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Adsorption Characteristics of CO₂ onto Carbon Nanotube for Adsorption Cooling/Capturing Applications

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Abstract: This article focuses on the possible applications of multi-walled carbon nanotube (MWCNT) in CO₂ capture and adsorption cooling applications. In this study, surface properties namely surface area and porosity of MWCNT are assessed employing N₂ adsorption/desorption method. It is observed that surface area and total pore volume of MWCNT are about 640 m² g⁻¹ and 1.151 cm³ g⁻¹, respectively. Moreover, adsorption isotherms of CO₂ onto MWCNT are investigated at temperature ranging from 30 to 70 °C and pressures up to 5000 kPa. Experimental adsorption uptake data are fitted with well-known Tóth and modified Dubinin-Astakhov (D-A) adsorption models. Adsorption characteristic analysis reveals that 1 gram MWCNT can adsorb up to 0.631cm³ amount of CO₂.

Keywords: Adsorption; CO₂; MWCNT; Porosity; Surface area.

1. INTRODUCTION

The concentration of CO_2 in atmosphere is rising promptly for rapid urbanization and industrialization. This excess concentration causes an imbalance in the carbon cycle, and results global warming. Hence, special care should be adopted to reduce CO_2 level in the atmosphere.

To control the CO_2 level in the atmosphere, CO_2 capture and storage have been attracted to the researchers. Several authors [1–6] investigated the adsorption of CO_2 onto different porous materials such as activated carbon (AC), zeolite, metal organic framework (MOF), silica gel etc for capture and storage applications. Nowadays, researchers are focusing on the utilization of the captured CO_2 . Gustav Lorentzen [7] firstly utilized CO_2 as refrigerant. Besides, Saha et al. [8], Pal et al. [9,10], Singh et al. [11], Mahbubul et al. [12] and many other researchers showed the exploitation of CO_2 as refrigerant for adsorption cooling and heating (ACH) system. CO_2 as refrigerant can mitigate the environmental adverse effect of conventional refrigerants (HFCs, CFCs).

Environmentally benign ACH system along with CO₂ as refrigerant is becoming popular for compact system design. Porous adsorbent materials are the key elements of adsorption system. However, the widely used adsorbents such as AC, zeolite, silica gel and MOF exhibit low thermal conductivity and packing density, which render the ACH system bulky. Therefore, porous materials having high thermal conductivity and adsorption capacity will be very promising for ACH applications. Multi-walled carbon nanotube (MWCNT) may be a good candidate for ACH system due to its pore like structure and high thermal conductivity. The key contributions of this article are:

- i) Investigation of N_2 adsorption/desorption onto MWCNT and estimating porous properties employing BET and NLDFT methods.
- ii) Measurement of adsorption characteristics of CO₂ onto MWCNT at temperature ranging from 30-70 °C and pressures up to 5000 kPa.

iii) Experimental data are correlated with well-known adsorption models

2. MATERIAL

Carbon nanotubes (CNT) are widely used in various electrical applications specially in VLSI interconnection [13,14] due to their high electrical conductivity. Nevertheless, they possess high thermal conductivity [15] which leads them to be used in ACH systems. In this study, MWCNT has been used which was provided by Raymor Nanotech, Canada.

3. N₂ ADSORPTION/DESORPTION AND POROUS PROPERTIES OF MWCNT

3FlexTM Surface Characterization Analyzer is widely used to investigate the N₂ adsorption/desorption isotherm which is one of the standard methods to estimate the porous properties of any material. Fig. 1 shows the N₂ adsorption/desorption isotherm of MWCNT.



Fig. 1. N₂ adsorption/desorption isotherm of MWCNT.

From Fig. 1, it is seen that N_2 adsorption increases gradually at low relative pressure, and rises sharply at high relative pressure, which correspond to Type II isotherm. The intermediate flat region of the isotherm indicates monolayer and multilayer formations. At high relative pressure, hysteresis is observed which restricts MWCNT to be used in ACH system at 0 to 0.8 relative pressure range.

Using the N₂ adsorption data, surface area analysis is carried out adopting Brunauer-Emmett-Teller (BET) method, and Fig. 2 shows the BET plot. It is observed that MWCNT exhibits surface area about $640 \text{ m}^2/\text{g}$.



Fig. 2. BET plot of MWCNT

Pore size distribution (PSD) is a fundamental information of any porous material. The PSD analysis is performed employing Non-Local Density Functional Theory (NLDFT). Fig. 3 shows the incremental and cumulative pore volume of MWCNT.



Fig. 3. Pore size distribution analysis of MWCNT

From Fig. 3 it is observed that most of the pores lie in the mesoporous and macroporous region, and the pore volume is $1.151 \text{ cm}^3 \text{ g}^{-1}$.

4. ADSORPTION OF CO2 ONTO MWCNT

To check the feasibility of MWCNT for the application of ACH system, adsorption isotherms of CO2 onto are investigated employing Magnetic MWCNT suspension adsorption measurement unit (MSB-GS-100-10M) supplied by BEL Japan. The details of this unit are available in literature [9]. This unit provides excess adsorption uptake data. The absolute adsorption uptake can be determined using the following equation.

$$C = C_{excess} + \rho_{CO_2} \times v_p \qquad (1$$

where, C is the absolute adsorption uptake [g g^{-1}], C_{excess} denotes excess adsorption uptake [g g⁻¹], ρ_{CO_2} refers to

the density of CO₂ [g cm⁻³], and v_p represents total pore volume $[cm^3 g^{-1}]$.

In this study, Tóth and modified Dubinin Astakhov (D-A) equations are employed to correlate the CO_2 adsorption uptake data onto MWCNT as given by equations (2) and (3). 0

$$\frac{C}{C_0} = \frac{b_0 e^{\frac{S_a}{RT}} P}{\left(1 + \left(b_0 e^{\frac{Q_a}{RT}} P\right)^t\right)^{V_t}}$$
(2)
$$C = \frac{W_0}{v_a} exp\left[-\left(\frac{RT \ln\left(\frac{P_s}{P}\right)}{E}\right)^n\right]$$
(3)

where, C_0 represents saturated amount of adsorption uptake [g g⁻¹], b_0 is equilibrium constant [kPa⁻¹], Q_{st} denotes isosteric heat of adsorption [J mol⁻¹], R stands for the molar gas constant [J mol⁻¹ K⁻¹], T refers to adsorption temperature [K], P denotes the equilibrium pressure [kPa], t refers to Tóth parameter, W_0 is the maximum volumetric adsorption capacity [cm3 g-1], E stands for adsorption characteristic energy $[J mol^{-1}]$ and nrepresents structural heterogeneity.

The adsorbed phase specific volume of adsorbate is defined as-

$$v_a = v_t \exp\left[\alpha \left(T - T_t\right)\right] \tag{4}$$

where, v_t is the specific volume of the liquid adsorbate $[\text{cm}^3 \text{ g}^{-1}]$ at triple point ($v_t = 0.84858 \text{ cm}^3 \text{ g}^{-1}$ for CO₂), α $(= 0.0025 \text{ K}^{-1} [16], 1/T [17])$ is the thermal expansion coefficient $[K^{-1}]$ of the superheated liquid, and T_t refers to triple point temperature [K].

Beyond the critical temperature, saturated vapor pressure is replaced by pseudo saturated vapor pressure, and can be expressed as-

$$P_{S} = \left(\frac{T}{T_{C}}\right)^{k} P_{C}$$
(5)

here, k is a fitting parameter, T_c and P_c represent critical temperature and pressure of CO₂, respectively.

Fig. 4 shows the experimental adsorption uptake data and the correlation between experimental data and adsorption models. Moreover, all the fitting parameters of the models and the root-mean square deviation (RMSD) values are listed in Table 1.



Fig. 4. Adsorption isotherms of CO₂ onto MWCNT.

From Fig. 4, it is observed that modified D-A equation shows good agreement with the measured adsorption isotherm data.

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Table 1. Fitting parameters and RMSD values of the studied isotherm models.

Model	Fitting	MWCNT/CO ₂
	parameters	pair
Tóth	$C_0 [g g^{-1}]$	1.530
	$b_0 [kPa^{-1}]$	1.72×10 ⁻⁰⁷
	Q _{st} [J mol ⁻¹]	15297.479
	t [-]	0.630
	RMSD [%]	1.095
Modified D-A	$W_0 [cm^3 g^{-1}]$	0.631
	E [J mol ⁻¹]	1753.740
	n [-]	0.694
	k [-]	2.362
	RMSD [%]	0.368

5. CONCLUSIONS

In this study, the possible applications of MWCNT in CO_2 capture and ACH system are investigated. From the N_2 adsorption/desorption analysis, it is observed that most of the pores of MWCNT are mesoporous and macroporous, and total pore volume is $1.151 \text{ cm}^3 \text{ g}^{-1}$. Besides, adsorption characteristic analysis reveals that MWCNT exhibits significant CO_2 adsorption capacity, and it can adsorb up to $0.631 \text{ cm}^3 \text{ g}^{-1}$. From this result, it is evident that MWCNT cannot replace highly porous AC as adsorbent in ACH application. However, it can be used as thermal conductive material along with activated carbon to enhance the heat transfer of adsorbent.

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