

Low pressure adsorption of CO₂ on multi-wall carbon nanotubes

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Abstract

Volumetric techniques were employed to study the adsorption of CO₂ on a purified multi-wall carbon nanotubes (MWNT's) sample, as a mesoporous material, at isothermal conditions of 288, 293 and 298 K and pressures ranging from 30 to 150 kPa. Langmuir, Freundlich and Sips equations were used to represent the isotherms. Also the parameters of these fitted isotherm models have been determined. The isosteric heat of adsorption was calculated using Clausius-Clapeyron equation that resulted in an average value of 10.19 kJ/mol (0.106 eV). Adsorption isotherms behavior with temperature and the average value of heat of adsorption confirmed that CO₂ adsorption phenomenon is physisorption at the studied ranges. The observed entropy changes related to the adsorption in the range of surface loading from 0.133 to 0.147 mol/kg were lower than the values of theoretical entropy changes for both of the mobile and localized adsorption models.

Keywords: Adsorption; Thermodynamics properties; Nano structures; Mesoporous structure.

1. INTRODUCTION

In recent years, carbon nanotubes (CNTs) have been widely studied due to their remarkable role as building blocks in nanotechnology. Their unique characteristics and special geometry offer a wide range of potential applications, such as gas adsorption [1-7]. Gas adsorption ability of CNTs is strongly dependent on the adsorption capability and structural properties of the nanotubes [1,2]. A wide range of adsorption surface areas (up to 3000 m²/g) has been reported for nanotubes in the literature, which is comparable to conventional carbon-based adsorbents such as activated carbons [3].

Adsorption of simple gases like CO₂, H₂ and Xe on single-wall carbon nanotubes (SWNTs) has been investigated for the past several years [1,2,4-7]. Among these gases, adsorption of CO₂ which is the most prevalent greenhouse gas has been studied by several researchers. Cinke et al. studied

the adsorption isotherm of CO₂ on SWNTs and activated carbon, at various temperatures (273-473 K) and noted that CO₂ adsorptive capacity of SWNT is nearly twice that of activated carbon although the surface area of the former is just 25% larger [1,4]. They also concluded that CO₂ is physisorbed side-on to the nanotube [1,4]. The later conclusion was confirmed by Agnihotri et. al. for the adsorption of organic vapors on SWNTs [3].

Applicability of common adsorption isotherm models to gas adsorption on SWNTs and identifying what equation can be used to represent the adsorption data, have been studied by some authors in literature. Freundlich, Langmuir and Sips isotherm equations are empirical adsorption isotherm equations to describe the physical adsorption of gases on microporous solids [8]. The Sips and Freundlich models are used as standard models with a wide range of application which represent heterogeneous adsorption systems

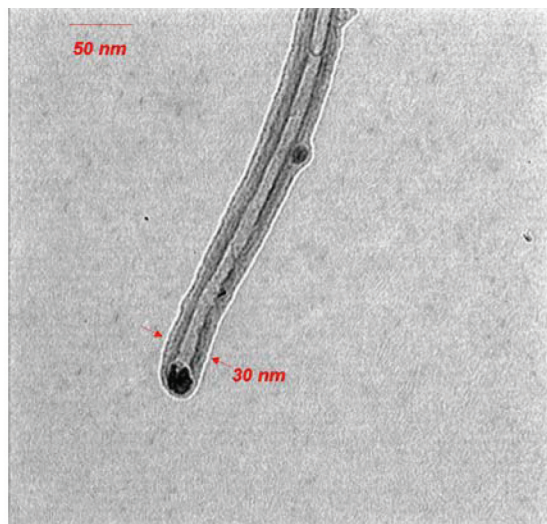
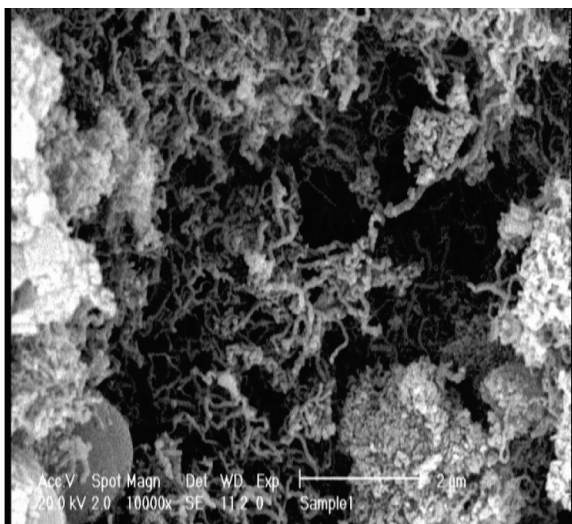


Figure1: SEM image of MWNTs (left) and TEM image of MWNT with 30 nm diameter (right)

properly [8], although the Langmuir model assumes a homogeneous adsorbent and is appropriate to represent homogeneous systems [8]; Fujiwara et al. [2] found that Langmuir-type adsorption isotherm can be applied for the adsorption of N_2 and O_2 on SWNT bundle, while Agnihotri et al. [3] showed that the Freundlich isotherm equation can be properly fitted for the experimental data of organic vapors adsorption on SWNTs more closely than the Langmuir or Dubinin-Rudkevich equation which were attributed to the heterogeneity of SWNTs adsorption sites. However, Hu and Ruckenstein [1] observed a perfect compatibility between the Dubinin-Astakhov equation and CO_2 adsorption data on SWNTs at temperatures 273 and 298 K. They also reported that CO_2 molecules are adsorbed on both internal and external surfaces of SWNTs and the porosity of SWNTs is heterogeneous. It can be concluded generally from literature that CNTs, especially SWNTs, are heterogeneous adsorbents [1,4,6,9], although some authors have suggested that CNTs may be homogeneous adsorbents [2]. However, further studies are needed to get more information about the heterogeneity or homogeneity of CNTs adsorption sites.

On the other hand, recently, the adsorption of simple gases and gaseous pollutants on multi-wall carbon nanotubes (MWNTs) has been studied by several authors [10, 11]. Some of these studies have

experimentally proved which shows that MWNTs can effectively adsorb gaseous pollutants [10,12]. Moreover these studies showed that MWNTs have excellent recoverability and high extraction ability [13,14]. Nevertheless, none of these researches has explored MWNTs in detail, as potential adsorbents for adsorption of CO_2 . Adsorption properties of CO_2 on MWNTs are important because of their potential in CO_2 separation. Although further researches are necessary to understand the adsorption properties of common adsorbates on MWNTs, before such potential can be used commercially.

The limited researches in the literature show the potential of CNTs for gas storage and it seems that the adsorption characteristics of CO_2 on MWNTs deserve to be considered more precisely.

This study presents applicable data on the use of MWNTs as adsorbents for CO_2 adsorption at pressure range of 30 to 150 kPa and isothermal conditions of 288, 293 and 298 K. The equilibrium adsorption capacities of CO_2 on the MWNTs sample have been measured volumetrically at experimental conditions. The adsorption data was fitted to common isotherm equations, including both heterogeneous and homogeneous equations, Freundlich, Langmuir and Sips, to identify the applicability of these isotherm models for CO_2 adsorption on MWNTs at the studied range. Furthermore, the isosteric heats of adsorption were

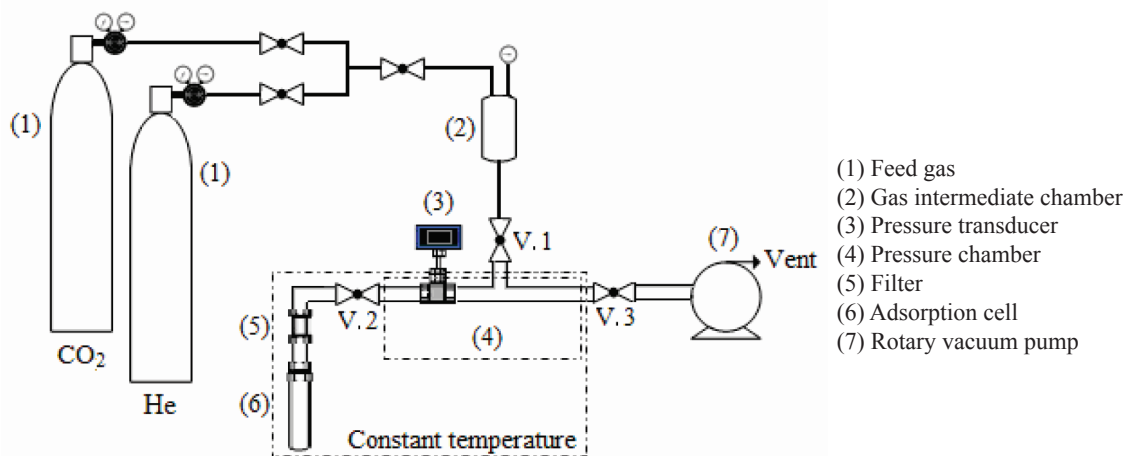


Figure 2: Schematic diagram of the volumetric adsorption system

calculated from isotherm equations using Clausius-Clapeyron equation. Thermodynamic analysis of the adsorption phenomenon was also presented.

2. EXPERIMENTAL

2.1. Sample description

The MWNT experimental sample was prepared by the floating catalyst chemical vapor deposition method [15, 16]. The sample was purified with acid wash. The amorphous carbons were removed by heating at 400 °C for 1 h as reported previously. The purity of MWNTs in the sample was determined to be 95% using TGA method. It was obtained by combustion of MWNT at temperature range from 550 to 700 °C [16]. The sample exhibited a BET surface area of 52 m²/g measured based on the adsorption isotherm of N₂ at 77 K. The sample was characterized using SEM and TEM. The corresponding images are shown in Fig.1. The TEM image shows that these entangled carbon nanotubes were almost composed of MWNTs with average diameter of about 30 nm.

2.2. Experimental apparatus and procedure

Adsorption experiments of CO₂ were carried out volumetrically in a stainless steel vacuum system at isothermal conditions of 288, 293 and 298 K and pressure ranging from 30 to 150 kPa. Fig. 2 shows a schematic diagram of the apparatus. It consisted of a gas chamber of approximately 62.2 ml volume connected to an adsorption chamber of 45.4 ml;

both submerged within a water/ice bath in which the temperature was controlled to within 1 K. The pressure was measured using a pressure transducer (Hanyoung, Korea) with 0.1 kPa error, calibrated in the pressure range studied (30 – 150 kPa). Cell volumes were estimated using water displacement method [17].

The experimental procedure to measure the adsorption isotherms of carbon dioxide was as follows.

A known mass of adsorbent was charged into the adsorption cell. The whole system was then evacuated by a rotary vacuum pump (P.V.R , Italy) capable of establishing vacuum up to 200 Pa absolute pressure. In continuation valves 1 and 3 (V.1 & V.3) were closed and pump was turn off. Then carbon dioxide was delivered into pressure chamber from the inlet valve 2 (V.2) until pressure reached a desired value. This valve was then closed. The pressure and temperature of pressure chamber were then measured to provide the initial number of moles of the gas, n_1 , using ideal gas PVT equation. An adequate amount of carbon dioxide was then allowed to contact the adsorbent by opening the valve 3 (V.3) for a short time which was located between pressure chamber and adsorption cell. After equilibrium had been achieved the pressure was measured to calculate the number of moles remaining in the constant temperature part (Pressure chamber + Adsorption cell) at new condition. The number of moles adsorbed to adsorbent can be obtained then by difference ($n_1 - n_2$). In order to

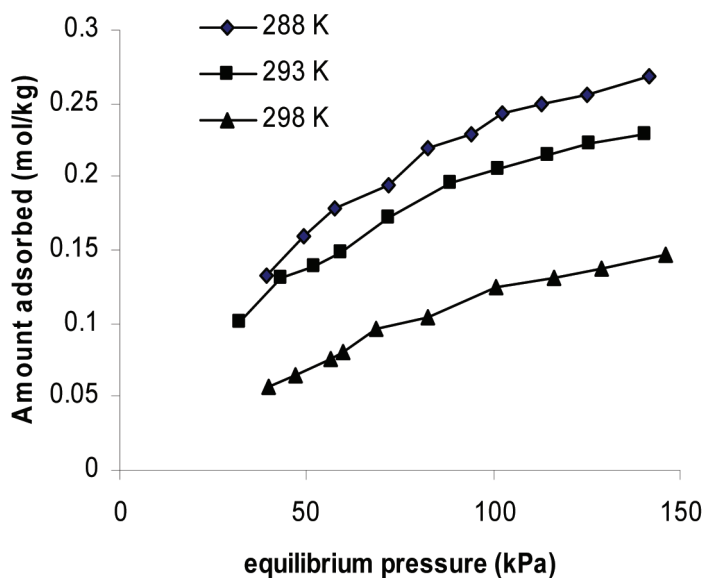


Figure 3: CO₂ adsorption isotherms on the MWNT sample at 288, 293 and 298 K

carry out the calculations it is needed to know the volume of the pressure chamber and free volume of the adsorption cell which is defined as the difference in the volume of adsorption cell and the volume occupied by the solid adsorbent. To measure these volumes, a similar operation can be done using a gas with negligible adsorption on adsorbent. Helium was used in the present study for this purpose. The gases used were of 99.9% purity obtained from Roham Gas Company, I. R. Iran.

3. RESULTS AND DISCUSSION

3.1. Adsorption isotherm curves

Fig.3 shows the adsorption isotherms for the MWNTs sample, at various temperatures. As shown, increasing the temperature decreases the adsorptive capacity of MWNT sample in a manner characteristic of exothermic physisorption. It is also interesting to note that a temperature decrease of 10 K could result to an increase of adsorption capacity up to 2 times which could show the significant effect of temperature condition on the CO₂ adsorption capacity of the MWNT sample. Moreover it was observed that the adsorptive capacity of the purified MWNTs sample was lower than that of activated carbon which was studied experimentally in the previous study [18]. The adsorption data was fitted to the standard

isotherm models, Freundlich, Langmuir and Sips [19] by Levenberg-Marquardt non-linear method. Tables 1-3 represent the estimated values of the parameters of the fitting isotherm models, along with the regression coefficients and the percent relative error between measured and predicted values.

The Freundlich equation is in the form of:

$$c_{\mu} = kp^{1/n} \quad (1)$$

Where C_{μ} is the concentration of the adsorbed species, and k and n are constants that are generally temperature dependent. The Freundlich equation is applicable to describe the gas phase adsorptive systems with heterogeneous surfaces which provide the range of pressure is not too wide. It is generally valid in the narrow range of the adsorption data although it is not usually used at high pressure [8]. The Langmuir and Sips equations take the below forms, respectively:

$$c_{\mu} = c_s \frac{bp}{1+bp} \quad (2)$$

$$c_{\mu} = c_s \frac{(bp)^{1/n}}{1+(bp)^{1/n}} \quad (3)$$

Where C_s is the maximum amount of adsorbed

Table 1: Constants of Freundlich isotherm model, regression coefficient and average relative error for adsorption of CO₂ on MWNT sample

Temperature (K)	Constants of the model	R-square	Average relative error (%)
288	K = 0.006636 n = 1.943	0.9926	2.7
293	K = 0.005425 n = 1.918	0.9929	3.02
298	K = 0.000908 n = 1.422	0.9904	3.95

Table 2: Constants of Langmuir isotherm model, regression coefficient and average relative error for adsorption of CO₂ on MWNT sample

Temperature (K)	Constants of the model	R-square	Average relative error (%)
288	C _s = 0.44 b = 0.001144	0.9902	1.61
293	C _s = 0.37 b = 0.001203	0.9973	1.84
298	C _s = 0.35 b = 0.000501	0.9903	2.7

Table 3: Constants of Sips isotherm model, regression coefficient and average relative error for adsorption of CO₂ on MWNT sample

Temperature (K)	Constants of the model	R-square	Average relative error (%)
288	C _s = 0.35 b = 0.0017 n = 0.7795	0.9902	2.17
293	C _s = 0.33 b = 0.0015 n = 0.8981	0.9975	1.75
298	C _s = 0.21 b = 0.0012 n = 0.6968	0.9982	1.95

Table 4: Comparison of the results of the present study with Su et al.'s at temperature of 293 K and flue gas pressure.

Adsorbent	Adsorbed value (mmol/g)	BET surface area (m ² /g)	Av. pore diameter (nm)
MWNT (present study)	0.2	52	30
MWNT (Su et al.)	0.63	96	23

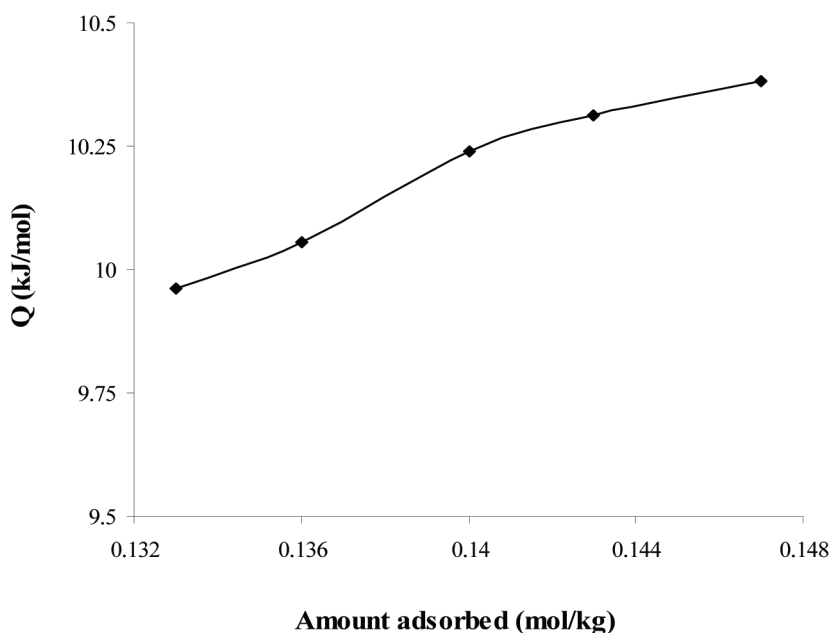


Figure 4: Isosteric heat of adsorption as a function of adsorbed amount

species. In Sips equation the parameter n can be regarded as the parameter characterizing the system heterogeneity. If this parameter n is unity, we recover the Langmuir equation applicable for ideal surfaces. The isotherm modeling in this study could not provide useful insights into the heterogeneous nature of MWNTs as adsorbents, because both of the Langmuir and Sips equation could be properly fitted to the experimental data without large errors. On the other hand, decrease of average relative error with increase of temperature is typical behavior of heterogeneous adsorbents [3] that was not observed here, although the heterogeneous isotherm models, Sips and Freundlich, showed a good compatibility with experimental data. The reason of these opposite observations can be due to the narrow range of pressure which was considered in the experiment, in the present study.

Su et al. [20] found multi-walled carbon nanotube (MWNT) as an effective separation media for removing CO_2 from flue gas at low temperatures. They measured CO_2 adsorption on as-grown MWNT at temperature range of 293-393 K and flue gas pressure. They also observed the adsorption capacities of CO_2 on MWNT decreased with temperature indicating the exothermic nature of

this adsorption process which is consistent with the result of the present study.

The CO_2 adsorption uptake reported by these researchers at temperature of 293 K and flue gas pressure has been compared with the present study result in Table 4.

3.2. Isosteric heat of adsorption

The isosteric heat of adsorption refers to the strength of adsorbate-adsorbent interaction and so characterizes the activation energy for adsorption process [3]. The heat released upon adsorption can be adsorbed partly by the adsorbent, which increases the temperature of adsorbent and slows the rate of adsorption, so quantification of isosteric heat of adsorption values is important for kinetic investigations [3].

The isosteric heat of the adsorption of CO_2 , Q , at a given surface coverage was calculated from the adsorption isotherms at different temperatures using Clausius-Clapeyron equation as:

$$Q = -R \left[\frac{\partial \ln P}{\partial \left(\frac{1}{T}\right)} \right]_{c_u} \quad (4)$$

Here T is temperature, P is pressure and R is the gas

constant. The best fitting isotherm models at each temperature were used to calculate Q in the present study. The ideal gas law was assumed in calculations since errors in isosteric heat of adsorption due to non-ideality are not noticeable when pressure is below 460 kPa [21]. Fig. 4 shows the isosteric heat of adsorption at surface coverage range of 0.13 to 0.15 for the MWNT sample. The value of heat of adsorption on MWNT sample increased slightly from 9.96 to 10.38 kJ/mol when the surface loading increased from 0.133 to 0.147. An average value of 10.19 kJ/mol or 0.106 eV was calculated for CO₂ heat of adsorption on MWNT sample, in this study. A rule of thumb in adsorption is that adsorption heat of smaller than 80 kJ/mol is representative of physisorption [4]. An adsorption heat of about 10 kJ/mol and the manner with temperature in Fig.3 proves that the adsorption of CO₂ on MWNT sample is physisorption. The observed increase in the heat of adsorption with increase of surface loading may be due to strong repulsive interaction between adsorbed carbon dioxide molecules.

3.3. Gibbs energy and entropy of adsorption

The thermodynamic data for the adsorption at surface loading of 0.14 mol/kg have been presented in Table 5. The values of free energy and entropy changes due to adsorption were calculated from the obtained adsorption data using the following relations [19]:

$$\Delta G = RT \ln(P_s/P) \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$S_a = S_g + \Delta S \quad (7)$$

Where, ΔS , ΔH , and ΔG stand for the standard free entropy, enthalpy and energy changes respectively. S_g is the entropy of the adsorbate at standard

pressure P_s (101325 Pa). S_a and P are the entropy of the adsorbed phase and the equilibrium pressure of the adsorbate, respectively. The values of S_g for CO₂ gas at various temperatures were estimated from the data given elsewhere [19] by linear regression. The results of calculation showed that the values of ΔG and $-\Delta S$ decreased with increase of both surface loading on the MWNTs sample and temperature. Moreover the entropy of the adsorbed phase for the MWNTs sample (S_a) and hence mobility increased as carbon dioxide coverage and adsorption temperature increased. The increase of mobility as a result of adsorbate loading increase suggests that the sites of highest adsorption potential were first occupied in the initial stages of adsorption. These adsorption sites might be in the narrowest of the microporosity. In continuation of adsorption, the adsorption sites changed to pores of lower adsorption potential and the quantity of carbon dioxide molecules which were mobile on the surface got more and more.

The theoretical entropy changes at various operating temperatures for the mobile film model [19] in the adsorption process can be calculated using the following expression:

$$\Delta S_t = S_{t3D} - S_{t2D} \quad (8)$$

where S_{t2D} and S_{t3D} represent for the translational entropies for the two-dimensional and three-dimensional adsorbate vapors, respectively. These quantities can be calculated from the following equations [19]:

$$S_{t3D} = R \ln(M^{1.5}T^{2.5}) - 9.61 \quad (9)$$

$$S_{t2D} = 0.667 S_{t3D} + 2.7 \ln T - 12.71 \quad (10)$$

It is expected that the values of the theoretical entropy changes for the localized and mobile adsorption models be equal to S_{t3D} and $(S_{t3D} - S_{t2D})$ respectively. These values also have been calculated and presented in Table 5.

Table 5: Thermodynamic data for the adsorption of CO₂ on MWNT sample at the surface loading 0.14 (mol/kg)

Temperature (K)	ΔG (kJ/mol)	$-\Delta S$ (J/(mol.K))	S_g^* (J/(mol.K))	S_a (J/(mol.K))	ΔS_t (J/(mol.K))	S_{t3D} (J/(mol.K))
288	2.13	42.94	212.3	169.36	48.79	155.28
293	1.67	40.65	212.9	172.25	48.86	155.64
298	-0.71	31.96	213.5	181.54	48.93	155.99

• Values have been calculated by linear regression using data from reference [19].

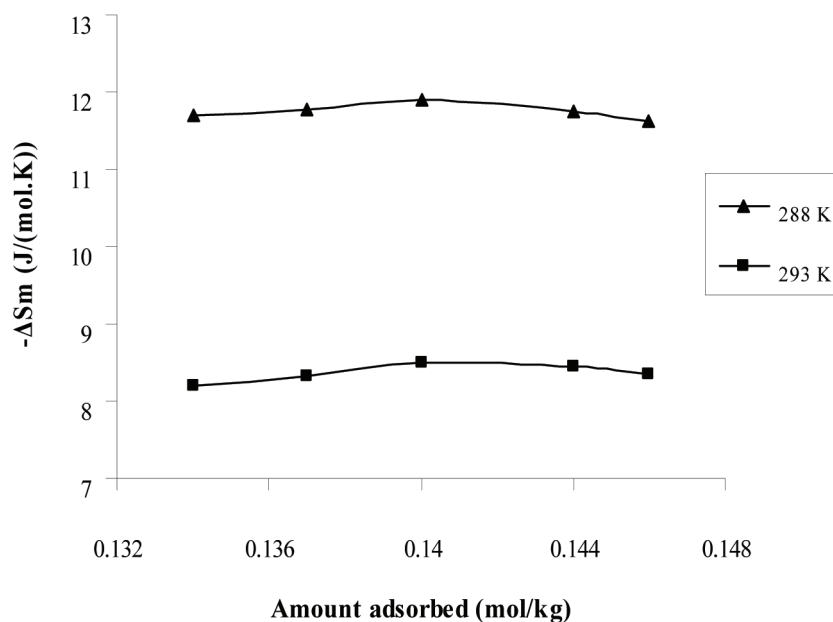


Figure 5: Observed entropy changes at different adsorbed amounts and temperatures in the adsorption of CO₂ on the MWNT sample.

The observed entropy change related to the adsorption can be determined from ΔS using the relation:

$$\Delta S_m = \Delta S + R \ln (A^+/A) \quad (11)$$

Where A is the molecular area of the adsorbate estimated using the data given elsewhere [19]. A⁺ is the standard molecular area (4.08 T×10⁻¹⁶ cm²).

Fig. 5 represents the observed entropy change (ΔS_m) at different surface loadings relating to temperature conditions of 288 and 298 K. These observed entropy changes can be compared with theoretical entropy change for mobile adsorption at temperatures 288 and 298 K considering Table 5.

As shown in Fig. 5, the observed entropy change for the MWNT sample increased slightly with increase of adsorbed amount in the range of 0.133 to 0.14 and decreased with more increase of adsorbed amount in the range of 0.144 to 0.147. Bo Guo et al. (2006) showed that the latter trend existed for the observed entropy change of CO₂ adsorption on four activated carbon samples which decreased slightly with increasing surface loading in all studied samples. As presented in Table 5, the theoretical entropy changes for mobile and localized adsorption of CO₂ on the

MWNT sample were about 49 and 156 J/mol.K. Comparison of these values with the data in Fig. 5 show that the observed entropy change was lower than the values of theoretical entropy changes for both of the mobile and localized adsorption models in the entire range of adsorbate loading studied for the MWNT sample.

4. CONCLUSION

Adsorption of CO₂ on multi-wall carbon nanotubes has been studied volumetrically at various temperatures (288-298 K) and pressures ranging from 30 to 150 kPa. The applicability of popularly used isotherms models including, the Freundlich, Langmuir and sips equation, to CO₂ adsorption data at experimental conditions have been investigated and the related parameters have been determined. Also, sips isotherm has been the best fitted isotherm at temperatures of 288 and 298 K. The experimental data resulted in a heat of adsorption of 10.19 kJ/mol (0.106 eV). An adsorption heat of about 10 kJ/mol and the adsorption isotherm behavior with temperature showed that CO₂ adsorption on MWNTs was physisorption at the studied pressure range. Thermodynamic analysis showed that the values of

ΔG and $-\Delta S$ were decreased with increasing of the both surface loading on the MWNTs sample and temperature. Also, the theoretical entropy changes for mobile and localized adsorption of CO_2 on the MWNT sample were about 49 and 156 J/mol.K. Further, the observed entropy change was lower than the values of theoretical entropy changes for both of the mobile and localized adsorption models. It was also suggested by thermodynamic analysis of the data that the mobility for the adsorption of CO_2 on the MWNT sample increased as the surface loading increased. The presents study provided a preliminary insight into the application of MWNTs for flue gas cleaning however the proposed application need to be studied further in detail.

Symbols used

A	molecular area of adsorbate (cm^2)
A^+	standard molecular area (cm^2)
b	adsorption affinity (1/kPa)
C_s	maximum adsorbed concentration (mol/kg)
C_μ	adsorbed concentration (mol/kg)
K	Fruendlich constant
M	molecular weight (kg/kgmol)
n	temperature dependent constant
P	pressure (kPa)
P_s	standard pressure (kPa)
Q	isosteric heat of adsorption (kJ/mol) or (eV)
R	the gas constant (J/mol.K)
S_a	entropy of adsorbed phase (J/(mol.K))
S_g	entropy of adsorbate at standard pressure (J/(mol.K))
S_{2D}	translational entropy for two-dimentional adsorbate vapor (J/(mol.K))

S_{3D} translational entropy for three-dimentional adsorbate vapor or theoretical entropy change for localized adsorption model (J/(mol.K))

T temperature (K)

Greek letters

ΔG standard free energy change(kJ/mol)

ΔH standard enthalpy change (kJ/mol)

ΔS standard entropy change (J/(mol.K))

ΔS_m observed entropy change (J/(mol.K))

ΔS_l heoretical entropy change for mobile adsorption model (J/(mol.K))

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