



Equilibrium and Thermodynamic Studies of Methane Adsorption on Multi-Walled Carbon Nanotube

^{1,2}Sanaz. Monemtabary, ²Mojtaba Shariati Niasar, ²Mohsen Jahanshahi and ²Ali Asghar Ghoreyshi

¹Nanotechnology and Transport Phenomena Lab,
Faculty of Chemical Engineering, Tehran University, Iran
²Nanotechnology Research Institute, Faculty of Chemical Engineering,
Babol University of Technology, Iran

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Abstract: In this work, The adsorption of methane onto multi-walled carbon nanotubes (MWCNTs) was studied, in which the influences of temperature and pressure were investigated. The physical properties of the MWCNT were systematically characterised by Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) surface area measurements. The equilibrium adsorption data were analyzed using three common adsorption models: Langmuir, Freundlich and Sips. All of the models fit the experimental results well. The adsorption thermodynamic was carried out at 283.15, 298.15 and 313.15 K. The isosteric heat of adsorption (ΔH) was calculated for CH₄ and H₂, using Clausius-Clapeyron equation. The small amounts of that indicated physical nature of adsorption mechanism. All values were negative, indicating that the adsorption is feasible and exothermic process in nature.

Key words: Gas separation • Gas adsorption • Multi-walled carbon nanotubes • Methane • Hydrogen

INTRODUCTION

Syngas (synthetic gas or synthesis gas) is a gas mixture that contains different gases with different ratios. Syngas consists primarily of hydrogen, carbon monoxide and very often some carbon dioxide and has less than half the energy density of natural gas. More than 80 percent of this gas is hydrogen. Hydrogen is an important gas for many chemical reactions (Hydrogen is considered to be a clean energy carrier) such as oil reforming, sulfur reduction from oil, purification of metals, hydrogenation and reduction of fine-chemicals. It is also used in many semiconductor processes as a carrier gas [1]. Hydrogen purification with different process such as membrane separation and adsorption is essential to remove impure gases such as methane, Because a trace of methane could cause detrimental effects on the reactors operation and their efficiency. Methane is the main component of natural gas. In addition to the natural gas is commonly

considered as a suitable, non-polluting, energy source for the future [2]. But membrane separation requires high cost and creates problems in industries. Hence adsorption is developed as one of the best methods. Many sorbents have been used for adsorption process. Some of these sorbents are zeolites, silica, carbon molecular sieves, polymeric materials and activated carbon. In recent years, Since the carbon nanotube (CNT) was discovered by Iijima in 1991 [3], extensive research efforts have been carried out for this new kind of material due to its unique properties based on their large specific surface areas, high uniform porosity, high permeability, high selectivity and highly uniform pore size and attractive surface potentials, that it is very promising for gas absorption processes. Previous studies have been carried out on separation of CH₄/H₂ mixtures in different adsorbents both experimentally and theoretically. For instance, Mac Elroy and Boyle used a non-equilibrium molecular dynamics (NEMD) simulation technique to investigate the transport

of binary mixtures of hydrogen and methane through a model carbon membrane of varying thickness [4]. Also Vieira-Linares and Seaton used non-equilibrium molecular dynamics simulations of gas separation in a “selective surface flow” membrane. The studied gas mixture was hydrogen/methane at pressure of 1.7 bar and at a fixed temperature of 295.15 K. They showed that the permeability is sensitive to small variations on the pore size. The simulations gave the more strongly adsorbing species (methane) in a dense layer near the pore wall, with the less strongly adsorbed species (hydrogen) diffusing through a less dense region close to the Centre of the pore [5]. Mei Hong used a SAPO-34 membrane for separation H_2/CH_4 mixtures at feed pressures up to 1.7MPa. They have showed that the SAPO-34 membrane separated H_2 from CH_4 , because CH_4 is close to the SAPO-34 pore size and has a lower diffusivity than H_2 [6]. Haibin Chen, David S. Sholl used atomically detailed simulations to predict the binary permeance of CH_4/H_2 mixtures through defect-free (10, 10) single walled carbon nanotubes acting as membranes at room temperature. Their simulations indicated that single-component gas diffusion in carbon nanotubes is extremely rapid compared to other known nanoporous materials [7].

The main objective of the present research is to assess the potential of MWCNT as an effective adsorbent for separation of CH_4 from syngas. Therefore, adsorption of methane and hydrogen on multi-walled carbon nanotube is investigated.

MATERIALS AND METHODS

Materials: The multi-walled carbon nanotube was purchased from Alpha Nanotechnology Company, Ltd (China). It was synthesized by Chemical Vapor Deposition (CVD) method with 95% purity. Methane and hydrogen with purity of 99.999% and helium with purity of 99.995% were purchased from Technical Gas Services Company, UAE. helium was employed to estimate the dead volumes.

Physical Characterization: Scanning Electron Microscopy (SEM) micrograph of the sample was detected in order to obtain supplementary information regarding the MWCNT structure. The SEM used in this reaserch was obtained by TESCAN VegaII model microscope. The porous structure of MWCNTs sample was also examined by means of N_2 porosimetry. A nitrogen adsorption–desorption isotherm at 77K was measured with Belsorp mini II model (manufactured by BelJapan Company) apparatus. The amount adsorbed at each

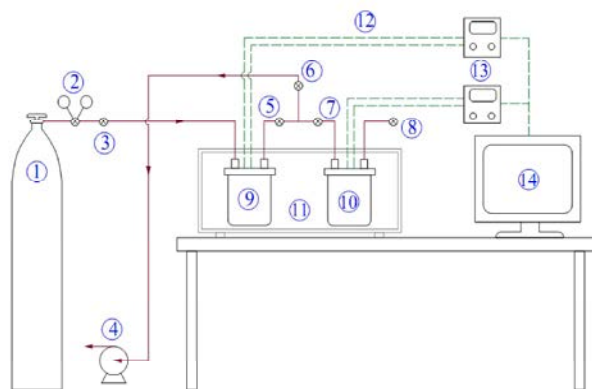


Fig. 1: Schematic design of the volumetric adsorption system.

(1) methane cylinder; (2) regulator; (3) valve; (4) vacuum pump; (5, 6 and 7) valves; (8) vent; (9) loading cell; (10) adsorption cell; (11) water bath; (12) pressure and temperature transducers; (13) indicators; (14) computer.

relative pressure (P/P_0 , where P is the pressure of nitrogen vapor and P_0 is the saturation pressure of N_2 at 77K) range of 0.0001-0.99 was obtained by admitting appropriate volumes of high purity nitrogen gas into the sample cell at 77K and measuring the equilibrium vapor pressure. Analysis of the adsorption and desorption data was carried out to investigate the structure of the sample. The Brunauer–Emmett–Teller (BET) [8] method was applied to determine the BET surface area (S_{BET}) and the adsorbent monolayer capacity.

Apparatus: The schematic apparatus presented in Figure 1 was set up to measure volumetrically adsorbed methane at temperatures of 283.15K, 298.15K and 313.15K under the pressures up to 40 bar. Degassing of the adsorbent was performed under vacuum and high temperature of 473.15 K before each experiment and the system was evacuated by vacuum pump to 8 mbar. About 10 grams of MWCNTs were used as the sample in each experiment. During the experiments the apparatus used for methane and hydrogen adsorption experiments was comprised of two high-pressure stainless steel cylinders, the loading and the adsorption vessels that were located in the water bath (WB22 memmrt germany WNB 7-45) to maintain constant temperature (with working temperature range of 283-363K). The loading cell was connected to the adsorption cell and a regulator via a needle valve to control entrance gas rate. The regulator was connected to a high-pressure cylinder. Each one of the cells has a pressure transducer

(CA CP 2R), which they were connected to a computer to show and record experimental pressures. Before entering the gases into the adsorption vessel, the pressure of loading vessel was set at the required initial level for each adsorption measurement. After starting the experiments, a time was required to approach to the equilibrium condition at a constant pressure and the isotherm temperature. The adsorption capacity was calculated using the mass balance (Eq. 1) on the base of the temperature and pressure measured before and after the equilibrium state.

$$\frac{PV}{ZRT}\Big|_{L_1} + \frac{PV}{ZRT}\Big|_{a_1} = \frac{PV}{ZRT}\Big|_{L_2} + \frac{PV}{ZRT}\Big|_{a_2} + N \quad (1)$$

RESULT AND DESSCUTION

Material Characterization: The MWCNT was characterized using the SEM techniques and by means of N₂ porosimetry and determination of the specific area by the BET method. Figure 2 shows SEM images of the specific sample. As it is obvious in the SEM image, the length of MWCNT is very short and this short length caused to increase of BET surface area. The short length of MWCNT maybe occurred during purification of CNT with concentrated acids. The N₂ adsorption–desorption isotherm for the MWCNTs at 77 K is shown in Figure 3. The textural properties such as BET surface area, pore diameter and pore volume are listed in Table 1.

Adsorption Experiments: The experiments were carried out with a sample of multi-walled carbon nanotubes at various temperatures of 283.15K, 298.15K and 313.15K in pressures ranging 0 to 50 bar. Results showed this type of multi-walled carbon nanotube is strongly capable for methane adsorption. The maximum value of methane adsorption onto MWCNT at T= 283.15 K and P= 40 bar were achieved to 5.44 mmol/g. The most important experimental parameters affecting the gas adsorption and separation are temperature and pressure. As it can be seen in Figures 4, at a given temperature, the amount of gas adsorbed is only a function of the pressure. Increasing gas pressure cause to increase of gas

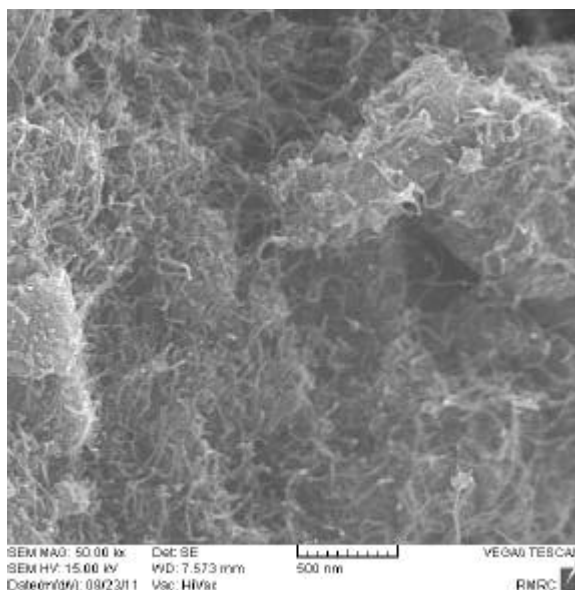


Fig. 2: SEM image of MWCNT.

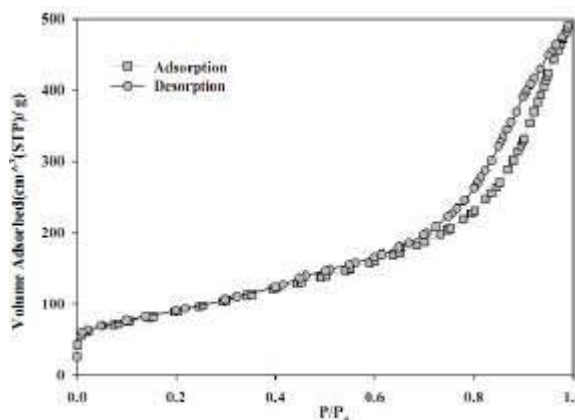


Fig. 3: N₂ adsorption–desorption isotherms of MWCNT.

adsorption, but Increasing the temperature leads to decrease of gas adsorption [9]. Also according to the obtained results it is observed that the amount of methane adsorption on MWCNT is more than hydrogen adsorption. This fact can be explained with regarding to the stronger Van der Waals interactions between methane molecules and MWCNT in comparison with hydrogen and also the higher molecular mass of CH₄ compared to H₂. These results are illustrated in Table 2.

Table 1: Technical data of the MWCNT

| Impurity (Ca) | Impurity (Au) | S _{BET} (m ² /g) | Pore volume (cm ³ /g) | Mean pore diameter (nm) |
|---------------|---------------|--------------------------------------|----------------------------------|-------------------------|
| 0.25 | 2.49 | 324 | 0.76 | 9.36 |

Table 2: Effect of temperature on adsorption process

| Temperature | H_2 | | CH_4 | |
|-------------|--------------|--------------|--------------|--------------|
| | q (P=20 bar) | q (P=30 bar) | q (P=20 bar) | q (P=30 bar) |
| 283.15 | 1.9141 | 2.6822 | 3.0590 | 4.2178 |
| 298.15 | 1.8622 | 2.6107 | 2.6027 | 3.5572 |
| 313.15 | 1.5895 | 2.2218 | 2.3784 | 3.1978 |

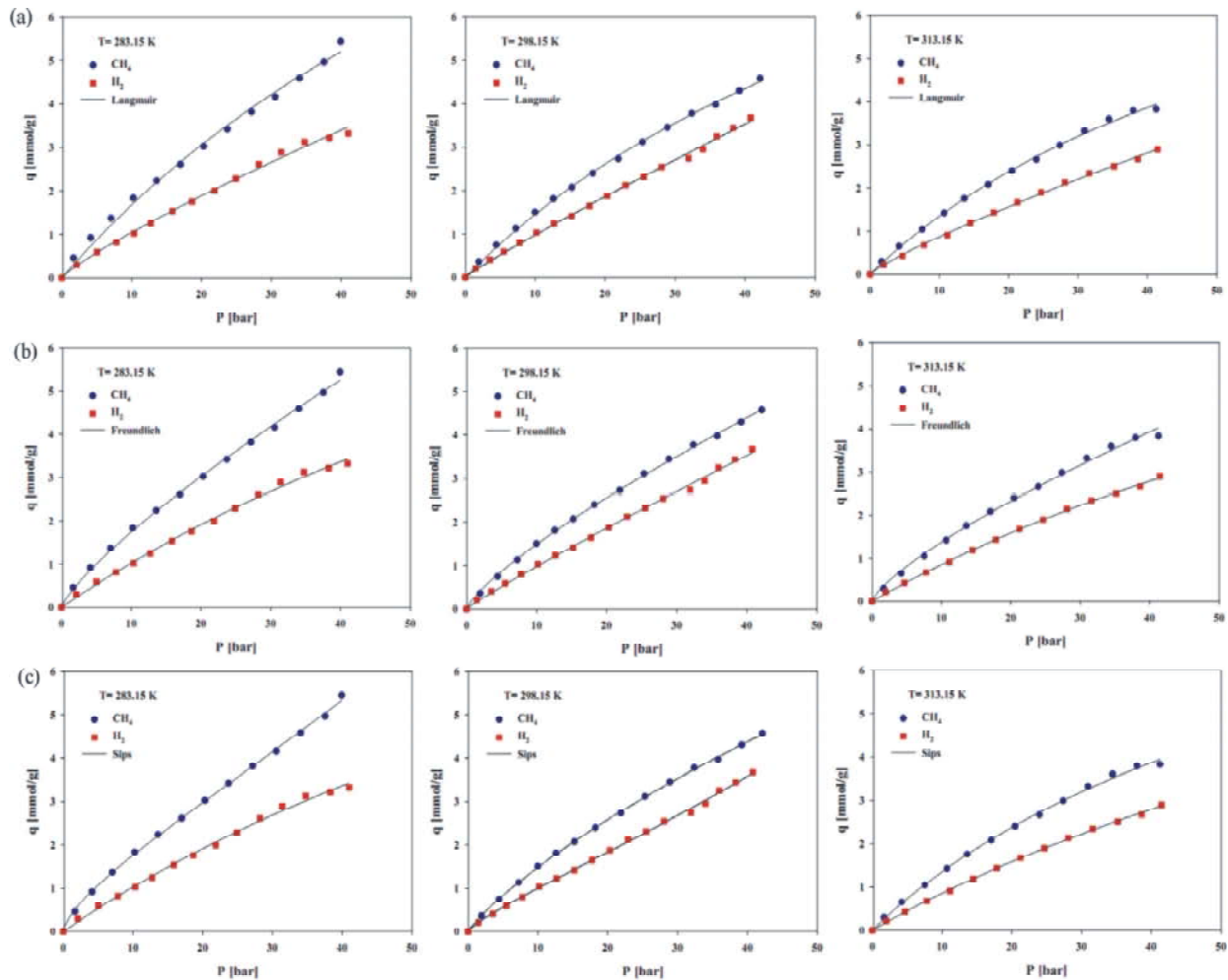


Fig. 4: Comparison of methane and hydrogen adsorption on MWCNT fitted with a) Langmuir, b) Freundlich and c) Sips isotherms equation at different temperatures.

Adsorption Isotherms Model: Equilibrium data, commonly known as adsorption isotherms, describe how the adsorbate interacts with adsorbents and give a comprehensive understanding of the nature of interaction. It is important to optimize the design of an adsorption system. There are several methods of mathematically representing adsorption isotherms, with different models used to describe the adsorption process [10]. To study the adsorption behavior three prevalent isotherm models

such as, Langmuir (Eq. 2), Freundlich (Eq. 3) and Sips (Eq. 4) have been used. The Langmuir model assumes that there is no interaction between the adsorbate molecules and the adsorption is localized in a monolayer. In fact the Langmuir model is based on assumption of monolayer adsorption on a structurally adsorbent [11]. In which the attraction between adsorbate molecules and their mobility along the surface can be ignored. The Freundlich isotherm model is an empirical relationship describing the

adsorption of adsorbate to a adsorbent surface and assumes that different sites with several adsorption energies are involved. Adsorption equilibrium is described with the Langmuir isotherm equation, so:

$$q_e = q_m \frac{K_L P}{1 + K_L P} \quad (2)$$

where q_e is the amount of methane adsorbed per unit mass of MWCNT [mmol/gr]; q_m is the maximum amount of methane adsorbed [mmol/g]; P is the equilibrium pressure of methane [bar]; and K_L is a constant related to the adsorption energy.

Freundlich isotherm is expressed by the following equation:

$$q_e = K_F P^{1/n} \quad (3)$$

where K_F and n are the Freundlich constants that point to relative capacity and adsorption intensity respectively and n giving an indication of how favorable the adsorption process [12]. $1/n$ is the heterogeneity factor. whereby values $n > 1$ represent favorable adsorption condition. The Freundlich isotherm indicates reversible adsorption process [13, 14].

The first effort to extend the Langmuir model to adsorption on an energetically heterogeneous solid was exercised by Sips in 1948. Based on the assumption of quasi-Gaussian energy distribution, Sips derived an isotherm containing the surface heterogeneity factor, $1/n$, as follows:

$$q = q_m \frac{(bP)^{(1/n)}}{1 + (bP)^{(1/n)}} \quad (4)$$

where p is an equilibrium pressure of adsorbed gas molecules and b is a Langmuir constant containing the characteristic adsorption energy U_0 (i.e., $\bar{A} = A_0 \exp(U_0/RT)$, where A_0 is a pre-exponential factor) [15]. The Langmuir, Freundlich and Sips isotherm parameters

and the correlation coefficients (R^2) are shown in table 3 and 4. As indicates that n is greater than one, which proves that CH_4 and H_2 molecules are favorably adsorbed on multi-walled carbon nanotubes at all temperatures. Also it is observed the correlation coefficients is in the range of 0.9949–0.9997. Therefore it can be said that three models are able to fit the adsorption data for all of the studied gas adsorption at all temperatures.

Thermodynamic Studies: The isosteric heat of adsorption (ΔH) provides a direct measure of the strength of the binding forces between the adsorbate molecules and the adsorbent surface [16]. It can be calculated using a Clausius–Clapeyron equation (Eq. 5). The value of ΔH is determined from the slope of $\ln P$ versus $1/T$. Where P [bar] is the vapor pressure, ΔH [kJ/mol] is the gas enthalpy changes, T [K] the gas temperature and R [8.314 J/mol K] is the gas constant. The isosteric heat for methane and hydrogen is shown in Figures 5 and 6 and table 5 and 6. It shows that the reactions are exothermic and amount of adsorbed hydrogen is less than adsorbed methane, due to the high interaction between MWCNTs and methane molecules.

$$\left(\frac{\partial \ln P}{\partial \frac{1}{T}} \right)_q = \frac{\Delta H}{R} \quad (5)$$

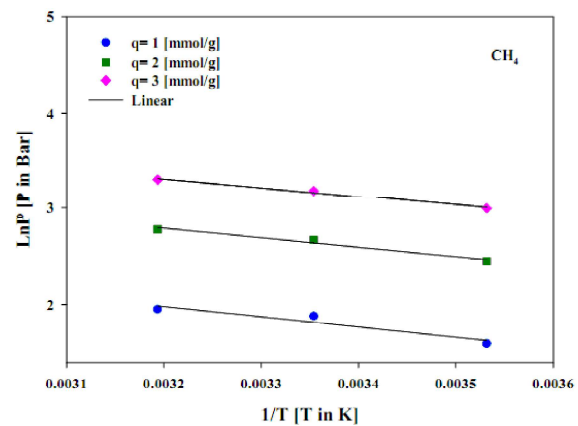


Fig. 5: Isosteric heat of adsorption of CH_4 on MWCNT.

Table 3: Langmuir, Freundlich isotherm parameters and correlation coefficients for adsorption of methane on MWCNT

| T(K) | Langmuir | | | Freundlich | | Sips | | | | |
|--------|----------|--------|--------|------------|-------|--------|-------|-------|-------------|--------|
| | q_m | K_L | R^2 | K_F | n | R^2 | q_m | n | b | R^2 |
| 283.15 | 36.58 | 0.0107 | 0.9949 | 0.2784 | 1.255 | 0.9984 | 28.30 | 1.549 | $7.6e^{-3}$ | 0.9993 |
| 298.15 | 14.05 | 0.0125 | 0.9991 | 0.2457 | 1.278 | 0.9994 | 13.14 | 1.154 | $6.5e^{-3}$ | 0.9997 |
| 313.15 | 11.61 | 0.0150 | 0.9984 | 0.2385 | 1.316 | 0.9967 | 11.05 | 1.025 | $4.4e^{-3}$ | 0.9985 |

Table 4: Langmuir, Freundlich isotherm parameters and correlation coefficients for adsorption of hydrogen on MWCNT

| T(K) | Langmuir | | | Freundlich | | | Sips | | | |
|--------|----------|--------|--------|------------|-------|--------|-------|-------|-------------|--------|
| | q_m | K_L | R^2 | K_F | n | R^2 | q_m | n | b | R^2 |
| 283.15 | 17.40 | 0.0079 | 0.9967 | 0.1477 | 1.176 | 0.9960 | 14.30 | 1.003 | $3.6e^{-3}$ | 0.9967 |
| 298.15 | 13.05 | 0.0027 | 0.9974 | 0.1151 | 1.077 | 0.9981 | 13.13 | 1.292 | $3.5e^{-3}$ | 0.9989 |
| 313.15 | 10.28 | 0.0079 | 0.9993 | 0.1228 | 1.178 | 0.9988 | 10.19 | 1.022 | $2.7e^{-3}$ | 0.9994 |

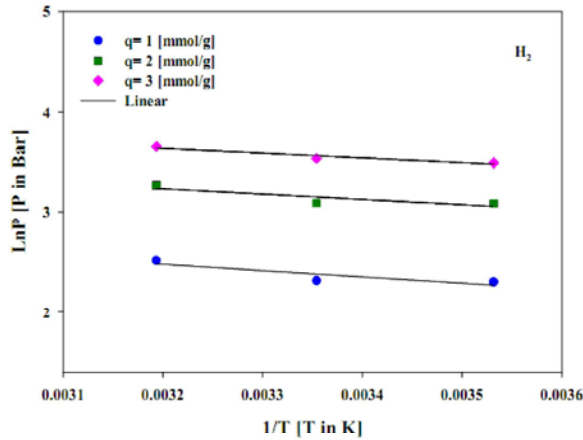


Fig. 6. Isosteric heat of adsorption of H₂ on MWCNT.

Table 5: The amount of isosteric heat of adsorption of CH₄ onto MWCNT

| MWCNT | | |
|----------------|--------|--------------------------|
| q_c [mmol/g] | R^2 | ΔH_{st} [kJ/mol] |
| 1 | 0.9086 | -8.84 |
| 2 | 0.9712 | -8.18 |
| 3 | 0.9875 | -7.77 |

Table 6: The amount of isosteric heat of adsorption of H₂ onto MWCNT

| MWCNT | | |
|----------------|--------|--------------------------|
| q_c [mmol/g] | R^2 | ΔH_{st} [kJ/mol] |
| 1 | 0.7792 | -5.15 |
| 2 | 0.7453 | -4.47 |
| 3 | 0.9123 | -3.97 |

CONCLUSIONS

The adsorption of methane and hydrogen on MWCNT was systematically investigated at temperature range of 283.15-313.15 K and pressure up to 40 bar. The Langmuir, Freundlich and Sips isotherm models fitted the experimental results well. According to the value of n which was greater than one the adsorption was favorable. The results emphasized that lower temperature and higher pressure is needed to improve the gas adsorption by MWCNT. Also due to negative value of ΔH the reaction

was exothermic. In addition, the obtained values of ΔH showed that adsorption of methane was more than adsorption of hydrogen. In general results obtained from equilibrium thermodynamic studies indicated that MWCNTs is a promising adsorbent for separation of CH₄ from H₂.

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