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Chapter

Experimental Study of Adsorption on Activated Carbon for CO$_2$ Capture

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Abstract

The adsorption of carbon dioxide (CO$_2$) 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 CO$_2$ sorption capacity on AC ranged from 109.5 to 35.46 and from 129.65 to 35.55 mg CO$_2$/g of AC for initial concentrations 10 and 13.725% vol., respectively. Different isotherm models are applied to mathematically model the CO$_2$ adsorption, and on the basis of the estimated adsorption capacity by model and determination coefficient (r^2), the Langmuir model provides a perfect fit to the experimental data owing to closeness of the r^2 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 CO$_2$ 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 CO$_2$ 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 CO$_2$ emissions is capture and storage. CO$_2$ capture means separating the CO$_2$ from other gases in flue. The advanced technologies being used worldwide for CO$_2$ capture in different arrangements are post-combustion, pre-combustion, and oxy-fuel processes [1].

Numerous investigations have been done for CO$_2$ 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 CO$_2$ 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 CO$_2$-N$_2$ 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 CO$_2$ on AC estimates the values of enthalpy, free energy, and entropy. Also, effects of the interaction between CO$_2$ 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.

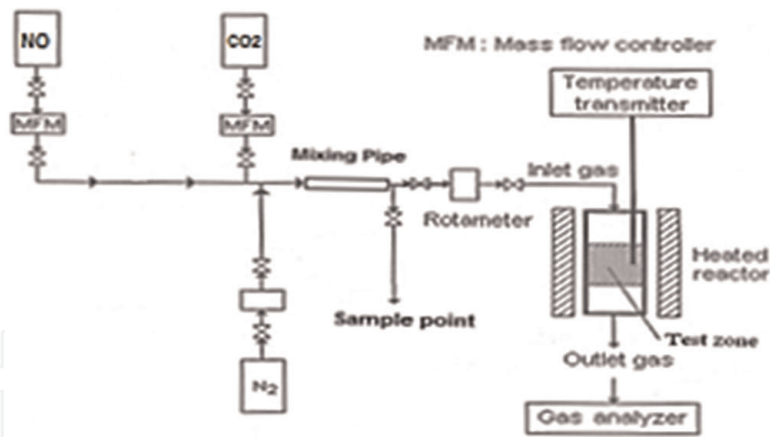- Ending zone with 6.5 cm diameter and 8 cm length containing spherical particles of carbon steel.

Figure 1.
Schematic of the experimental set-up.

N_2 and CO_2 were supplied by pressurized cylinders. The purity for CO_2, NO, and N_2 cylinders was 99.9, 99, and 99.99% (vol.%), respectively. The used concentrations of CO_2 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 N_2, NO, and CO_2 of 0.1 ppm, 0.1 ppm, and 0.1% vol., respectively. The total flow was kept constant for 12 l/min; whereas the N_2 and CO_2 were controlled precisely according to the required balance gas N2 during binary experiments. The dynamic adsorption capacity of CO_2 onto AC column was calculated using Eqs. (1) and (2) [10]:

$$t = \int_0^t \left(1 - \frac{c}{c_o}\right) dt \tag{1}$$

$$q_i = \frac{Q_v . y_i . t . \rho_i}{m} * 1000 \tag{2}$$

where t is the time of adsorption (min.), C is the outlet concentration of CO_2 gas (mg/l), C_o is the inlet concentration of CO_2 gas (mg/l), q_i is the amount of adsorbed gases (mg gas/g adsorbent), Q_v is the volumetric flow rate of CO_2 gas (l/min.), y_i is the mole fraction of inlet CO_2, ρ_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 CO_2 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.

2.3.4 Dubinin-Radushkevich isotherm

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

$$q_e = q_m \, e^{-\beta \varepsilon^2} \tag{9}$$

A linear form of Dubinin-Radushkevich isotherm is

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{10}$$

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

$$\varepsilon = \frac{RT}{M} \ln \left(1 + \frac{1}{C_e} \right) \tag{11}$$

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 β 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]:

$$E = \frac{1}{\sqrt{2\beta}} \tag{12}$$

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:

$$C_t = C_o e^{k_1 t} \tag{13}$$

that can be rearranged to obtain a linear form

$$\log C_t = \frac{k_1}{2.303} t + \log C_o \tag{14}$$

where C_t and C_o 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]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{15}$$

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

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303}t \tag{16}$$

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

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \tag{17}$$

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]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{18}$$

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

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \tag{19}$$

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \tag{20}$$

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

The slopes and intercepts of plots t/q_e 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]

$$q_t = k_p t^{0.5} + c \qquad (21)$$

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]:

$$\Delta G^o = -RT \ln a_L \qquad (22)$$

$$\ln a_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (23)$$

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

Characteristic	Value	Unit
Particle diameter	5	mm
Bed porosity	0.304	—
Weight of bed	500	g
BET surface area	602	m²/g
Pore volume	0.61	cm³/g

Table 1.
Characteristics of used AC depending on particle diameter.

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