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Molecular dynamic simulation of carbon dioxide, methane, and nitrogen adsorption on Faujasite zeolite

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ABSTRACT

Removing impurities such as carbon dioxide and nitrogen from natural gas is a technical challenge and one of the major concerns in natural gas treatment process. In this study, adsorption of CH₄, N₂, and CO₂ on the Faujasite (FAU) zeolite has been studied using molecular dynamics simulation at temperatures of 293, 308, and 323 K and pressures up to 1 MPa. COMPASS force field was used to model the interactions between zeolite and guest molecules. Ewald and atom-based summation methods were used for the calculation of electrostatic and van der Waals forces, respectively. Simulated results were modeled using Langmuir, Freundlich, Toth, and Sips adsorption isotherms. Sips isotherm for CO₂, and Toth isotherm for CH₄ and N₂ pure compounds showed the best performance. Heat of adsorption for CH₄, CO₂, and N₂ were calculated to be −15.48, −24.1, and −13.31 kJ·mol^{−1}, respectively. A comparative study showed that the simulation model was successful in predicting the overall trend of the adsorption with acceptable accuracy.

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1. Introduction

Natural gas, as a fuel source, provides a quarter of the world's total energy. It is estimated that the demand for natural gas will rise by 50 percent in the next 20 years [1]. Natural gas constituents depend heavily on the source from which it was extracted, but essentially, it consists of methane (typically 80%–95%), C₂+ hydrocarbons, and a small percentage of nitrogen and carbon dioxide as impurities [2]. Some sources have higher concentrations of impurities, such as CO₂ [1]. Levels of carbon dioxide in the atmosphere have increased by about 30% after industrialization, and is anticipated to become doubled or tripled by the end of the 21st century [3]. Necessity of removing these impurities has encouraged researchers to study natural gas purification processes [4,5]. Presence of carbon dioxide and nitrogen in natural gas decreases the energy density of natural gas and causes corrosion in pipelines. As a result, the amount of N₂ and CO₂ should be less than 2% and 4%, respectively [5,6]. Methane produces less carbon dioxide when burned, compared to coal and oil (45% and 30% respectively), and is

more attractive financially [2]. Adsorption using aqueous amine solutions [7], membranes [8], and using nanoporous materials, including zeolites, is recommended for CH₄/CO₂ mixture separation. Adsorption processes are also used in CH₄ separation from coal bed and landfill gas treatment [9–11]. Due to the financial and environmental concerns, and difficulties in conducting experiments, separation of carbon dioxide and methane mixture is quite challenging. Researchers are trying to find new materials which are not only effective adsorbents but also inexpensive and easy to produce. Among many materials that have been tested, zeolite has proven to be a good candidate. Zeolites can act as heterogeneous catalysts, adsorbents, and molecular sieves in gas separation process [12,13]. Many studies have focused on the separation of CO₂ and CH₄ using zeolites [2,14]. Among different zeolites, zeolite 13X is the most efficient and most common adsorbent due to its polar surface, high specific surface area, and big pore volume. Accuracy of adsorbent models can be evaluated by comparing the simulation results and the experimental data [15,16].

In recent years, adsorption of CH₄, N₂, and CO₂ on zeolites has been studied using atomistic molecular dynamics simulation methods such as Monte Carlo method [17–19]. Molecular dynamics simulation has an important role in helping us understand how gas is adsorbed on zeolites, at molecular level [20–22]. Macedonia *et al.* [23] studied the adsorption of methane, ethane, and argon on mordenite, using Monte Carlo simulation method. Evaluating the

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results using experimental data, they found the simulation results consistent with empirical data. Ahunbay *et al.* [24] surveyed methyl tertiary butyl ether (MTBE) adsorption on silicalite-1 using Grand Canonical Monte Carlo (GCMC) simulation and reported good agreement with experimental data except for lower loadings, which was caused by the limitations of the Polymer Consistent Force Field (PCFF). Purdue *et al.* [25] studied the adsorption of wet flue gas on zeolite 13X in the pressure of 1 atm, and temperature range of 298–348 K using molecular dynamics simulation. Simulated equilibrium isotherm data showed that presence of small amounts of steam in the gas mixture has a profound effect on the loading of adsorbed gas species on zeolite 13X. Recent studies revealed that Monte Carlo is a great method for simulating adsorption and separation of gases using zeolite [15,26].

Aim of this work is to simulate adsorption of CH_4 , N_2 , and CO_2 on zeolite FAU at 293, 308, and 323 K and pressures up to 1 MPa with molecular dynamics. Adsorption isotherms were modeled using Langmuir, Freundlich, Langmuir-Freundlich, and Toth methods, and deviations for each model was calculated. In the end, adsorption enthalpy was calculated for CH_4 , N_2 , and CO_2 .

2. Methodology

Molecular dynamics simulation is a way of solving Newton's equation of motions by iteration, in a specified time frame. Solving the equations will yield the trajectory of each atom or molecule in the system, which can then be used to calculate physical datasets of the system, such as diffusivity and adsorption isotherms [27]. All the simulations were carried out using BIOVIA Materials Studio 2017. Simulations were done in the zeolite structure of FAU with the composition of $\text{Si}_{96}\text{Al}_{96}\text{O}_{384}$ and cell dimensions of $25.028 \times 25.028 \times 25.028 \times 10^{-30} \text{ m}^3$. Faujasite (FAU) is from the zeolite family of silicate minerals [17]. The schematic diagram of FAU zeolite structure is shown in Fig. 1. Because the ratio of Si/Al in the structure is 1:1, the cell has a negative charge. This negative charge can be compensated by adding Na^+ cations to the zeolite structure [17,28]. The number of required sodium ions was determined with cation locator module in Materials Studio and have been inserted into FAU zeolite structure [29]. Cation locator module was used to insert cations in the zeolite structure, which uses Consistent Valence Force-

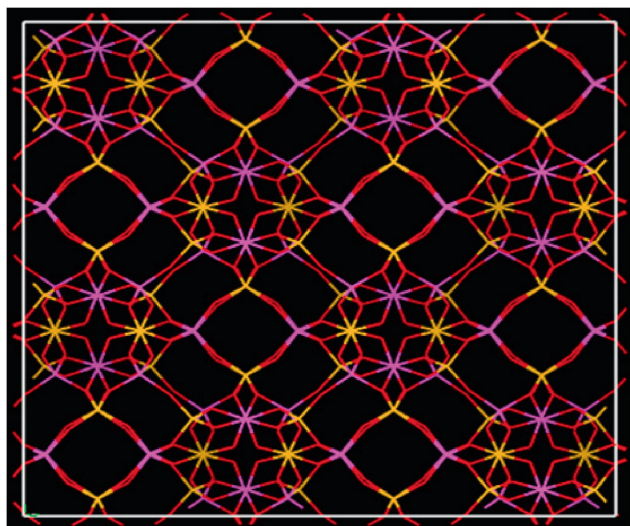


Fig. 1. Schematic structure of FAU zeolite: red: O, yellow: Si, and purple: Al.

Field (CVFF) [30]. Sodium cations (Na^+) were inserted into the simulation box randomly and were able to move freely in the exerted force section [17].

GCMC method was used with periodic boundary conditions to simulate adsorption of CH_4 , N_2 , and CO_2 on FAU zeolite. All the interactions of guest molecules (Na^+ , CH_4 , N_2 , and CO_2) with FAU zeolite structure was modeled using Lennard-Jones potential 12–6 (LJ) [31] and COMPASS force field. Ewald summation method was used with the accuracy of $0.01 \text{ kcal}\cdot\text{mol}^{-1}$ ($1 \text{ cal}=4.184 \text{ J}$) to calculate the long-range electrostatic interactions [32]. Additionally, using atom-based summation method with the cut off distance of $12.5 (\text{\AA}) \times 10^{-10} \text{ m}$, van der Waals potential energy was calculated [33]. The number of calculations for achieving the equilibrium was considered 1×10^6 steps for equilibrium and 1×10^7 steps for production. The duration of each timestep was 1 fs. In GCMC calculations, temperature (T), volume (V), and chemical potential (μ) are kept constant in the system [34,35]. When the chemical potential of the bulk gas (outside the framework) and

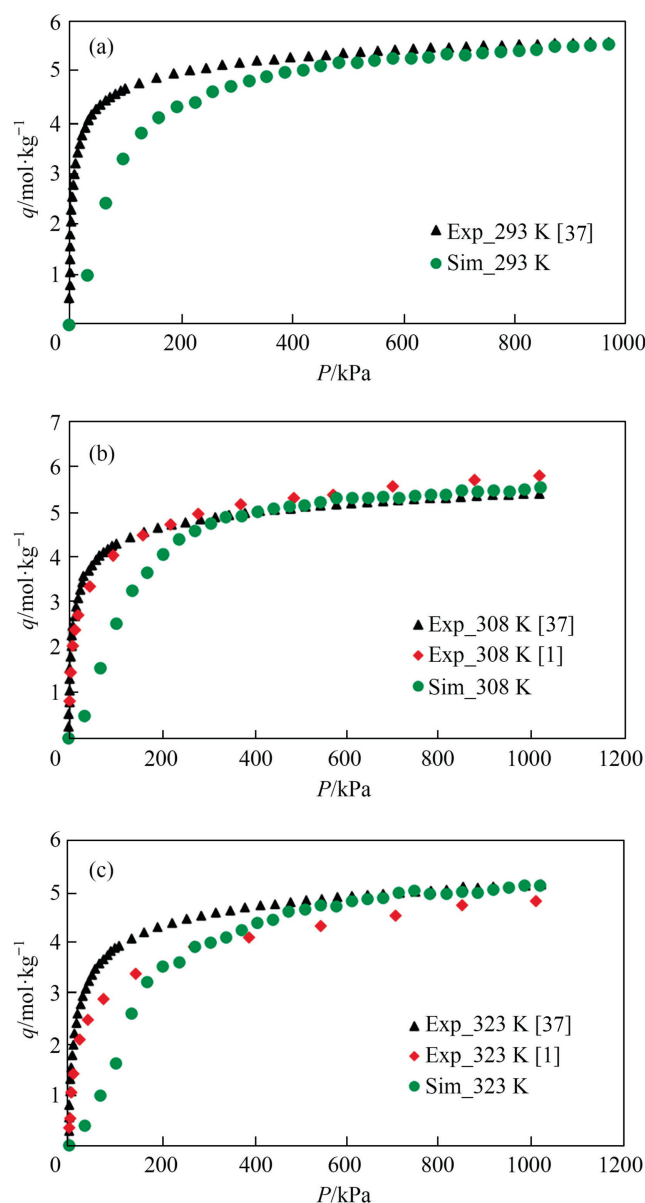


Fig. 2. Adsorption equilibrium isotherm of CO_2 on FAU zeolite at (a) 293 K, (b) 308 K, (c) 323 K.

the gas inside are equal at certain temperature and pressure, equilibrium will be achieved. The required partial pressure for evaluating the chemical potential of adsorbed molecules was calculated by ideal gas equation. Since the adsorption condition (temperature and pressure) is constant during the adsorption measurement, comparing experimental and simulation results would be possible [33].

3. Results and Discussion

3.1. Adsorption of pure component

Adsorption of pure components of CH₄, N₂, and CO₂ on zeolite FAU was investigated using molecular dynamics simulation at temperatures of 293, 308, and 323 K and pressures up to 1 MPa. Results of molecular dynamics simulation were compared with experimental data to validate adsorption isotherms. Experimental data for adsorption isotherms of methane and nitrogen at temperatures of 293, 308, and 323 K was obtained from Park *et al.* [36] and Cavenati (red squares) [1] was used for the adsorption isotherm of carbon dioxide at 293, 322, and 308 K. As can be seen in Figs. 2–4, the effect of temperature on adsorption isotherms of CO₂ (Fig. 2),

CH₄ (Fig. 3), and N₂ (Fig. 4) on FAU zeolite using molecular dynamics and experimental data is illustrated. As the charts suggest, the adsorption is very pressure-dependent at low pressures but the dependence gradually decreases as the pressure increases until the effect becomes almost negligible at very high pressures. Between the three gases, N₂ has the lowest molecular diameter and its diffusion is considered as micropore, whereas the CO₂ and CH₄ have macropore diffusion [37]. Despite its big diameter and large tetrahedral structure, CH₄ has low heat of adsorption, which contributes to its adsorption rate. The CO₂ has the highest affinity among the three gases, making its adsorption rate the largest. It can be seen from experimental adsorption isotherms of CO₂ obtained from Park [36] and Cavenati [1] results that adsorption capacities are different at the same pressure and temperature. This could be the result of the difference in the purity of zeolites or in the apparatus used to carry out the experiments [33]. Adsorption isotherms of CH₄, CO₂, and N₂ at 293, 308, and 323 K are depicted in Figs. 2–4. It can be seen from the figures that simulated isotherms of CH₄ and N₂ are more consistent with the experimental data than CO₂ adsorption isotherms. There is a slight discrepancy between simulated adsorption isotherm of CO₂ and the experimen-

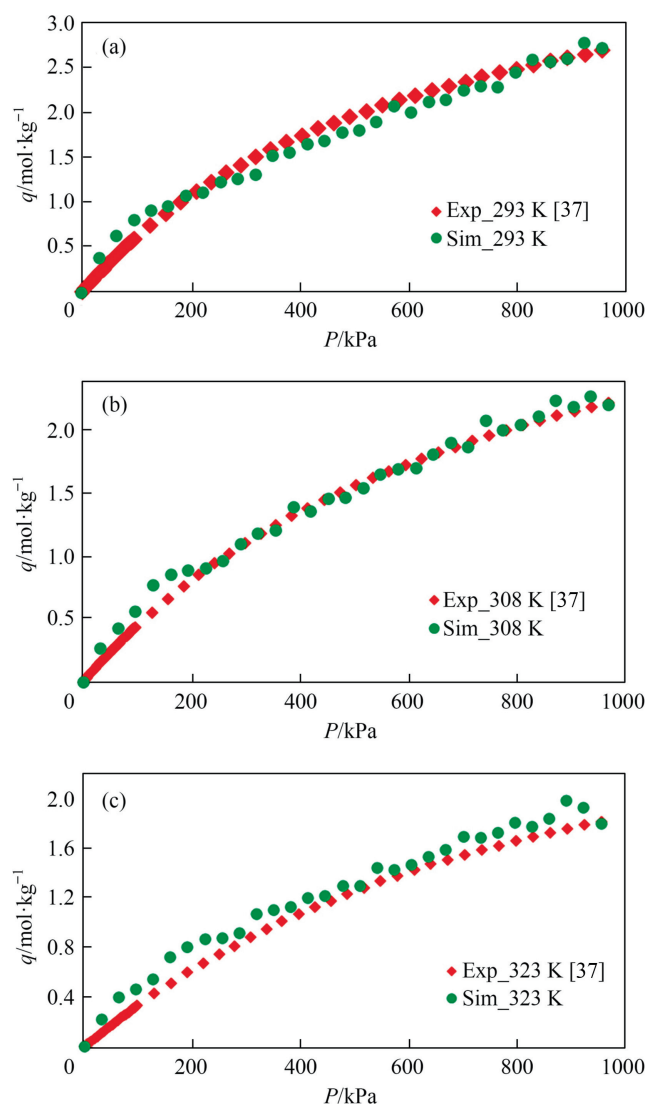


Fig. 3. Adsorption equilibrium isotherm of CH₄ on FAU zeolite at (a) 293 K, (b) 308 K, (c) 323 K.

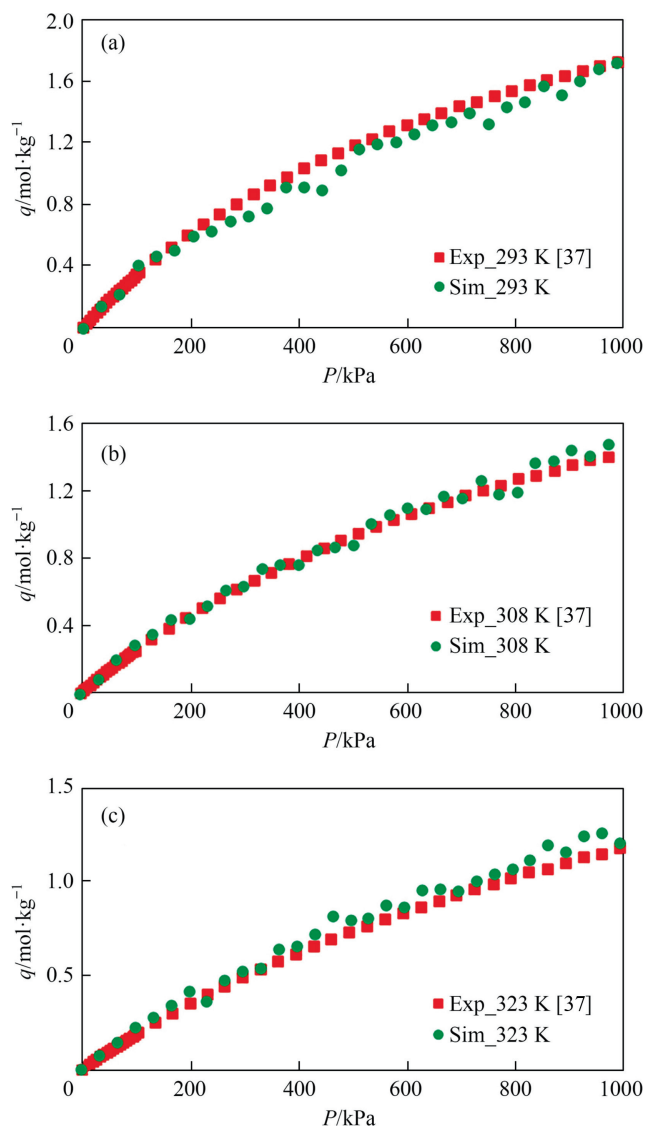


Fig. 4. Adsorption equilibrium isotherm of N₂ on FAU zeolite at (a) 293 K, (b) 308 K, (c) 323 K.

Table 1Adsorption parameters of Langmuir model of CO₂, CH₄ and N₂ adsorption on FAU

Temperature	Gas	R^2	RMS	Model's parameters	
				$q_{\max}/\text{mol}\cdot\text{kg}^{-1}$	K/kPa^{-1}
293	CO ₂	0.9638	0.2479	5.65	0.015222
	CH ₄	0.9746	0.1136	4.203	0.001582
	N ₂	0.9880	0.0532	3.12	0.001105
308	CO ₂	0.9119	0.4293	5.56	0.013217
	CH ₄	0.9854	0.0751	4.08	0.001198
	N ₂	0.9918	0.0382	3.03	0.000909
323	CO ₂	0.9082	0.4281	5.2	0.010022
	CH ₄	0.9780	0.0778	3.995	0.000969
	N ₂	0.9931	0.0303	2.93	0.000744

Table 2Adsorption parameters of Freundlich model of CO₂, CH₄ and N₂ adsorption on FAU

Temperature	Gas	R^2	RMS	Model's parameters		
				$q_{\max}/\text{mol}\cdot\text{kg}^{-1}$	K/kPa^{-1}	n
293	CO ₂	0.9088	0.3934	5.85	0.001039	3.903839
	CH ₄	0.9935	0.0571	4.18	0.000477	1.691584
	N ₂	0.9932	0.0401	3.06	0.000432	1.454086
308	CO ₂	0.8834	0.4942	5.76	0.001138	3.2638
	CH ₄	0.9940	0.0480	4.05	0.00039	1.654679
	N ₂	0.9920	0.0377	3.021	0.000367	1.423011
323	CO ₂	0.9049	0.4358	5.35	0.001112	2.735831
	CH ₄	0.9923	0.0462	3.95	0.000305	1.69041
	N ₂	0.9919	0.0329	2.98	0.000318	1.365291

Table 3Adsorption parameters of Sips model of CO₂, CH₄ and N₂ adsorption on FAU

Temperature	Gas	R^2	RMS	Model's parameters		
				$q_{\max}/\text{mol}\cdot\text{kg}^{-1}$	K/kPa^{-1}	n
293	CO ₂	0.9967	0.0747	5.69	0.011416	0.740445
	CH ₄	0.9752	0.1124	4.225	0.001559	1.030964
	N ₂	0.9884	0.0524	3.04	0.00118	0.945846
308	CO ₂	0.9991	0.0439	5.645	0.008573	0.591249
	CH ₄	0.9877	0.0690	4.105	0.001177	1.075368
	N ₂	0.9918	0.0382	3.021	0.000918	0.991172
323	CO ₂	0.9918	0.1282	5.59	0.006229	0.70808
	CH ₄	0.9903	0.0518	4.05	0.000863	1.178105
	N ₂	0.9932	0.0302	3.006	0.00071	1.011237

Table 4Adsorption parameters of Toth model of CO₂, CH₄ and N₂ adsorption on FAU

Temperature	Gas	R^2	RMS	Model's parameters		
				$q_{\max}/\text{mol}\cdot\text{kg}^{-1}$	K/kPa^{-1}	n
293	CO ₂	0.9906	0.1269	6.05	0.009358	1.09167
	CH ₄	0.9752	0.1122	4.3	0.00155	0.982209
	N ₂	0.9895	0.0497	3.15	0.000976	1.110833
308	CO ₂	0.9946	0.1068	5.645	0.004902	0.003754
	CH ₄	0.9867	0.0718	4.095	0.001378	0.906369
	N ₂	0.9919	0.0379	3.034	0.00088	1.030302
323	CO ₂	0.9881	0.1542	4.957	0.003754	2.836549
	CH ₄	0.9887	0.0557	4	0.001414	0.761091
	N ₂	0.9931	0.0303	2.96	0.000736	0.995365

tal data at low pressures. This inconsistency could be caused by the defects in zeolite structure (in contrast, simulated structure is perfect and periodic) or by uncertainty in the position of cation [31,38]. In low pressures of carbon dioxide, cations in site III will be occupied, but in high pressures, cations in site II will be occu-

pied, instead [37]. In Maurin *et al.* study [37], which investigated the carbon dioxide adsorption on NaY, NaX, and DAY, the experimental and simulation results were also different in high pressures. This was due to the deviation of adsorbent behavior from ideal gas behavior. The figures also show that loadings are

decreased by increasing temperature. Since there are differences between the experimental data for the adsorption isotherms, Comparison between simulation and experimental results should be focused on the trend of the graph, and levels of adsorption. In general, it has been observed that COMPASS force field has good accuracy in simulating adsorption isotherms of pure materials. Adsorption loading follows the order of $\text{CO}_2 > \text{CH}_4 > \text{N}_2$ which is due to the strength of binding forces.

3.2. Adsorption isotherms

In this work, adsorption models of Langmuir, Freundlich, Sips (Langmuir-Freundlich), and Toth were used to describe the simulation results. In Langmuir adsorption model (Eq. (1)), it is assumed that the surface contains a number of equivalent sites, and each site can only adsorb one molecule [38].

$$\frac{q}{q_{\max L}} = \frac{K_L P}{1 + K_L P} \quad (1)$$

Where q stands for adsorption capacity with the unit of $\text{mol} \cdot \text{kg}^{-1}$, P is equilibrium pressure (kPa), $q_{\max L}$ is maximum adsorption capacity, and K_L is Langmuir equilibrium constant.

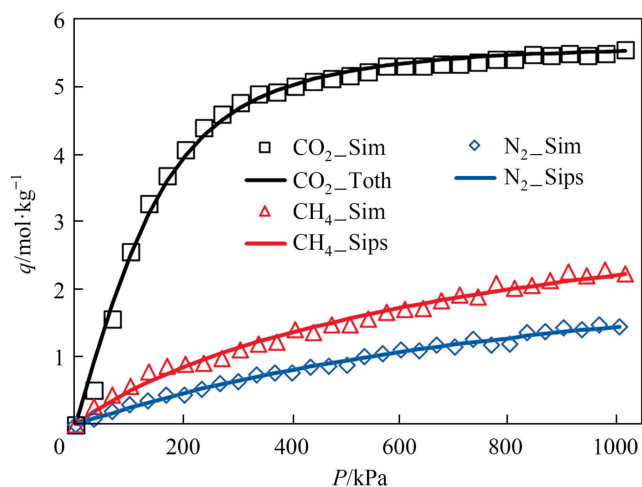


Fig. 5. Comparison between simulated isotherms and Toth model for CO_2 and Sips model for CH_4 and N_2 at 308 K.

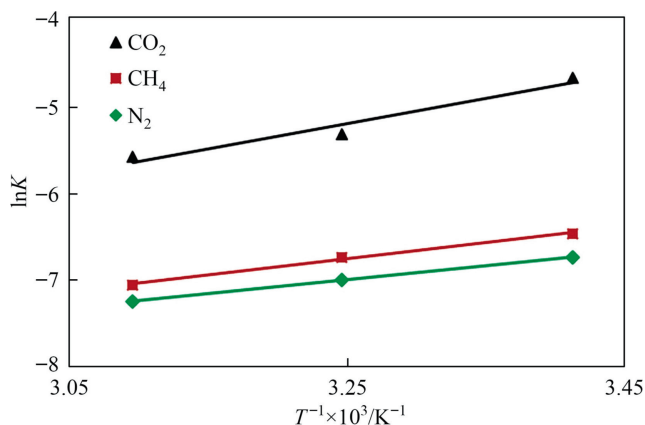


Fig. 6. Arrhenius plot for determining heat of adsorption and Arrhenius constant for CO_2 , CH_4 , and N_2 .

Freundlich model (Eq. (2)) is an empirical model used for heterogeneous systems and reversible adsorption, and also takes into account multilayer adsorption [39].

$$\frac{q}{q_{\max F}} = (K_F P)^{\frac{1}{n}} \quad (2)$$

Where n , $q_{\max F}$, and K_F are Freundlich isotherm parameters.

Sips adsorption model is the combination of Langmuir and Freundlich models, and thus is also called the Langmuir-Freundlich adsorption model [40].

$$\frac{q}{q_{\max S}} = \frac{(K_S P)^{\frac{1}{n}}}{1 + (K_S P)^{\frac{1}{n}}} \quad (3)$$

Where n , $q_{\max S}$, and K_S are Sips isotherm parameters. Sips isotherm is equal to Langmuir isotherm in the case of $n = 1$.

Toth isotherm model (Eq. (4)) is suitable for heterogeneous systems [41].

$$\frac{q}{q_{\max T}} = \frac{K_T P}{[1 + (K_T P)^m]^{\frac{1}{m}}} \quad (4)$$

Where $q_{\max T}$, K_T and m are maximum adsorption capacity, Toth equilibrium constant, and heterogeneity parameter, respectively. Toth isotherm is equal to Langmuir isotherm in the case of $m = 1$.

Results of simulation were compared with isotherm models using root mean square (RMS) (Eq. (5)) and coefficient of determination (R^2) (Eq. (6)).

$$\text{RMS} = \left(\frac{\sum_{i=1}^N (q_i^{\text{sim}} - q_i^{\text{cal}})^2}{N} \right)^{0.5} \quad (5)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{i=n} (q_i^{\text{cal}} - q_i^{\text{sim}})^2}{\sum_{i=1}^{i=n} (q_i^{\text{sim}} - q_m)^2} \quad (6)$$

Where N is the number of data and q_i^{cal} , q_i^{sim} , and q_m are adsorption loading of models, simulated adsorption capacity, and mean capacity of adsorption simulated by molecular dynamics. Values of R^2 and RMS, and Langmuir, Freundlich, Sips, and Toth adsorption model parameters are presented in Tables 1–4. Isotherm parameters were calculated using Polymath professional version 6.1. According to the RMS values, best adsorption isotherm for CO_2 was found to be the Toth isotherm due to the high affinity of CO_2 molecules toward zeolite and adsorbate heterogeneity [2] while Sips isotherm showed better results for adsorption of pure methane and nitrogen. Simu-

Table 5

Heat of adsorption and Arrhenius constants for CO_2 , CH_4 , and N_2

Gas	$\Delta H_{\text{ads}}/\text{kJ} \cdot \text{mol}^{-1}$	K_0/kPa^{-1}
CO_2	−24.0989604	4.48212×10^{-7}
CH_4	−15.4856564	2.72784×10^{-6}
N_2	−13.31071	5.02×10^{-6}

Table 6

Comparison of heat of adsorption and Arrhenius constant for CO_2 , CH_4 , and N_2

$-\Delta H/\text{kJ} \cdot \text{mol}^{-1}$			Ref.
CO_2	CH_4	N_2	
37.2	15.3	12.8	[1]
35.4	17.2	17.1	[2]
34.65	15.43	–	[14]
43.1	9.2	–	[44]

lated isotherms, Toth isotherm for CO₂, and Sips isotherm for CH₄ and N₂ are shown in Fig. 5. In the entire range of pressure, isotherm models predicted the simulation results with an error of less than 2.54% and RMS of less than 0.1136, except for Langmuir and Freundlich models for CO₂ isotherms, which had errors in the range of 3.62%–9.18% and 9.12%–11.66%, respectively.

3.3. Heat of adsorption

Part of the heat of adsorption will increase the temperature of adsorbent particles, which influences the adsorption kinetics and separation performance of bed by using adsorbent [42,43]. Equilibrium constants are dependent on the temperature, which is governed by Arrhenius equation (Eq. (7)).

$$\ln K = K_0 \exp\left(-\frac{\Delta H_{\text{ads}}}{RT}\right) \quad (7)$$

In Arrhenius equation, K_0 is the rate constant (kPa⁻¹), ΔH_{ads} is the activation energy, and R is the universal gas constant.

Fig. 6 shows the linear regression of Arrhenius equation for the adsorption of carbon dioxide, methane, and nitrogen on zeolite at 293, 308, and 323 K, in which the y-intercept is $\ln K_0$ and the slope is equal to $\Delta H_{\text{ads}}/R$. As deduced in last section and according to Tables 1–4 and Fig. 5, Toth model had the best accuracy in adsorption of CO₂ and Sips model had the best accuracy for N₂ and CH₄. It is clear from Fig. 6 that Sips model for CH₄ and N₂ and Toth model for CO₂ have high accuracy in explaining adsorption behavior on FAU. According to Table 5, the values of ΔH_{ads} and K_0 are given for the three pure gases. Heat of adsorption for CO₂, CH₄, and N₂ were calculated from Arrhenius equation and were equal to -24.1, -15.48, and -13.31 kJ·mol⁻¹, respectively, which was in good agreement with the reported data, in except for carbon dioxide (Table 6) [1,2,14,44]. It seems that the discrepancy between the results for carbon dioxide is related to the differences between simulated and experimental adsorption isotherms of CO₂.

4. Conclusions

Molecular dynamics simulation of CH₄, N₂, and CO₂ adsorption on FAU zeolite was performed using Monte Carlo method at temperatures of 293, 308, and 323 K and pressures up to 1 MPa. Interaction between the molecules was modeled with Lennard-Jones potential and COMPASS force field. Effect of temperature on the adsorption loadings was simulated and the results were compared with experimental data from previous studies. Adsorption models of Langmuir, Freundlich, Sips (Langmuir-Freundlich), and Toth were used to describe the simulation results. According to the calculated RMS and R^2 values, Toth adsorption model for CO₂, and Sips model for CH₄ and N₂ had the best performance and accuracy. Finally, heat of adsorption for the adsorption of CH₄, N₂, and CO₂ on FAU zeolite was calculated from Arrhenius equation, which was in good agreement with the reported experimental data.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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