

Study of Methane Storage and Adsorption Equilibria in Multi-Walled Carbon Nanotubes

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ABSTRACT: *Adsorbed natural gas has various advantages and is relatively more economical than liquefaction and compression. Carbon nanotubes can be introduced as a new candidate for natural gas storage. In this study, adsorption of methane was firstly studied on the as-prepared multi-walled carbon nanotubes, and then chemical and physical treatment of MWCNTs was performed to enhance the methane adsorption. Treatment by acid washing and annealing with air improved purity, surface area and methane adsorption. The adsorption and equilibrium isotherm data of T-MWCNTs, were measured by a static volumetric technique at different temperatures of 298, 291, 273 and 263 K and pressures up to 7 MPa. The maximum value of methane storage at normal temperature of 298 K was achieved to 2.81 mmole/g in our experiments. This amount of methane adsorption is equal to 108 v/v, meanwhile the target value of the adsorbed natural gas is 120 v/v to become as the accepted material for ANG process. The isosteric heat of adsorption of T-MWCNTs was determined in the studied range of pressures and temperatures. The results revealed an energetically heterogeneous surface in methane adsorption. Furthermore, different isotherm models were fitted on the experimental adsorption data and the model parameters were correlated. Within the different studied isotherms, Sips equation provided best fitting to the experimental data.*

KEY WORDS: *Methane storage, Multi-walled carbon nanotubes, Adsorption equilibria.*

INTRODUCTION

Methane as a major component of natural gas, which is receiving tremendous attentions for consideration as the future fuel for energy generation, is being studied extensively [1, 2]. Due to the low critical temperature (191 K), methane can not be liquefied by only implementing pressure at room temperature. Compressed natural gas (CNG) is an alternative solution, although has some

disadvantages such as requirements of costly multi-stage compression to 20-25 MPa high pressures. Compared to CNG, adsorbed natural gas (ANG) is promising and efficient by storing natural gas in porous media. Novel adsorbents are being sought to provide new adsorption materials such as carbon fibers, carbon nanotubes, carbon nanohorns, etc. for the storage and transport of methane.

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Table 1: Properties of as-prepared and T- MWCNTs.

Adsorbent	BET (m ² .g ⁻¹)	Packing density (g.dm ⁻³)	Purity (wt %)	Int. diameter (μm)
As prepared	300	0.5	75	<1
T- MWCNT	385	0.79	89.4	<1

Discovery and synthesis of CNTs has contributed much to the research in carbon chemistry perhaps mainly due to the cylindrical structure of this novel carbon structures and to their potential applications in gas storage [3,4]. CNTs can be prepared in single-walled carbon nanotubes (SWCNTs) or multiple-walled carbon nanotubes (MWCNTs). By the literature reviews, we found some of the researches working on the experimental measurements and some others on simulation and theoretical predictions [5-10].

For instance, *Lee et al.* [5] produced multi-walled carbon nanotubes by CVD methods with purity of greater than 95 %. They determined the amount of adsorbed methane about 1.886 mmole/g at 303.15 K and 2.745 MPa. *Bekyarova et al.* [6] investigated the adsorption of methane on single-walled carbon nanohorns (SWCNHs). They reported the total amount of adsorbed methane, about 160 v/v 303 K and 3.5 MPa. *Yulong et al.* [7] studied methane storage in MWCNTs at ambient temperature and pressures of 0-10.5 MPa, with a quantity of 80 g samples and achieved 11.7 % wt at 298 K and 10.5 MPa.

Tanaka et al. [8] studied the adsorption of methane on isolated SWCNT by density functional theory (DFT), and predicted the capacity of 12.3 mmole /g at room temperature. *Cao et al.* [9] studied methane adsorption on triangular arrays of SWCNT by the grand canonical Monte Carlo (GCMC) simulation, the maximal gravimetric capacity achieved to 13.4 mmole/g by this model.

Zhang et al. [10] simulated methane adsorption on SWCNTs by GCMC and DFT method and predicted 22 mmole/g adsorbed gas at 300 K and 6 MPa. Although different amount of adsorbed methane are reported by the literature and most of them are focused on SWCNTs, it is concluded that CNTs could be a good candidate for methane storage. MWCNTs with small internal diameters are expected to be appropriate material for methane adsorption. Higher surface area and lower cost of production are promising potential of MWCNTs for gas storage process [5]. The major of our work, is the experimental study on the Iranian made MWCNTs

and improving the methane adsorption by some chemical and physical treatment. Furthermore, modeling the equilibrium state of methane/treated- MWCNTs system is studied at different temperatures and pressures to obtain the adsorption parameters which are necessary for design and simulation of the adsorption- desorption cycles.

EXPERIMENTAL

Materials

The as-prepared MWCNTs were purchased from Research Institutes of Petroleum Industries (RIPI) of IRAN. This material was produced by chemical vapor deposition (CVD) of methane. The properties of this material are shown in table 1. Acid solutions of HCl (33 wt %), HNO₃ (6M) and distilled water were prepared for purification of the raw MWCNTs. A high pressure methane cylinder with high purity of 99.995 % was used as the adsorbate. Helium gas of 99.999 % purity was employed to estimate the dead volumes and adsorbent pores.

Treatment of MWCNTs

Purification and treatment of the as-prepared MWCNTs performed by three following steps in this work:

1- Raw MWCNTs sample were soaked in 33 wt % HCl solution for 24 hours, then they were washed several times with distilled water. This stage was used to remove the amount of catalyst in MWCNTs.

2- At the second stage, reflux in 6M HNO₃ solution was employed to MWCNTs for three hours, and then MWCNTs were washed several times with distilled water and filtered. Finally, the samples were dried in an oven at 100 °C for 24 hours. The aim of this step was removing the remained catalyst as well as oxidation of the amorphous carbon content.

3- At the final stage of treatment, oxidation was carried out in a furnace with hot air at 420 °C for 20 minutes. This step was used to remove the residual coke and amorphous carbon and to open the end of the tubes. The prepared material was attributed as T-MWCNTs.

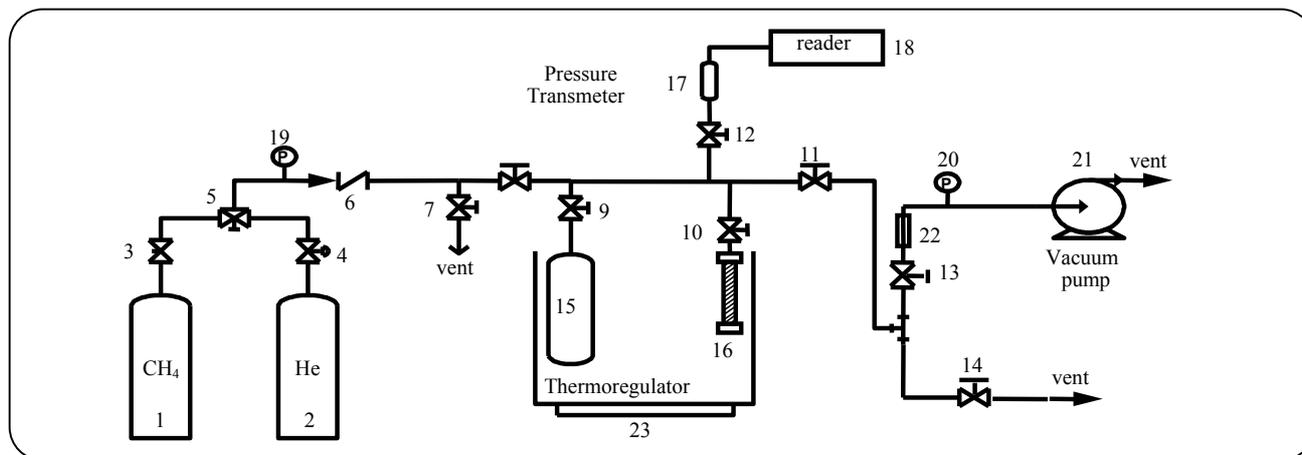


Fig. 1: Experimental apparatus (3,4) regulators, 5 tree-wave valve, (19,20) pressure gauges, 6 check valve, (7-14) valves, 15 reference vessel, 16 adsorption vessel, 17 pressure transducer, 18 reader, 21 vacuum pump, 22 filter.

Apparatus and procedures

The schematic apparatus presented in Fig.1 was set up to measure volumetrically adsorbed methane at temperatures of 260-350 K under the pressures of 0.1-10 MPa. During the experiments, the reference and the adsorption vessels were kept in a constant temperature by a circulation bath (LCP-R133, LapTech) with a fluctuation of ± 0.3 K. A pressure transducer (ECO-1, WIKA) with an accuracy of 0.1 % was used to monitor the pressure. Degassing of the adsorbents was performed under vacuum and high temperature (423 K for 4 hr) with a high temperature circulation bath (Tu-20D, Techne) before each experiment.

About 5.2 grams of MWCNTs were used as the sample in each experiment. Before entering methane into the adsorption vessel, the pressure of reference vessel was set at the required initial level for each adsorption measurement. After starting the experiments, the 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:

$$\left(\frac{PV}{ZRT}\right)_r + \left(\frac{PV}{ZRT}\right)_a = \left(\frac{PV}{ZRT}\right)_{eq} + N \quad (1)$$

Where P is pressure, T is temperature, V is volume, R is gas constant, Z is the compressibility factor and N is the amount of adsorbed material, r, a and eq represent, the reference vessel and its connections; adsorption vessel

and the final equilibrium state, respectively. The amount of methane adsorbed per mass of adsorbent was obtained by Eq. (2):

$$m = \frac{NM}{\text{adsorbent mass}} \quad (2)$$

Here M is the molecular weight of methane.

RESULTS AND DISCUSSION

T-MWCNTs properties

The surface area, packing density and purity of the raw and T-MWCNTs are presented comparatively in table 1. The other properties of T-MWCNTs such as TEM image, Raman spectroscopy and TGA are shown in Figs. 2 to 4. Table 1 presents an improvement of surface area, packing density and purity of the MWCNTs after acid washing and hot air treatment. TEM image of T-MWCNTs in Fig. 2 shows the CNTs with lower diameter than 10 nm (around 5 nm).

In Fig. 3, Raman spectra of T-MWCNTs reveals the split tangential modes (G-line) at 1500-1600 cm^{-1} which indicates the presence of MWCNT in the sample. The band corresponding to disordered carbon (D-band) around 1350 cm^{-1} is appeared at a low intensity, that indicates low amount of defect carbon structures ($I_G/I_D = 3.5$). The result of TGA in Fig. 4 shows that combustion of T-MWCNTs is occurred in the range of 400-500 $^{\circ}\text{C}$. According to TGA, the weight amorphous carbon is obtained 0.85 wt % and the inorganic impurity of 9.74 wt % is observed in the treated product.



Fig. 2: TEM image of T-MWCNT.

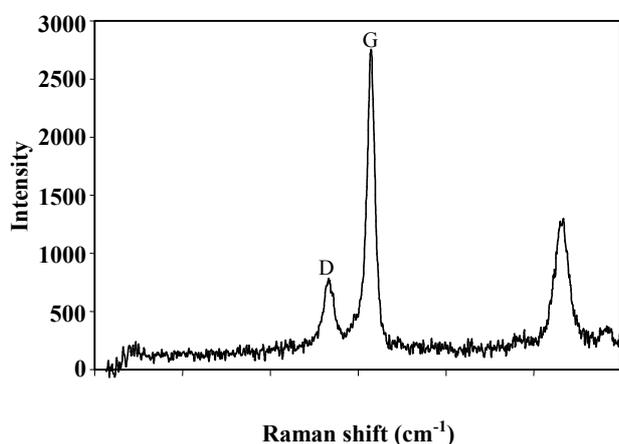


Fig. 3: Raman spectra of the T-MWCNT.

The equilibrium data of methane adsorption on the raw MWCNTs and T-MWCNTs are measured at 298 K and pressures up to 7 MPa and presented in Fig. 5, comparatively. The experiments were replicated again at normal temperature to find out the reproducibility of the experiments and a good degree of accuracy was observed in the total range of the pressure studied.

The results revealed enhancement of methane adsorption capacity after treatment operations. The results show higher improved methane adsorption at lower pressures (<4 MPa). As the working pressure of methane storage in ANG technology is usually around 3 to 4 MPa, we conclude that purification and treatment of the MWCNTs should be necessary for these processes [1]. Actually, acid washing removes inorganic compounds and amorphous carbons in which presence of both materials reduce adsorption capacity. Also, oxidation

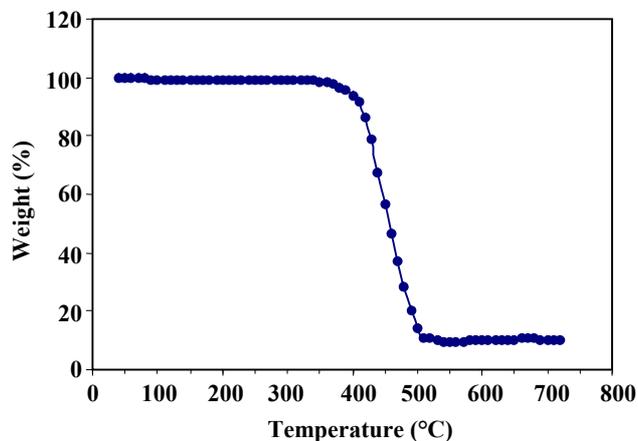


Fig. 4: TGA diagram of T-MWCNT.

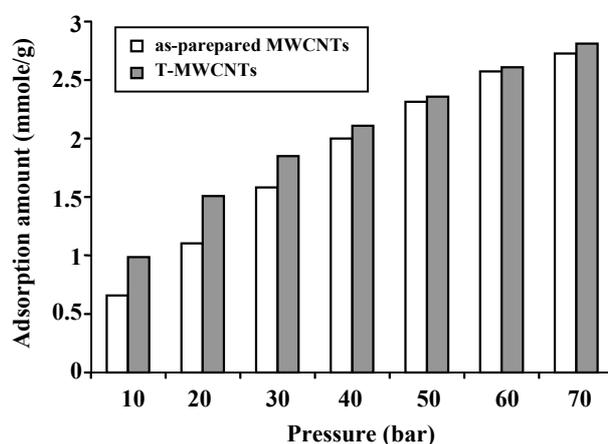


Fig. 5: Experimental isotherms of methane adsorption on as-prepared and T-MWCNTs.

process could lead to opening the end of closed tubes therefore increasing the adsorption sites [3].

Gas delivery is the other important function in ANG technology that should be investigated during the bed pressure reduction. In the range of studied temperatures and pressures, no hysteresis effect was observed. It is concluded that capillary condensation was not occurred inside the adsorbent pores. The total gas delivery of the MWCNTs was determined at constant temperature of 298 K by reducing the system pressure from 7 to 0.1 MPa and it showed 82 % desorption of methane from T-MWCNTs. It seems that 18 % of methane was adsorbed irreversibly on the active sites.

The effect of temperature on the adsorption capacity was studied on T-MWCNTs in the following part and the experimental isotherms are presented in Fig. 6. The maximum amount of adsorbed methane at 298 and 263 K

were obtained 2.81 and 3.99 mmol/g, respectively. As shown in Fig. 6, the amount of adsorbed methane increases with an increase in the pressure of the system. In fact, increasing the pressure increases the van der Waals attraction forces between the gas and adsorbent molecules also, it can be seen that decreasing the temperature increases heat removal from the system and enhances the storage capacity.

The isosteric heat of adsorption can be obtained by the Clausius-Clapeyron equation:

$$Q_{st} = -R \left[\frac{\partial \ln P}{\partial (1/T)} \right]_{C_u} \quad (3)$$

Where P is the pressure, T is the temperature R is the gas constant and Q_{st} is the isosteric heat of adsorption. The logarithmic form of the equilibrium pressures was plotted against the reciprocal temperature at the constant coverage in T-MWCNTs in Fig. 7 for five different adsorbed capacities. The slopes of these lines (A) were calculated as the isosteric heat of adsorption:

$$Q_{st} = -R(A) \quad (4)$$

The isosteric heat of adsorption (IHOA) values are exposed in Fig. 8 versus surface loadings. As can be seen, IHOA rises from -8.4 kJmol^{-1} to -14.8 kJmol^{-1} by increasing the loading then reduces to -12.6 kJmol^{-1} . This observation is due to the increased interaction between adsorbed molecules as the loading increases (8.4 to 14.8 kJmol^{-1}). With increasing the surface coverage, repulsive forces between molecules dominate on the attractive forces and IHOA reduces from 14.8 to 12.6. Such a decrease does not necessarily mean that the interaction among adsorbed molecules is repulsive, and it could also show the heterogeneity of the surface which is composed of sites having different energy of adsorption [11].

Lee *et al.* declared similar consequence. Their experimental results showed that the MWCNTs adsorbents had an energetically heterogeneous surface because of IHOA variations from -40 to -50, then decreasing to -15 kJmol^{-1} , against increasing the loading [5].

Adsorption isotherms

Different isotherm models were correlated on the experimental results of methane adsorption on T-MWCNTs. The proposed isotherm models are represented in Appendix 1.

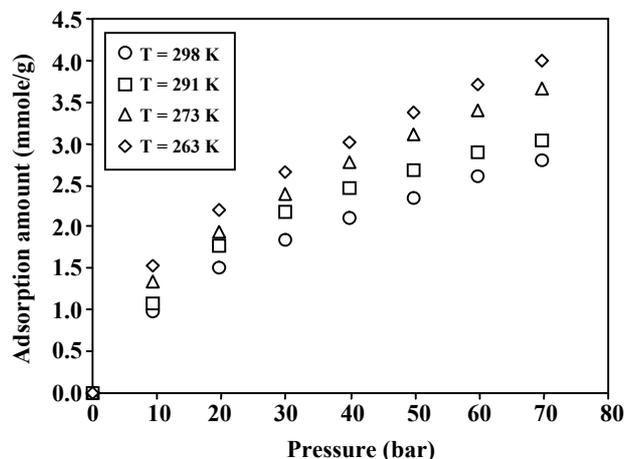


Fig. 6: Experimental isotherms of methane adsorption on T-MWCNT.

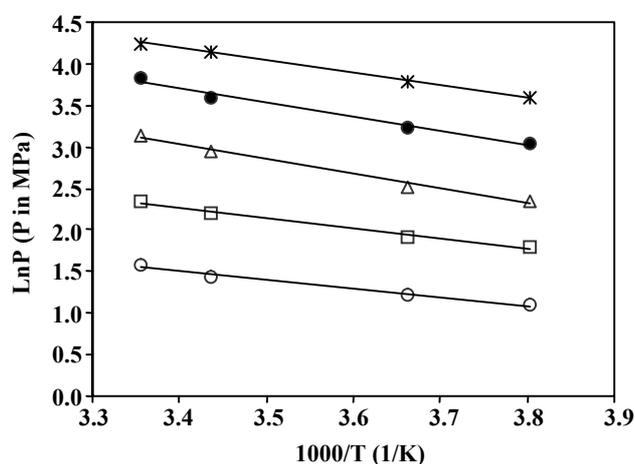


Fig. 7: Isotheres of methane on the T-MWCNTs sample at constant coverages: (○) 0.01; (□) 0.02; (Δ) 0.03, (●) 0.04, (*) 0.05.

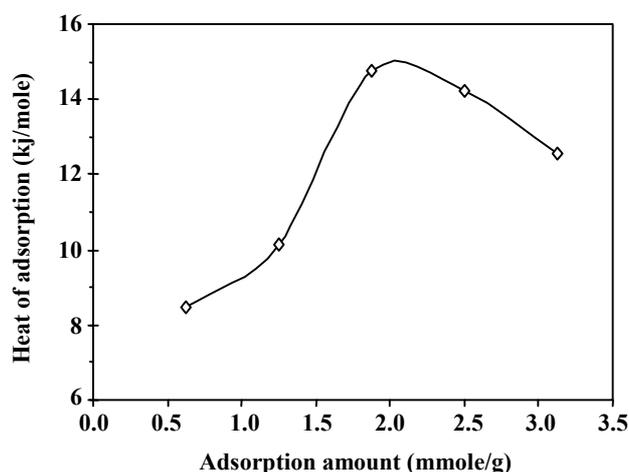


Fig. 8. Isosteric heat of adsorption as a function of adsorption amount.

Table 2: The calculated isotherms parameters at each temperature.

Temperature	Isotherms	Isotherms parameters					
		$^*C_{\mu_s}$	*b	n	t	s	*E
298 K	Langmuir	4.00	0.0324	—	—	—	—
	Volmer	9.74	0.0096	—	—	—	—
	Sips	13.28	0.0017	1.6462	—	—	—
	Toth	76.95	0.0237	—	0.1959	—	—
	Unilan	11.96	0.0017	—	—	3.8644	—
	DR	3.91	—	—	—	—	6832.2
	DA	6.43	—	0.9980	—	—	4746.8
291 K	Langmuir	4.27	0.0325	—	—	—	—
	Volmer	10.10	0.0101	—	—	—	—
	Sips	13.39	0.0019	1.6584	—	—	—
	Toth	80.39	0.0290	—	0.1923	—	—
	Unilan	11.97	0.0018	—	—	3.9573	—
	DR	3.96	—	—	—	—	6832.2
	DA	6.44	—	0.9980	—	—	4746.8
273 K	Langmuir	5.06	0.0329	—	—	—	—
	Volmer	11.08	0.0116	—	—	—	—
	Sips	13.68	0.0025	1.6938	—	—	—
	Toth	89.95	0.0511	—	0.1820	—	—
	Unilan	12	0.0024	—	—	4.2182	—
	DR	4.09	—	—	—	—	6832.2
	DA	6.47	—	0.9980	—	—	4746.8
263 K	Langmuir	5.56	0.0331	—	—	—	—
	Volmer	11.66	0.0125	—	—	—	—
	Sips	13.84	0.0030	1.7163	—	—	—
	Toth	95.75	0.0723	—	0.1757	—	—
	Unilan	12.01	0.0028	—	—	4.378	—
	DR	4.16	—	—	—	—	6832.2
	DA	6.49	—	0.9980	—	—	4746.8

*) C_{μ_s} : mmole.g⁻¹, b: bar⁻¹, E: J.mole⁻¹

Table 3: The AARD of the different models against experiments.

Isotherms	Langmuir	Volmer	Sips	Toth	Unilan	DR	DA
AARD %	3.91	7.26	2.08	1.94	3.67	5.26	2.31

Appendix 1: Adsorption isotherm models and their parameters.

Model	Equation	Fitting parameters
Langmuir	$C_{\mu} = C_{\mu s} \frac{bp}{1 + bp}$	$C_{\mu s}, b$
Volmer	$bP = \frac{C_{\mu}}{C_{\mu s} - C_{\mu}} \exp\left(\frac{C_{\mu}}{C_{\mu s} - C_{\mu}}\right)$	$C_{\mu s}, b$
Sips	$C_{\mu} = C_{\mu s} \frac{(bp)^{1/n}}{1 + (bp)^{1/n}}$	$C_{\mu s}, b, n$
Toth	$C_{\mu} = C_{\mu s} \frac{bp}{\left(1 + (bp)^t\right)^{1/t}}$	$C_{\mu s}, b, t$
Unilan	$C_{\mu} = \frac{C_{\mu s}}{2s} \operatorname{Ln}\left(\frac{1 + be^s P}{1 + be^{-s} P}\right)$	$C_{\mu s}, b, s$
Dubinin – Radushkevich (DR)	$C_{\mu} = C_{\mu s} e^{-\left(\frac{RT \ln(P_0/P)}{E}\right)^2}$	$C_{\mu s}, E$
Dubinin – Astokhov (DA)	$C_{\mu} = C_{\mu s} e^{-\left(\frac{RT \ln(P_0/P)}{E}\right)^n}$	$C_{\mu s}, E, n$

C_{μ} is the adsorbed amount, P is the equilibrium pressure; T is temperature; R is gas constant; P_0 is the vapor pressure; $C_{\mu s}$ is the maximum adsorbed amount; b is the affinity parameter which is a measure of how strong an adsorbate molecule is attracted onto a surface; n, t and s are the heterogeneity parameters and E in DR and DA models is the characteristic energy which is a measure of the strength of interaction between adsorbent and the volume of adsorbate residing within the micropores.

The fitted parameters are assumed as a function of temperature and dependent equations of the fitted parameters were estimated by the proposed equations in Appendix 2. The unknown parameters were determined by the direct search method of Nelder-Mead simplex method. The absolute average relative deviations (AARD) of experimental and fitted results are calculated by equation (5):

$$\text{AARD} = \frac{1}{28} \sum_{i=1}^{28} \frac{|C_{\mu_i}^{\text{experiment}} - C_{\mu_i}^{\text{model}}|}{C_{\mu_i}^{\text{experiment}}} \quad (5)$$

AARD is calculated for 28 experimental points refer to four temperatures and seven pressure steps in adsorption experiments.

Table 2 presents the value of the fitting parameters obtained from correlation of several adsorption isotherms on the experimental data at four temperatures. As it is observed, decreasing the temperature increases the maximum adsorbed amount ($C_{\mu s}$) in all isotherms. In other words, increasing temperature will decrease the amount adsorbed at a given pressure. Also, it can be seen that affinity parameter (b) increases with a decrease in

temperature. In fact at lower temperatures, the surface is covered more by the molecules which lead to the stronger affinity of adsorbate molecules towards the surface.

The calculated heterogeneity parameters for Sips, Toth, Unilan and DA isotherms (n) deviate from the related value for homogeneous systems [11]: $n_{\text{Sips}}=1$, $t=1$, $s=0$ and $n_{\text{DA}}=3$. This deviation suggests some degree of heterogeneity of the methane/MWCNT system.

The AARD of each model is summarized in table 3. According to this table, Sips and Toth isotherms are introduced as the best fitted model, although the adsorbed capacity of Toth isotherm ($C_{\mu s}$) usually grows up from the other models because parameter t is less than one.[11]. Sips isotherm is presented in Fig. 9. for different temperatures.

CONCLUSIONS

In this research the small diameter MWCNTs were studied for methane storage application. Chemical and thermal treatment of MWCNTs caused enhancement of methane adsorption by 36.6 %, at 2 MPa and 298 K. The adsorption isotherms were measured and modeled on T-MWCNTs at temperatures of 298 K, 291 K,

Appendix 2: Temperature dependence of fitting parameters.

Model	Temperature dependent equations
Langmuir, Volmer, DR and DA	$C_{\mu s} = C_{\mu s0} \exp[-\delta(T - T_0)]$
Sips and Toth	$C_{\mu s} = C_{\mu s0} \exp\left[\chi\left(1 - \frac{T}{T_0}\right)\right]$
Langmuir and Volmer	$b = b_{\infty} e^{(Q/RT)}$
Sips and Toth	$b = b_0 \exp\left[\frac{Q}{RT_0}\left(\frac{T_0}{T} - 1\right)\right]$
Unilan	$b = b_0 \exp\left[-\frac{\bar{E}}{RT_0}\left(1 - \frac{T_0}{T}\right)\right]$ and $\bar{E} = \frac{E_{\max} + E_{\min}}{2}$
Sips	$\frac{1}{n} = \frac{1}{n_0} + \alpha\left(1 - \frac{T_0}{T}\right)$
Toth	$t = t_0 + \alpha\left(1 - \frac{T_0}{T}\right)$
Unilan	$s = \frac{E_{\max} + E_{\min}}{2RT}$

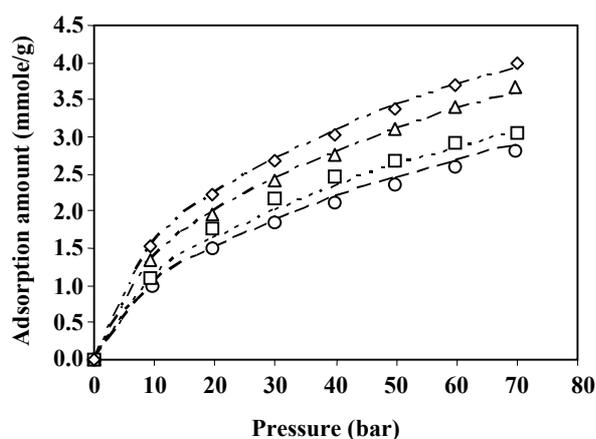


Fig. 9: Experimental data: (○) 298 K; (□) 291 K; (Δ) 273 K; (◇) 263 K. isotherms from Sips model: (---) 298 K; (···) 291 K; (- · - ·) 273 K; (- - - -) 263 K.

273 K, 263 K and pressures from normal to 7 MPa. Several empirical isotherm models were correlated on the experimental data to predict the parameters and follow the mechanism of adsorption. Sips model was concluded as the best correlated model with lower AARD among the other isotherms. Attending to this model, mechanism of methane adsorption on MWCNTs would be a surface

coverage with a heterogeneous behavior of methane/T-MWCNTs system referring to deviation of heterogeneity parameter n from unit value. In addition, variation of IHOA along with loading amount revealed the heterogeneity of the adsorption surfaces.

The presented isotherm model could be used as a base for design and scale up in the adsorbed-methane process for these new porous materials. Other improvement procedures such as cutting and functionalizing the MWCNTs with additional modifications would be the future work of this study to approach to the target value of methane storage as a suitable container at medium pressures and normal temperature.

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