Carbon dioxide capture using nonwoven activated carbon nanofiber

B I Waisi, J T Majeed and N S Majeed
Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad, Iraq
*Corresponding author Email: basmawaisi@coeng.uobaghdad.edu.iq

Abstract. The adsorption isotherms and kinetic uptakes of Carbon Dioxide (CO2) on fabricated electrospun nonwoven activated carbon nanofiber sheets were investigated at two different temperatures, 308 K and 343 K, over a pressure range of 1 to 7 bar. The activated carbon nanofiber-based on polymer (PAN) precursor was fabricated via electrospinning technique followed by thermal treatment to obtain the carbbonous nanofibers. The obtained data of CO2 adsorption isotherm was fitted to various models, including Langmuir, Freundlich, and Temkin. Based on correlation coefficients, the Langmuir isotherm model presented the best fitting with CO2 adsorption isotherms' experimental data. Raising the equilibrium adsorption temperature decreased the total amount adsorbed, indicating an exothermic adsorption process of CO2 on CNF and ACNF. It was also observed from the adsorption kinetic data that increasing the flow rate decreased the breakthrough point and the saturation time in the adsorption column. The efficiency of CO2 adsorption on ACNF (82%) was better than that on nonwoven carbon nanofiber (CNF) (67%) due to the high specific surface area and pore volume of ACNF (375 m2/g, 0.051 m3/g) comparing to CNF (20 m2/g, 0.0167 m3/g).

Keywords: Carbon dioxide, Activated carbon nonwoven nanofibers, Adsorption, Isotherm study, and Kinetic study.

1. Introduction
The most massive greenhouse gas emissions due to human activities are from burning fossil fuels for electricity, heat, and transportation. Carbon dioxide (CO2) is a major anthropogenic greenhouse gas, contributing to more than 60% of global warming. Also, about 40% of the world's current CO2 emission has been emitted by power generation plants [1,2]. Furthermore, relevant emissions are growing exponentially due to the increase in global energy demand. As a result, CO2 captured from large stationary sources has recently attracted great attention to reduce the significant harm of CO2 emission in the environment and the climate system [3].

Several techniques have been proposed to capture CO2 including chemical absorption, physical absorption, cryogenics, and membrane separation [4][5]. Accordingly, over the last decade, new technologies and materials for CO2 capture and storage have been gaining increasing attention. The adsorption method using solid sorbents is one of the most promising ways to reduce the potential energy and possibility of regenerating the used adsorbents [6–8]. In the last decade, adsorptive CO2 removal processes employed various solid adsorbents such as metal–organic frameworks (MOFs) [4][9][10], zeolites [7][11], and activated carbons [3][12].

Although the activated carbon is one of the promising adsorbent materials for CO2 adsorption due to its availability, low cost, high surface area, and high thermal stability, its usage is restricted by a high-pressure gas treatment [13]. Recent researches focused on how carbon adsorption and selectivity can be improved by enhancing the pore structure and surface properties using various precursors or processing systems.

Nonwoven activated carbon nanofibers (ACNF) is a unique nanomaterial form of activated carbon that is used in several applications such as energy storage in batteries, sensors, catalysts, water treatment, and...
fuel cells due to its high porosity and its accessible large surface area combined with its nonwoven membrane structure [14][15]. Besides, an activated carbon nonwoven nanofibers membrane is a mesoporous material with high porosity to facilitate rapid diffusion of the pollutants and offers surface modification scope to enhance specific contaminant adsorption [16]. As a result, ACNF was used as an adsorbent for removing emulsified oil [17] and methylene blue dye [18]. Also, ACNF was applied in the air-cleaning system as a filter membrane for formaldehyde adsorption [19] and volatile organic compounds [20].

Therefore, this carbon nanofiber sheet is typically fabricated via electrospinning technology using a specific type of polymers as a precursor. The electrospinning technique has been widely used to fabricate nonwoven polymeric nanofibers membranes under electrostatic forces to drive the fiber-forming process. Polyacrylonitrile (PAN) is the most common polymers used in synthetic carbon nanofibers due to its heat resilience, low cost, and high carbon yield [17][21]. The fabricated polymeric nonwoven nanofibers membranes can be converted to carboneses ones after passing through several thermal decomposition steps, including carbonization and activation. The optimized processing conditions to produce nonwoven activated carbon with strong mechanical efficiency, high specific surface area, and high hydrophobicity have been documented in our previous work [14].

The purpose of this work is to explore the adsorption capacity of CO2 on this new form of the activated carbon adsorbent sheet (ACNF). The adsorption equilibrium and kinetic are investigated to optimize the performance of the fabricated adsorbents. The equilibrium adsorption of CO2 on ACNF and CNF was done at 308 and 343 K, while the kinetic adsorption was done at different gas flow rates at pressure up to 7 MPa. The efficiency of ACNF was compared with CNF.

2. Materials and methods

2.1. Materials

Carbon dioxide (purity of 99.70 (0.01 vol. %)) and nitrogen (purity of 99.99 (0.001 vol. %)) were supplied from the Gulf gas company located in Baghdad to prepare the adsorbate gas mixture. Polyacrylonitrile (PAN) powder (MW avg. 150.000) was from Scientific Polymer Products Inc., while Dimethylformamide (DMF) solvent was purchased from Acros Organics.

2.2. Adsorbent fabrication

A precursor solution of 14 wt.% PAN in DMF was prepared by mixing a specific amount of Polyacrylonitrile (PAN) with dimethylformamide (DMF) under constant stirring at 60 °C for two hours. The precursor solution was used to fabricate the nonwoven activated carbon nanofibers via an electrospinning system, as explained in our previous work [17]. Briefly, a syringe pump (KD Scientific) was used to dispense the solution at a flow rate of 1ml/h from a 20-gauge needle. The collector was a rotating grounded drum at 70 rpm and humidity of 20 ± 5%. The collection distance was 17 cm, with a voltage difference of 24 kV. To convert the precursor nanofibers to carboneses ones, they need to pass through three heat treatment steps. Firstly, the precursor nanofibers were stabilized in a muffle furnace (Carbolite) in an air atmosphere at 280 °C for one hour. Secondly, the carbonization step was done by a tube furnace (Lindberg Blue M, Thermo Scientific) in an inert nitrogen atmosphere at 600 °C for two hours producing nonwoven carbon nanofibers (CNF). Finally, the activation step was done by the same furnace at 750 °C for 1 hour with introducing 60 g/h of steam to produce the nonwoven activated carbon nanofiber (ACNF).

2.3. Adsorbents characterization

The surface morphologies of ACNF and CNF were explored using field emission scanning electron microscopy (FESEM, JEOL 6335F). A Physisorption Analyzer (Micromeritics Instrument Corporation) was used for obtaining the Nitrogen adsorption/desorption isotherms and the BET specific surface area of
the adsorbent samples. Besides, the sample’s surfaces' hydrophobicity was specified by evaluating their contact angle with water (water droplet volume of \(5 \pm 0.5 \, \mu\text{l}\)), using a contact angle goniometer (CAM 101 series).

2.4. Adsorption isotherm method

The schematic diagram shown in Fig. 1 describes the used system for investigating the carbonized nanofibers (ACNF and CNF) for CO\(_2\) uptake; more details are explained in our previous work [17]. Briefly, the system consists of two identical iron cylinders (reservoir and adsorption chambers) with a volume of 20 cm\(^3\) for each. The gas pressure was monitored by a gauge (Helicoid gauge, 1 % accuracy). The chambers were put in a water bath with an electrical hot plate to maintain a constant temperature in the enclosure. The gas cylinder of CO\(_2\) was connected to a regulator pressure to supply the gas feed to the system. After packing the nanofibers adsorbents in the adsorption chamber, the carbonized nanofibers were regenerated using a vacuum pump (Stuart, RE3022C) to evacuate the system (-100 Kpa) for 10 minutes.

The amount of adsorbed CO\(_2\) at equilibrium can be determined according to the mass balance [7] using the following equation:

\[
q = \frac{(C_{rt} - C_{rf})V_r - C_{rf}V_a}{W}
\]  

In which \(q\) is the adsorbed CO\(_2\) at equilibrium (mmol/g). The initial and final concentrations (mmol/l) in the reservoir and adsorber vessels are \(C_{rt}\) and \(C_{rf}\), respectively. The volume of reservoir and adsorber vessels are \(V_r\) and \(V_a\), respectively. The values of \(W\) and \(\varepsilon_0\) are the weight of the adsorbent in the adsorber vessel (g) and the overall bed void fraction, respectively.

**Figure 1:** Schematic diagram of the apparatus used for adsorption equilibrium measurement

2.5. Adsorption kinetics method

In gas adsorption units, evaluating the velocity of gas diffusion into the porous structure helps understand the adsorption kinetic over a pressure range of 1 to 7 bar. Thus, diluted breakthrough experiments were used to predict the multicomponent adsorption equilibrium [6]. A schematic diagram in Fig. 2 explained the used system for doing the adsorption kinetic. One gram of the nanofibers adsorbent was packed into the adsorption column, which was an iron column of 625 cm\(^3\) volume, Gauze plates of mesh were sited at both ends of the column to hold the packing in position. Before each experiment, the adsorbent material was evacuated under a vacuum pump for 1 hr at the required temperature of 308 K and 343 K. To study the isotherm of CO\(_2\), a flow of gas mixture (10% CO\(_2\) and 90% N\(_2\)) was introduced via a control valve to the
mixer column and then to the adsorber vessel where the adsorption process accurses. A rotameter measured the quantity of inlet flow rate (5-20 L/min), and then the outlet CO$_2$ concentration was analyzed by a gas analyzer (type Biogs 5000 Geotech, UK) periodically (each 5 sec) until reaching equilibrium.

Figure 2. Schematic diagram of the apparatus used for adsorption kinetics

3. Results and discussion

3.1. Adsorbent characterizations

The shown images in Figure 3 a and b represented the surface morphologies of the nonwoven carbon nanofiber (CNF) and activated carbon nanofiber (ACNF), respectively. The results revealed that both CNF and ACNF sheets have long and continuous tubes in nanoscale sizes with an average fiber diameter of 350 and 250 nm, respectively. The SEM images showed the nanofibers had been fabricated in a nonwoven structure creating a high porosity of CNF (0.92) and ACNF (0.96), one of the desired characterizations in suitable adsorbents [17].

Figure 4 shows the average pore diameter relation with the pore volume for the fabricated adsorbents according to the BJH adsorption model. The results showed that 80 % and 50 % of the overall pores in ACNF and CNF are micro and mesoporous (pore diameter between 2 and 100 nm), the desired characterization of the good adsorbent material. The BET specific surface area and BJH overall pore volume of the used adsorbents are shown in Table1. The obtained ACNF and CNF sheets showed high hydrophobicity (126° and 133°, respectively), as shown in Figure 5 a and b. The hydrophobicity surface is the desired characterization in the adsorbent used to trap CO$_2$ molecules due to repelling the diffusion of water molecules from the environment [22].
Figure 3 the SEM images of the external surface of the different adsorbents (a) CNF and (b) ACNF

Figure 4. The pore size distribution of the prepared ACNF and CNF sheets

| Adsorbent type | Surface area (m²/g) | Overall pore volume (cm³/g) |
|---------------|---------------------|-----------------------------|
| ACNF          | 375                 | 0.051037                    |
| CNF           | 20                  | 0.016684                    |

Figure 5 The images of contact angle measurement of the fabricated adsorbent (a) ACNF and (b) CNF
3.2. Adsorption isotherm
The adsorption isotherm is essential to evaluate the selectivity of the used adsorbents to separate CO₂ from CO₂/N₂ mixtures and describe the CO₂ adsorption mechanism of the adsorbent [3]. The adsorption isotherm was studied at 308 and 343 K to investigate the effect of temperature on CO₂ adsorption using CNF and ACNF, as shown in Fig. 6 and 7. The results showed that increasing the equilibrium adsorption temperature decreases the total amount adsorbed on both CNF and ACNF, indicating exothermic adsorption. With the increase in temperature, the adsorbed CO₂ becomes unstable on the activated carbon nanofiber surface because of increased molecular diffusion, which leads to more desorption of CO₂ molecules. This behavior has also been mentioned by previous studies [23].

Figure 6 Adsorption equilibrium isotherm of carbon dioxide on (a) CNF and (b) ACNF
Amongst the several available isothermal models, Langmuir, Freundlich, and Temkin models were applied to evaluate the interaction of CO₂ adsorbed on the fabricated ACNF and CNF. The Langmuir model suggests that adsorption occurs at some uniform locations making monolayer adsorption on the homogeneous surface of the adsorbent expressed in the following equation [17]:

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]

(2)

Where \( q_e \) (mmol/g) is the adsorbed amount at equilibrium, while \( q_m \) (mmol/g) is the maximum adsorbed amount corresponding to complete coverage of the surface. \( K_L \) (L/mmol) is the Langmuir equilibrium constant. \( C_e \) (mmol/l) is the adsorbate concentration at the equilibrium.

The Freundlich model suggests that the adsorbed molecules interact with each other, creating a multi-layer on the adsorbent's heterogeneous surfaces, and it is defined as the following empirical equation [17]:

\[ q_e = K_F C_e^{\frac{1}{n}} \]

(3)

Where \( K_F \) and \( n \) are the Freundlich equilibrium constant (L/mmol) and the degree of non-linearity, respectively.

The Temkin isotherm model assumes that the binding energies are uniformly distributed of the binding energies up to the maximum binding energy. Also, by this model, the heat of gas adsorption is assumed to be linearly decreased with increasing the equilibrium adsorption capacity. The Temkin equation is expressed in the following equation [7]:

\[ q_e = \beta \ln \ln K_T + \beta \ln \ln C_e \]

(4)

Where the terms of \( \beta \) and \( K_T \) are the heat of adsorption (J/mol) and the Temkin isotherm constant related to equilibrium energy (L/mmol), respectively.

Values of the isotherm constants and error analysis (R²) obtained from the plot of each model at 308 °C are listed in Table (2), which shows that for carbon dioxide adsorption on CNF and ACNF; the highest correlation coefficient (R²) value was for the Langmuir isotherm as compared to that of both Freundlich and Temkin ones at 308 K. Langmuir isotherm describes adsorbate-adsorbent systems in which the extent of adsorbate coverage is limited to one molecular layer.

| Isotherms | Parameters | CNF | ACNF |
|-----------|------------|-----|------|
| Langmuir  | \( q_m \)  | 1.4620 | 0.8557 |
|           | \( K_L \)  | 0.0013 | 0.0019 |
|           | \( R^2 \)  | 0.9964 | 0.9903 |
| Freundlich| \( K_F \)  | 0.0027 | 0.0023 |
|           | \( n \)    | 1.1099 | 1.1233 |
|           | \( R^2 \)  | 0.9856 | 0.9870 |
| Temkin    | \( K_T \)  | 0.0616 | 0.0717 |
|           | \( \beta \) | 0.0928 | 0.0489 |
|           | \( R^2 \)  | 0.9827 | 0.9189 |
3.3. Adsorption kinetics
The effect of the CO₂ flow rate on the breakthrough curve using CNF and ACNF is shown in Fig. 6 a and b. It can be seen that if the flow rate of the feed increased, it decreases breakthrough time and, therefore, the amount of CO₂ that can be adsorbed. Also, increasing the flow rates of CO₂ from 0.5 to 2 L/min decreased the required time for column saturation from 120 to 60 sec (using 1 g of CNF) and from 210 to 90 sec (using 1 g of ACNF). The longer saturation time of the column with ACNF is related to the high specific surface area of ACNF compared to CNF, which means more available adsorption sites in ACNF. At a higher flow rate, the breakthrough curve became steeper, indicating low utilization of the adsorbents' surface area in the column due to the short contact time between CO₂ and the adsorbate resulting in early breakthrough time. The long breakthrough time is desired to decrease the need for adsorbent regeneration, which means less consumed energy and less process operation cost.

![Graph](a)

![Graph](b)

Figure 7. The effect of feed flow rate on the breakthrough curve using (a) CNF and (b) ACNF

4. Conclusions
In sum, Electrospun activated carbon nonwoven nanofibers were successfully fabricated via PAN electrospinning, followed by heat treatment to convert the precursor nanofibers to carbonaceous ones (an
average fiber diameter of 250 nm) as an adsorbent sheet. The characterization analysis of the prepared activated carbon nonwoven nanofibers (ACNF) showed a high accessible specific surface area (375 m²/g) and a hydrophobic surface with a micro- and mesoporous structure. The adsorbents' CO₂ adsorption capacity was studied using an adsorber chamber under various temperatures and inlet CO₂ flow rates to understand the adsorption isotherms and kinetics on ACNF. Also, the adsorption efficiency of ACNF was compared with CNF. The results revealed the highest removal efficiency of ACNF 82%, compared to that of CNF 67%. The adsorption isotherm data were well fitted with the Langmuir isotherm at 308 K, indicating a monolayer adsorption mechanism. Increasing the temperature resulted in lower adsorption of CO₂, indicating an exothermic adsorption process. The adsorption kinetics showed that increasing the inlet gas flow rate decreased the breakthrough time and the column's saturation time.

References
[1] Ruddiman W F, Kutzbach J E and Vavrus S J 2011, Can natural or anthropogenic explanations of late Holocene CO₂ and CH₄ increases be falsified? The Holocene, 21(5): 865-879. doi:10.1177/0959683610387172.
[2] Albo J, Luis P and Irabien A, 2010, Carbon Dioxide Capture from Flue Gases Using a Cross-Flow Membrane Contactor and the Ionic Liquid 1-Ethyl-3-methylimidazolium Ethylsulfate, Industrial & Engineering Chemistry Research, 49, 11045–51.
[3] Drage T C, Kozynchenko O, Pevida C, Plaza M G, Rubiera F, Pis J J, Snape C E and Tennison S 2009. Developing activated carbon adsorbents for pre-combustion CO₂ capture. Energy Procedia, 1(1):599-605. doi: 10.1016/j.egypro.2009.01.079.
[4] Lu C, Bai H, Wu B, Su F and Hwang J F 2008. Comparative study of CO₂ capture by carbon nanotubes, activated carbons, and zeolites. Energy & Fuels, 22(5):3050-6.
[5] White C M, Strazisar B R, Granite E J, Hoffman J S and Pennline H W 2003 Separation and capture of CO₂ from large stationary sources and sequestration in geological formations—coalbeds and deep saline aquifers. Journal of the Air & Waste Management Association, 53(6):645-715. doi:10.1080/10473289.2003.10466206.
[6] Shen C, Grande C A, Li P, Yu J and Rodrigues A E 2010 Adsorption equilibria and kinetics of CO₂ and N₂ on activated carbon beads. Chemical Engineering Journal, 160(2):398-407. doi: 10.1016/j.cej.2009.12.005.
[7] Majeed N S and Majeed J T 2017 Study the Performance of Nanozeolite NaA on CO₂ Gas Uptake. Iraqi Journal of Chemical and Petroleum Engineering, 18(2):57-67.
[8] Abdeen F R, Mel M, Jami M S, Ihsan S I and Ismail A F 2016 A review of chemical absorption of carbon dioxide for biogas upgrading. Chinese Journal of Chemical Engineering, 24(6):693-702.
[9] Krishna R and van Baten J M 2012 A comparison of the CO₂ capture characteristics of zeolites and metal–organic frameworks. Separation and Purification Technology, 87, pp.120-6. doi: 10.1016/j.seppur.2011.11.031.
[10] Liu J, Thallapally P K, McGrail B P, Brown D R and Liu J 2012. Progress in adsorption-based CO₂ capture by metal–organic frameworks. Chemical Society Reviews, 41(6):2308-22. doi:10.1039/c1cs15221a.
[11] Lee S C, Hsieh C C, Chen C H, Chen Y S 2013 CO₂ Adsorption by Y-Type Zeolite Impregnated with Amines in Indoor Air, Aerosol and Air Quality Research, 13, 360–6. doi:10.4209/aaqr.2012.05.0134.
[12] Saha B B, Jribi S, Koyama S and El-Sharkawy I I 2011 Carbon dioxide adsorption isotherms on activated carbons. Journal of Chemical & Engineering Data, 56(5):1974-81. doi:10.1021/je100973t.
[13] Yu C H, Huang C H and Tan C S, 2012 A review of CO₂ capture by absorption and
adsorption. *Aerosol and Air Quality Research*, **12**(5):745-69. doi:10.4209/aaqr.2012.05.0132.

[14] Waisi B I, Manickam S S, Benes N E, Nijmeijer A and McCutcheon J R, 2019. Activated Carbon Nanofiber Nonwovens: Improving Strength and Surface Area by Tuning Fabrication Procedure. *Industrial & Engineering Chemistry Research*, **58**(10):4084-9. https://pubs.acs.org/doi/10.1021/acs.iecr.8b05612.

[15] Waisi B I, Al-Jubouri S M and McCutcheon J R 2019. Fabrication and Characterizations of Silica Nanoparticle Embedded Carbon Nanofibers. *Industrial & Engineering Chemistry Research*, **58**(11):4462-7. doi: 10.1021/acs.iecr.8b05825.

[16] Zhang J, Wang S, Xu M, Wang Y, Zhu B, Zhang S, Huang W and Wu S 2009. Hierarchically porous ZnO architectures for gas sensor application. *Crystal Growth and Design*, **9**(8):3532-7.

[17] Waisi B I, Arena J T, Benes N E, Nijmeijer A and McCutcheon J R 2020. Activated carbon nanofiber nonwoven for removal of emulsified oil from water. *Microporous and Mesoporous Materials*, **296**, p.109966.

[18] Ibupoto A S, Qureshi U A, Ahmed F, Khatri Z, Khatri M, Maqsood M, Brohi R Z and Kim I S, 2018. Reusable carbon nanofibers for efficient removal of methylene blue from aqueous solution. *Chemical Engineering Research and Design*, **136**, pp.744-52. doi:10.1016/j.cherd.2018.06.035.

[19] Lee K J, Shiratori N, Lee G H, Miyawaki J, Mochida I, Yoon S H and Jang J 2010. Activated carbon nanofiber produced from electrospun polyacrylonitrile nanofiber as a highly efficient formaldehyde adsorbent. *Carbon*, **48**(15):4248-55. doi: 10.1016/j.carbon.2010.07.034.

[20] Jahangiri M, Adl J, Shahtaheri S J, Rashidi A, Ghorbanali A, Kakooe H, Forushani A R and Ganjali M R, 2013 Preparation of a new adsorbent from activated carbon and carbon nanofiber (AC/CNF) for manufacturing organic-vacbopur respirator cartridge. *Iranian journal of environmental health science & engineering*, **10**(1):15.

[21] Mataram A, Ismail A F, Abdullah M S, Ng B C and Matsuura T 2011. A review of assembled polyacrylonitrile-based carbon nanofiber prepared electrospinning process. *International Journal of Nanoscience*, **10**(03):455-69. doi:10.1142/S0219581X11008228.

[22] Ding N, Li H, Feng X, Wang Q, Wang S, Ma L, Zhou J and Wang B 2016. Partitioning MOF-5 into confined and hydrophobic compartments for carbon capture under humid conditions. *Journal of the American Chemical Society*, **138**(32):10100-3. doi:10.1021/jacs.6b0605.

[23] Pham T, Lee B, Kim J and Lee C 2016 Enhancement of CO2 Capture by Using Synthesized Nano-Zeolite. *Journal of the Taiwan Institute of Chemical Engineers* 0: 1–7. https://doi.org/10.1016/j.jtice.2016.04.026.