions of CO$_2$:CH$_4$ and pressures shown in Figure 7a at 303 K. If the composition of CO$_2$ increased, the selectivity also increased because the interaction of CO$_2$ molecules with the atoms of the zeolite 4A structure was stronger than that with CH$_4$ molecules. In addition, CO$_2$ molecules particularly adsorbed well in the pores of zeolite 4A and hindered the diffusion of the weaker adsorbing CH$_4$ molecules. 
The obtained selectivity from IAST and EL models for different compositions are shown in Figure 7a. It was indicated that the EL selectivity of CO$_2$/CH$_4$ was constant for all gas compositions and pressures. On the other hand, the IAST selectivity showed various results for both total pressure and composition. From this prediction of IAST, the composition of CO$_2$ would affect selectivity when the pressure was increased. Figure 7b shows the different temperatures on selectivity of 50:50 of CO$_2$:CH$_4$ ratio, at 1 bar. The selectivity increased with rising temperature [49] which is the same in both models. For this reason, the pressure and temperature had a positive impact on the adsorption selectivity of CO$_2$ over CH$_4$. Therefore, to predict the selectivity of CO$_2$-CH$_4$, the IAST calculation was based on Langmuir and EL calculations.

As mentioned above, the use of an adsorbent must be considered for high efficiency separation. Therefore, the comparison of the adsorption capacity in each adsorbent can be used as analytical data for improving the adsorbent. Table 4 shows the adsorption capacity for the CO$_2$-CH$_4$ binary gas mixture with zeolite compared to others. It can be seen that the adsorption values of both CO$_2$ and CH$_4$ from zeolite 4A showed similar trends to those of 13 X and 5A zeolites at the same conditions. The BET specific surface area of zeolite 4A was close to that of zeolite 13X. Therefore, the adsorption capacities of CO$_2$ were similar to CH$_4$. There were no different adsorption effects in each zeolite in Table 4. The adsorption capacity of CO$_2$ showed greater than CH$_4$.

The selectivity of the binary gas mixture has an important parameter because it can form zeolite into an ideal material adsorbent for CO$_2$ and CH$_4$ mixture gas separation.

Table 4. Comparison of the adsorption capacity for CO$_2$-CH$_4$ binary gas mixture with different adsorbents at 323 K.

| Adsorbent | P (Bar) | CO$_2$:CH$_4$ | $q_{CO_2}$ (mmol/g) | $q_{CH_4}$ (mmol/g) | Ref. |
|-----------|---------|----------------|---------------------|---------------------|------|
| Zeolite 4A | 6       | 40:60          | 4.076               | 0.159               | This work |
| Zeolite 5A | 10      | 50:50          | 4.400               | 0.102               | [38] |
| Zeolite 13X | 5.8     | 40:60          | 2.852               | 0.150               | [44] |
3.4. Dynamic Simulation of Adsorption Experiment

Figure 8 shows the kinetic adsorption of CO$_2$ and CH$_4$ on zeolite 4A at different temperatures (273, 303, 343 K) and pressures (1, 5, 10 bar).

It was observed that at the beginning of the adsorption, the amount of CO$_2$ adsorbed on the adsorbent was slightly fast and then slowly decreased until it reached equilibrium. In the initial stages, CO$_2$ molecules directly contacted with the adsorbent, resulting in great interaction between adsorbate and adsorbent [50]. After total pores were adsorbed without any further adsorption of CO$_2$ molecules, the process of adsorption went to saturation. In addition, when the temperature increased, faster saturation was observed due to the exothermic process for CO$_2$ adsorption. In the exothermic process, increasing temperature caused adsorption to decrease because of the decreased of the attraction between the adsorbate and the adsorbent [37,39,44].

The mass transfer coefficient was increased with increased temperature as shown in Table 5. This is caused by CO$_2$ and CH$_4$ molecules moving faster with higher temperature from the increased kinetic energy [28,51].

Table 5. Mass transfer coefficient CO$_2$ and CH$_4$ adsorption on zeolite 4A (0.2 cm) at different conditions of pressure and temperature.

| T (K) | P (Bar) | D$_P$ (cm$^2$/s) | k (s$^{-1}$) |
|-------|---------|------------------|-------------|
|       |         | CO$_2$           | CH$_4$      | CO$_2$   | CH$_4$   |
| 273   | 1       | 0.0196           | 0.0386      | 0.3222   | 0.6357   |
|       | 5       | 0.0046           | 0.0093      | 0.0749   | 0.1524   |
|       | 10      | 0.0023           | 0.0047      | 0.0382   | 0.0781   |
|       | 1       | 0.0232           | 0.0450      | 0.3820   | 0.7400   |
| 303   | 5       | 0.0055           | 0.0102      | 0.0906   | 0.1684   |
|       | 10      | 0.0030           | 0.0057      | 0.0489   | 0.0942   |
|       | 1       | 0.0283           | 0.0546      | 0.4662   | 0.8985   |
| 343   | 5       | 0.0069           | 0.0127      | 0.1137   | 0.2089   |
|       | 10      | 0.0036           | 0.0071      | 0.0584   | 0.1174   |

From the simulation adsorption model, it was found that pressure affected the adsorption capacity and mass transfer coefficient. The mass transfer coefficient decreased with the rising pressure because of effective diffusivity decreased from decreased molecular dif-
The relation of mass transfer coefficient, effective diffusivity and molecular diffusivity are shown in Equations (12)–(14), respectively. Equation (15) shows Knudsen diffusion which depends on temperature. Figure 8b shows that CH$_4$ adsorption took a long time to adsorb, due to the decrease in the polarizability and kinetic diameter of CH$_4$, which was larger than CO$_2$ as shown in Table 2.

### 3.4.1. The Effect of the Physical Properties of Zeolite 4A on Kinetic Adsorption

The physical properties of various zeolite 4A with different particle size, pore volume and pore diameter are shown in Table 6. Three types of zeolites were compared in this study: zeolite 4A-0.2 cm, zeolite 4A (HSD, high bulk density)-0.2 cm and zeolite 4A-0.4 cm.

**Table 6.** Physical properties of zeolite 4A with different types.

| Type of Zeolite          | Particle Size (cm) | Pore Volume (cm$^3$/g) | Pore Diameter (nm) | BET Surface (m$^2$/g) |
|-------------------------|--------------------|-------------------------|--------------------|-----------------------|
| Zeolite 4A-0.2 cm       | 0.2                | 0.3147                  | 361                | 501.4                 |
| Zeolite 4A (HSD)-0.2 cm | 0.2                | 0.1606                  | 320                | 509.8                 |
| Zeolite 4A-0.4 cm       | 0.4                | 0.3012                  | 314                | 510.4                 |

To study the physical properties of the zeolite 4A adsorbents, the model developed to predict the breakthrough curves of CO$_2$ and CH$_4$ adsorptions on zeolite 4A was shown in Figure 9. It was found that small particle sizes of zeolite went into saturation and balance more quickly than large ones because of long diffusion inside the pores [52]. For different pore volumes with the same particle size, at large pore volumes could go into saturation quickly because the adsorption capacity was greater for larger pore volumes. Moreover, after all the pores were occupied by the adsorbate, the adsorbent could no longer adsorb CO$_2$ molecules. The efficiency was high if the amount of porosity was large. Less pore diameter affects the kinetic adsorption on fast diffusion. The effect of pore diameter on the adsorption is mentioned in Section 3.2.

![Figure 9](image-url)

**Figure 9.** Breakthrough curves on the effect of physical properties of zeolite 4A at 303 K and 10 bar (a) CO$_2$ and (b) CH$_4$.

The mass transfer coefficient of large particles was smaller than the small ones as shown in Table 7. From Equation (12), the mass transfer coefficient was inverse to the particle radius. Therefore, the particle radius was large; the mass transfer coefficient was reduced.
Table 7. Mass transfer coefficients of CO$_2$ and CH$_4$ adsorption on different types of zeolites 4A at 303 K and 10 bar.

| Type of Zeolite          | $D_P$ (cm$^2$/s) | $k$ (s$^{-1}$) |
|-------------------------|------------------|----------------|
| Zeolite 4A-0.2 cm       | 0.0030           | 0.0489         | 0.0942        |
| Zeolite 4A (HSD)-0.2 cm | 0.0028           | 0.0269         | 0.0546        |
| Zeolite 4A-0.4 cm       | 0.0028           | 0.012          | 0.0244        |

3.4.2. The Effect of Binary CO$_2$-CH$_4$ Mixed Gas

Figure 10a,b showed the effect of the composition ratios of CO$_2$ and CH$_4$ of 80:20, 50:50 and 30:70 at 303 K and 10 bar pressure.

When CO$_2$ composition increased, the saturation of the breakthrough curve was decreased, representing the faster kinetics of the adsorption process with a high CO$_2$ content [53]. It was predicted that CO$_2$ had a higher adsorption with zeolite 4A than CH$_4$. As a result, when CO$_2$ composition was high, competition of CO$_2$ and CH$_4$ for adsorption was less than with less composition of CO$_2$ [54,55].

3.4.3. Modeling of Breakthrough Curves

Modeling of the breakthrough curves were obtained from experiments using the Thomas and Yoon-Nelson model. The experimental data of the adsorption of CO$_2$ on zeolite 4A at 573.15 K and flow rate of 5 L/h were obtained from Tobarameekul [56].

Figure 11 shows the ability of the Thomas and Yoon-Nelson model to predict the experimental breakthrough curves. The prediction of the Yoon-Nelson model is better than Thomas’s model. Both models were formed according to the experimental data. The parameters from fitting the different models to experimental breakthrough curves were shown in Table 8. The correlation coefficient ($R^2$) of the Yoon-Nelson model is greater than that of Thomas.
Processes 2021, 9, x FOR PEER REVIEW 16 of 19

Figure 11. Comparison of the prediction of the Thomas and Yoon-Nelson model with the experimental breakthrough curve.

Table 8. Thomas and Yoon-Nelson model parameters.

| Model          | Parameter          | Value               |
|----------------|--------------------|---------------------|
| Thomas         | $k_{Th}$ (L/mg min) | $1.232 \times 10^{-3}$ |
|                | $q_0$ (mg/g)       | 654,490.9           |
|                | $R^2$              | 0.948               |
| Yoon-Nelson    | $k_{YN}$ (min$^{-1}$) | 0.567               |
|                | $\tau$ (min)       | 3.347               |
|                | $R^2$              | 0.974               |

4. Conclusions

Adsorption isotherms of pure CO$_2$ and pure CH$_4$ on zeolite 4A with 273 to 343 K, and pressure up to 10 bar using the Langmuir model were performed. Adsorption generally depended on the temperature. Adsorption decreased with increasing temperature because adsorption processes were exothermic reaction. On the other hand, at a constant temperature, the adsorption capacity increased with pressure. Therefore, the highest CO$_2$ and CH$_4$ adsorption from this study was found at 273 K and 10 bar. The properties of CO$_2$ and CH$_4$ affected on the adsorption capacity so that the adsorption capacity of CO$_2$ was much higher than CH$_4$. The effect of temperature and pressure on the binary gas mixture had the same effect on the pure component of adsorption. However, the adsorption of the mixed gas increased with the amount of CO$_2$ entered. The effect of pore size on adsorption showed that CO$_2$ with a smaller kinetic diameter could be separated from CH$_4$ with a larger kinetic diameter as CO$_2$ diffuses more quickly in narrow pores than CH$_4$. In addition, Zeolite 4A has pore window apertures that are similar to the kinetic diameter of CH$_4$, then CO$_2$ could enter the zeolite 4A freely, but CH$_4$ was blocked. Simulation models for gas mixtures were IAST and EL models. The amount of adsorption of the IAST model was greater than the EL model and the selectivity also increased with the amount of CO$_2$ entered, and the results showed that selectivity rose with the temperature. Moreover, the amount of CO$_2$ adsorbed from dynamic adsorption simulation increased with increasing pressure because of effective diffusivity decreased from decreased molecular diffusion. At the same time, CH$_4$ showed the same trend as CO$_2$, but its adsorption capacity was less than CO$_2$. In addition, the rising temperature could reach the equilibrium faster than the low temperature. Small adsorbent particles and large pore volume could enter the saturation fast. For the kinetic adsorption simulation of the CO$_2$-CH$_4$ binary mixture gas adsorption, the increased composition of CO$_2$ would greatly benefit the efficiency of CO$_2$
adsorption in the mixed gas system. Moreover, the prediction of the breakthrough curves from the Yoon-Nelson model was better than Thomas’s model.

**Author Contributions:** Conceptualization, S.P. and P.W.; methodology, S.P. and P.W.; software, S.P.; validation, S.P. and P.W.; formal analysis, S.P. and P.W.; investigation, P.W.; data curation, S.P. and P.W.; writing—original draft preparation, S.P.; writing—review and editing, P.W.; visualization, S.P.; supervision, P.W.; project administration, P.W.; funding acquisition, P.W. Both authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by King Mongkut’s University of Technology North Bangkok. Contract no. KMUTNB-63-KNOW-043.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

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

**References**

1. Jawaharraj, K.; Shrestha, N.; Chilkoor, G.; Dhiman, S.S.; Islam, J.; Gadhamshetty, V. Valorization of methane from environmental engineering applications: A critical review. *Water Res.* 2020, 187, 116400. [CrossRef]

2. Paraschiv, S.; Paraschiv, L.S. Trends of carbon dioxide (CO2) emissions from fossil fuels combustion (coal, gas and oil) in the EU member states from 1960 to 2018. *Energy Rep.* 2020, 6, 237–242. [CrossRef]

3. Qin, Y.; Wang, X. Conversion of CO2 into Polymers. In *Green Chemistry and Chemical Engineering*; Han, B., Wu, T., Eds.; Springer: New York, NY, USA, 2019; pp. 323–347.

4. Yousef, A.M.; El-Maghlany, W.M.; Eldrainy, Y.A.; Attia, A. Low-Temperature Distillation Process for CO2/CH4 Separation: A Study for Avoiding CO2 Freeze-Out. *J. Heat Transf.* 2017, 140. [CrossRef]

5. Qin, C.; Jiang, Y.; Zhou, J.; Song, X.; Liu, Z.; Li, D.; Zhou, F.; Xie, Y.; Xie, C. Effect of supercritical CO2 extraction on CO2/CH4 competitive adsorption in Yanchang shale. *Chem. Eng. J.* 2021, 412, 128701. [CrossRef]

6. Zhang, Y.; Sunarso, J.; Liu, S.; Wang, R. Current status and development of membranes for CO2/CH4 separation: A review. *Int. J. Greenh. Gas. Control.* 2013, 12, 84–107. [CrossRef]

7. Klewiah, I.; Berawala, D.S.; Alexander Walker, H.C.; Andersen, P.O.; Nadeau, P.H. Review of experimental sorption studies of CO2 and CH4 in shales. *J. Nat. Gas. Sci. Eng.* 2020, 73, 103045. [CrossRef]

8. Wankat, P.C. A review of: “Gas Separation Technology”. *Sep. Purif. Methods* 1991, 20, 199–200. [CrossRef]

9. Álvarez-Gutiérrez, N.; Gil, M.V.; Rubiera, F.; Pevida, C. Adsorption performance indicators for the CO2/CH4 separation: Application to biomass-based activated carbons. *Fuel Process. Technol.* 2016, 142, 361–369. [CrossRef]

10. Tamnanloo, J.; Fatemi, S.; Golmakani, A. Binary Equilibrium Adsorption Data and Comparison of Zeolites with Activated Carbon for Selective Adsorption of CO2 from CH4. *Adsorp. Sci. Technol.* 2014, 32, 707–716. [CrossRef]

11. Zhang, Y.; Chen, K.; Lv, C.; Wu, T.; Wen, Y.; He, H.; Yu, S.; Wang, L. Adsorption Separation of CO2/CH4 from Landfill Gas by Ethanolamine-Modified Silica Gel. *Water Air Soil Pollut.* 2021, 232. [CrossRef]

12. Liang, D.; Hu, Y.; Bao, Q.; Zhang, J.; Feng, J.; Sun, P.; Ma, Y.; Zhang, H. A suitable zeolite Rho for separating CO2/CH4 in pressure swing adsorption (PSA) process. *Inorg. Chem. Soil Pollut.* 2021, 127, 108547. [CrossRef]

13. Verma, M.; Kaur, G. A mini review on zeolite. *Mater. Today Proc.* 2021. [CrossRef]

14. Dusselier, M.; Davis, M.E. Small-Pore Zeolites: Synthesis and Catalysis. *Chem. Rev.* 2018, 118, 5265–5329. [CrossRef]

15. Li, Y.; Li, L.; Yu, J. Applications of Zeolites in Sustainable Chemistry. *Chem. 2017*, 3, 928–949. [CrossRef]

16. Chong, L.; Myshakin, E.M. Molecular simulations of competitive adsorption of carbon dioxide—Methane mixture on illitic clay surfaces. *Fluid Phase Equilibria* 2018, 472, 185–195. [CrossRef]

17. Al Mesfer, M.K.; Amari, A.; Danish, M.; Al Alwan, B.A.; Shah, M. Simulation study of fixed-bed CO2 adsorption from CO2/N2 mixture using activated carbon. *Chem. Eng. Commun.* 2020, 01–10. [CrossRef]

18. Brea, P.; Delgado, J.A.; Águeda, V.L.; Uguna, M.A. Modeling of breakthrough curves of N2, CH4, CO, CO2 and a SMR type off-gas mixture on a fixed bed of BPL activated carbon. *Sep. Purif. Technol.* 2017, 179, 69–71. [CrossRef]

19. Seabra, R.; Ribeiro, A.; Gleichmann, K.; Ferreira, A.; Rodrigues, A. Adsorption equilibrium and kinetics of carbon dioxide, methane and nitrogen on binderless zeolite 4A adsorbents. *Microporous Mesoporous Mater.* 2018, 277. [CrossRef]

20. Wood, K.; Liu, Y.; Yu, Y. *Simulation of Adsorption Processes*; Wiley: Hoboken, NJ, USA, 2018; pp. 1–153.

21. Plaza, M.G.; Durán, I.; Querejeta, N.; Rubiera, F.; Pevida, C. Experimental and Simulation Study of Adsorption in Postcombustion Conditions Using a Microporous Biochar. 1. CO2 and N2 Adsorption. *Ind. Eng. Chem. Res.* 2016, 55, 3097–3112. [CrossRef]

22. Azizian, S.; Eris, S. Chapter 6—Adsorption isotherms and kinetics. In *Interface Science and Technology*; Ghaedi, M., Ed.; Elsevier: Amsterdam, The Netherlands, 2021; Volume 33, pp. 445–509.
23. Kapoor, A.; Ritter, J.A.; Yang, R.T. An extended Langmuir model for adsorption of gas mixtures on heterogeneous surfaces. *Langmuir* **1990**, *6*, 660–664. [CrossRef]

24. Goel, C.; Bhunia, H.; Bajpai, P. Prediction of Binary Gas Adsorption of CO\(_2\) /N\(_2\) and Thermodynamic Studies on Nitrogen Enriched Nanostructured Carbon Adsorbents. *J. Chem. Eng. Data* **2017**, *62*, 214–225. [CrossRef]

25. LeVan, M.D.; Vermeulen, T. Binary Langmuir and Freundlich isotherms for ideal adsorbed solutions. *J. Phys. Chem.* **1981**, *85*, 3247–3250. [CrossRef]

26. McIntyre, S.M.; Shan, B.; Wang, R.; Zhong, C.; Liu, J.; Mu, B. Monte Carlo Simulations to Examine the Role of Pore Structure on Ambient Air Separation in Metal–Organic Frameworks. *Ind. Eng. Chem. Res.* **2018**, *57*, 9240–9253. [CrossRef]

27. Hauchhum, S.; Mahanta, P.; De Wilde, J. Capture of CO\(_2\) from Flue Gas onto Coconut Fibre-Based Activated Carbon and Zeolites in a Fixed Bed. *Transp. Porous Media* **2015**, *110*. [CrossRef]

28. Krishna, R.; van Baten, J.M. Investigating the validity of the Bosanquet formula for estimation of diffusivities in mesopores. *Chem. Eng. Sci.* **2012**, *69*, 684–688. [CrossRef]

29. Thomas, H.C. Heterogeneous Ion Exchange in a Flowing System. *J. Am. Chem. Soc.* **1944**, *66*, 1664–1666. [CrossRef]

30. Afroz, S.; Sen, T.K.; Ang, H.M. Adsorption performance of continuous fixed bed column for the removal of methylene blue (MB) dye using Eupatorium eyssianum bark biomass. *Res. Chem. Intermed.* **2016**, *42*, 2343–2364. [CrossRef]

31. Yoon, Y.H.; Nelson, J.H. Application of Gas Adsorption Kinetics I. A Theoretical Model for Respirator Cartridge Service Life. *J. Am. Chem. Soc.* **1944**, *66*, 684–688. [CrossRef]

32. El-Naas, M.H.; Alhaija, M.A.; Al-Zuhair, S. Evaluation of an activated carbon packed bed for the adsorption of phenols from petroleum refinery wastewater. *Environ. Sci. Pollut. Res.* **2017**, *24*, 7511–7520. [CrossRef]

33. Khalili, S.; Khoshandam, B.; Jahanshahi, M. A comparative study of CO\(_2\) and CH\(_4\) adsorption using activated carbon prepared from pine coke by phosphoric acid activation. *Korean J. Chem. Eng.* **2016**, *33*, 2943–2952. [CrossRef]

34. Romero-Pérez, A.; Aguilar-Armenta, G. Adsorption Kinetics and Equilibria of Carbon Dioxide, Ethylene, and Ethane on 4A(CECA) Zeolite. *J. Chem. Eng. Data* **2010**, *55*, 3625–3630. [CrossRef]

35. Harper, R.J.; Stief, G.R.; Anderson, R.B. Adsorption of gases on 4A synthetic zeolite. *Can. J. Chem.* **1969**, *47*, 4661–4670. [CrossRef]

36. Wei, M.; Yu, Q.; Duan, W.; Hou, L.; Liu, K.; Qin, Q.; Liu, S.; Dai, J. Equilibrium and Kinetics Analysis of CO\(_2\) Adsorption on Waste Ion-exchange Resin-based Activated Carbon. *J. Taiwan Inst. Chem. Eng.* **2017**, *77*, 161–167. [CrossRef]

37. Golchoobi, A.; Pahlavanzadeh, H. Molecular simulation, experiments and modelling of single adsorption capacity of 4A molecular sieve for CO\(_2–\)CH\(_4\) separation. *Sep. Sci. Technol.* **2016**, *51*, 2138–2135. [CrossRef]

38. Mofarahi, M.; Gholipour, F. Gas adsorption separation of CO\(_2)/\text{CH}_4 \text{ system using zeolite }5\text{A. Microprocess Mesoporous Mater.} \text{2014, }200,1–10. [CrossRef]

39. Wu, Y.-J.; Yang, Y.; Kong, X.-M.; Li, P.; Yu, J.-G.; Ribeiro, A.M.; Rodrigues, A.E. Adsorption of Pure and Binary CO\(_2\), CH\(_4\), and N\(_2\) Gas Components on Activated Carbon Beads. *J. Chem. Eng. Data* **2015**, *60*, 2684–2693. [CrossRef]

40. Cornelius, M.-L.U.; Price, L.; Wells, S.A.; Petrik, L.F.; Sartbaeva, A. The steric influence of extra-framework cations on framework flexibility: An LTA case study. *Z. Krist. Cryst. Mater.* **2019**, *234*, 461–468. [CrossRef]

41. Rzepka, P.; Bacsik, Z.; Smeets, S.; Hansen, T.C.; Hedin, N.; Wardecki, D. Site-Specific Adsorption of CO\(_2\) in Zeolite NaA-K-A. *J. Phys. Chem. C* **2018**, *122*, 27005–27015. [CrossRef]

42. Grajciar, L.; Čejka, J.; Zváček, A.; Areán, C.O.; Palomino, G.T.; Nachtigall, P. Controlling the Adsorption Enthalpy of CO\(_2\) in Zeolites by Framework Topology and Composition. *ChemSusChem* **2012**, *5*, 2011–2022. [CrossRef] [PubMed]

43. Zváček, A.; Areán, C.O.; Delgado, M.R.; Nachtigall, P.; Pulido, A.; Mayerová, J.; Čejka, J. Combined volumetric, infrared spectroscopic and theoretical investigations of CO\(_2\) adsorption on Na-A zeolite. *Microporous Mesoporous Mater.* **2011**, *146*, 97–105. [CrossRef]

44. Abdul Kareem, F.A.; Shariff, A.M.; Ullah, S.; Mellon, N.; Keong, L.K. Adsorption of pure and predicted binary (CO\(_2\)/CH\(_4\)) mixtures on 13X-Zeolite: Equilibrium and kinetic properties at offshore conditions. *Microporous Mesoporous Mater.* **2018**, *267*, 221–234. [CrossRef]

45. Pino, D.; Bessières, D. CH\(_4\)/CO\(_2\) Mixture Adsorption on a Characterized Activated Carbon. *J. Chem. Eng. Data* **2017**, *62*. [CrossRef]

46. Zhou, F.; Le-Hussain, F.; Guo, Z.; Yanici, S.; Cinar, Y. Adsorption/desorption characteristics for methane, nitrogen and carbon dioxide of coal samples from Southeast Qinshui Basin, China. *Energy Explor. Exploit.* **2013**, *31*, 645–666. [CrossRef]

47. Cheung, O.; Hedin, N. ChemInform Abstract: Zeolites and Related Sorbents with Narrow Pores for CO\(_2\) Separation from Flue Gas. *ChemInform* **2014**, *45*. [CrossRef]

48. Rios, R.B.; Straglilotti, F.M.; Peixoto, H.R.; Torres, A.E.B.; Bastos-Neto, M.; Azevedo, D.C.S.; Cavalcante, C.L., Jr. Studies on the adsorption behavior of CO\(_2–\)CH\(_4\) mixtures using activated carbon. *Braz. J. Chem. Eng.* **2013**, *30*, 939–951. [CrossRef]

49. Khalili, S.; Ghoreyshi, A.A.; Jahanshahi, M.; Khoshandam, B. Predictions of the adsorption equilibrium of CO\(_2)/\text{O}_2 \text{ mixture on multi-walled carbon nanotube using Ideal Adsorbed Solution Theory.} J. Water Environ. Nanotechnol. **2016**, *1*, 9–17. [CrossRef]

50. Singh, V.K.; Kumar, E.A. Comparative Studies on CO\(_2\) Adsorption Kinetics by Solid Adsorbents. *Energy Procedia* **2016**, *90*, 316–325. [CrossRef]

51. Malekbala, M.; Soltani, S.; Abdul Rashid, S.; Luqman Chuah, A.; Rashid, U.; Imededdine, N.; Choong, T.; Teo, S.H. Optimization the Process of Chemically Modified Carbon Nanofiber Coated Monolith via Response Surface Methodology for CO\(_2\) Capture. *Materials* **2020**, *13*, 1775. [CrossRef] [PubMed]
52. Gomez, L.; Zacharia, R.; Bénard, P.; Chahine, R. Simulation of binary CO$_2$/CH$_4$ mixture breakthrough profiles in MIL-53(Al). J. Nanomater. 2015. [CrossRef]

53. Pino, L.; Italiano, C.; Vita, A.; Fabiano, C.; Recupero, V. Sorbents with high efficiency for CO$_2$ capture based on amines-supported carbon for biogas upgrading. J. Environ. Sci. 2016, 48, 138–150. [CrossRef]

54. Ahn, H.; Moon, J.-H.; Hyun, S.-H.; Lee, C.-H. Diffusion Mechanism of Carbon Dioxide in Zeolite 4A and CaX Pellets. Adsorption 2004, 10, 111–128. [CrossRef]

55. Arefi Pour, A.; Sharifnia, S.; Neishabori Salehi, R.; Ghodrati, M. Adsorption separation of CO$_2$/CH$_4$ on the synthesized NaA zeolite shaped with montmorillonite clay in natural gas purification process. J. Nat. Gas. Sci. Eng. 2016, 36, 630–643. [CrossRef]

56. Tobarameekul, P.; Sangsured, S.; Chat, N.; Worathanakul, P. Enhancement of CO$_2$ Adsorption Containing Zinc-ion-exchanged Zeolite NaA Synthesized from Rice Husk Ash. Appl. Sci. Eng. Prog. 2020. [CrossRef]