THE EFFECT OF CHEMICAL TREATMENT ON ADSORPTION OF NATURAL GAS BY MULTI-WALLED CARBON NANOTUBES: SORPTION EQUILIBRIA AND THERMODYNAMIC STUDIES

In this study, adsorption of methane as the main constituent of natural gas was studied on pristine multi-walled carbon nanotubes (MWCNTs), after which purification and different chemical treatments of MWCNTs were performed to enhance the natural gas adsorption capacity. The results revealed that chemical treatment of the MWCNTs in the presence of H₂SO₄/HNO₃ acidic mixture in 3:1 volume ratio enhanced considerably the adsorption capacity of natural gas (an optimal up to 45 mmol/g) at a temperature of 298.15 K and pressure of 50 bar, compared to the pristine MWCNTs (about 27 mmol/g) at the same operating conditions. This effect can be attributed to the opening of the nanotubes caps with a major alteration in their structural properties due to chemical treatment. The experimental data of adsorption were almost equally well described by Langmuir, Freundlich and Sips Equations to determine the model isotherms. The best fit was obtained by the Sips model isotherm with the r-squared value near to unity. Furthermore, using the experimental data obtained in different temperatures the isosteric heat of natural gas adsorption onto pristine MWCNTs was also calculated in the interested range of pressures and temperatures using the thermodynamic-based Clausius-Clapeyron Equation from the Sips Isotherm model. The results revealed an energetically heterogeneous surface of MWCNTs in natural gas adsorption. Also the natural gas adsorption process was kinetically studied through pseudo-second order and intra-particle diffusion models, which indicated the intra-particular diffusion is the rate limiting step in adsorption of methane on MWCNTs.

Keywords: carbon nanotube, methane, adsorption, chemical treatment, kinetic, isosteric heat of adsorption.

In recent years, a series of attempts was made to develop new fuel technologies to meet the energy requirement for transportation and reduce dependence on petroleum products such as diesel and gasoline. Among the possible fuels, natural gas (NG) (mainly consisting of methane) was one of the best candidates due to its clean properties, cheap price as well as its vast proved reservoirs in the world [1]. New development is necessary to make NG as a fuel competitive with the other types of conventional fuels in the market. For this purpose, an adequate amount of natural gas must be stored in the on-board fuel tank. There are several ways for storing natural gas in on-board tanks such as compression, liquefaction and storage in porous media. Compressed natural gas (CNG) is an alternative solution, but high pressures (20-30 MPa) are needed to store considerable amount of gas into tanks which makes the operation costly due to high energy and heavy steel cylinders requirement. NG also cannot be liquefied only by implementation of pressure at room temperature due to the low critical temperature. Therefore, costly cryogenic systems are required for liquefaction at -160 °C. Compared to CNG and LNG (liquefied natural gas), adsor-
bed natural gas (ANG) represents a promising and efficient technique for storing NG in porous media [2]. For ANG, lower pressures are required for storing natural gas compared to CNG, namely only 4 MPa, in lightweight containers. Therefore, adsorbed natural gas offers an obviously lower cost of storage. Many types of porous media have been developed such as molecular sieves, zeolite, activated carbon, etc., to adsorb gases [3,4]. Activated carbons with diversified microporous structures constitute an important category of potential adsorbents for natural gas storage. Arami-Niya et al. [5] used granular activated carbon prepared by impregnation of oil palm shell by ZnCl$_2$. Their results showed maximum methane adsorption of 12 cm$^3$ STP/g (0.5 mmol/g) at a pressure of 800 mmHg, which increased by 100% under further physical activation with CO$_2$. However, their results have been obtained at relatively low pressures near to atmospheric pressure and cannot be compared with results of the present study. Monge et al. [6] investigated the adsorption of methane on a series of microporous activated carbon (AC), activated carbon fibers (ACF) and superactivated carbon (SAC) at 298 K and 4 MPa (40 bar). They have reported maximum storage capacity of 13 mmol/g with SAC due to its higher micropore volume. Adsorption of methane on porous metal carboxylates was compared with other adsorbents such as activated carbon and zeolite [7]. The results of this study reveal that the metal carboxylates demonstrated one of the highest adsorption capacities for methane with a maximum of 282 cm$^3$ STP/g (12.6 mmol/g) at 50 bar and 298 K. The authors have suggested that porous adsorbents for methane adsorption should have high porosities rather than high specific adsorption sites or structures. Adsorption of methane on corn cobs based activated carbons with different BET surface areas at various pressures was studied in a volumetric adsorption apparatus [8]. The highest methane storage capacity was found to be 0.27 g/g (17 mmol/g) at 298 K and 500 psi (35 bar). Natural gas storage capacity and the effect of its composition on the amount of adsorption by activated carbon were evaluated by measuring isotherms in a magnetic suspension microbalance [9]. The highest adsorption capacity of methane reported in this study was around 6 mmol/g at 35 bar and 298 K. However, the authors emphasized on preferential adsorption of heavier hydrocarbons and CO$_2$, which should be taken into account for the evaluation of adsorption behavior.

Recently, carbon nanotubes (CNTs) have been posed as potential materials in different fields due to their exceptional properties [10-17]. They were particularly implemented as porous media, because of their unique features in terms of highly uniform pore size, high surface areas and attractive surface potentials that renders them as promising materials for gas adsorption processes. With respect to these interesting properties of CNTs, representation of appropriate gas storage properties by ANG method is an interesting projected area. At present, investigations around gas storage on CNTs mainly focus on hydrogen storage. Little attention has been paid to other gases, such as methane and oxygen, that majority of these attempts were concentrated on the SWCNTs as adsorbent [18-21]. There are limited researches regarding methane adsorption on MWCNTs with undesired results and deserves further investigations [22]. Thus, investigation of natural gas storage on MWCNTs and promotion of its adsorption properties by different treatment techniques is an interesting research work topic.

For some potential applications (gas adsorption in this work), it is necessary to treat CNTs under a coarse treatment method to obtain highly purified materials. From the literature reviews, it can be found that a number of studies have been concentrated on purification techniques and improving the structural and surface properties of CNTs by chemical and physical treatments [23-30]. Yulong et al. [22] found that treatments can affect pore structure and surface properties significantly. Datsyuk et al. [28] applied four different agents for purification and chemical oxidation of MWCNTs and found that increasing acidic strength increases the morphology variations in MWCNTs and alkaline treatment has no remarkable effect on its structural properties. Chiang et al. [23] investigated the variation in the structure of MWCNTs subjected to different degrees of oxidation and claimed that by means of this process the tubes became thinner and shorter. In the other research, CNT purification by microwave assisted acid digestion was investigated [24]. The main idea in most of the research studies has been to find the effect of key variables such as acid type and concentration, temperature, duration and pressure and finally determining the optimum conditions through correct experimental procedures [31-33]. As mentioned above, although different methods were performed for purification and treatment of CNTs, but except for a few of them [22], correlation of treatments effects on gas, especially natural gas, adsorption capacity was not investigated. Thus, further work is required to make CNTs a practical natural gas storage medium.

The primary aim of this study was to investigate the influence of different chemical treatments of MWCNTs for applying in natural gas adsorption by experimental methods and comparing it to pristine...
MWCNTs adsorption capacity results. The modeling of equilibrium adsorption isotherm as well as the adsorption kinetics of CNTs materials was performed. The isosteric heats of adsorption on MWCNTs were evaluated and compared.

EXPERIMENTAL

Materials and methods

MWCNTs synthesized by CVD method with purity greater than 95%, outer diameter ranging between 15-20 nm, about 4 nm in inner diameter and about 30 μm in length were purchased from Alpha Nanotechnologies Company, Ltd. (China) and employed in this study. The measured apparent density was only 0.066 g/cm³ (very light). Figure 1 shows the TEM images of this kind of MWCNTs. Methane with purity of 99.99% was purchased from Technical Gas Services, UAE.

Before the chemical treatments, the nanotubes were sonicated in a proportion of 50 mg MWCNTs in 500 mL ethanol for 40 min to eliminate the amorphous phase. Then, resulting solution were filtered and dried for 2 hours in a vacuum oven at 90 °C.

In this study, purification and chemical treatments of MWCNTs was carried out with three different methods; alkaline treatment (sample 1) in presence of 2 M sodium hydroxide solution; acidic treatment in the presence of nitric acid (sample 2); acidic treatment in the presence of sulfuric acid/nitric acid mixture in 3:1 volume ratio (sample 3).

In the first method (sample 1), prepared MWCNTs were doused in 2 M sodium hydroxide and sonicated in water bath for 4 h at a temperature of 30 °C. Finally, the sample was sufficiently washed with deionized water until pH of filtered water reached 7, then dried at 100 °C for 8 h in vacuum oven. In the second method (sample 2), prepared MWCNTs were doused in 200 ml concentrated nitric acid 63% for 2 h under sonication at the temperature of 30 °C. The black concentrated solution was then refluxed for 4 h at a temperature of 90 °C. The resulting solution was adequately filtered and washed with deionized water until pH of filtered water reached 7, then dried at 100 °C for 8 h in a vacuum oven. In the third method (sample 3), prepared MWCNTs were doused in 200 ml of concentrated mixture of sulfuric acid/nitric acid (98 and 63%, respectively) in 3:1 volume ratio for 2 h under sonication at a temperature of 30 °C. Then the acidic concentrated solution was refluxed for 4 h at a temperature of 90 °C. After that, acidic solution was frequently filtered and washed with deionized water until pH of filtered water reached neutral condition, then dried at 100 °C for 8 h in vacuum oven. After drying, all three prepared samples were taken out of filters and applied as adsorbents in methane adsorption experiments.

The most important properties of any adsorbent associated with adsorption applications are surface characteristic and pore structures. Surface characteristics of the original untreated MWCNTs as well as chemically treated MWCNTs samples used as adsorbents were determined with BET analysis and microscopic observations. The BET analysis was carried out based on the adsorption isotherm of N2 at 77 K measurement (Micromeritics ASAP 2010). Microscopic observation of the samples was conducted using SEM (Tescan Vega). The Transmission electron microscopy image was taken by TEM System, model 2085. The main goal in the experimental adsorption studies was to determine the amount of methane equilibrium uptake on the adsorbents at various pressures and temperatures and compare the obtained results for untreated and treated MWCNTs employed as adsorbents.

Adsorption apparatus

Adsorption experiments were conducted in agreement with the volumetric (pressure decay) method, the pressure drop due to adsorption was measured in a closed system. A dual sorption vessel apparatus was fabricated and used in this study for the assessment of methane storage by MWCNTs. The experimental set up is shown in Figure 2.

The gas was introduced from the gas cylinder into the pressure cell using valve 1. The temperature of pressure cell was monitored by a temperature probe located in the pressure cell. The pressure in pressure cell was measured by a pressure transducer.
with the precision of 0.01 bar located in the pressure cell. The gas was then spread in the adsorption cell loaded with 15 g adsorbent through valve 3 and valve 5. The volumes of both the pressure cell and the adsorption cell were 325 cm$^3$. The pressure of the adsorption cell was read using the pressure transducer located in the adsorption cell with the same precision. The temperature of the adsorption cell was measured by a temperature probe located in the adsorption cell. The installation temperature was controlled by a water bath. Before each experimental run, the whole system was vacuumed by a vacuum pump (supplied by Edward Company, UK, model E2M2) to near full vacuum (less that 0.1 mbar) to remove any adsorbed gases. The pressure and temperature of each cell were continuously recorded and transmitted to a computer. The maximum allowable operating pressure was 50 bar and the allowable operating temperature range was 283-343 K. The air tightness of pressure vessel was guaranteed using a special air tight O-ring. Since the volumetric method is sensitive to gas leakage, before each experiment the cells were tested against any probable leakage by taking it under high pressure with pressurized air. Hence, any contribution of leakage to pressure drop due to adsorption can be ruled out.

Due to the methane adsorption, the cell pressure reduced until the equilibrium conditions was reached. The amount of adsorbed gas was calculated using material balance and a suitable equation of state (SRK in this study) at equilibrium condition. The material balance equation for calculation of adsorbed amount is shown below:

$$\left( \frac{PV}{zRT} \right)_{A_1} + \left( \frac{PV}{zRT} \right)_{A_2} = \left( \frac{PV}{zRT} \right)_{A_3} + nM$$

where $P$ is pressure, $T$ is temperature, $V$ is volume, $R$ is the gas constant, $M$ is adsorbent mass, $z$ is the gas compressibility factor (obtained from SRK state equation) and $n$ is the adsorbed amount (the subscript $I$ refers to the initial state and $2$ represents the final equilibrium state).

**THEORY**

**Adsorption isotherm models**

Experimental data of methane adsorption on CNTs material can be simulated by several isotherm models such as Langmuir, Freundlich and Sips. Such isotherm models are semi-empirical equations that are used to describe the physical adsorption of gases on porous solids [28]. Applicability of the mentioned adsorption model isotherms for description of gas adsorption on single wall carbon nanotubes (SWCNTs) has been reported in the literature [34]. Application of the Langmuir isotherm model has been extensively referenced in adsorption literature [35-37]. In addition, the Sips adsorption isotherm model was applied for simulation of experimental adsorption data in some works [38]. This model offers several advantages such as ability to fit experimental isotherms, mathematical simplicity and easy extension to multicomponent adsorption. These reasons justify the frequent applications of the Sips model in modeling and design of adsorbents [34]. Equations (2)-(4) represent Langmuir, Freundlich and Sips Equations, respectively.

$$q = \frac{q_m bP}{1+bP}$$  \hspace{1cm} (2)

$$q = kp^{1/n}$$  \hspace{1cm} (3)

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

where $q_m$ (mmol/g) is the maximum amount adsorbed on a monolayer of adsorbents, $b = K_a/K_b$, $K_a$ and $K_b$ are adsorption and desorption constants, respectively. The coefficients $k$ and $n$ are constants that are generally temperature dependent and $n$ describes the adsorbate/adsorbent interaction.

**Isosteric heat of adsorption**

For proper design and operation of any gas-phase adsorption process, it is necessary to have some information about adsorption capacity as well as heat of adsorption. An evaluation of the possible interaction between adsorbent lattice atoms and adsorbate molecules is provided by the isosteric heat of adsorption which is usually determined from the temperature dependence of the adsorption isotherms [40-
Therefore, for accurate design and optimal operation of gas-phase adsorption processes, it is essential to use a well-defined correlation that captures correctly the temperature dependence of parameters over a wide range pressure [43-45]. For any specific isotherm model, the isosteric heat of adsorption, $Q_{st}$ is estimated using the Clausius-Clapeyron Equation as follows [46]:

$$Q_{st} = RT^2 \left( \frac{\partial \ln P}{\partial T} \right)_q$$

(5)

Herein, the isosteric heat of adsorption is calculated by the Sips isotherm model (Eq. (4)). The $b$ and $n$ parameters in the Sips Equation (Eq. (4)) can be written as:

$$b = b_0 \exp \left[ \frac{Q}{RT_0} \left( \frac{T_0}{T} - 1 \right) \right], \quad \frac{1}{n} = \frac{1}{n_0} + \alpha \left( 1 - \frac{T_0}{T} \right)$$

(6)

where $\gamma = Q/RT_0$ is the heat coefficient, $n_0$ and $\alpha$ are the model parameters, and $Q$ (KJ/mol) is the isosteric heat of adsorption at half loading. The $n$ temperature dependency was incorporated into Sips isotherm model. To evaluate isosteric heat of adsorption, the Sips isotherm model was used in this study. Applying Eq. (5) to the Sips isotherm model, with the parameters defined by Eq. (6), gives:

$$Q_{st} = Q - \alpha nRT_0 \ln\left( bP \right)$$

(7)

The derivation of Eq. (7) is given in Appendix 1.

### Adsorption kinetic study

An adsorption kinetic study is essential for control of the process efficiency. In this study, the kinetic data of adsorption was analyzed by different kinetic models. Here, two models, namely a pseudo-second order model and an intra-particle diffusion model were used for this purpose.

#### Pseudo-second order kinetic model

The pseudo-second order model is described as follow [47]:

$$t = \frac{1}{k_2 q_e^2} + \frac{q_e}{q_i} \frac{t}{q_e}$$

(8)

where, $q_i$ (mmol/g) is the amount of gas adsorbed on MWCNTs at time $t$ (min), $q_e$ is the amount of gas adsorbed on MWCNTs at equilibrium time (mmol/g), $k_2$ is the second order rate constant of sorption (g mmol⁻¹ min⁻¹). If second-order kinetics prevails, then the plot of $t/q$ versus time gives a straight line from which $q_e$ and $k_2$ can be determined from the slope and intercept of the plot, respectively.

### Intra-particle diffusion model

In general, adsorption of a gaseous adsorbate on porous adsorbents may consist of several steps including the transport of the adsorbate in bulk phase as well as solid phase (by either pore diffusion and/or surface diffusion). The overall rate of adsorption is controlled by the slowest transport step [48]. Intraparticle diffusion model is characterized by the relationship between specific adsorption and the square root of time, according to the following equation [49]:

$$k_t = q_e l^0.5$$

(9)

If the plot of $q_i$ versus $t^{0.5}$ exhibits multi-linear plots, then two or more steps influence the adsorption process. Similar studies were done for different adsorbents by different researchers [50-54]. Adsorption kinetic data obtained in this study was further used to estimate possible mechanism of methane adsorption on MWCNTs whether the intra-particle diffusion is the rate limiting step and also to find the diffusion rate constant, $k_i$ (mmol g⁻¹ min⁻⁰.⁵).

### RESULTS AND DISCUSSION

#### Experimental adsorption data and isotherm model

Figure 3 shows the variation of methane equilibrium uptake by original (untreated) MWCNTs versus pressure at different temperatures. As it is clear from the presented data in Figure 3, excellent results of methane adsorption capacity are obtained from the unique surface properties of this kind of MWCNTs such as highly uniform pore size and high pore volume. Since the average size of methane molecules are 0.388 nm, they can be easily loaded within this kind of MWCNTs with uniform pore size of about 4 nm.

![Figure 3. Methane adsorption isotherms on pristine MWCNTs at different temperatures.](image-url)
In general, the amount of uptake increased with an increase in the pressure and decreased with an increase in temperature. It is obvious that adsorption of methane on MWCNTs seems to continue beyond this pressure. It can be concluded that MWCNTs can be a favorable adsorbent for methane storage compared to other adsorbents, if it is manufactured and purified with a good pore size, high pore volume and proper surface properties.

For the pristine and treated MWCNTs, the measured specific surface area (SSA), mean pore diameter and total pore volume were listed in Table 1. Figure 4 shows the scanning electron microscopy images of pristine and chemically treated MWCNTs. Improvement in above characteristics is obvious from the values of Table 1 for all treated samples compared to the pristine one. SEM and BET analysis have clearly shown that acidic treatment under reflux condition has a greater effect compared to alkaline treatment. It causes breakdown in nanotube structure (reducing its length) and creating more defects in its network. Alkaline treatment although caused removal of all impurities including amorphous carbon, but the treatment had no actual effect on MWCNTs structure. Indeed, NaOH is a good dispersing agent; it prevents the agglomeration of nanotubes. As it is obvious from SEM image in Figure 4B, most of MWCNTs particles are segregated from each other compared to pristine one. Removal of impurities by alkaline and then acidic treatment causes formation of cavities and defects in MWCNs structure, therefore increases the surface area by opening of closed ends, as it can be observed in Figure 4C. Results have also indicated that the best improvement was achieved by chemical treat-

<table>
<thead>
<tr>
<th>Property</th>
<th>Pristine</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area m²/g</td>
<td>293.86</td>
<td>317.34</td>
<td>346.69</td>
<td>394.08</td>
</tr>
<tr>
<td>Mean pore diameter, nm</td>
<td>4.6788</td>
<td>4.058</td>
<td>3.685</td>
<td>2.945</td>
</tr>
<tr>
<td>Total pore volume, cm³/g</td>
<td>0.6231</td>
<td>0.6401</td>
<td>0.6921</td>
<td>0.7861</td>
</tr>
</tbody>
</table>

Figure 4. Scanning electron microscopy (SEM) images of MWCNTs: A) pristine, B) sample 1, C) sample 2 and D) Sample 3.
ment of MWCNTs with a mixture of H$_2$SO$_4$/HNO$_3$ in 3:1 volume ratio. The shortening of MWCNTs length can be clearly seen in Figure 4D. Similar deductions have been made using SEM images by the other researchers [55].

In general, acidic treatment could alter the lattice structure of MWCNTs more effectively compared to the other methods. As the values of Table 1 show, chemical treatment in acidic environment led to remarkable increase in the specific area and decrease in mean pore diameters. The major change achieved in the material’s structure promoted considerably its capacity for methane storage compared to original untreated nanotubes as well as treated ones under alkaline condition. Figure 5 shows different chemical treatment effects of MWCNTs on methane adsorption capacity at a temperature of 298.15 K and pressure of 50 bar compared to the original MWCNTs. Methane adsorption capacities for samples of 1-3 were estimated to be 30, 35 and 45 mmol/g, respectively, which is obviously higher than the results for original MWCNTs (about 27 mmol/g).

Several isotherm models were used to simulate experimental data of methane adsorption on MWCNTs. It was found that Langmuir, Freundlich and Sips isotherm models give almost perfect fits to the experimental adsorption data. The parameters of Langmuir, Freundlich and Sips isotherm models recovered from a nonlinear fit to experimental data are summarized in Tables 2 and 3 for original untreated MWCNTs at various temperatures and treated MWCNTs at 298.15 K, respectively. Regression coefficient values ($R^2$) near to unity shown in Table 2 indicated a perfect match between experimental data and the fitted values. The fitted values were also shown along with experimental data for comparison in Figures 6-8. Similar results were obtained for all treated samples with different methods (Figures 9-11). The best fit was obtained by the Sips model isotherm. Therefore, it was used for the calculation of isosteric heat of adsorption in this study.

![Figure 5. Comparison of methane adsorption capacity on chemical treated MWCNTs and pristine MWCNTs at 298.15 K.](image)

### Isosteric heat of adsorption

The isosteric heat of methane adsorption was calculated using Sips isotherm model. Table 4 lists the optimal isotherm parameters obtained by fitting the adsorption equilibrium data at different temperatures for methane. These parameters obtained using MATLAB software (version 7.0.4) assuming a temperature independent $q_{max}$ value. In every case, the obtained regression coefficient, $R^2$, is greater than

| Table 2. Langmuir, Freundlich and Sips parameters for methane adsorption on pristine MWCNTs at different temperatures |
|---|---|---|---|
| Equation | Parameter | $T / \text{K}$ |
| | | 283.15 | 298.15 | 318.15 |
| Langmuir | $q_{max} / \text{mmol g}^{-1}$ | 128.9 | 111.32 | 102.86 |
| | $b$ | 0.006976 | 0.006891 | 0.006594 |
| | $R^2$ | 0.9993 | 0.9969 | 0.9985 |
| | RMSE | 0.2638 | 0.5228 | 0.3156 |
| Freundlich | $k$ | 1.188 | 0.806 | 0.7763 |
| | $n$ | 1.167 | 1.083 | 1.11 |
| | $R^2$ | 0.9972 | 0.9986 | 0.9985 |
| | RMSE | 0.5326 | 0.3512 | 0.3199 |
| Sips | $q_{max} / \text{mmol g}^{-1}$ | 80.92 | 77.158 | 72.164 |
| | $b$ | 0.01435 | 0.01306 | 0.0119 |
| | $n$ | 0.8881 | 0.8461 | 0.8778 |
| | $R^2$ | 0.9998 | 0.9996 | 0.9998 |
| | RMSE | 0.129 | 0.7504 | 0.1548 |

*Root mean square error*
0.999. The excellent agreement between the fitted values based on Sips model and the experimental data indicated that this isotherm model can be confidently employed to correlate precisely the adsorption equilibria of methane on MWCNTs adsorbents. The maximum amount of methane adsorbed at saturation conditions ($q_{\text{max}}$), as predicted by the Sips isotherm model for MWCNTs is equal to 80.92 mmol/g at 283.15 K.

![Figure 6. Comparison of experimental adsorption data to predicted values by Langmuir isotherm model.](image1)

![Figure 7. Comparison of experimental adsorption data to predicted values by Freundlich isotherm model.](image2)

![Figure 8. Comparison of experimental adsorption data to predicted values by Sips isotherm model.](image3)

**Table 3. Langmuir, Freundlich and Sips parameters for methane adsorption on treated MWCNTs at 298.15 K**

<table>
<thead>
<tr>
<th>Equation</th>
<th>Parameter</th>
<th>$T / K$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>283.15</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_{\text{max}} / \text{mmol g}^{-1}$</td>
<td>97.4</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>0.009855</td>
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<td></td>
<td>$R^2$</td>
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<tr>
<td></td>
<td>$RMSE^a$</td>
<td>0.3233</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$k$</td>
<td>1.456</td>
</tr>
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<td></td>
<td>$n$</td>
<td>1.256</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
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<tr>
<td></td>
<td>$RMSE^a$</td>
<td>0.4022</td>
</tr>
<tr>
<td>Sips</td>
<td>$q_{\text{max}} / \text{mmol g}^{-1}$</td>
<td>134.5</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>0.005802</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>1.075</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9993</td>
</tr>
<tr>
<td></td>
<td>$RMSE^a$</td>
<td>0.3075</td>
</tr>
</tbody>
</table>

$^a$ Root mean square error

Figure 12 depicts the variation of the isosteric heat of adsorption with the amount of adsorbed methane determined from the temperature dependence of the Sips isotherm model. Selected temperatures for plotting the curves are those at which the adsorption equilibria were measured. The values of $Q_{st}$ for methane adsorption are quite satisfactory when compa-
Figure 9. Comparison of experimental data of methane adsorption on treated MWCNTs to values predicted by Langmuir isotherm model.

Figure 10. Comparison of experimental data of methane adsorption on treated MWCNTs to values predicted by Freundlich isotherm model.

red with the values reported in the literature [37].

Figure 12 shows a drastic decreasing trend for \( Q_{st} \) with an increase in loading level of methane on MWCNTs. At low amount of adsorption the isosteric heat of adsorption is high. This can explained by knowing that at low methane loading, the surface coverage by the adsorbed molecules is low. This causes a stronger interaction between methane molecules and adsorbent surfaces accompanied by a high isosteric heat of adsorption. However, at higher surface coverage, interaction between the adsorbate and adsorbent surface becomes weak due to pore filling and lack of uncovered surface. This leads to a decreasing trend in the isosteric heat of adsorption with the methane loading level onto MWCNTs.

**Adsorption kinetic study**

Figures 13 and 14 show variation of methane uptake by original MWCNTs and pressure *versus*
Figure 11. Comparison of experimental data of methane adsorption on treated MWCNTs to predicted values by Sips isotherm model.

Table 4. Sips model parameters for methane adsorption on pristine MWCNTs

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Parameter</th>
<th>( q_{\text{max}} / \text{mmol g}^{-1} )</th>
<th>( b_0 / \text{bar}^{-1} )</th>
<th>( \alpha )</th>
<th>( n_0 )</th>
<th>( Q / \text{kJ mol}^{-1} )</th>
<th>( T_0 / \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine MWCNTs</td>
<td></td>
<td>80.92</td>
<td>0.01434</td>
<td>0.726</td>
<td>0.884</td>
<td>7.595</td>
<td>283.15</td>
</tr>
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</table>

Figure 12. Variation in isosteric heat of adsorption of methane on pristine MWCNTs with the amount of adsorption; ○, *, Δ indicate 283.15, 298.15 and 318.15 K, respectively.

variation of contact time at different initial loading pressures at constant temperature of 298.15 K, respectively.

Figures 13 and 14 show opposite trends, where a decrease in the adsorption cell pressure with time accompanied with an increase in methane uptake. The recorded data reveals fast kinetics for the adsorption of methane on MWCNTs in which most of the adsorption occurs at an early time of adsorption experiments and the adsorbent is saturated by the adsorbate.
The experimental and model predicted data are shown in Table 5. The correlation coefficients for the pseudo-second order kinetic are desired. Moreover, the calculated $q_e$ value obtained from Eq. (8) was in agreement with the experimental $q_e$ value (Table 4). It can be concluded that the pseudo-second order kinetic model fits well the adsorption of methane onto MWCNTs.

**Intra-particle diffusion model**

The plot of $q_t$ versus $t^{0.5}$ for methane adsorption on MWCNTs is shown in Figure 16 and particularly Figure 17 at equilibrium pressure of 45 bar. As shown in Figure 16, the uptake rates exhibits a double-linear region. The uptake rate is initially very fast, and then it becomes slow. The slope of line at early stage of adsorption gives a measure of external residence to mass transfer surrounding the particle. The second linear region with a lower slope is characterized by intra-particle diffusion. Therefore, the controlling mechanism in overall transport of methane adsorption on MWCNTs is intra-particle diffusion.

**CONCLUSIONS**

In this study, the adsorption of methane at equilibrium conditions on original untreated MWCNTs and
chemically treated MWCNTs adsorbents was experimentally determined by volumetric technique. A series of experiments was conducted at different temperatures and pressures to evaluate the amount of methane storage on these adsorbents. The results revealed that treatment and purification of MWCNTs samples can dramatically affect the surface area and pore structure. Chemical treatment in general has led to the opening of the nanotube ended caps and increasing the active site for gas adsorption and thus enhancing the methane storage capacity.

SEM Results revealed that the acidic treatment with a mixture of H$_2$SO$_4$/HNO$_3$ at 3:1 volume ratio under reflux condition resulted in the highest structural change, such as producing nanotubes with shorter length. Alkaline treatment led to removal of any impurities including the amorphous carbon, but caused no structural change. The best improvement was achieved with the chemical treatment in acidic environment, enhancing considerably the specific surface area and pore volume of MWCNTs. Superior methane adsorption capacity was achieved for treated MWCNTs in acidic conditions with a mixture of H$_2$SO$_4$/HNO$_3$ at 3:1 volume ratio at a temperature of 298.15 K and pressure of 50 bar (about 45 mmol/g) that is considerably higher than methane adsorption capacity on original untreated MWCNTs (about 27 mmol/g) at the same conditions.

It was found that increasing the pressure and decreasing the temperature increases the amount of adsorption for all samples. Subsequently the experimental data was fitted to model isotherms for prediction purposes. The results indicated that the trend of variation in the amount of methane uptake by original MWCNTs follows the Sips isotherm model. Evaluation of methane isosteric heat of adsorption on MWCNTs from the Sips isotherm model using the thermodynamic based Clausius-Clapeyron Equation showed that decreasing temperature or increasing methane uptake decreases the isosteric heat of adsorption. Rapid decrease in methane isosteric adsorption heat due to increase in the loading amounts on the MWCNTs, revealed that MWCNTs adsorbents have heterogeneous surface in methane adsorption.

Also the methane kinetic adsorption study has shown that pseudo-second order and intra-particle diffusion models well fitted the adsorption data of methane onto MWCNTs.

It can be concluded that MWCNTs can be a more favorable adsorbent for methane storage, if it is manufactured and modified with a good pore size, high pore volume and proper surface properties. To the best of our knowledge, the current study revealed the potential for natural gas storage upon MWCNTs and deserves further study.

Acknowledgments
The authors gratefully acknowledge National Iranian Oil Products Refining and Distribution Company (NIOPRDC) for their valuable supports and funding of this research project.

REFERENCES

APPENDIX 1

Sips isotherm:

\[ q = \frac{q_m (bq)^{1/n}}{1 + (bq)^{1/n}} \]  

with the following temperature dependent parameters:

\[ \begin{align*}
    b &= b_0 \exp \left( \frac{Q}{RT} \left( \frac{T}{T_0} - 1 \right) \right) \\
    \frac{1}{n} &= \frac{1}{n_0} + \alpha \left( 1 - \frac{T}{T_0} \right)
\end{align*} \]

Isosteric heat of ads is given as:

\[ Q_{st} = RT^2 \left( \frac{\partial \ln b}{\partial T} \right)_q \]

To calculate \( \partial \ln p / \partial T \) we need an explicit expression for \( \ln p \) vs. \( T \). For this purpose, Eq. (1) can be written as follows:

\[ P^{1/n} = \frac{q / q_m}{b^{1/n} (1 - q / q_m)} \quad \text{or} \quad P = \frac{(q / q_m)^n}{b(1 - q / q_m)^n} \]

\[ \ln P = n \ln \left( \frac{q / q_m}{b^{1/n} (1 - q / q_m)} \right) = \ln b + n \ln(1 - q / q_m) \]

Now, derivation of Eq. (3) with respect to \( T \) at constant \( q \), gives:

\[ \frac{\partial \ln P}{\partial T} = \ln \left( \frac{q / q_m}{b^{1/n} (1 - q / q_m)} \right) \frac{\partial n}{\partial T} + \frac{\partial \ln b}{\partial T} - \ln(1 - q / q_m) \frac{\partial n}{\partial T} = \]

\[ = \frac{\partial n}{\partial T} \left[ \ln \left( \frac{q / q_m}{b^{1/n} (1 - q / q_m)} \right) - \ln(1 - q / q_m) \right] - \frac{\partial \ln b}{\partial T} \]

Now, we need an expression for partial derivatives, \( \ln b / \partial T \) and \( \ln b / \partial T \):

\[ \frac{\partial n}{\partial T} = \frac{1}{n_0} + \alpha \left( 1 - \frac{T}{T_0} \right) \]

\[ \frac{1}{n} = \frac{1}{n_0} + \alpha \left( 1 - \frac{T}{T_0} \right) \]

Now, derivatives of Eq. (5) with respective to \( T \) gives:

\[ \frac{\partial \ln b}{\partial T} = -\frac{Q}{RT^2} \]

\[ \frac{\partial n}{\partial T} = -\frac{\alpha T}{T_0} \frac{T}{n^2} = \frac{\alpha T n^2}{T_0} \]

From Eq. (2), we have:

\[ \frac{\partial \ln P}{\partial T} = \frac{\partial n}{\partial T} \ln \left( \frac{q / q_m}{b^{1/n} (1 - q / q_m)} \right) - \frac{\partial \ln b}{\partial T} \]

\[ \Rightarrow \ln \left( \frac{q / q_m}{b^{1/n} (1 - q / q_m)} \right) = \frac{1}{n} \left( \ln b + \frac{Q}{RT^2} \right) \]

\[ \Rightarrow \ln \left( \frac{q / q_m}{b^{1/n} (1 - q / q_m)} \right) = \frac{1}{n} \left( \ln b + \frac{Q}{RT^2} \right) \]

Equation (4) can be also written as follows:

\[ \frac{\partial \ln P}{\partial T} = \frac{\partial n}{\partial T} \ln \left( \frac{q / q_m}{b^{1/n} (1 - q / q_m)} \right) - \frac{\partial \ln b}{\partial T} \]

Putting Eqs. (6)-(8) into Eq. (9) leads to:

\[ \frac{\partial \ln P}{\partial T} = -\frac{\alpha T n^2}{T_0} \left( \frac{1}{n} \ln b + \frac{Q}{RT^2} \right) \]

\[ Q_{st} = RT^2 \left( \frac{\partial \ln P}{\partial T} \right)_q = RT^2 \left[ -\frac{\alpha T n^2}{T_0} \left( \frac{1}{n} \ln b + \frac{Q}{RT^2} \right) \right] \]

And finally:

\[ Q_{st} = -\alpha R T \ln (b P) \]
UTICAJ HEMIJSKOG TRETMANA NA ADSORPCIJU PRIRODNOG GASA NA VIŠESLOJNE UGLJENIČNE NANOCEVI: RAVNOTEŽA SORPCIJE I TERMODINAMIČKA ISTRAŽIVANJA

U ovom radu ispitivana je adsorpcija metana, glavnog sastojka prirodnog gasa, na ne-
modifikovanim višeslojnim ugljeničnim nanocevima (VSUNC), nakon čega je vršeno
prečišćavanje i različiti hemijski tretmani VSUNC u cilju poboljšanja kapaciteta adsorp-
cije prirodnog gasa. Rezultati su pokazali da je hemijski tretman VSZUNC u prisustvu
smješe kiseline H2SO4/HNO3 u zapreminskom odnosu 3:1 značajno pospešio kapacitet
adsorpcije prirodnog gasa (optimalno do 45 mmol/g) na temperaturi od 298.15 K i
pritisku 50 bar u poređenju sa nemodifikovanim VSUNC (oko 27 mmol/g) pri istim opera-
tivnim uslovima. Ovaj uticaj može se pripisati otvaranju poklopaca nanocevi i time zna-
čajnoj promeni njihovih strukturnih svojstava usled hemijskog tretmana. Eksperimentalni
podaci adsorpcije skoro su podjednako dobro opisani Langmuir-ovom, Freundlich-ovom
i Sips-ovom jednačinom. Najbolje slaganje postignuto je primenom Sips-ovog modela
izoterme sa vrednošću r2 blizu jedan. Dalje, primenom eksperimentalnih podataka dobi-
jenih na različitim temperaturama, izosterna toplota adsorpcije prirodnog gasa na nemo-
difikovanim VSUNC izračunata je za dati opseg pritiska i temperature primenom termo-
dinamičke Clausius-Clapeyron-ove jednačine iz Sips-ovog modela izoterme. Rezultati su
pokazali postojanje energetski heterogene površine VSUNC pri adsorpciji prirodnog
gasa. Takođe, proces adsorpcije prirodnog gasa kinetički je proučavan preko modela
pseudo-drugog reda i unutar-čestičnog difuzionog modela, koji su pokazali da je intra-
čestična difuzija korak koji određuje brzinu adsorpcije metana na MZUNC.

Ključne reči: ugljenične nanocevi, metan, adsorpcija, hemijski tretman, kinetika, izosterna toplota adsorpcije.