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Experimental Study of Adsorption on Activated Carbon for CO₂ Capture

Hesham G. Ibrahim and Mohamed A. Al-Meshragi

Abstract

The adsorption of carbon dioxide (CO₂) on activated carbon (AC) prepared from olive trees has been investigated by using a fixed bed adsorption apparatus. The adsorption equilibrium and breakthrough curves were determined at different temperatures 30, 50, 70, and 90°C in order to investigate both kinetic and thermodynamic parameters. Maximum CO₂ sorption capacity on AC ranged from 109.5 to 35.46 and from 129.65 to 35.55 mg CO₂/g of AC for initial concentrations 10 and 13.725% vol., respectively. Different isotherm models are applied to mathematically model the CO₂ adsorption, and on the basis of the estimated adsorption capacity by model and determination coefficient (r²), the Langmuir model provides a perfect fit to the experimental data owing to closeness of the r² to unity. From the correlation coefficient, it is found that the pseudo-second-order model is well-fitted with the experimental data. In addition, it indicates that CO₂ adsorption is a physical adsorption process and demonstrates a behavior of an exothermic reaction, which is consistent with the thermodynamic analysis. The results obtained in this study conclude that AC prepared from olive trees can be considered as adequate for designing a fixed bed cycle to separate carbon dioxide from flue gases and serve as a benchmark while searching for inexpensive and superior activated carbon production in future studies.

Keywords: adsorption, breakthrough, equilibrium, kinetic, thermodynamic

1. Introduction

The emissions of CO₂ from burn fossil fuels are the major reason for the increase in the concentration of this gas in the atmosphere [1]. The amount of carbon dioxide in the atmosphere is currently increasing globally by around 6 billion tons per year [2].

A feasible technique method used industrially in reduction of CO₂ emissions is capture and storage. CO₂ capture means separating the CO₂ from other gases in flue. The advanced technologies being used worldwide for CO₂ capture in different arrangements are post-combustion, pre-combustion, and oxy-fuel processes [1].

Numerous investigations have been done for CO₂ capture field by using adsorption, which are indicating to the effective usage of a post-combustion treatment of gas emissions of flue. The proposed schemes in a cycle process of capture by adsorption include pressure swing adsorption (PSA) and temperature swing...
adsorption (TSA) [1, 3–5]. The capture of carbon dioxide by adsorptive process is mainly based on preferential adsorption of this gas on a porous adsorbent. Thus, the first and most important step is to find a suitable adsorbent [1]. Carbon materials are relatively insensitive to moisture and are suitable candidates for CO₂ capture due to their pore structure and surface chemistry properties [6].

In recent years, considerable attention has been focused on removal of pollutants by using adsorbents derived from low-cost agro-wastes. Olive trees (Olea europaea) are abundantly found and easily available in the Mediterranean countries generally and especially Libya. Thus, the aim of the present study is to describe the dynamics and equilibrium of CO₂-N₂ mixture adsorption on local activated carbon (AC) prepared from olive trees using the breakthrough curve method. Experimental breakthrough curves are used to obtain equilibrium data, and then Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich equilibrium adsorption models were applied. Kinetic models examined herein are simple first-order, pseudo-first-order, pseudo-second-order, and intra-particle diffusion. Model validity with experimental data is assessed by using the coefficient of determination ($r^2$); the closer the value to unity means that the model will be better. Thermodynamic analysis of adsorption of CO₂ on AC estimates the values of enthalpy, free energy, and entropy. Also, effects of the interaction between CO₂ and NO are studied.

2. Materials and methods

2.1 Preparation of activated carbon

The prepared activated carbon based on charcoal was prepared from olive trees for low cost and was abundantly available. The used activated carbon was obtained from the local area. The raw material of charcoal as received was crushed, ground, and sieved, and only the fraction of particle size 5 mm was chosen as the mean particle diameter. Then it is heated in an oven for 48 h up to 115°C to dry and activate (to remove the absorbed gases and moisture it contains) [7, 8]. The produced activated carbon is then stored in a tightly closed container to be used as required. The total pore volume and surface area of AC were determined using Gemini VII 2390a analyzer. The particle size is obtained by using standard mesh sieves (standard sieve AS 200), and average value of bed porosity is calculated in terms of the average diameter of particles [9].

2.2 Dynamic adsorption capacity of carbon dioxide

A laboratory system used for measuring breakthrough curve was set up and shown in Figure 1. The adsorber which is made of carbon steel tube, consists of three zones:

- Calming zone with 6.5 cm diameter and 8 cm length containing spherical particles of carbon steel.
- Active zone with 8.44 cm diameter and 39 cm length containing the activated carbon particles, and it was surrounded by a shell containing a heating medium.
- Ending zone with 6.5 cm diameter and 8 cm length containing spherical particles of carbon steel.
N₂ and CO₂ were supplied by pressurized cylinders. The purity for CO₂, NO, and N₂ cylinders was 99.9, 99, and 99.99% (vol.%), respectively. The used concentrations of CO₂ were 10 and 13.725% (vol.%). Delivery of the feed gas was controlled by mass flow meter. After mixing in a mixing chamber (2.45 cm diameter and 15 cm length), simulated gas was fed into the inlet of the adsorber. Prior to all measurements, an initial degassing of the sample was performed at a given temperature (30, 50, 70, and 90°C) by the flow of nitrogen until reaching steady state. Then mixed gas was passed through the fixed bed column at constant temperature. The inlet and outlet concentrations were analyzed by a Testo 350XL flue gas, which has a resolution for N₂, NO, and CO₂ of 0.1 ppm, 0.1 ppm, and 0.1% vol., respectively. The total flow was kept constant for 12 l/min; whereas the N₂ and CO₂ were controlled precisely according to the required balance gas N₂ during binary experiments. The dynamic adsorption capacity of CO₂ onto AC column was calculated using Eqs. (1) and (2) [10]:

\[ t = \int_0^t \left(1 - \frac{C}{C_0}\right) dt \] (1)

\[ q_i = \frac{Q_v y_i t \rho_i}{m} * 1000 \] (2)

where \( t \) is the time of adsorption (min.), \( C \) is the outlet concentration of CO₂ gas (mg/l), \( C_0 \) is the inlet concentration of CO₂ gas (mg/l), \( q_i \) is the amount of adsorbed gases (mg gas/g adsorbent), \( Q_v \) is the volumetric flow rate of CO₂ gas (l/min.), \( y_i \) is the mole fraction of inlet CO₂, \( \rho_i \) is the density of inlet gas (mg/l), and \( m \) is the weight of the adsorbent (g).

The interval times for measurements were 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70, and 80 min. The experimental procedures and measurements are replicated three times for accuracy.

2.3 Adsorption isotherm studies

In order to optimize the design of a sorption system to capture CO₂ on AC, the suitable isotherm model for equilibrium curves must be established. Equilibrium models that have been examined herein are Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich. The conformity between the predicted values of models and experimental data is expressed by comparing the experimental adsorption
capacity with the adsorption capacity estimated by these models, by means of the
determination coefficient ($r^2$, values close or equal to 1) [11, 12].

2.3.1 The Langmuir isotherm

The widely used Langmuir isotherm found as a successful application in many
real sorption processes [12] is expressed as

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{3}$$

A linear form of this expression is

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{4}$$

where $q_e$ is the amount of adsorbed CO$_2$ per unit weight of AC at equilibrium
(mg/g) and $C_e$ is the unadsorbed CO$_2$ concentration in effluent at equilibrium
(mg/l). $K_L$ is the Langmuir equilibrium constant, and $K_L/a_L$ value is used to estimate
the theoretical monolayer capacity of AC, $Q_o$ (mg/g). Therefore, the plot of $C_e/q_e$
versus $C_e$ enables one to determine the constants $a_L$ and $K_L$.

2.3.2 The Freundlich isotherm

The well-known Freundlich isotherm is often used for heterogeneous surface
energy systems [12]. The Freundlich equation is given as

$$q_e = K_F C_e^{1/n} \tag{5}$$

A linear form of this expression is

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

where $K_F$ is the Freundlich constant (mg/g) and $n$ is the Freundlich exponent. $K_F$
and $n$ can be determined from the linear plot of $\log q_e$ versus $\log C_e$.

2.3.3 Temkin isotherm

The Temkin isotherm [13, 14] has been used in the following form:

$$q_e = \frac{RT}{b} \ln (AC_e) \tag{7}$$

A linear form of the Temkin isotherm can be expressed as

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \tag{8}$$

where $A$ is the Temkin isotherm equilibrium binding constant (l/g), $b$ is the
Temkin isotherm constant, $R$ is the universal gas constant (8.314 J/mol.K), $T$ is the
temperature, and $B$ (=RT/b) is the constant related to heat of adsorption (J/mol).

The sorption data can be analyzed according to Eq. (8). Therefore, the plot of $q_e$
versus $\ln(C_e)$ enables one to determine the constants $A$ and $B$. 

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*CO$_2$ Sequestration*
2.3.4 Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich equation in Eq. (9) is as follows [15]:

\[ q_e = q_m e^{-\beta \varepsilon^2} \]  

(9)

A linear form of Dubinin-Radushkevich isotherm is

\[ \ln q_e = \ln q_m - \beta \varepsilon^2 \]  

(10)

where \( q_m \) is the Dubinin-Radushkevich monolayer capacity (mg/g), \( \beta \) is the Dubinin-Radushkevich isotherm constant (mol\(^2\)/kJ\(^2\)), and \( \varepsilon \) is the Polanyi potential, and it’s related with equilibrium concentration as follows:

\[ \varepsilon = \frac{RT}{M} \ln \left( 1 + \frac{1}{C_e} \right) \]  

(11)

where \( R \) is the universal constant of gases (8.314 J/mol.K), \( T \) is the experiment temperature (K), and \( M \) is the molecular weight of CO\(_2\). The constant \( \beta \) gives the mean free energy of adsorption \( (E) \) for CO\(_2\) molecules transported from the gas bulk to the surface of AC which is calculated by using Eq. (12) [14, 16]:

\[ E = \frac{1}{\sqrt{2\beta}} \]  

(12)

2.4 Kinetic models of adsorption

To determine an appropriate kinetic model is necessary to analyze the experimental data to investigate the mechanism of adsorption process that may include mass transfer or chemical reaction. Also, other extensive models applied to many models such as homogenous surface diffusion model and heterogeneous diffusion model (also known as pore and diffusion models, respectively) have been extensively applied to expound the adsorbate transfer onto the particles of adsorbent [17-19]. The determination coefficient \( (r^2) \) is used to examine the confirmation of the predicted values of models with experimental data (determination coefficient value close or equal to 1). The validity of these models is evaluated by the determination coefficient \( (r^2) \), which is within the range of 0–1, in which \( r^2 \) closer to unity implies the best fitting toward the particular kinetic model [20].

2.4.1 Simple first-order model

The sorption kinetic may be described by a simple order equation [21, 22]. The following simple first-order equation describes the change in bulk concentration:

\[ C_t = C_0 e^{k_1 t} \]  

(13)

that can be rearranged to obtain a linear form

\[ \log C_t = \frac{k_1}{2.303} t + \log C_0 \]  

(14)

where \( C_t \) and \( C_0 \) are the concentration of adsorbate at time \( t \) and initially (mg/l), respectively, and \( k_1 \) is the first-order rate constant, (1/min).
Furthermore, Sparks [23] and Hossain et al. [21] proposed that the simple kinetic models such as first- or second-order rate equations are not applicable to the adsorption system with solid surfaces.

2.4.2 Pseudo-first-order model

The sorption kinetics may be described by pseudo-first Eq. (15) [13, 21, 24–26]:

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]  

Integration of Eq. (15) and using the initial conditions \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_t \) at \( t = t \) yield

\[
\log \left( \frac{q_e}{q_e - q_t} \right) = \frac{k_1}{2.303} t
\]  

(16)

By rearrangement of Eq. (16), a linear form is obtained:

\[
\log (q_e - q) = \log q_e - \frac{k_1}{2.303} t
\]  

(17)

where \( q_e \) is the amount of \( CO_2 \) adsorbed at equilibrium (mg/g), \( q \) is the amount of \( CO_2 \) adsorbed at time \( t \) (mg/g), and \( k_1 \) is the pseudo-first-order constant (1/min).

The pseudo-first-order constant \( k_1 \) and equilibrium adsorption \( q_e \) are determined by plot of \( \log(q_e - q) \) versus \( t \).

2.4.3 Pseudo-second-order model

The adsorption kinetics may also be described by pseudo-second-order Eq. (17) [13, 26–30]:

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]  

(18)

Integrating Eq. (18) and applying the initial boundaries yield

\[
\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t
\]  

(19)

By rearrangement Eq. (19), a linear form is obtained:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \frac{t}{q_t}
\]  

(20)

where \( k_2 \) is the equilibrium rate constant of pseudo-second-order adsorption (g/mg.min).

The slopes and intercepts of plots \( t/q_t \) versus \( t \) are used to calculate the pseudo-second-order rate constants \( k_2 \) and \( q_e \).
2.4.4 Intra-particle diffusion model

The intra-particle diffusion model is expressed as [31–33]

\[ q_t = k_p t^{0.5} + c \]  

(21)

where \( k_p \) is a rate factor (present CO\(_2\) adsorbed per minute). The plot of this model is multi-linear that indicates there are two or more steps occurring consecutively. The external surface/instantaneous adsorption stage occurred first in sharp portion. Then a gradual adsorption stage is in the second portion, where the controlled rate is the intra-particle diffusion. Final equilibrium stage occurs where intra-particle diffusion begins to slow down because of extremely low adsorbate concentrations in the bulk [24, 34].

2.5 Thermodynamic studies

Thermodynamic parameters were estimated from Langmuir isotherms by using the Van’t Hoff’s equation as in Eqs. (22) and (23). The thermodynamic parameters can be estimated from Langmuir isotherms by using the Van’t Hoff’s equation as follows [12, 35]:

\[ \Delta G^o = -RT \ln a_L \]  

(22)

\[ \ln a_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \]  

(23)

where \( a_L \) is a Langmuir constant (l/mol), \( R \) is the universal constant of gases (8.314 J/mol.K), and \( T \) is an absolute temperature of gas.

3. Results and discussion

3.1 Adsorbent characterization

The main characteristics of AC (particle diameter, bed porosity, weight of bed, BET surface area, and pore volume) are shown in Table 1. Due to a high value BET surface area for used AC, its good pore structure makes it a suitable candidate for CO\(_2\) capture.

3.2 Dynamic studies

Two mixtures of CO\(_2\) and N\(_2\) gases have been used in experiments (initial concentrations of CO\(_2\) are 10 and 13.725% vol., respectively). Figure 2 shows that

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter</td>
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<td>mm</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.304</td>
<td></td>
</tr>
<tr>
<td>Weight of bed</td>
<td>500</td>
<td>g</td>
</tr>
<tr>
<td>BET surface area</td>
<td>602</td>
<td>m(^2)/g</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.61</td>
<td>cm(^3)/g</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of used AC depending on particle diameter.
the rate of CO$_2$ adsorption gradually decreased with time, until equilibrium condition was achieved. This behavior is observed for each line in Figures 2 and 3 throughout a gradual increase of the concentration ratio of (outlet/initial) concentrations of CO$_2$ (C/C$_o$).

The CO$_2$ adsorption was most intensive during 50 min. and thereafter remains unchanged until saturation was attained. Adsorption process to carbon dioxide for different temperatures (30, 50, 70, and 90°C) on AC reaches equilibrium for increased temperature. The same behavior is shown in Figure 3 when using a high concentration of carbon dioxide but fast (30 min. to reach the equilibrium), due to high CO$_2$ concentration, and this behavior is compatible with previous results when using AC prepared from coconut residue to remove carbon dioxide [36]. It is noted that breakthrough curves become shorter and steeper for high temperatures; this indicates the adsorption process here is exothermic and that’s compatible with previous results for some of the previous adsorption of carbon dioxide on the zeolite [1]. The adsorption of carbon dioxide carbon process was not affected by the presence of nitrogen gas, and this is due to the strength of the links formed by carbon dioxide with AC particles [36].

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**Figure 2.**
Breakthrough curve for CO$_2$ adsorption onto AC (initial conc. = 10%vol., avg. particle diameter = 5 mm, and volumetric rate = 12 l/min).

**Figure 3.**
Breakthrough curve for CO$_2$ adsorption onto AC (initial conc. = 13.725%vol., avg. particle diameter = 5 mm, and volumetric rate = 12 l/min).
In post-combustion process, the flue gas temperature is typically within the range of 50–120°C [36, 37]. Thus, an adsorption study was conducted at 30–90°C to investigate the CO$_2$ adsorptive properties at elevated temperatures. Figures 4 and 5 show that the CO$_2$ adsorption capacity of solid adsorbent decreases with temperature, and it implies the existence of physical adsorption (physisorption) between the CO$_2$ molecules and carbonaceous adsorbent. Adsorption capacity decreased with increasing temperature because of exothermic adsorption process as shown in Figures 4 and 5. This behavior is also identical with the results of previous studies [3, 38]. The adsorption capacities recorded in Figure 4 are 109.529, 74.57, 50.61, and 35.46 mg$_{(CO_2)}/$g$_{AC}$, whereas they recorded in Figure 5 as 129.651, 89.2, 53.079, and 35.546 mg$_{(CO_2)}/$g$_{AC}$ at temperatures 30, 50, 70, and 90°C, respectively. Thus, the optimum temperature for the removal process is 30°C. It also notices that the adsorption process occurs in the beginning quickly and be a decline in the curves and clear because of the abundance of the active sites and the presence of small surface resistance on the surface of adsorbents, then more smoothness gradually less steep and alignment over time because of the fullness of all the active sites on the surface of adsorbents and that the process has become controlled by internal diffusion within the adsorbents in accordance with what has been presented previously [39]. Also the results of comparison for both Figures 4 and 5 together note

Figure 4.
Adsortion capacity of CO$_2$ onto AC (initial concn. = 10%vol., avg. particle diameter = 5 mm, and volumetric rate = 12 l/min.).

Figure 5.
Adsortion capacity of CO$_2$ onto AC (initial conc. = 13.725%vol., avg. particle diameter = 5 mm, and volumetric rate = 12 l/min.).
that the amount of the CO$_2$ adsorbed onto AC increases due to increase of the concentration difference of CO$_2$ between bulk and surface of AC leading to an increase of mass transfer [9, 40].

3.3 Equilibrium isotherm studies

The equilibrium data can be approximated using common and practical adsorption isotherms, which provide the basis for the design of adsorption systems. The amount of adsorbed CO$_2$ onto adsorbent (AC) as a function of its concentration at constant temperature can be described by different adsorption isotherm models (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich). The predicted isotherm constants for the CO$_2$ adsorption and the determination coefficient $r^2$ value from the linear regression method are shown in Table 2.

Based on tabulated data, the maximum capacity ($Q_o$) of AC and $a_L$ values (Langmuir parameters) for CO$_2$ adsorption decreased with increasing temperature; this reveals a physisorption process occurred. The decline in values of maximum adsorption capacity with increased in the adsorption temperature is due to the exothermic nature of the CO$_2$ adsorption on AC. It is confirmed by $n$ values higher than 1 in the Freundlich isotherm model that the adsorption is favorable for AC.

<table>
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<tr>
<th>$C_o$ (Vol. %)</th>
<th>$T$ (°C)</th>
<th>$a_L$ (l/mg)</th>
<th>$q_o$ (mg/g)</th>
<th>$K_F$ (mg/g)</th>
<th>$n$ (-)</th>
<th>$Q_L$ (mg/g)</th>
<th>$r^2$</th>
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<th>$q_m$ (mg/g)</th>
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<th>$c$ (kJ/mol)</th>
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<td>35.63</td>
<td>0.9947</td>
<td>35.43</td>
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</table>

Table 2. Parameters of isotherm models at different temperatures via linearized technique for adsorption of CO$_2$ onto AC.
In addition, the Dubinin-Radushkevich isotherm will provide a useful information related to the energy parameters, in terms of \( E \) (mean free energy of adsorption). The calculated \( E \) values which are within the range of 1.213–8 and 0.626–2.193 kJ/mol for both initial concentrations 10 and 13.725% vol., respectively, suggest that the CO\(_2\) adsorption is physical in nature, as the magnitude of \( E \) is below 8 kJ/mol, whereas the value of \( 8 < E < 16 \) is an indicator of the chemical adsorption \[41\]. Also, \( B \) (value of heat adsorption) in Temkin isotherm ranged between 15.47 and 35.826 J/mol indicating a physisorption process occurs.

On the basis of corresponding \( r^2 \) values and adsorption capacity estimated by each model shown in Table 2, the Langmuir model gives the best fit toward the experimental data over the entire temperature range. Therefore, it implies that the surface of the activated carbon is heterogeneous and a restricted monolayer CO\(_2\) adsorption occurs, as results of adsorption CO\(_2\) onto activated carbon prepared from coconut fiber studied by Hauchhum and Mahanta \[3\].

### 3.4 Kinetic studies

An analysis of kinetic adsorption process is a useful tool to estimate the time of residence for the adsorption process to complete and to determine the dynamics of adsorption and its performance in industrial scale of fixed bed or in flow-through systems. Thus, simple first-order, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were performed in this study. Kinetic parameters of these models are shown in Table 3.

Table 3 shows the simple first-order kinetic model for activated carbon did not fit well with the experimental data, with \( r^2 \) value found to be within the range of 0.4344–0.7873 and 0.319–0.734 for both initial concentrations 10 and 13.725% vol., respectively. Also, Table 3 shows the pseudo-first-order kinetic model for activated carbon did not fit well with the experimental data, with \( r^2 \) value found to be within the range of 0.9521–0.967 also from 0.9175 to 0.9487 for both initial concentrations 10 and 13.725% vol., respectively.

Comparing the values of determination coefficients as stated in Table 3, pseudo-second-order model gives better fit than the pseudo-first-order and intra-particle diffusion models with experimental data, with \( r^2 \) value within the range of 0.963–0.996 and 0.955–0.998 for both initial concentrations 10 and 13.725% vol., respectively. Also, the values of adsorption capacity of equilibrium (\( q_e \)) were observed to decrease with respect to temperature. The kinetic energy of CO\(_2\) adsorbed at elevated temperatures is high, and it leads to its increasing tendency to escape from the AC surface. Maroto-Valer et al. \[42\] reported that physisorption process involves high surface adsorption energy and molecule diffusion at elevated temperatures, which result in instability of the adsorbed gas on the surface of activated carbon, and consequently desorption process will occur.

In similarity to pseudo-first-order and pseudo-second-order models, the intra-particle diffusion model provides insight of the mechanism in adsorption process. Adsorption contains of few steps involved in the transfer of adsorbate (CO\(_2\)) from the phase of bulk to the solid surface of AC and is followed by the molecule diffusion into the interior of the pores of AC. Intra-particle diffusion is typically described as a slow process and is a limiting step in many adsorption processes. Theoretically, if the adsorption process obeys the intra-particle diffusion model, a straight linear plot that passes through the origin is expected. However, results of the variation of gradient with respect to time show that the intra-particle diffusion is not the sole rate-limiting step in this adsorption process. Note that the first steeper region (2–4 min.) could be due to surface sorption, while the second
region (4–9 min.\(^{1/2}\)) may be attributed by the intra-particle diffusion rate controlled.

### 3.5 Thermodynamic studies

The values of thermodynamic parameters of CO\(_2\) adsorption process on AC based on Van’t Hoff plot for Eqs. (22) and (23) are shown in Figure 6. The estimated values of the thermodynamic parameters are tabulated in Table 4. For significant adsorption to occur, the Gibbs free energy change of adsorption (\(\Delta G^o\)) must be negative [43]. Table 4 shows that the (\(\Delta G^o\)) was negative values for all five temperatures studied, which indicates the feasibility and spontaneity of the adsorption process. In addition, decreased negative \(\Delta G^o\) value with increasing temperature implies that the CO\(_2\) adsorption process is more favorable at 30°C rather than at 90°C; this behavior is also noticed by Rashidi et al. [44] and Hauchhum and Mahanta [3].

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>(C_v) (vol. %)</th>
<th>Parameter</th>
<th>Temperature (°C)</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
</tr>
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<tr>
<td>Simple first-order</td>
<td>10</td>
<td>(k_1)</td>
<td></td>
<td>2.633</td>
<td>1.974</td>
<td>1.394</td>
<td>0.955</td>
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<tr>
<td></td>
<td></td>
<td>(C_a)</td>
<td></td>
<td>(4.1 \times 10^3)</td>
<td>(1.75 \times 10^{12})</td>
<td>(1.67 \times 10^{12})</td>
<td>(6.73 \times 10^{12})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(r^2)</td>
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<td>0.434</td>
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<td></td>
<td>13.725</td>
<td>(k_1)</td>
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<td>3.293</td>
<td>2.404</td>
<td>1.457</td>
<td>1.091</td>
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<tr>
<td></td>
<td></td>
<td>(C_a)</td>
<td></td>
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<td>(8.414 \times 10^{34})</td>
<td>(6.52 \times 10^{34})</td>
<td>(1.023 \times 10^{34})</td>
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<td></td>
<td></td>
<td>(r^2)</td>
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<td>0.319</td>
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<td></td>
<td></td>
<td>(q_e)</td>
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<td>159.48</td>
<td>143.481</td>
<td>84.94</td>
<td>62.22</td>
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<tr>
<td></td>
<td></td>
<td>(r^2)</td>
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<td>0.96</td>
<td>0.915</td>
<td>0.952</td>
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<td></td>
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<td>0.918</td>
<td>0.927</td>
<td>0.944</td>
<td>0.949</td>
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<tr>
<td>Pseudo-second-order</td>
<td>10</td>
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<td>(1.6 \times 10^3)</td>
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<td>(1.69 \times 10^4)</td>
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<tr>
<td></td>
<td></td>
<td>(q_e)</td>
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<td>144.93</td>
<td>87.719</td>
<td>55.56</td>
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<td></td>
<td></td>
<td>(r^2)</td>
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<td>0.968</td>
<td>0.976</td>
<td>0.989</td>
<td>0.995</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>(q_e)</td>
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<td>161.29</td>
<td>102.04</td>
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<tr>
<td></td>
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<td>(r^2)</td>
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<td>0.96</td>
<td>0.982</td>
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<td>Intra-particle diffusion</td>
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<td></td>
<td></td>
<td>(c)</td>
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<td>12.25</td>
<td>13.025</td>
<td>11.775</td>
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<tr>
<td></td>
<td></td>
<td>(r^2)</td>
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<td>5.219</td>
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<tr>
<td></td>
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<td>(c)</td>
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<td>14.137</td>
<td>17.633</td>
<td>17.693</td>
<td>14.578</td>
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<tr>
<td></td>
<td></td>
<td>(r^2)</td>
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<td>0.841</td>
<td>0.788</td>
<td>0.677</td>
<td>0.601</td>
</tr>
</tbody>
</table>

Table 3.
Kinetic parameters of CO\(_2\) onto AC.
According to findings of the experimental data, the negative sign of $\Delta H^0$ value indicates an exothermic nature of the CO$_2$ adsorption process onto AC, and the negative value of $\Delta S^0$ suggests high orderliness of the adsorbate molecules (CO$_2$) upon adsorption. Zhao et al. [45] mentioned that the negative value of $\Delta S^0$ can be interpreted by the behavior of the CO$_2$ molecules upon the adsorption process, which is from randomized to an ordered form on the surface of the adsorbent. The decline in the entropy value upon the adsorption process is due to a lesser degree of freedom of the CO$_2$ molecules, due to minimum free space on the surface of AC. Moreover, the value of $\Delta H^0$ indicates the type of CO$_2$ adsorption process, whether it belongs to the physisorption or chemisorption. It has been reported that the value of $\Delta H^0$ for the physisorption process is $<$20 kJ/mol, while for the chemisorption process, the value is within 80–200 kJ/mol [45, 46]. Therefore, the calculated values of $\Delta H^0$ approximately ranging between 18 and 28 kJ/mol suggest that the CO$_2$ adsorption can be attributed to a physi-intra-particle diffusion adsorption process rather than a pure physisorption or chemisorption process. Also, this supports the isotherm study results that reveal the adsorption mechanism is physisorption and obeys Langmuir isotherm model.

<table>
<thead>
<tr>
<th>Conc. (vol.%)</th>
<th>Temp. (K)</th>
<th>$a_L$ (mol/l)</th>
<th>$\Delta G^0$ (J/mol)</th>
<th>$\Delta H^0$ (J/mol)</th>
<th>$\Delta S^0$ (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>303</td>
<td>2164.79</td>
<td>$-19347.21$</td>
<td>$-28038.965$</td>
<td>$-29.7716$</td>
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<td>807.71</td>
<td>$-17976.75$</td>
<td></td>
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<tr>
<td></td>
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<td>$-17566.61$</td>
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<td></td>
</tr>
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<tr>
<td>13.725</td>
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<td>753.38</td>
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<td>$-18630.843$</td>
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<td>363</td>
<td>204.91</td>
<td>$-16063.38$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Thermodynamic parameters of CO$_2$ adsorption onto AC.

According to findings of the experimental data, the negative sign of $\Delta H^0$ value indicates an exothermic nature of the CO$_2$ adsorption process onto AC, and the negative value of $\Delta S^0$ suggests high orderliness of the adsorbate molecules (CO$_2$) upon adsorption. Zhao et al. [45] mentioned that the negative value of $\Delta S^0$ can be interpreted by the behavior of the CO$_2$ molecules upon the adsorption process, which is from randomized to an ordered form on the surface of the adsorbent. The decline in the entropy value upon the adsorption process is due to a lesser degree of freedom of the CO$_2$ molecules, due to minimum free space on the surface of AC. Moreover, the value of $\Delta H^0$ indicates the type of CO$_2$ adsorption process, whether it belongs to the physisorption or chemisorption. It has been reported that the value of $\Delta H^0$ for the physisorption process is $<$20 kJ/mol, while for the chemisorption process, the value is within 80–200 kJ/mol [45, 46]. Therefore, the calculated values of $\Delta H^0$ approximately ranging between 18 and 28 kJ/mol suggest that the CO$_2$ adsorption can be attributed to a physi-intra-particle diffusion adsorption process rather than a pure physisorption or chemisorption process. Also, this supports the isotherm study results that reveal the adsorption mechanism is physisorption and obeys Langmuir isotherm model.
3.6 Effects of interaction between gases in mixture

The adsorption amount for each component in a complex mixture of (CO$_2$, NO, and N$_2$) was compared with that under the single-component conditions, with the results shown in Figure 7. In the single-component condition, the adsorption amount was 109.24 mg CO$_2$/g AC and 0.245 mg NO/g AC in 50 and 40 min for each one, respectively. When all of the components were present in a mixture of CO$_2$, NO, and N$_2$, the CO$_2$ adsorption amount decreased by 6%, and the NO adsorption amount also decreased by 7.6%. The adsorption capacity of CO$_2$ in complex mixture is not changed compared with that under the single-component conditions but is favorable due to decreased equilibrium time required. The adsorption capacities of complex mixture were 103.2 mg CO$_2$/g AC in 40 min and 0.229 mg NO/g AC in 30 min. This decrease in adsorption capacity is due to the competition between both gases on the active sites, whereas the CO$_2$ adsorption capacity is higher than NO gas because of the presence of CO$_2$ gas at high concentrations. NO and CO$_2$ display fast breakthrough, and high adsorption amounts were observed in the pure component adsorption experiments. When the interaction effect of CO$_2$ and NO was considered, a very interesting phenomenon appeared. After the initial breakthrough, the CO$_2$ concentration descends to a minimum and then gradually ascends with the breakthrough ending point of NO. This is observed from the arrival time of the

![Figure 7](image1)

**Figure 7.**
Breakthrough curves for mixture gas (CO$_2$, NO, and N$_2$) (initial conc. = 10% vol. of CO$_2$, and 550 ppm of NO, avg. particle diameter = 5 mm, temperature = 30°C, and volumetric rate = 12 l/min.)

![Figure 8](image2)

**Figure 8.**
Breakthrough curves for mixture gas (CO$_2$, NO, and N$_2$) (initial conc. = 13.725% vol. of CO$_2$, and 550 ppm of NO, avg. particle diameter = 5 mm, temperature = 30°C, and volumetric rate = 12 l/min.)
equilibrium state which was 30 min for the NO gas and 40 min for the CO₂ gas; the same behavior is shown for the single-component conditions; the difference between them was reached in the equilibrium stage fast approximately 10 min. In Figure 8 the adsorption capacities of complex mixture were 124.4 mgCO₂/gAC in 40 min and 0.22 mgNO/gAC in 30 min by using different initial concentrations of gases. This is confirmed by the fact that free Gibbs energy values of both gases are very different, as they have NO gas higher in value, while in the case of CO₂, they are much lower. This behavior is shown in previous study for adsorption on activated carbon prepared from coconut husk residues [47].

4. Conclusion

In this study, the fixed bed adsorption of carbon dioxide from CO₂/N₂ mixtures on activated carbon was studied. The adsorption dynamics was investigated at different operating temperatures (30–90°C). The results show that the low-cost activated carbon can be prepared from olive trees as potential carbonaceous material serving as porous media for CO₂ capture. Based on the experimental results, it is concluded that the CO₂ adsorption onto the olive tree activated carbon follows the physisorption behavior, whereby the CO₂ adsorption capacity decreases with respect to increasing temperature. Based on the equilibrium models of isotherm used herein to fit the experimental data of adsorption, the Langmuir model was the best fit with experimental data over the whole temperature range, due to the highest estimated adsorption capacity and determination coefficient (r²) closeness to unity, thus implying a perfect fit to the experimental data. Besides, thermodynamic analysis proves that the CO₂ adsorption is a spontaneous process at low temperature, physisorption, and intra-particle diffusion and exothermic in nature. Also, the negative values of the entropy of the adsorption manifest the restricted randomness of the adsorbate molecules on the surfaces of adsorbent. CO₂ adsorption capacity has been reduced slightly when NO appears, but the process of adsorption has been faster as a result of competition on carbon-active sites. Olive trees are dominant and easily available in the Mediterranean countries generally and especially Libya, and because charcoal is prepared from olive trees, it is cheap in Libya. According to the obtained result, this study concludes that AC prepared from olive trees can be considered as adequate for designing a fixed bed cycle to separate carbon dioxide from flue gases and serve as a benchmark while searching for inexpensive and superior activated carbon production in future studies that concerned of capturing CO₂ from flue gases of the industrial sectors (such as cement plants and power stations) that are prevailing in Libya.
Author details

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