



Carbon dioxide capture using functionalized multi-wall carbon nanotubes by EDA

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Abstract

Carbon dioxide (CO₂) is the primary factor considered to be responsible for global warming. CO₂ capture technology has been considered an important issue to decrease greenhouse gas emissions. The current research investigates the functionalization of Multi-Wall Carbon nanotubes (MWCNTs) by Ethylenediamine (EDA) solution which is used for CO₂ capture at various operating conditions. Surface functionality groups and morphology of MWCNTs and physical properties were analyzed by X-ray diffraction (XRD), Fourier Transforms Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), surface area Brunauer Emmett and Teller (BET). The physical and chemical properties of CNTs have changed after the functionalization process, which enhances MWCNTs adsorption for CO₂ gas. According to the study's results, during the functionalization process, amine groups bound to carbonaceous surfaces created CO₂ adsorption sites on multi-walled CNTs, increasing the adsorption capacity of MWCNTs. The CO₂ adsorption capacity was determined by volumetric technique at temperatures from 309 to 333 °K and a pressure of 1 to 7 bar. The exothermic nature of the adsorption process was indicated by the decreasing of CO₂ adsorption capabilities via MWCNTs and MWCNTs-EDA with temperature rising. The results showed that the MWCNTs-EDA are a potential low-temperature adsorbent for CO₂ capture. In addition, 0.6968 mmol g⁻¹ of CO₂ was adsorbed by MWCNT-EDA at 309 °K, while raw MWCNT adsorbed only 0.3428 mmol g⁻¹ at the same condition. Both the Freundlich and Langmuir adsorption isotherms were used to model the experimental data, with the conclusion being that the Freundlich model fits the data well.

Keywords: MWCNTs; Amine Functionalization; ethylenediamine; CO₂ adsorption; Functional groups.

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1- Introduction

Climate change has been significantly impacted by the dramatic increase in greenhouse gas emissions in the past decade. As science and technology advance, human activity is placing a growing strain on the environment, requiring the development of new approaches for preventing environmental disasters [1, 2]. In recent years, there has been a global increase in awareness of the need to reduce carbon dioxide (CO₂) emissions from the production of energy and other manufacturing processes [3]. Industrial byproducts, such as the manufacture of synthesis gas, natural gas sweetening, and flue gases from fossil fuel-fired power plants, industrial furnaces, cement plants, engine exhausts, and lime kiln exhausts, are the main sources of CO₂ [4]. Although opinions on the causes of environmental issues and global warming vary, many scientists agree that the majority of environmental issues are caused by greenhouse gas emissions. Of all the greenhouse gases produced by humans, CO₂ is the most significant. Carbon dioxide emissions are responsible for around 60% of the consequences of global warming [5]. One of the most critical environmental problems facing humanity is the rising atmospheric CO₂ level, which has risen by 100 parts per million since the beginning of the

industrial revolution. Therefore, as a way of maintaining atmospheric CO₂ at a level that may reduce the global climate impact, many technologies for CO₂ capturing from flue gas are being investigated globally [6]. Various methods such as chemical absorption, physical absorption, and membrane separation have been suggested for CO₂ capture. Consequently, there has been a growing interest in novel materials and technology for CO₂ capture and storage within the past ten years [7]. Among the most promising approaches to the potential for regenerating used adsorbents is the adsorption method employing solid sorbents. In order to reduce the impact of CO₂ emissions on global warming effect. With its low cost and great efficiency, adsorption separation is considered a promising approach for separation. In this regard, a wide range of recognized and novel nonporous materials, such as carbon nanotubes (CNTs), activated carbons, metal-organic frameworks (MOFs), and zeolites, have been developed and investigated. Specifically, have large specific surface areas and significant adsorptive affinities. These characteristics, when combined with the superior transport qualities of CNTs, may further enhance the adsorption potential of CNTs for CO₂ collection. [8]. Comparing CNT to amorphous carbons and activated



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carbon fiber, it has a higher CO₂ /CH₄ selectivity and a superior adsorption capacity for CO₂ at ambient temperature and atmospheric pressure.

Over the past ten years, there has been a lot of interest in gas adsorption using carbon nanotubes (CNTs). Because of their clearly defined morphology and surface features, CNTs provide excellent model systems [9]. Furthermore, several methods can be used to change the functionalization of their chemical surface including supramolecular complexation, exohedral and endohedral functionalization, defect and sidewall functionalization, and covalent and noncovalent functionalization [10]. These important characteristics enable quick reaction kinetics, effective regeneration, and easily adjustable properties, which make these materials a desirable class of gas adsorbents for both theoretical and practical uses [11]. CNTs offer exceptional mechanical, electrical, and thermal capabilities because of their special structure. They are among the most promising carbon-based adsorbents due to their huge specific area, lightweight, well-defined structure, and reproducibility [12].

Multiwalled carbon nanotubes (MWCNTs) have been evaluated for their ability to adsorb CO₂ from flue gases [9]. Discovering that, in comparison to zeolites or granular activated carbons, they can exhibit higher CO₂ adsorption capabilities following the appropriate chemical modification. Furthermore, it has been discovered through experimentation that carbon nanotubes' electrical resistance is susceptible to the adsorption of gaseous molecules, such as those generated during the combustion of fossil fuels [13]. Ethylenediamine is preferred among amine molecules because it can act as a medium for attaching various substances to carbon nanotubes (CNTs). The diamine is made up of two amino groups (-NH₂) present; one can bind to carbon nanotubes (CNTs), while the other can bond to other functional groups [14]. The adsorption capacity of carbon nanotubes has already been increased using different amines. The aim of this work is to modify MWCNTs using ethylenediamine (EDA), and then test the adsorption capacity for CO₂. ethylenediamine, which is readily available, is less expensive than other amines and hasn't been employed in the amine functionalization process yet. The multiwall carbon nanotubes were characterized using XRD, BET, SEM, and FTIR. Also, investigate the effect of bed weight and flow rate on the adsorption process performance.

2- Experimental work

2.1. Materials and equipment

In the present work, different materials are used to functionalize multi-wall carbon nanotubes are shown in Table 1.

Table 1. Laboratory used material

Material	Company	Purity %
MWCNTs	cheap tubes	90
EDA	Thomas Baker (Chemicals)	99
Toluene	scharlau chemicals	98.8
Deionized water	/	100

2.2. Functionalization method

The functionalization of MWCNTs has been done by dispersing 200 mg of carbon nanotubes into a flask containing ethylenediamine, EDA (10 mL of 99% EDA+150 mL of 99.8% toluene+3.2 mL of deionized H₂O). The mixture was then refluxed for 2 hours at 100 °C. Once the mixture had reached room temperature, it was filtered using 45 µm filter paper. The resulting solid was then dried in an electrical oven (Gallenamp Size Two INCUBATOR model IH-100, Germany) at 100 °C for eight hours [14].

2.3. Adsorption equilibrium isotherm apparatus and method

Fig. 1 shows a schematic diagram of the apparatus. All 3/8-inch copper tubes were joined together using fittings. The reservoirs and adsorption chamber were made of iron sample cylinders with a volume of around 20 cm³. A Helicoid gauge, with a range of 0 to 200 psig, was used to measure the gas pressure. Its accuracy was 1% and its sensitivity was 0.02% of the full scale throughout. In order to maintain a constant temperature, the reservoir and adsorption chamber were submerged in water [15].

2.3.1. Procedure of equilibrium isotherm process

All equipment was evacuated by a vacuum pump (675 mmHg, power 100w, output airflow 26 LPM, Sparmax, tiwan) after each experiment. The feed gas was supplied with a gas cylinder controlled with a pressure regulator (Excel Instrument, EN 837-1, and India. The adsorbent was placed into the adsorption vessel to regenerate the adsorbent (carbon nanotubes) and evacuated for one hour under a vacuum pump. Without affecting the adsorbents, this pre-treatment enabled the measurements of adsorption. Following the pretreatment of the adsorbent, the vacuum pump was turned off. The water bath with the electrical hot plate (type Heidolph MR Hei-Tec, Germany) was turned on until the temperature reached a steady state. Through valve V1, carbon dioxide gas was introduced into the reservoir chamber until a sufficient concentration was attained, then V1 closed, and the concentration was measured. Following that, valve 2 was opened, enabling the system to establish equilibrium. Using a mass balance, the amount of gas adsorbed at equilibrium was calculated. The mass balance can be written as follows:

$$C_i V_r = C_f V_r + C_f \epsilon_0 V_a + W q \quad (1)$$

Where W is the weight of the adsorbent in the adsorber vessel (g), ϵ_0 is the overall bed void fraction, V is a volume (l), C is a concentration (mmole/l), and q is the adsorbent loading at equilibrium (mmole/g). The reservoir vessel, adsorber vessel, initial state, and final condition are denoted by the subscripts r, a, i, and f, respectively.

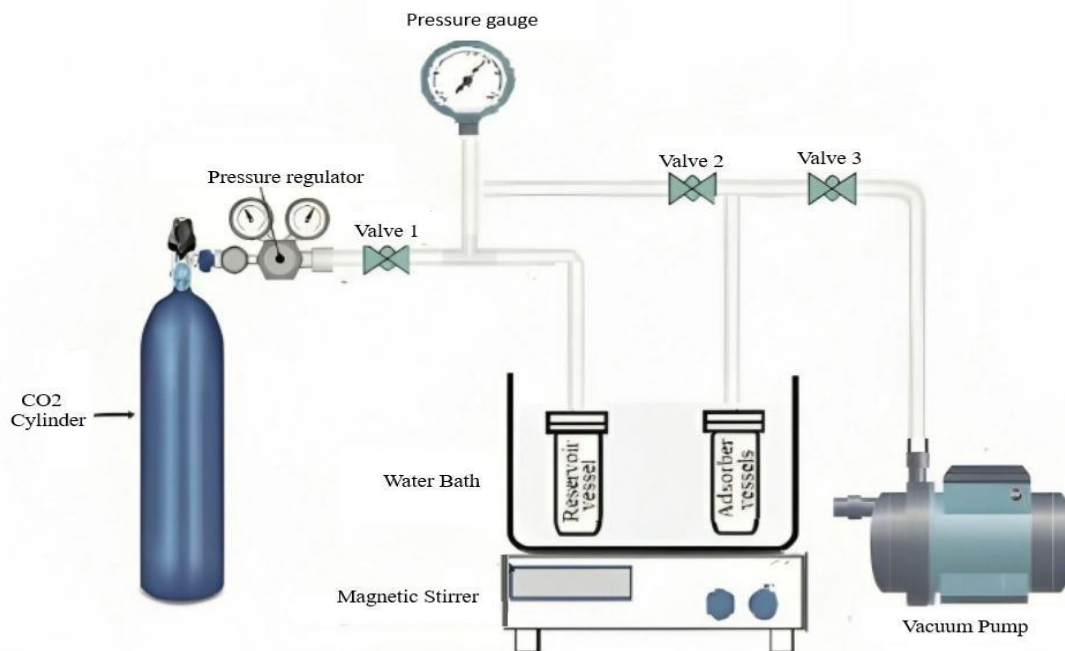


Fig. 1. Schematic diagram of apparatus used for adsorption equilibrium measurement procedure

2.4. Adsorption kinetics and pressure swing adsorption (PSA) procedure

Fig. 2 shows a schematic diagram of the apparatus. All 3/8-inch copper tubes were connected with a fitting. An iron pipe with an ID of 3.5 cm and a length of 65 cm was used as the adsorption column. Steel mesh is used to hold the MWCNTs in the adsorption column. For measuring the process pressure, a gauge pressure was attached to the top of the column. A rotameter was used to measure the inlet gas flow rate, while a gas analyzer was used for determining the outlet gases. The adsorbent regenerate

(carbon nanotubes), was placed into the adsorption vessel and evacuated under a vacuum pump for one hour. After the adsorbent pretreatment, the vacuum pump was turned off. The adsorption process was then started by introducing carbon dioxide and nitrogen (10/90 v/v), the flow rate of the inlet gases measured by a rotameter, and then allowing the gases to enter the mixer column and adsorption column. Until equilibrium was reached, the gas analyzer (Geotechnical Instruments, BIOGAS 5000, UK, ISO17025 certified) periodically (every 5 seconds) examined the exit gas from the adsorption column.

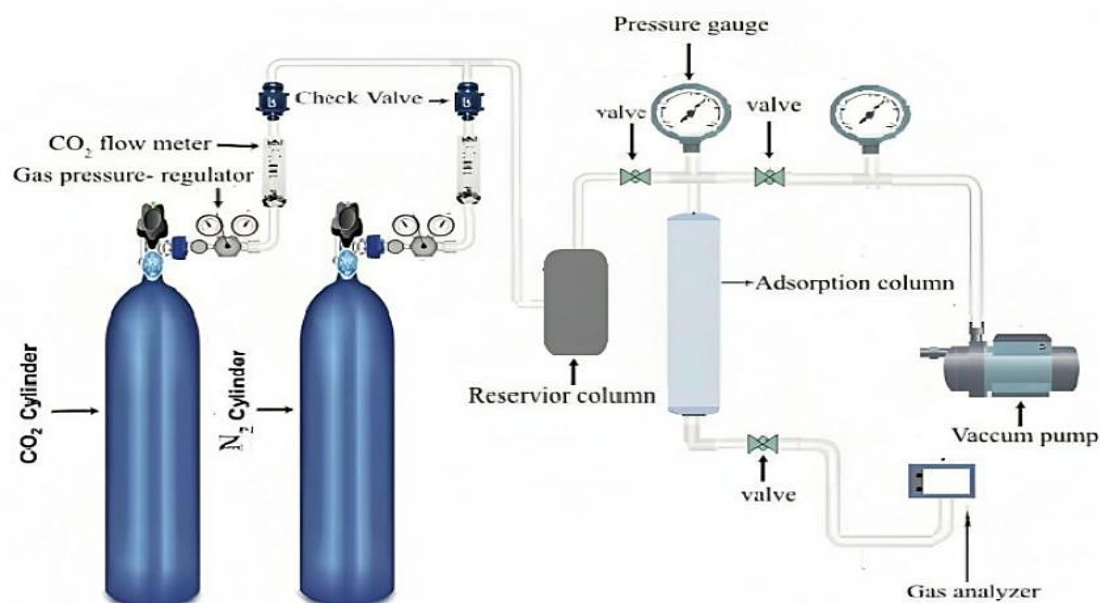


Fig. 2. Schematic Diagram of Apparatus Used for Adsorption Kinetics

2.5. Characterization of adsorbent samples test

1. X-Ray Diffraction

X-ray diffraction is used to determine the phase purity and material crystallinity for MWCNT and functionalize MWCNT. X-ray diffraction analysis was carried out using X-ray diffractometer type Shimadzu 6000, Japan.

2. Fourier Transforms Infrared Spectroscopy (FTIR)

The FTIR analysis was done to investigate the structure of MWCNT. Analysis was carried out using the device of Sigmadzu 8400S type with wave number range (400-4000cm⁻¹).

3. Scanning Electron Microscopy (SEM)

The SEM analysis was done to investigate the Morphology and particle size of MWCNT. Analysis was carried out using the device of Tescan MIRA III/ Czech.

4. Surface Area and Pore Volume (BET)

The surface area analyzer manufactured by Thermo/USA was used to measure the surface area and pore volume of the MWCNT_s, using the Brunauer Emmett and Teller (BET) method.

3- Result and discussion

3.1. Characterization of MWCNT_s

1. X-ray diffraction

Researchers used X-ray diffraction (XRD) analyses to discover how the functionalization impacted the crystallographic growth of MWCNTs [16]. The two samples Fig. 3 and Fig. 4 show distinctive peaks situated nearly in the same places, indicating that the crystalline structures remain unchanged throughout the functionalization process. [17]. On the other hand, peaks with nearly identical positions show varied intensities. The graphite (002), (100), (004) and (110) lattice planes correspond to the strong diffraction peak at $2\theta = 25.6^\circ$ and weak diffraction peaks at $2\theta = 42.9^\circ$, 51° and 78° of MWCNTs. Sometimes there are additional peaks connected to the metallic catalyst [14, 16, 19]. Peaks between 38° and 50° that are likewise connected to metallic catalysts such as Fe, Si, Al, and Co. A number of chemical changes can reduce the crystalline degree of CNTs. [18]. Any change in the crystallinity order of MWCNT will cause the XRD peaks to become larger and move the peak diffraction towards lower angles. Therefore, the peak's sharpness at 25.6° has decreased, indicating that the treated MWCNT's graphite structure was treated without suffering severe damage. [20].

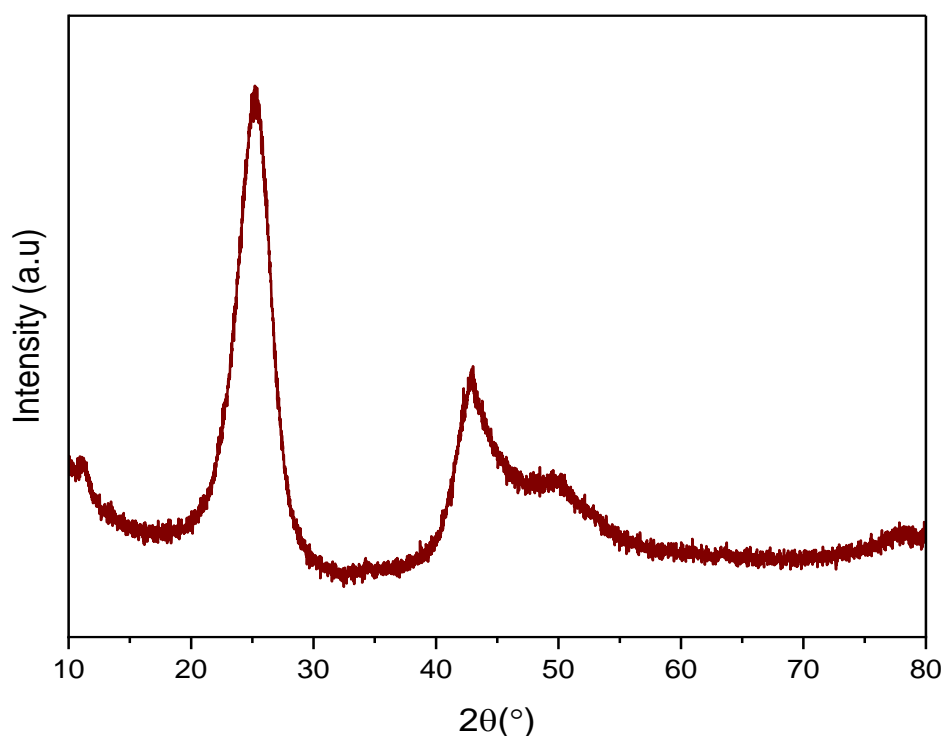


Fig. 3. XRD patterns for MWCNTs

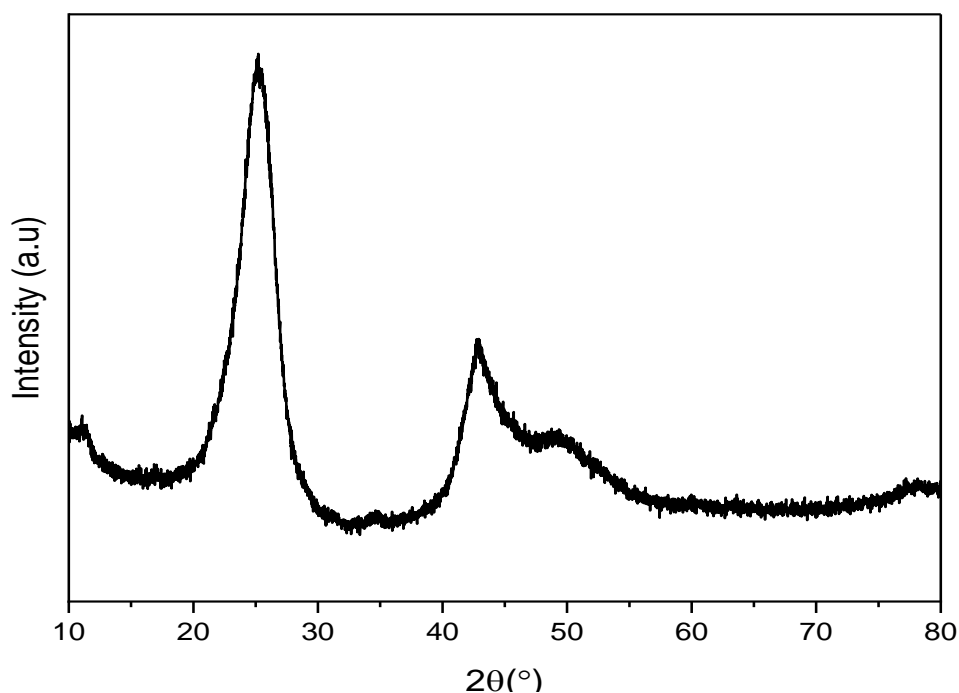


Fig. 4. XRD patterns for EDA-functionalized MWCNT

2. Fourier transforms infrared spectroscopy (FT-IR)

The qualitative method for determining whether functional groups are present in the MWCNT's surface is Fourier transform infrared spectroscopy (FTIR). As shown in Fig. 5 of the MWCNTs FTIR results, the existence of bands at 3441 cm^{-1} and $1770\text{--}1697\text{ cm}^{-1}$ signifies the existence of vibrations involving O-H stretching and C=O stretching, respectively [23, 24]. The C-N peaks appeared at 1338 and 1512 cm^{-1} [14, 21, 22]. The C=C bond of the carbon structure of MWCNT is given the peaks at $879\text{--}779\text{ cm}^{-1}$ and $1643\text{--}157\text{ cm}^{-1}$, while the C-O bond stretching peak is at $1149\text{--}1045\text{ cm}^{-1}$ [20, 25, 26]. Fig. 6 of the MWCNT-EDA FTIR analysis shows that the stretching frequencies of the C=C bonds,

and the hydroxyl groups (O-H) are at 1622 and 3442 cm^{-1} , respectively. The amine-functionalized MWCNTs show an Al-O-Al peak at 474 cm^{-1} and a number of peaks between 2926 and 2854 cm^{-1} , which match the alkanes' C-H stretching absorption bands [16, 22, 27]. The C=O stretching of the carboxylic acid group is indicated by the peak between 1749 and 1720 cm^{-1} . Additionally, peaks at 3250 , 1523 , and 1438 cm^{-1} correspond to the N-H bending of the amine and amide groups, respectively. Stretch vibrations between carbon and nitrogen cause the peaks at 1211 and 1340 cm^{-1} . The aromatic amine groups' stretching mode caused the peak at $796\text{--}727\text{ cm}^{-1}$. The C-O stretching vibrations of the carboxylic acid group can be attributed to the peaks $1093\text{--}1039\text{ cm}^{-1}$ [25, 28- 30].

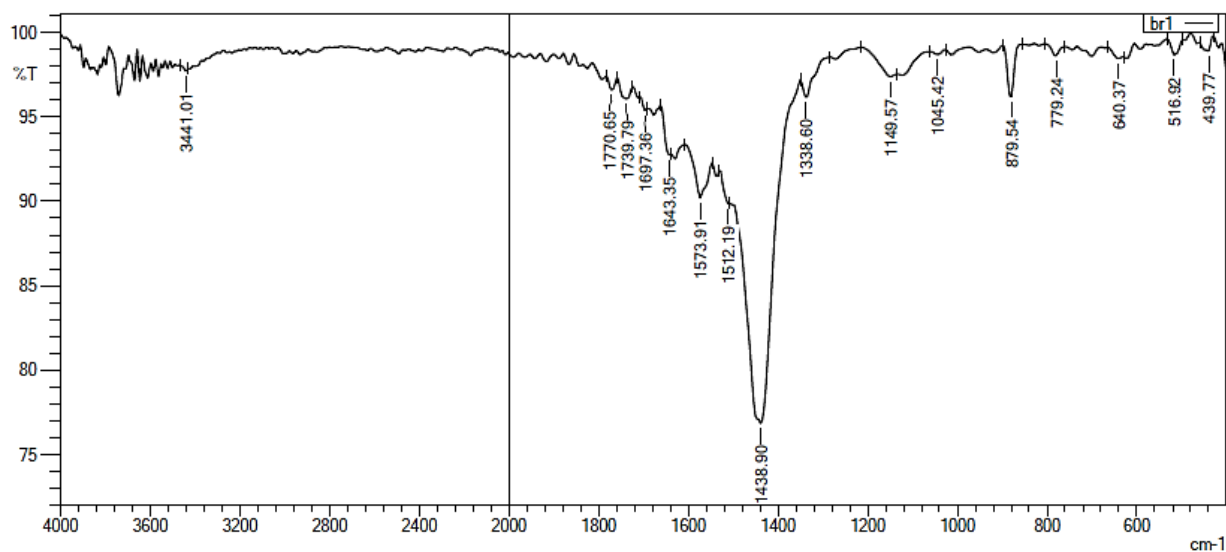


Fig. 5. FTIR spectra of the pristine MWCNT

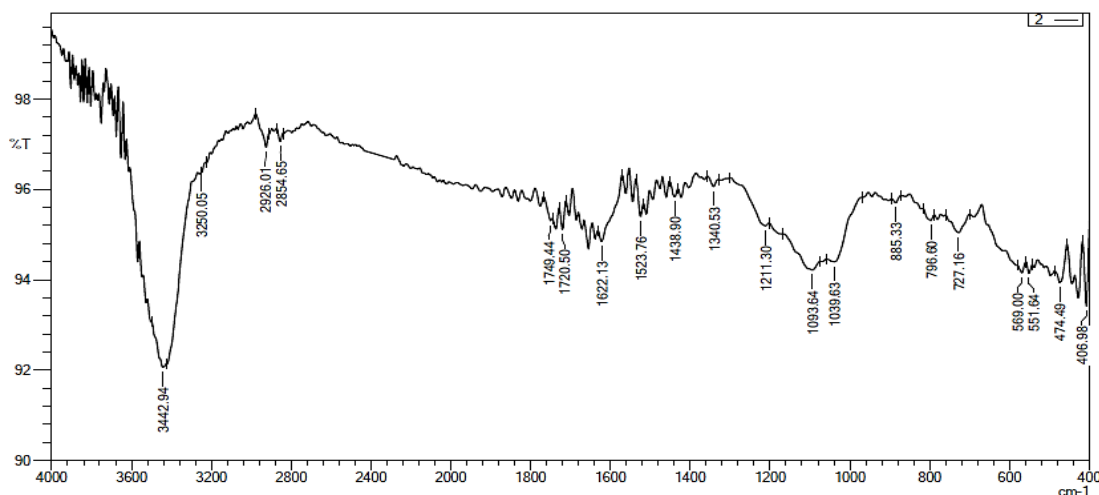


Fig. 6. FTIR spectra of the EDA-functionalized MWCNT

3. Scanning electron microscopy SEM

Scanning electron microscopy (SEM) shows how functionalization affected MWCNTs. The shape of the MWCNT is unaffected during functionalization, as demonstrated in Fig. 7 and Fig. 8 which display the scanning electron micrographs of the pristine and modified MWCNTs, respectively. It appears that MWCNT is sufficiently strong to resist the functionalization process since no evidence of destruction or damage was found. Images of functionalized MWCNTs showed more obvious ends than those of unmodified MWCNTs. That is because the lengths of MWCNTs were fragmented as a result of the walls being etched by a modified process [25-27]. A picture of MWCNTs-EDA Fig. 8 demonstrates that the multilayer MWCNTs structure has a homogeneous shape with swelling in the tubular structure, which could be due to the introduction of carboxyl groups and amine chains into the pores. Can be noticed that the MWCNTs surface is partially covered with functional groups leading to a decrease in the effective surface area for CO₂ adsorption [31, 33]. As a result of the treatment, the MWCNTs structure transformed into agglomerates and layers [34].

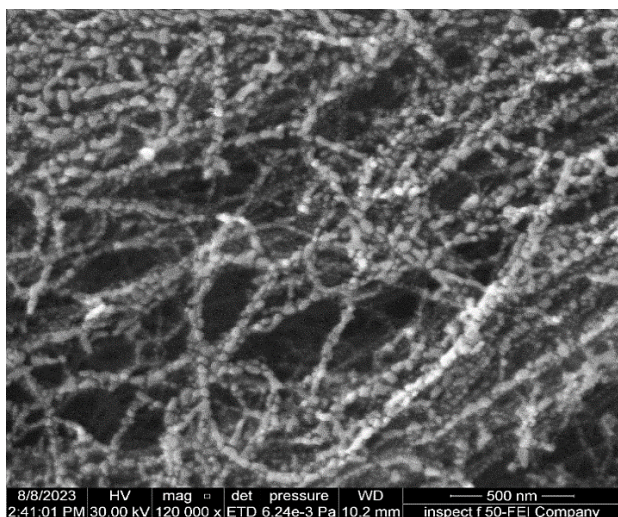


Fig. 7. SEM images of the pristine MWCNT

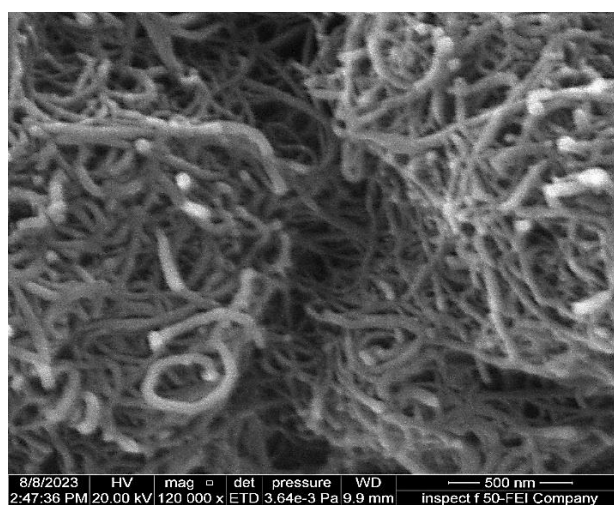


Fig. 8. SEM images of the EDA-functionalized MWCNT

4. Surface area, pore volume, and pore size

Using nitrogen physical adsorption at liquid nitrogen temperature, the BET (Brunauer, Emmett, and Teller) method was used to estimate the surface area of both pristine and functionalized MWCNTs [35]. The analysis below Table 3 shows that the grafting of functional groups into the surface of CNTs considerably changes the porosity structure and pore size, leading to the adsorption capacity increasing [17]. The difference between the adsorbent's physical properties before and after functionalization is shown in Table 2. After the functionalization process, the surface area and pore volume of MWCNT were significantly reduced. This reduction is a result of nitrogen gas being unable to enter some pores due to the development of amine groups during modification. The results are not far from values obtained by [14, 26, 27, 37]. The pure MWCNTs had the highest surface area and pore volume. It is found that the main reason for the decrease in surface area and pore volume in chemically modified MWCNTs, as compared to their pristine, is the blockage of pore openings with primary amine groups [31].

Table 2. Structural properties of pristine and functionalized MWCNT measured by BET technique

Sample	Surface Area (m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹)	Pore Size (nm)
MWCNTs	281.315	1.42	20.23
MWCNT-EDA	196.37	1.122	22.86

3.2. CO₂ adsorption

Experiments on adsorption were conducted at two distinct temperatures (309 and 333 °K) and pressures (up to 7 bar). Fig. 9 and Fig. 10 show the experimental CO₂ adsorption isotherms for unmodified and functionalized MWCNTs, respectively. The CO₂ adsorbed amount was only a function of pressure at any given temperature. It is obvious that temperature rising from 309 to 333 °K reduced carbon dioxide capacity, for both MWCNTs and MWCNT-EDA adsorbents. Because of the exothermic reaction and reduced chemical bonding between amino groups and CO₂ molecules [9, 38, 39]. Functionalized MWCNT has a greater capacity for adsorption of 0.6968 mmol/g at 309 °K than unmodified MWCNT at 0.3428 mmol/g over the investigated range of pressure and temperature. This is despite the fact that following EDA functionalization, the MWCNT's pore volume and surface area are reduced. This behavior can be related to the strong attraction that CO₂ molecules have at low pressures for basic amine sites on the MWCNT-EDA and Lewis acid sites. As a result, at low pressures, the amount of CO₂ adsorbed increased quickly. The pore volume of MWCNT decreased in the present study following the amine functionalization, although this cannot indicate a decrease in CO₂ adsorption. [7, 11, 40]. Adsorption isotherms are widely used and effective methods for estimating equilibrium data. These isotherms serve as the basis for the design of adsorption systems. It is possible to represent the amount of material adsorbed onto an adsorbent as a function of pressure at constant temperature using several adsorption isotherm models [12, 13]. The Langmuir equation, which is based on the three fundamental assumptions that adsorption cannot proceed beyond monolayer coverage, adsorption sites are equivalent, and sites are independent, is the most often used isotherm equation for modeling the adsorption data, and is given by the Eq. 2 [41, 42]:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (2)$$

Where k_L is the adsorption equilibrium constant, C_e is the equilibrium concentration of the adsorbate, q_e is the amount adsorbed at equilibrium, and q_m is the maximum monolayer adsorption uptake (mmole/g). To determine the constants k_L and q_m Eq. 3 may be used to produce a graph $1/q_e$ against $1/C_e$:

$$\frac{1}{q_e} = \left(\frac{1}{q_m k_L}\right) \frac{1}{C_e} + \frac{1}{q_m} \quad (3)$$

Eq. 4 provides the Freundlich adsorption isotherm. It is an empirical equation that may be applied to non-ideal sorption on heterogeneous surfaces and is not limited to monolayer sorption [43]:

$$q_e = k_f C_e^{1/n} \quad (4)$$

Where C_e is the equilibrium concentration of the adsorbate, q_e is the amount adsorbed at equilibrium, K_f is the Freundlich constant, and n = the heterogeneity factor. To determine the constants K_f and, the linear form of Eq. 4 may be used to produce a graph of $\text{Log}(q_e)$ against $\text{Log}(C_e)$ Eq. 5:

$$\text{Log } q_e = \text{Log } K_f + 1/n \text{ Log } C_e \quad (5)$$

Reversible adsorption is indicated by the Freundlich isotherm [44]. A nonlinear fit of isotherm models to experimental data produced the isotherm parameters. Table 4 lists the values of the Freundlich and Langmuir isotherm parameters. The results presented here showed that the adsorption process was exothermic, as evidenced by the negative relationship between temperature and the affinity between CO₂ and both adsorbents. This indicates that at low temperatures, CO₂ adsorption on both adsorbents is more desirable [45]. A better fit for MWCNTs and modified MWCNTs was found by employing the Freundlich isotherm after evaluating the calculated coefficients (R^2 values in Table 3. The comparatively fast adsorption of CO₂ on MWCNT-EDA was an indication of the easily accessible adsorption sites in comparison to MWCNTs. This may be the result of a higher affinity between the functional groups and adsorbate on the surface of the MWCNT-EDA adsorbent [14, 16]. The standard deviation for MWCNTs Fig. 9 is (0.081 at 309 k and 0.0438 at 333k), and for MWCNTs-EDA Fig. 10 are (0.1775 at 309k and 0.1021 at 333k).

Table 3. Langmuir and Freundlich isotherm constants for adsorption of CO₂ on MWCNT and MWCNT-EDA samples

Iso therm	Adsorbent	Parameters	Temperature (K)	
			309	333
Langmuir	MWCNT _s	q_m	0.453	0.282
		k_L	0.016	0.03
		R^2	0.9809	0.9857
	MWCNT-EDA	q_m	1.0711	0.6044
		k_L	0.01	0.013
		R^2	0.9876	0.988
Freundlich	MWCNT _s	k_f	0.02	0.033
		n	1.767	2.471
		R^2	0.9963	0.9908
	MWCNT-EDA	k_f	0.023	0.0194
		n	1.497	1.61
		R^2	0.9914	0.9931

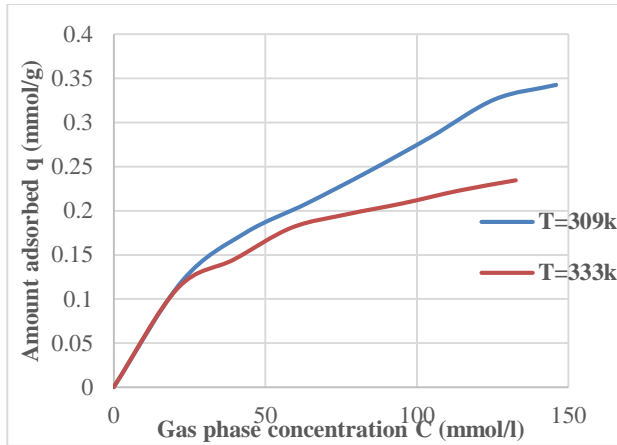


Fig. 9. Adsorption equilibrium isotherm of carbon dioxide on MWCNT_s

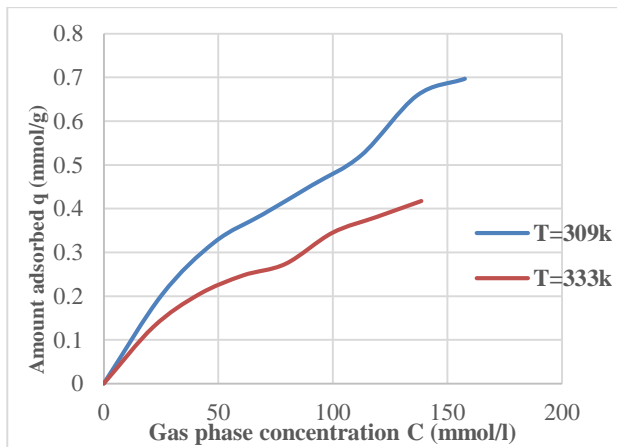


Fig. 10. Adsorption equilibrium isotherm of carbon dioxide on MWCNT-EDA

3.3. Adsorption kinetics (Breakthrough Curves)

1. Effect of feed flow rate

CO₂ flow rate affection the breakthrough curve on raw and functionalized MWCNT is shown in Fig. 11 and Fig. 12. The bed weight is 1.5 g and the flow rate change from 0.5 l/m to 1.5 l/m. The breakthrough curves were modified as the gas flow rates increased, shifting them to a shorter time. Using high flow rates minimizes the contacting time of adsorbate with the adsorbent, which allows adsorption to happen faster and results in an early adsorbate breakthrough. Longer breakthrough periods are also preferred because they reduce the frequency of adsorbent particle regeneration, which has an impact on process energy consumption and costs. This behavior has been brought up by [46, 47]. The standard deviation values are shown in Table 4.

2. Effect of bed weight

The weight of the adsorbent causes varying bed lengths because the adsorption column's diameter remains constant. Short bed lengths decrease the amount of transfer area and minimize the contacting time of the adsorbate with the adsorbent. As shown in Fig. 13 and

Fig. 14, the adsorption capacity for carbon dioxide adsorption increases as bed length increases because an increase in bed length results in an increase in the surface area available for adsorption [48]. The standard deviation values are shown in Table 4.

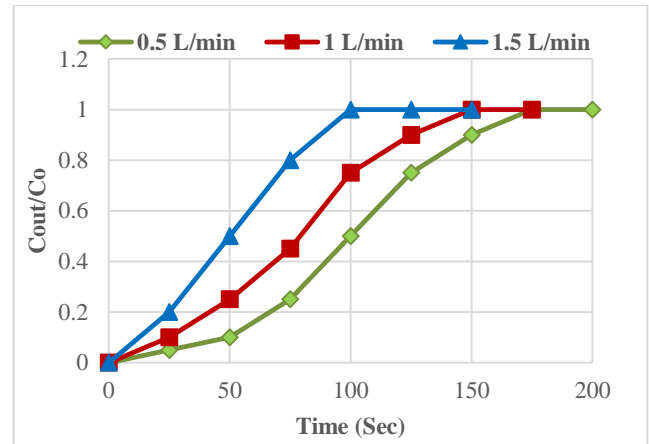


Fig. 11. The effect of feed flow rate on the breakthrough time for (10% CO₂, 90%N₂ at 309K and 1.5 g for MWCNT_s)

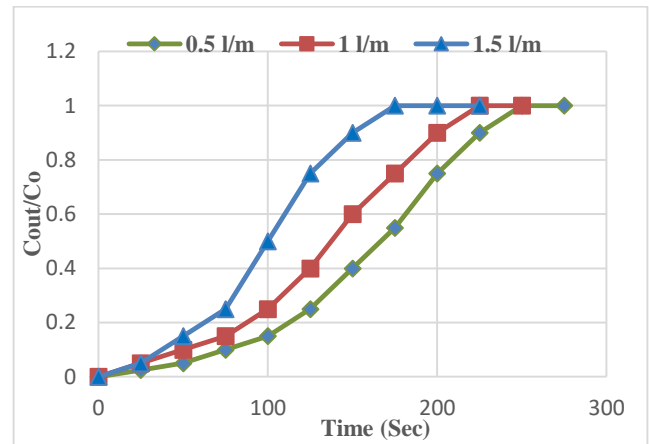


Fig. 12. The effect of feed flow rate on the breakthrough time for (10% CO₂, 90%N₂ at 309K, and 1.5 g for MWCNT-EDA)

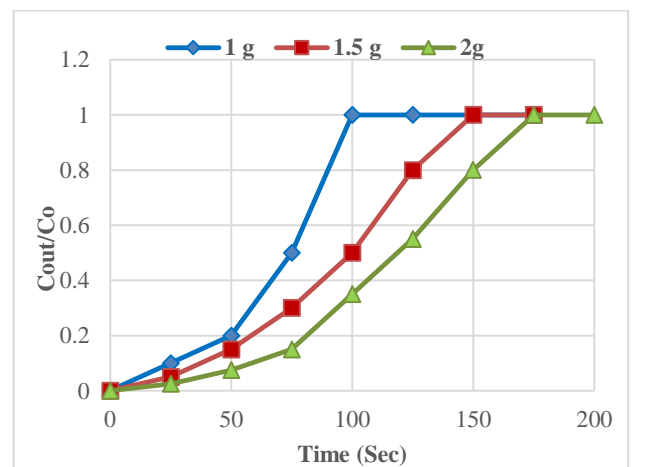


Fig. 13. The effect of bed weight on the breakthrough time for MWCNT_s (10% CO₂, 90%N₂ at 309K, and 0.5 l/min of CO₂)

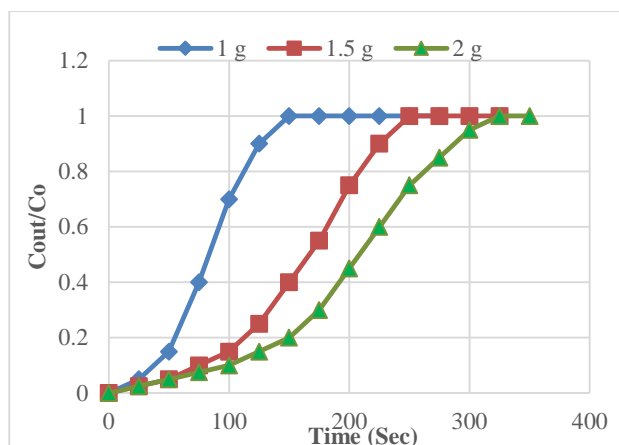


Fig. 14. The effect of bed weight on the breakthrough time for MWCNT-EDA (10% CO₂, 90%N₂ at 309K and 0.5 l/min of CO₂)

Table 4. Standard deviation values for breakthrough curves

sample	0.5 l/m	1 l/m	1.5 l/m	1 g	1.5 g	2 g
MWCNT	0.40	0.397	0.41	0.403	0.384	0.379
MWCNT-EDA	0.367	0.369	0.395	0.412	0.367	0.368

4- Conclusion

Multi-walled carbon nanotubes (MWCNTs) have been functionalized by using a mixture of ethylenediamine and toluene. The SEM and XRD investigations revealed that the MWCNTs have enough strength to withstand amine functionalization and the crystalline structures remain unchanged throughout the functionalization process. Therefore, after the amine alteration, MWCNTs' tubular structure and crystallographic formation weren't damaged. Carboxylic groups have been observed on the surface of CNTs according to FTIR measurements. Additionally, the results show that the structure of MWCNTs contains amine functional groups, which increased MWCNTs' CO₂ adsorption capacity over the whole pressure and temperature range examined from 0.3428 mmol/g to 0.6968 mmol/g. The BET analysis verified that after the modification process, carbon nanotubes' pore volume and specific surface area decreased. Adsorption test results indicated that, regardless of temperature or pressure, MWCNT-EDA had greater CO₂ adsorption capacity than pristine MWCNTs. In addition, CO₂ molecules showed a higher reactivity towards amine groups. Furthermore, the adsorption capability of MWCNT and MWCNT-EDA reduced as the temperature increased. The results have suggested that the Freundlich model fits the experimental data more precisely.

Reference

[1] J. Gutsche, Ł. Muślewski, A. Dzioba, and S. Matyukh, "Identification and analysis of factors influencing climate change in terms of CO₂ emissions," *MATEC Web of Conferences*, 2021, vol. 332, p. 01002, <http://dx.doi.org/10.1051/mateconf/202133201002>

[2] M. S. Khasanova and M. A. Saidulgerieva, "Alternative methods of production and consumption as tools for solving global problems of modern society and implementing the principles of sustainable development," *BIO Web of Conferences*, 2024, vol. 82, p. 05034, <http://dx.doi.org/10.1051/bioconf/20248205034>

[3] K. Saidi and A. Omri, "Reducing CO₂ emissions in OECD countries: Do renewable and nuclear energy matter?," *Progress in Nuclear Energy*, vol. 126, p. 103425, Aug. 2020, <http://dx.doi.org/10.1016/j.pnucene.2020.103425>

[4] K. O. Yoro and M. O. Daramola, "CO₂ emission sources, greenhouse gases, and the global warming effect," *Advances in Carbon Capture*, 2020, pp. 3–28, <http://dx.doi.org/10.1016/b978-0-12-819657-1.00001-3>

[5] S. f. Jaber, Y. M. Abdul wahab, and S. M. Zboon, "Investigation of Factors Affecting the Efficiency of Carbon Dioxide Removal in a Single Perforated Sieve Tray Column," *Journal of Petroleum Research and Studies*, vol. 2, no. 2, pp. 35–43, May 2011, <http://dx.doi.org/10.52716/jprs.v2i2.36>

[6] A. W. Dhuyool and I. K. Shakir, "Carbon Dioxide Capturing via a Randomly Packed Bed Scrubber Using Primary and Poly Amine Absorbents," *Journal of Ecological Engineering*, vol. 24, no. 11, pp. 14–29, Nov. 2023, <https://doi.org/10.12911/22998993/170205>

[7] L. Liu and S. K. Bhatia, "Molecular Simulation of CO₂ Adsorption in the Presence of Water in Single-Walled Carbon Nanotubes," *The Journal of Physical Chemistry C*, vol. 117, no. 26, pp. 13479–13491, Jun. 2013, <http://dx.doi.org/10.1021/jp403477y>

[8] B. I. Waisi, J. T. Majeed, and N. S. Majeed, "Carbon dioxide capture using nonwoven activated carbon nanofiber," *IOP Conference Series: Earth and Environmental Science*, Jun. 2021, vol. 779, no. 1, p. 012056, <http://dx.doi.org/10.1088/1755-1315/779/1/012056>

[9] Y. Su, S. Liu, and X. Gao, "Impact of Impure Gas on CO₂ Capture from Flue Gas Using Carbon Nanotubes: A Molecular Simulation Study," *Molecules*, vol. 27, no. 5, p. 1627, Mar. 2022, <https://doi.org/10.3390/molecules27051627>

[10] A. Hirsch and O. Vostrowsky, "Functionalization of Carbon Nanotubes," *Topics in Current Chemistry*, Jan. 2005, pp. 193–237, <http://dx.doi.org/10.1007/b98169>

[11] L. Liu, D. Nicholson, and S. K. Bhatia, "Exceptionally high performance of charged carbon nanotube arrays for CO₂ separation from flue gas," *Carbon*, vol. 125, pp. 245–257, Dec. 2017, <https://doi.org/10.1016/j.carbon.2017.09.050>

[12] D. J. Babu, M. Lange, G. Cherkashinin, A. Issanin, R. Staudt, and J. J. Schneider, "Gas adsorption studies of CO₂ and N₂ in spatially aligned double-walled carbon nanotube arrays," *Carbon*, vol. 61, pp. 616–623, Sep. 2013, <https://doi.org/10.1016/j.carbon.2013.05.045>

- [13] M. I. Romero-Hermida, J. M. Romero-Enrique, V. Morales-Flórez, and L. Esquivias, "Flue gas adsorption by single-wall carbon nanotubes: A Monte Carlo study," *The Journal of Chemical Physics*, vol. 145, no. 7, Aug. 2016, <https://doi.org/10.1063/1.4961023>
- [14] F. Su, C. Lu, W. Cnen, H. Bai, and J. F. Hwang, "Capture of CO₂ from flue gas via multiwalled carbon nanotubes," *Science of The Total Environment*, vol. 407, no. 8, pp. 3017–3023, Apr. 2009, <https://doi.org/10.1016/j.scitotenv.2009.01.007>
- [15] N. S. Majeed and J. T. Majeed, "Study the Performance of Nanozeolite NaA on CO₂ Gas Uptake," *Iraqi Journal of Chemical and Petroleum Engineering*, vol. 18, no. 2, pp. 57–67, Jun. 2017, <https://doi.org/10.31699/IJCPE.2017.2.5>
- [16] K. Rahimi, S. Riahi, M. Abbasi, and Z. Fakhroueian, "Modification of multi-walled carbon nanotubes by 1,3-diaminopropane to increase CO₂ adsorption capacity," *Journal of Environmental Management*, vol. 242, pp. 81–89, Jul. 2019, <https://doi.org/10.1016/j.jenvman.2019.04.036>
- [17] H. Hu, T. Zhang, S. Yuan, and S. Tang, "Functionalization of multi-walled carbon nanotubes with phenylenediamine for enhanced CO₂ adsorption," *Adsorption*, vol. 23, no. 1, pp. 73–85, Nov. 2016, <https://doi.org/10.1007/s10450-016-9820-y>
- [18] Q. Liu, Y. Shi, S. Zheng, L. Ning, Q. Ye, M. Tao, & Y. He, "Amine-functionalized low-cost industrial grade multi-walled carbon nanotubes for the capture of carbon dioxide," *Journal of Energy Chemistry*, vol. 23, no. 1, pp. 111–118, Jan. 2014, [https://doi.org/10.1016/S2095-4956\(14\)60124-8](https://doi.org/10.1016/S2095-4956(14)60124-8)
- [19] F. V. Ferreira, W. Franceschi, B. R. C. Menezes, F. S. Brito, K. Lozano, A. R. Coutinho and G. P. Thim, "Dodecylamine functionalization of carbon nanotubes to improve dispersion, thermal and mechanical properties of polyethylene based nanocomposites," *Applied Surface Science*, vol. 410, pp. 267–277, Jul. 2017, <https://doi.org/10.1016/j.apsusc.2017.03.098>
- [20] S. Gómez, N. M. Rendtorff, E. F. Aglietti, Y. Sakka, and G. Suárez, "Surface modification of multiwall carbon nanotubes by sulfonitric treatment," *Applied Surface Science*, vol. 379, pp. 264–269, Aug. 2016, <https://doi.org/10.1016/j.apsusc.2016.04.065>
- [21] L. S. Salah, N. Ouslimani, D. Bousba, I. Huynen, Y. Danlée, and H. Aksas, "Carbon Nanotubes (CNTs) from Synthesis to Functionalized (CNTs) Using Conventional and New Chemical Approaches," *Journal of Nanomaterials*, vol. 2021, pp. 1–31, Sep. 2021, <https://doi.org/10.1155/2021/4972770>
- [22] E. Molyanyan, S. Aghamiri, M. R. Talaie, and N. Iraj, "Experimental study of pure and mixtures of CO₂ and CH₄ adsorption on modified carbon nanotubes," *International Journal of Environmental Science and Technology*, vol. 13, no. 8, pp. 2001–2010, Apr. 2016, <http://dx.doi.org/10.1007/s13762-016-0989-0>
- [23] J. M. Ngoy, N. Wagner, L. Riboldi, and O. Bolland, "A CO₂ Capture Technology Using Multi-walled Carbon Nanotubes with Polyaspartamide Surfactant," *Energy Procedia*, vol. 63, pp. 2230–2248, 2014, <https://doi.org/10.1016/j.egypro.2014.11.242>
- [24] M.-S. Lee, S.-Y. Lee, and S.-J. Park, "Preparation and characterization of multi-walled carbon nanotubes impregnated with polyethyleneimine for carbon dioxide capture," *International Journal of Hydrogen Energy*, vol. 40, no. 8, pp. 3415–3421, Mar. 2015, <https://doi.org/10.1016/j.ijhydene.2014.12.104>
- [25] S. Khalili, A. A. Ghoreyshi, M. Jahanshahi, and K. Pirzadeh, "Enhancement of Carbon Dioxide Capture by Amine-Functionalized Multi-Walled Carbon Nanotube," *CLEAN – Soil, Air, Water*, vol. 41, no. 10, pp. 939–948, May 2013, <https://doi.org/10.1002/clen.201200339>
- [26] M. Irani, A. T. Jacobson, K. A. M. Gasem, and M. Fan, "Modified carbon nanotubes/tetraethylenepentamine for CO₂ capture," *Fuel*, vol. 206, pp. 10–18, Oct. 2017, <https://doi.org/10.1016/j.fuel.2017.05.087>
- [27] A. Maleki, U. Hamesadeghi, H. Daraei, B. Hayati, F. Najafi, G. McKay, & R. Rezaee, "Amine functionalized multi-walled carbon nanotubes: Single and binary systems for high capacity dye removal," *Chemical Engineering Journal*, vol. 313, pp. 826–835, Apr. 2017, <https://doi.org/10.1016/j.cej.2016.10.058>
- [28] S. S. Narwade, S. M. Mali, and B. R. Sathe, "Amine-functionalized multi-walled carbon nanotubes (EDA-MWCNTs) for electrochemical water splitting reactions," *New Journal of Chemistry*, vol. 45, no. 8, pp. 3932–3939, 2021, <https://doi.org/10.1039/D0NJ05479H>
- [29] X. Zhong, X. Zhang, X. Sun, B. Liu, Y. Kuang, And J. Chen, "Pt and Pt-Ru Nanoparticles Dispersed on Ethylenediamine Grafted Carbon Nanotubes as New Electrocatalysts: Preparation and Electrocatalytic Properties for Ethanol Electrooxidation," *Chinese Journal of Chemistry*, vol. 27, no. 1, pp. 56–62, Jan. 2009, <https://doi.org/10.1002/cjoc.200990026>
- [30] Z. Zhao, Z. Yang, Y. Hu, J. Li, and X. Fan, "Multiple functionalization of multi-walled carbon nanotubes with carboxyl and amino groups," *Applied Surface Science*, vol. 276, pp. 476–481, Jul. 2013, <https://doi.org/10.1016/j.apsusc.2013.03.119>
- [31] S. Shukrullah, M. Y. Naz, N. M. Mohamed, K. A. Ibrahim, N. M. AbdEl-Salam, and A. Ghaffar, "CVD Synthesis, Functionalization and CO₂ Adsorption Attributes of Multiwalled Carbon Nanotubes," *Processes*, vol. 7, no. 9, p. 634, Sep. 2019, <https://doi.org/10.3390/pr7090634>
- [32] M. M. Gui, Y. X. Yap, S.-P. Chai, and A. R. Mohamed, "Multi-walled carbon nanotubes modified with (3-aminopropyl triethoxysilane) for effective carbon dioxide adsorption," *International Journal of Greenhouse Gas Control*, vol. 14, pp. 65–73, May 2013, <https://doi.org/10.1016/j.ijggc.2013.01.004>

- [33] L. Thi Mai Hoa, "Characterization of multi-walled carbon nanotubes functionalized by a mixture of HNO₃/H₂SO₄," *Diamond and Related Materials*, vol. 89, pp. 43–51, Oct. 2018, <https://doi.org/10.1016/j.diamond.2018.08.008>
- [34] N. Janudin, L. C. Abdullah, N. Abdullah, F. Md Yasin, N. M. Saidi, and N. A. Mohd Kasim, "Comparison and Characterization of Acid Functionalization of Multi Walled Carbon Nanotubes Using Various Methods," *Solid State Phenomena*, vol. 264, pp. 83–86, Sep. 2017, <https://doi.org/10.4028/www.scientific.net/SSP.264.83>
- [35] Z. Zhou, "The Investigation of Functionalized Carbon Nanotubes for the Carbon Dioxide Capture and Ethane Oxidative Dehydrogenation Catalysts," 2020. Theses and Dissertations. 8417, *BYU ScholarsArchive*.
- [36] C. Lu, H. Bai, B. Wu, F. Su, and J. F. Hwang, "Comparative Study of CO₂ Capture by Carbon Nanotubes, Activated Carbons, and Zeolites," *Energy & Fuels*, vol. 22, no. 5, pp. 3050–3056, Jul. 2008, <https://doi.org/10.1021/ef8000086>
- [37] G. D. Vuković, Marinković, A. D., Čolić, M., Ristić, M. Đ., Aleksić, R., Perić-Grujić, A. A., & Uskoković, P. S, "Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes," *Chemical Engineering Journal*, vol. 157, no. 1, pp. 238–248, Feb. 2010, <https://doi.org/10.1016/j.cej.2009.11.026>
- [38] M. R. Mello, D. Phanon, G. Q. Silveira, P. L. Llewellyn, and C. M. Ronconi, "Amine-modified MCM-41 mesoporous silica for carbon dioxide capture," *Microporous and Mesoporous Materials*, vol. 143, no. 1, pp. 174–179, Aug. 2011, <https://doi.org/10.1016/j.micromeso.2011.02.022>
- [39] D. J. N. Subagyono, Z. Liang, G. P. Knowles, and A. L. Chaffee, "Amine modified mesocellular siliceous foam (MCF) as a sorbent for CO₂," *Chemical Engineering Research and Design*, vol. 89, no. 9, pp. 1647–1657, Sep. 2011, <https://doi.org/10.1016/j.cherd.2011.02.019>
- [40] J. Wei, L. Liao, Y. Xiao, P. Zhang, and Y. Shi, "Capture of carbon dioxide by amine-impregnated as-synthesized MCM-41," *Journal of Environmental Sciences*, vol. 22, no. 10, pp. 1558–1563, Oct. 2010, [https://doi.org/10.1016/S1001-0742\(09\)60289-8](https://doi.org/10.1016/S1001-0742(09)60289-8)
- [41] S. Hong, C. Wen, J. He, F. Gan, and Y. S. Ho, "Adsorption thermodynamics of Methylene Blue onto bentonite," *Journal of Hazardous Materials*, vol. 167, no. 1–3, pp. 630–633, Aug. 2009, <https://doi.org/10.1016/j.jhazmat.2009.01.014>
- [42] S. Khalili, A. A. Ghoreyshi, M. Jahanshahi, and K. Pirzadeh, "Enhancement of Carbon Dioxide Capture by Amine-Functionalized Multi-Walled Carbon Nanotube," *CLEAN – Soil, Air, Water*, vol. 41, no. 10, pp. 939–948, May 2013, <https://doi.org/10.1002/clen.201200339>
- [43] S. J. Allen, G. McKay, and J. F. Porter, "Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems," *Journal of Colloid and Interface Science*, vol. 280, no. 2, pp. 322–333, Dec. 2004, <https://doi.org/10.1016/j.jcis.2004.08.078>
- [44] C. L. Hsueh, Y.-W. Lu, C.-C. Hung, Y.-H. Huang, and C.-Y. Chen, "Adsorption kinetic, thermodynamic and desorption studies of C.I. Reactive Black 5 on a novel photoassisted Fenton catalyst," *Dyes and Pigments*, vol. 75, no. 1, pp. 130–135, Jan. 2007, <https://doi.org/10.1016/j.dyepig.2006.05.020>
- [45] Q. Fu et al., "Equilibrium, kinetic and thermodynamic studies on the adsorption of the toxins of *Bacillus thuringiensis* subsp. *kurstaki* by clay minerals," *Applied Surface Science*, vol. 255, no. 8, pp. 4551–4557, Feb. 2009, <https://doi.org/10.1016/j.apsusc.2008.11.075>
- [46] Q. Ye, J. Jiang, C. Wang, Y. Liu, H. Pan, and Y. Shi, "Adsorption of Low-Concentration Carbon Dioxide on Amine-Modified Carbon Nanotubes at Ambient Temperature," *Energy & Fuels*, vol. 26, no. 4, pp. 2497–2504, Mar. 2012, <https://doi.org/10.1021/ef201699w>
- [47] S. Yasyerli, G. Dogu, I. Ar, and T. Dogu, "Activities of Copper Oxide and Cu–V and Cu–Mo Mixed Oxides for H₂S Removal in the Presence and Absence of Hydrogen and Predictions of a Deactivation Model," *Industrial & Engineering Chemistry Research*, vol. 40, no. 23, pp. 5206–5214, Aug. 2001, <https://doi.org/10.1021/ie0010621>
- [48] A. Naghizadeh, S. Nasserli, A. H. Mahvi, R. Nabizadeh, R. R. Kalantary, and A. Rashidi, "Continuous adsorption of natural organic matters in a column packed with carbon nanotubes," *Journal of Environmental Health Science and Engineering*, vol. 11, no. 1, Jul. 2013, <https://doi.org/10.1186/2052-336X-11-14>

التقاط ثاني أكسيد الكربون باستخدام أنابيب نانوية كربونية متعددة الجدران

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الخلاصة

ثاني أكسيد الكربون (CO_2) هو العامل الرئيسي الذي يعتبر المسؤول عن ظاهرة الاحتباس الحراري. تعتبر تكنولوجيا احتجاز ثاني أكسيد الكربون قضية مهمة لتقليل انبعاثات الغازات الدفيئة وبالتالي تأثير تغير المناخ. في هذه الدراسة تم تفعيل الأنابيب النانوية الكربونية متعددة الجدران (MWCNTs) بواسطة خليط من الإيثيلين ثنائي الأمين. تم تحليل مجموعات الوظائف السطحية MWCNTs والخصائص الفيزيائية بواسطة (XRD)، (FTIR)، (SEM)، والمساحة السطحية (BET). تم تحديد قدرة امتصاص ثاني أكسيد الكربون بواسطة التقنية الحجمية عند درجات حرارة ٣٠٩ إلى ٣٣٣ درجة كلفن وضغوط من ١ إلى ٧ بار. تمت الإشارة إلى الطبيعة الباعثة للحرارة لعملية الامتزاز من خلال انخفاض قدرات امتصاص ثاني أكسيد الكربون عبر MWCNTs و MWCNTs-EDA مع ارتفاع درجة الحرارة. يشير هذا إلى أن MWCNTs-EDA عبارة عن مادة ممتزة ممتازة في درجة حرارة منخفضة لالتقاط ثاني أكسيد الكربون. أظهرت النتائج أن ٠,٦٩٦٨ ملي مول/غم من ثاني أكسيد الكربون تم امتزازه بواسطة MWCNT-EDA عند ٣٠٩ درجة كلفن بينما تم امتزاز MWCNT الخام فقط ٠,٣٤٢٨ ملي مول/غم في نفس الحالة. لقد تغيرت الخصائص الفيزيائية والكيميائية للأنابيب النانوية الكربونية بعد عملية التشغيل، مما يعزز امتصاص الأنابيب النانوية الكربونية لغاز ثاني أكسيد الكربون. وفقاً لنتائج الدراسة، أثناء عملية التشغيل، أنشأت مجموعات الأمين المرتبطة بالأسطح الكربونية مواقع لامتصاص ثاني أكسيد الكربون على الأنابيب النانوية الكربونية متعددة الجدران، مما يزيد من قدرة الامتزاز للأنابيب MWCNT. بالإضافة إلى ذلك، مع زيادة درجة الحرارة، انخفضت قدرة الامتزاز لكل من الممتزات MWCNT و MWCNT-EDA. أظهرت النتائج أن نموذج Freundlich ملائم بشكل أفضل مع النتائج العملية.

الكلمات الدالة: انابيب الكربون النانوية متعددة الجدران، التفعيل الاميني، إيثيلين ثنائي أمين، امتزاز ثاني أكسيد الكربون، المجاميع الوظيفية.