



Investigation of mass transport characteristics of CO₂ adsorption onto activated carbon: An experimental and numerical study

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ABSTRACT

This study experimentally and numerically investigated CO₂ adsorption characteristics onto a highly porous activated carbon. Adsorption kinetics and isotherms experiments were conducted using a high-precision thermogravimetric analyzer. The effects of key parameters, specifically adsorbent bed thickness, temperatures, and pressure, were considered. The two isotherm models were employed to correlate the measured data, and they showed a decent fit. Numerical simulations were carried out using COMSOL Multiphysics software under a coupled heat and mass transfer model. The simulated results showed a reasonable agreement with the experimental uptakes for all studied parameters. The results also showed that the diffusion time constant (D_{s0}/R_p^2) is pressure-dependent and varies with the adsorbent bed thickness. The D_{s0}/R_p^2 at each adsorption temperature is calculated and fitted with the Arrhenius equation. Estimated averaged values of limiting D_{s0}/R_p^2 for adsorbent bed thicknesses of 0.9, 5, and 25 mm, respectively, equal to 2.18×10^{-1} , 8.64×10^{-2} , and 2.05×10^{-2} 1/s. Linearly increasing adsorbent bed thickness causes a rapid nonlinear drop in D_{s0}/R_p^2 . The findings from this research provide valuable information on the mass transfer characteristics of CO₂ onto activated carbon. So, engineers can design optimized heating/cooling systems that operate more effectively, resulting in higher efficiency, reduced system costs, and lower carbon emissions.

1. Introduction

Carbon dioxide (CO₂) is a substantial contributor to global warming, primarily stemming from the burning of fossil fuels and the leaking of high global warming potential (GWP) refrigerants directly into the atmosphere from conventional heating/cooling systems [1–4]. The adsorption cooling/heating systems (ACHS) could be a viable substitute for conventional compression-based cooling/heating systems as they can be driven by heat from renewable energy sources (like solar heat) or waste heat [5–9] and several natural refrigerants can be used as a working fluid. Therefore, the ACHS can reduce CO₂ emissions to the environment directly and indirectly. However, ACHS has low performance, high cost, and large size compared to conventional cooling/heating systems. Consequently, researchers are actively exploring ways

to enhance ACHS performance by employing different adsorbate/adsorbent pairs, for instance, water/metal-organic frameworks (MOFs) [10], ethanol/activated carbon [11], water/zeolite [12], R134/activated carbon [13], silica gel/water [14], and CO₂/activated carbon [15].

The CO₂/activated carbon pair stands out as particularly promising among various pairs due to several advantages. Firstly, CO₂ possesses exceptional thermo-physical properties and high volumetric capacity compared to all other natural refrigerants (adsorbates). Additionally, it is non-flammable, harmless, and has zero ozone depletion potential with a very low GWP, as low as 1 [16]. Furthermore, unlike those using water, ACHS utilizing CO₂ as a refrigerant are not restricted solely above 0 °C for cooling and air-conditioning applications. It can also be effectively utilized for ice-making and freezing applications [17,18]. Another

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key element of ACHS is the adsorption/desorption bed, which is the porous material made by packing certain adsorbents. Numerous types of adsorbents have been investigated for CO₂ refrigerant, with activated carbons (ACs) [15] and carbon-based composites [17,19] emerging as promising options. This is due to their attributes, including appropriate pore size, high surface area, high thermal conductivity, large pore volume, moderate heat of adsorption, cost-effectiveness in large-scale production, low desorption temperature, and less susceptibility to moisture compared to other CO₂-philic materials. In addition, recently, it has been proven that high-quality, extremely porous, and benchmark adsorption of CO₂-based ACs have been prepared from waste biomass precursors [1,15,20]. Consequently, the overall system price is expected to be relatively low compared to MOF adsorbent. Moreover, using waste biomass as precursors of AC production can be regarded as an environmentally benign approach because it can reduce harmful gas emissions due to the natural degradation of that biomass [15,21].

Although the CO₂/activated carbon pair is promising for ACHS compared to all other pairs, its performance is still not satisfactory, and it is important to have an optimal design for it. Performance improvement and design optimization of any type of ACHS depends on many factors, such as adsorption/desorption bed thickness, operating conditions, available temperature of heat source, heat exchanger design, and so on. The adsorption/desorption bed is mainly responsible for cooling or heating by adsorbing and desorbing refrigerant gas. Numerous authors performed numerical and experimental investigations on the adsorption bed thickness and its influence on the kinetics and cooling/heating performances. For instance, Mohammed et al. [22] observed that the lower-thickness silica-gel bed can adsorb water vapor faster than a higher-thickness bed. Sharafian et al. [23] experimentally investigated the performance effectiveness of FAMZ02/water pair and observed that the decreasing of mass (thereby thickness) of this material used by 4 times led to the increase in the specific cooling power (SCP) by 82%; however, the COP (coefficient of performance) decreased by 37%. Fadar et al. [24] found a decreasing trend in the SCP with the rise of adsorbent bed thickness, although the COP of the system remained almost unchanged. They have indicated that an adsorbent bed with a thickness of >40 mm is not recommended for such type of cooling system. Some other notable studies can be found elsewhere [25–27]. It should also be mentioned that most studies on performance improvement are conducted based on the use of mathematical modeling techniques such as lumped parameters [28–32], distributed parameters [33], and coupled heat and mass transfer [34–38] models.

The development of ACHS is heavily reliant on optimizing the design and operational conditions of adsorption/desorption beds. Among the critical factors that influence the efficiency of these systems, the bed thickness of the adsorbent plays a significant role in determining the adsorption equilibria and kinetics. Despite this, there is a noticeable gap in the existing literature regarding the comprehensive understanding of how varying adsorbent bed thicknesses affect the adsorption performance, especially under different operational conditions. Addressing this gap is crucial for enhancing the performance and efficiency of ACHS, which are pivotal in applications ranging from industrial gas separation to environmental management. Therefore, this study is motivated by the need to fill this gap through experimental and numerical investigations, specifically focusing on CO₂ adsorption characteristics using activated carbon (AC) as the adsorbent.

It is evident from the literature that both experimental and numerical studies are needed to find an optimal design and operational conditions of adsorption/desorption beds, which are important tasks in the development of ACHS. Among the critical factors that influence the efficiency of this system, the bed thickness of the adsorbent plays a significant role in determining the adsorption equilibria and kinetics. Despite this, there is a noticeable gap in the existing literature regarding the comprehensive understanding of how varying adsorbent bed thicknesses affect the adsorption performance, especially under different operational conditions. Addressing this gap is crucial for enhancing the performance and

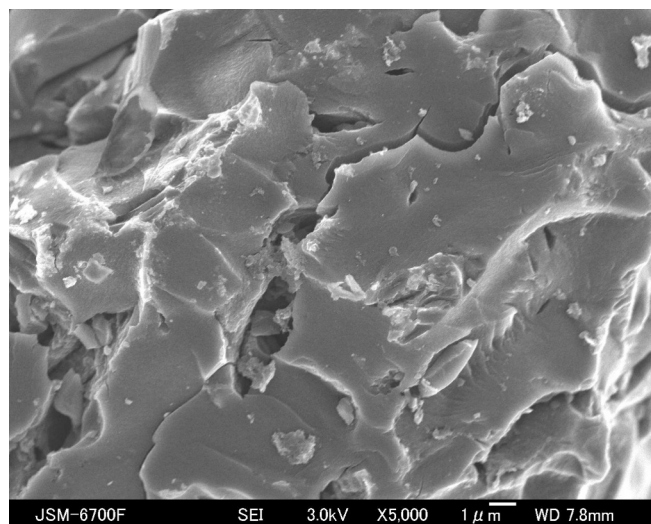


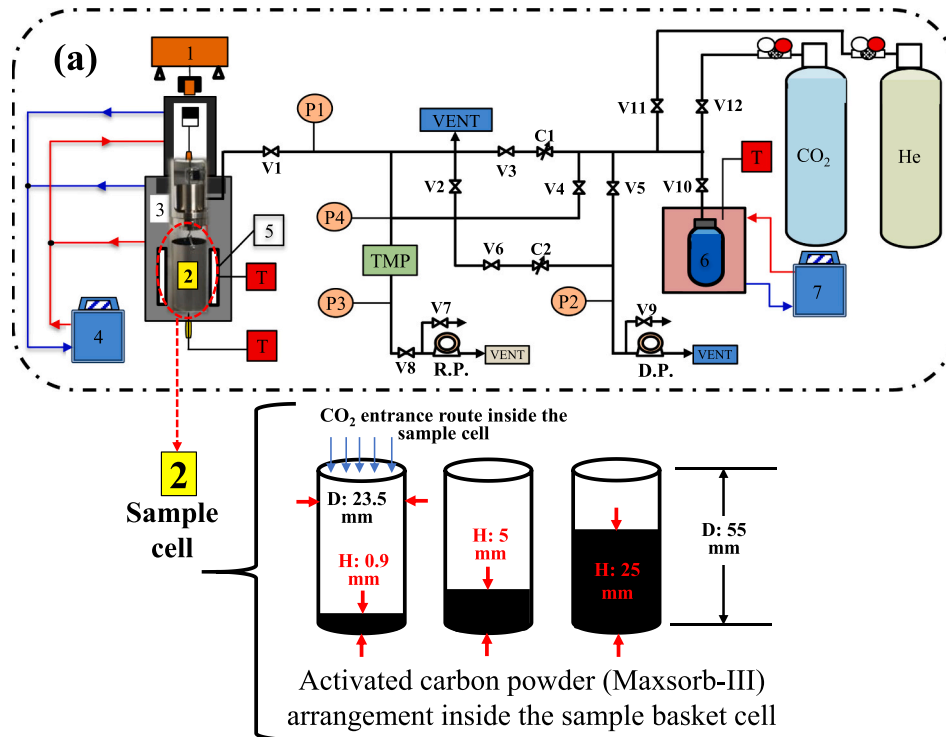
Fig. 1. SEM image of the studied adsorbent Maxsorb-III (activated carbon powder).

efficiency of ACHS, which are pivotal in applications ranging from industrial gas separation to environmental management. Therefore, this study is motivated by the need to fill this gap by conducting an experimental study on CO₂ adsorption characteristics in an adsorbent bed packed with different masses of activated carbon (AC) and a numerical study using a coupled heat and mass transfer model for understanding the insight of mass transport characteristics of CO₂ onto AC. The notable contributions of this study are summarized as follows:

- The adsorption kinetics and isotherms of CO₂ onto the Maxsorb-III (AC) are measured gravimetrically using a magnetic suspension measurement unit at three different adsorption temperatures: 30, 50, and 70 °C and pressure up to 4.5 MPa.
- To examine the effects of adsorbent bed thickness, three different mass amounts of Maxsorb-III are employed in this study: 66 mg, 369 mg, and 1843 mg, which provide the adsorbent bed's thicknesses as 0.9 mm, 5 mm, and 25 mm, respectively.
- Measured isotherms data are correlated with Tóth and modified Dubinin-Astakhov, whereas kinetics data are fitted with linear driving force model equation.
- The Arrhenius equation is used to fit the diffusion time constant predicted from each temperature.
- To predict CO₂ uptake, computational fluid dynamics (CFD) simulations are performed using COMSOL Multiphysics software.
- The predicted data of the CFD model are validated with the experimental data.
- The effects of the thickness of the adsorbent bed on diffusion time constant and adsorption kinetics are rigorously investigated.

2. Materials

The material employed in this work is commercially available and promising activated carbon called Maxsorb-III, developed by Kansai Coke and Chemical Co. Ltd. (Japan). It holds a pore volume and surface area of 1.7 cm³g⁻¹ and 3045 m²g⁻¹, respectively. Due to its high porosity, this adsorbent has a very high adsorption affinity towards many gasses [39,40]. Fig. 1 shows the scanning electron micrograph (SEM) of the studied Maxsorb-III, and the compositions ratio of different elemental are 95.13[%] C, 0.14[%] H, 0.25[%] N, 4.35[%] O(diff.), and 0.13 [%] ash [41–43].



1. Magnetic suspension balance; 2. Sample cell; 3. Circulation oil jacket; 4. Oil bath and circulator; 5. Sheathed heater; 6. Refrigerant container; 7. Isothermal oil bath; 8. CO₂; 9. Helium; TMP: Turbo-molecular pump; R.P.: Rotary pump; D.P.: Diaphragm pump; T: Thermocouple; P1-P4: Pressure gauges; C1-C2: Controlled valves; V1-V12: Valves.



Fig. 2. (a) Schematic diagram and (b) photograph of the experimental apparatus for measuring adsorption isotherms and kinetics of CO₂ onto Maxsorb-III. 1. Magnetic suspension balance; 2. Sample cell; 3. Circulation oil jacket; 4. Oil bath and circulator; 5. Sheathed heater; 6. Refrigerant container; 7. Isothermal oil bath; 8. CO₂; 9. Helium; TMP: Turbo-molecular pump; R.P.: Rotary pump; D.P.: Diaphragm pump; T: Thermocouple; P1-P4: Pressure gauges; C1-C2: Controlled valves; V1-V12: Valves.

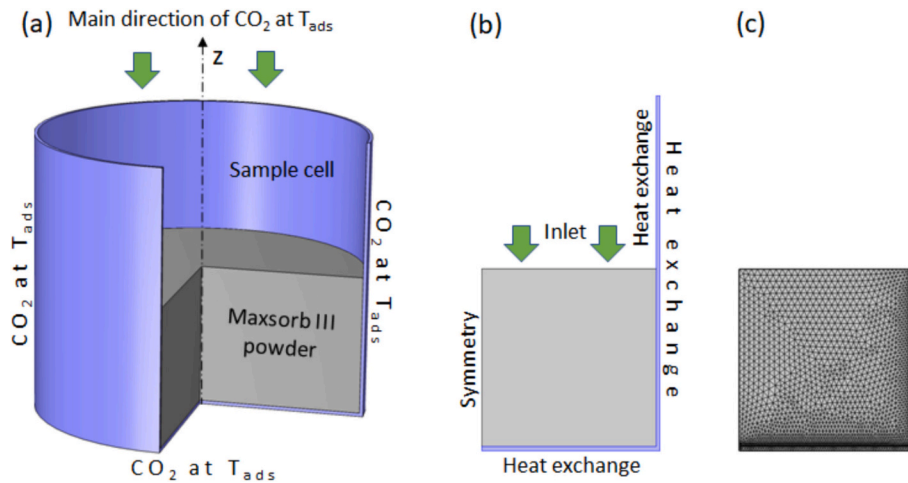


Fig. 3. 3D schematic of CO₂ adsorption onto (a) Maxsorb III, (b) simulation domain, and (c) mesh.

3. Experimental apparatus and procedure

The adsorption kinetics and isotherms of CO₂ onto the Maxsorb-III were measured using a magnetic suspended balance consisting of an adsorption measurement unit (MSB-GS-100-10 M) provided by Micro-tracBEL. The gravity formed between the electromagnet positioned on the balance and the loading mechanism, including a sample hanging from a permanent magnet, means that the adsorption quantity is determined as weight. The sample mass can be recorded with a precision of $\pm 10 \mu\text{g}$ using the magnetic suspension balance. The magnetic balance has a weight measurement repeatability of $\pm 30 \mu\text{g}$ and a relative inaccuracy of $\pm 0.002\%$ of the reading. The pressure is measured with an error of ± 0.1 of full scale using an absolute pressure gauge of type Keller PAA-35 $\times$, capable of measuring pressures up to 10,000 kPa. [15,27].

Fig. 2 shows the schematic drawing and photograph of the measurement unit. It consists of a magnetic suspension balance, a temperature-controlled oil-circulated bath to maintain the adsorption/evaporation temperatures, a temperature-controlled air bath to prevent condensation inside the system, an evaporator, several vacuum pumps, pressure sensors, and temperature sensors. The system performs the whole experiment automatically by following the instructions provided in the control software. Compressed air is used in the system to operate the valves, and pressurized helium gas is used to check for leaks and calculate the void volume, which is necessary for measuring buoyancy. It should be noted that the machine automatically considers the buoyancy effect. Adsorption isotherms and kinetics of CO₂ onto the Maxsorb-III are investigated at three different adsorption temperatures, viz. 30, 50, and 70 °C, and pressure up to 4.5 MPa. To examine the effects of adsorbent bed thickness, three different mass amounts of Maxsorb-III are employed in this study: 66 mg, 369 mg, and 1843 mg, which provide the adsorbent bed's thicknesses as 0.9 mm, 5 mm, and 25 mm, respectively. The experimental procedure can be described as follows:

- i.) To begin, the Maxsorb-III sample amount (66 mg, for instance) is placed into the sample container and connected to the apparatus. Before every isotherm experiment, the sample is heated under vacuum for many hours at 130 °C to eliminate any gas that has been adsorbed.
- ii.) The CO₂ cylinder's gas is charged into the tube (between V1 and C1). As seen in Fig. 2(a), control valve C1 regulates the pressure.
- iii.) It is then directed to the magnetic suspension balance unit to measure the adsorption uptake at low to medium pressure ranges. The saturated pressure of carbon dioxide in the cylinder at a temperature of 20 °C is about 5.7 MPa.

4. Mathematical model

Adsorption of CO₂ occurs within the adsorbent bed (gray domain), which is packed in an elevated vertical cylinder with a height of 53 mm, as shown in Fig. 3(a). The inner diameter and wall thickness of the sample cell (basket) are $D = 23.5$ and $W = 0.2$ mm, respectively. The basket material is stainless steel of grade 316. The flow of CO₂ is described using the Navier-Stokes equation, including porous medium resistance. Energy conservation equations are used to estimate temperature distribution in a porous adsorbent bed and basket material. The traditional linear driving force (LDF) equation is employed to calculate mass transfer. Modified Dubinin-Astakhov (D-A) and Tóth isotherm models are utilized to fit measured equilibria data. The model equations are derived under the following assumptions that CO₂:

- CO₂ is considered an ideal gas;
- There is local thermal equilibrium between the adsorbate and adsorbent particle;
- Flow is laminar;
- Flow is axisymmetric.

4.1. Flow equation

The flow of carbon dioxide within the adsorbent bed is described using Darcy-Brinkman-Forchheimer and mass conservation equations and the ideal gas equation of state [22]. The right-hand side of the mass conservation eq. (1) accounts for the mass disappearance due to the adsorption. The last three terms in the momentum conservation eq. (2) correspond to the Darcy, Forchheimer, and adsorption effects. Incorporation of the Forchheimer term into the momentum equation allows us to account for the high velocities.

$$\frac{\partial(\epsilon \rho_g)}{\partial t} + \nabla \cdot (\rho_g \vec{u}) = S_m \quad (1)$$

$$\frac{\rho_g}{\epsilon} \left(\frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \nabla) \frac{\vec{u}}{\epsilon} \right) = -\nabla p + \nabla \cdot \sigma - \left(\frac{\mu}{k} + \beta \rho_g |\vec{u}| + \frac{S_m}{\epsilon^2} \right) \vec{u} \quad (2)$$

$$\rho_g = \frac{p}{R_g T} \quad (3)$$

where t refers to the time (s), $\vec{u}$ is the Darcy velocity (m/s), $R_g = 188.92 \text{ J}/(\text{kg} \cdot \text{K})$ is the CO₂ gas constant, ρ_g and ρ_p are the gas and adsorbent particle density (kg/m^3), respectively, $\sigma = \frac{\mu}{\epsilon} \left\{ \nabla \vec{u} + \right.$

$(\nabla \vec{u})^T - \frac{2}{3}(\nabla \bullet \vec{u})\mathbf{I}$ and $\mathbf{I}$ denote the viscous stress and identity tensor, respectively. The superscript 'T' in the above expression indicates the matrix transpose operation. p means the gas pressure (Pa), T is the gas temperature (K), μ represents the gas dynamic viscosity (Pa·s), $S_m = -(1 - \varepsilon)\rho_p \frac{dq}{dt}$ is the mass source term due to adsorption, q denotes the mass of the adsorbed phase (g/g), $\varepsilon = 1 - \rho_a/\rho_p - \nu_\mu \rho_a$ is the total porosity and $\nu_\mu = 1.7 \text{ cm}^3/\text{g}$ is the pore volume of the Maxsorb-III [44], the permeability k (m^2) and Forchheimer coefficient β (1/m) is calculated using the following equations

$$k = \frac{D_p^3 \varepsilon^3}{150(1 - \varepsilon)^2}$$

$$\beta = \frac{0.55}{\sqrt{k}},$$

where $D_p = 70 \text{ }\mu\text{m}$ is the average adsorbent particle diameter [45].

4.2. Energy equation

4.2.1. Energy equation for the adsorbent bed

Eq. (4) provides the energy equation for the adsorbent bed, considering the local thermal equilibrium between the adsorbent particle and adsorbate. The specific heat capacities of the adsorbent particle, intraparticle (adsorbed) adsorbate, and interparticle adsorbate are used to compute the effective specific heat capacity of the porous medium. The effective thermal conductivity of the porous medium is calculated from the thermal conductivities of interparticle adsorbate and adsorbent-adsorbate, respectively. The last term in the eq. (4) indicates the heat release during the CO₂ adsorption.

$$(\rho C_p)_{\text{eff}} \frac{\partial T}{\partial t} + \rho_g C_{p,g} \vec{u} \bullet \nabla T = \nabla \bullet (k_{\text{eff}} \nabla T) - S_m Q \quad (4)$$

where $(\rho C_p)_{\text{eff}} = \varepsilon \rho_g C_{p,g} + (1 - \varepsilon) \rho_p (C_{p,p} + q C_{p,l})$ is the effective volumetric heat capacity at constant pressure, $C_{p,g}$, $C_{p,p}$ and $C_{p,l}$ denote the gas phase, adsorbent particle, and adsorbed phase heat capacities at constant pressure (J/(kg·K)), respectively, T is the temperature (K), Q means the isosteric heat of adsorption (J/mol), $k_{\text{eff}} = \varepsilon k_g + (1 - \varepsilon) k_p$ refers to the effective thermal conductivity (W/(m·K)), k_g and k_p are gas phase and adsorbent-adsorbate thermal conductivities (W/(m·K)), respectively.

4.2.2. Energy equation for the basket

The basket material is made from SUS316, and a pure conduction equation is used to obtain the distribution of temperature as follows. The properties of basket material are considered constant.

$$\rho_s C_{p,s} \frac{\partial T_s}{\partial t} = \nabla \bullet (k_s \nabla T_s) \quad (5)$$

where $\rho_s = 7890 \text{ kg/m}^3$, $C_{p,s} = 500 \text{ J/(kg·K)}$ and $k_s = 16.3 \text{ W/(m·K)}$ denote respectively the density, heat capacity at constant pressure, and thermal conductivity of basket material [46], T_s is the basket temperature (K).

4.3. Adsorption rate equation

The adsorption rate of CO₂ onto Maxsorb-III particle is calculated using the first-order linear driving force (LDF) model equation. This model is simple in use and allows to reduce computational time, and given in the following form [47–50].

$$\frac{dq}{dt} = k(q^* - q) \quad (6)$$

where absolute adsorbed mass q^* (g/g) is calculated using a modified Dubinin-Astakhov (D-A) isotherm, k is the overall mass transfer coefficient (1/s) which, in general, depends on many factors, such as external and internal mass transfer coefficients, particle diffusivity and size, inlet concentration (in separation processes), and temperature [48,51–53].

In this paper, the Glueckauf approach is used to calculate the overall mass transfer coefficient k [54].

$$k = \frac{15D_s}{R_p^2}$$

where D_s is the diffusivity (m^2/s), $R_p = D_p/2$ is the average particle radius and the diffusion time constant D_s/R_p^2 is calculated by the Arrhenius equation [55,56].

$$\frac{D_s}{R_p^2} = \frac{D_{s0}}{R_p^2} e^{-\frac{E_a}{RT}} \quad (7)$$

where E_a is the activation energy (J/mol), D_{s0}/R_p^2 is the pre-exponential factor (1/s), $R = 8.314 \text{ J/(K·mol)}$. The diffusion time constant D_s/R_p^2 is obtained by fitting the LDF eq. (6) to the experimental data. It is worth noting that the diffusion time constant is obtained for each pressure level and adsorbent bed thickness at an adsorption temperature of 30, 50, and 70 °C. After that, the pre-exponential factor D_{s0}/R_p^2 and activation energy E_a were identified using eq. (7) on the semi-logarithmic plot, which are the main input parameters of the CO₂ adsorption kinetics for the CFD simulation.

4.4. Initial and boundary conditions

The adsorbent bed (gray domain in Fig. 3(b)) is initially at a constant pressure (P_{in}), which is the equilibrium pressure of the previous adsorption step for the current step (see Fig. 6). The first adsorption step has a small value. There is no flow field assumed to be at the initial time. Initially, the adsorbent bed and basket material (blue domain in Fig. 3(b)) have the same temperature, which is equal to the adsorption temperature. Finally, there is no adsorbed mass of CO₂ at the initial time for the first adsorption step, and equilibrium uptakes from the previous steps are used as an initial condition to the LDF equation when used for the next adsorption steps.

The CO₂ gas enters the adsorbent bed through its top boundary at a constant adsorption temperature T_{ads} and equilibrium pressure P . The left side of the adsorbent bed and basket material domain is treated as a boundary with a symmetry condition for momentum and energy conservation equations. The conjunction condition is applied on the surface between the adsorbent bed and basket for the adsorbent bed and basket energy equations that ensure the continuity of temperature and conductive heat flux. Also, along this surface, a no-slip boundary condition is imposed on the momentum conservation equation for the adsorbate gas. On all surfaces of the basket except surfaces that are in conjunction with the adsorbent bed and on the symmetry line, a Dirichlet boundary condition ($T_s = T_{ads}$) is applied to the energy conservation equation for the basket material.

5. Numerical simulation procedure

The fully coupled finite element method was used to solve the set of equations given in section 4, along with the previously stated initial and boundary conditions. COMSOL Multiphysics version 5.6, a commercial software, was used for this process. An implicit back differentiation time stepping method is used. The automatic Newton solver is used to linearize the coupled nonlinear equations, and the MUMPS direct solver is used to solve the system of linear equations. The maximum number of Newton iterations is set to 100, and the relative tolerance was chosen as 0.005. Free triangular mesh is used for both the adsorbent bed and

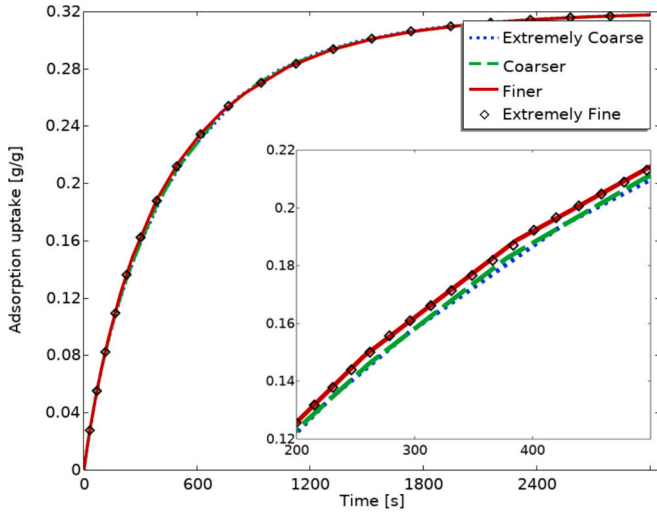


Fig. 4. Mesh sensitivity: CO₂ uptake distribution during adsorption.

basket material domain (Fig. 3(c)), and a grid independence test is conducted to calculate the volume-averaged mass of adsorbed CO₂ over adsorption time (Fig. 4). For the test, extremely coarse, coarser, finer and extremely fine meshes are used. Fig. 4 shows that the change in the calculated mass of adsorbed CO₂ is negligible after the use of finer mesh (with 10,146 elements), so it was selected for further analysis. It is worth noting that mesh was automatically refined near the conjunction wall between the adsorbent bed and basket, and in this region, quadrilateral boundary grids are used.

An essential component of the adsorption process is the adsorbents' specific heat capacity, $C_{p,p}$, which is a function of temperature and expressed as follows [57] and valid for the temperature range $303\text{ K} \leq T \leq 390\text{ K}$

$$C_{p,p} = 10^3 (11.547 - 0.119T + 4.797 \cdot 10^{-4}T^2 - 8.367 \cdot 10^{-7}T^3 + 5.39 \cdot 10^{-10}T^4)$$

The properties of many gases, including CO₂, significantly vary with temperature changes. Many authors analyzed the behavior of experimentally measured properties of CO₂ for a wide range of temperature and pressure changes and reported correlations for their estimation [58–60]. Their analysis is based on the estimation of properties as a sum of their critical and excess enhancement values for their zero-density limit (ideal gas part). Critical enhancement values of CO₂ properties are described by their behavior close to the critical point region. Its contribution decreases as conditions move away from the critical one. The excess enhancement part represents the contribution of all other effects. In this paper, CO₂ is considered an ideal gas, and its properties are calculated as an ideal part of overall properties. In fact, for a wide range of temperature and density, the contribution of critical and excess enhancement parts can be neglected [58–60]. Dynamic viscosity μ and thermal conductivity k_g of CO₂ are also functions of temperature and given by the following correlations [58,59], which have uncertainties <5% and are valid for temperature range $200\text{ K} \leq T < 1500\text{ K}$ and $200\text{ K} \leq T \leq 1000\text{ K}$, respectively, and pressures up to 100 MPa

$$\mu = \frac{1.00697 \cdot 10^{-6} \sqrt{T}}{\sigma_\mu}$$

$$k_g = \frac{4.75598 \cdot 10^{-4} \sqrt{T}}{\sigma_k} \left(1.4 + 0.4e^{\frac{183.5}{T}} \sum_{i=1}^5 c_i \left(\frac{T}{100} \right)^{2-i} \right)$$

where $\ln \sigma_\mu = \sum_{i=0}^4 a_i (\ln T_r)^i$, $\sigma_k = \sum_{i=0}^7 b_i / T_r^i$ and $T_r = T/251.196$.

Specific heat capacity $C_{p,g}$ of CO₂ calculated using the following

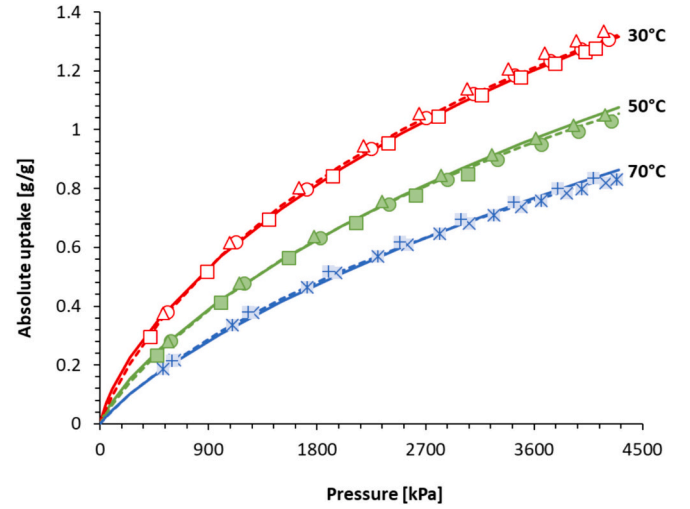


Fig. 5. Adsorption equilibria of CO₂ onto Maxsorb-III: Experimental data at $H = 0.9\text{ mm}$ (O, ●, ☐), $H = 5\text{ mm}$ (△, ▲, ▢) and $H = 25\text{ mm}$ (□, ■, ☒) fitted with modified D-A (solid lines) and Tóth (dashed lines) equations.

correlation [60], which has uncertainties <1.5% and is valid for temperature range $10\text{ K} \leq T \leq 1500\text{ K}$, and pressures up to 30 MPa

$$C_{p,g} = R_g \left(3.5 + \sum_{i=1}^5 d_i (\theta_i \tau)^2 \frac{e^{\theta_i \tau}}{(e^{\theta_i \tau} - 1)^2} \right)$$

where $\tau = T_c/T$, $T_c = 304.128\text{ K}$ and $R_g = 188.924\text{ J/(kg} \cdot \text{K)}$ denote CO₂ critical temperature and specific gas constant, respectively. It is worth noting that the table values of the coefficients a_i , b_i , c_i , d_i , and θ_i can be found in [58–60]. It should be noted that the calculation of the CO₂ properties in the REFPROP software is mainly based on the above equations.

6. Adsorption isotherms

After buoyancy adjustment, the adsorption data from the experimental measuring unit is excess adsorption. The absolute adsorbed mass could be obtained as the sum of excess adsorption and buoyancy correction factor [27].

$$q^* = q_{exc.} + \rho_g V_\mu$$

where $q_{exc.}$ denotes the excess adsorbed mass (g/g) and CO₂ density ρ_g is obtained using REFPROP software version 9.0.

A modified Dubinin-Astakhov (D-A) equation is used to fit the experimental data [27,61,62].

$$q^* = \frac{W_0}{V_m} e^{-\left(\frac{A}{E}\right)^n}$$

$$A = RT \ln \left[\frac{P_c}{P} \left(\frac{T}{T_c} \right)^k \right]$$

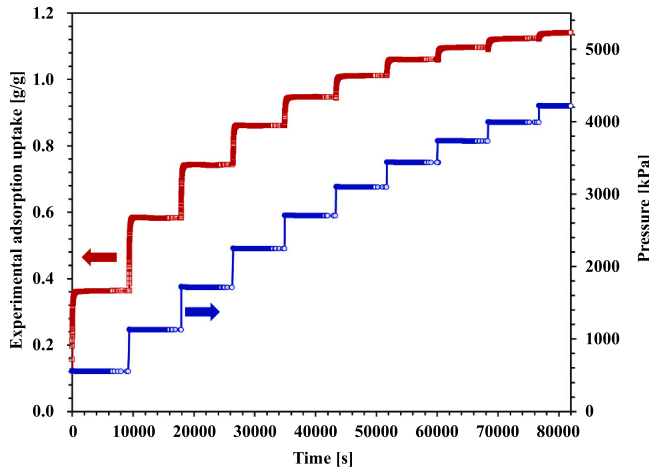
where $V_m = 0.84858e^{2.5 \cdot 10^{-3}(T-216.6)}$ is the CO₂ molar volume (cm^3/g), W_0 is the limiting micropore volume (cm^3/g), A is the adsorption potential (J/mol), E is the characteristic energy (J/mol), R is the universal gas constant ($\text{J/(K} \cdot \text{mol)}$), P_c and T_c is the critical pressure (kPa) and critical temperature (K), respectively, n is the structural heterogeneity parameter, and k is the parameter of adsorbent-adsorbate interactions.

Tóth equation is also used to fit the experimental data [27,61].

Table 1

Parameters of modified D-A and Tóth equation.

Parameters	D-A equation	Tóth equation
W_0 [cm ³ /g]	1.73	
E [J/mol]	4755.4	
n [–]	1.18	
k [–]	3.79	
q_0 [g/g]		4.54
Q [J/mol]		18,046.4
b_0 [1/kPa]		2.1×10^{-7}
t [–]		0.53
$rmsd$	2.46	1.73
R^2	0.9966	0.9979

**Fig. 6.** Temporal histories of uptake and pressure change with the time of CO₂ adsorption onto Maxsorb-III at 30 °C for an adsorbent bed thickness of 0.9 mm.

$$q^* = \frac{q_0 b P}{[1 + (bP)^t]^{1/t}}$$

where t is the heterogeneity parameter (–), P is the equilibrium pressure (kPa), q_0 is the saturated amount of adsorbed (g/g), $b = b_0 e^{\frac{Q}{RT}}$ is the adsorption affinity (kPa^{–1}) given by, b_0 is the adsorption affinity at infinite temperature (kPa^{–1}).

7. Results and discussion

7.1. Adsorption equilibria and kinetics

The absolute adsorbed mass of CO₂ onto Maxsorb III for adsorbent

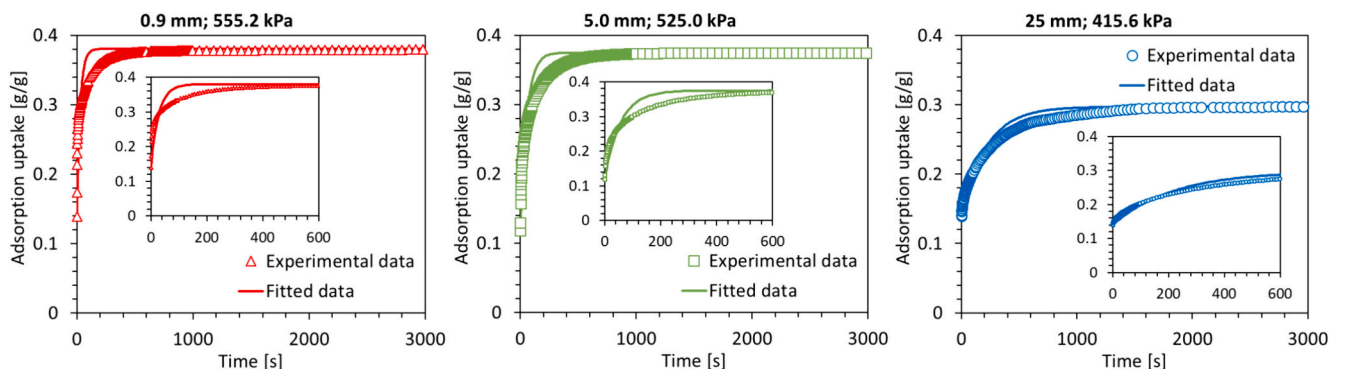
bed thickness of 0.9, 5, and 25 mm and adsorption temperature of 30, 50, and 70 °C is plotted in Fig. 5 (symbols). This figure plots the fitted values of the absolute adsorbed mass of CO₂ using modified D-A (solid lines) and Tóth (dashed lined) equations. As shown in Fig. 5, there is a good agreement between the experimental and fitted values of carbon dioxide uptake for all considered adsorption temperatures. The fitting parameters provided in Table 1 are used in CFD simulations.

The temporal histories of absorption and pressure change with CO₂ adsorption time onto Maxsorb-III at 30 °C for a 0.9 mm thick adsorbent bed are displayed in Fig. 6. The changes in adsorption pressures extend up to a maximum of 4200 kPa. The graphs clearly depict a consistent pattern in the adsorption kinetics seen throughout all stages of adsorption. Particularly, after an increase in pressure, there is a rapid initial increase in the adsorbed amount, gradually stabilizing to around the equilibrium uptake level as time goes on.

Fig. 7 depicts the fitting of the LDF equation to the experimental data for an adsorbent bed thickness of 0.9 (left), 5 (middle), and 25 (right) mm at 30 °C and given pressure considering constant equilibrium adsorption uptake. The comparison of two data for the first 600 s is given in the inserted sub-figures. In this figure, solid lines and symbols correspond to the fitted and experimental data. Fig. 7 shows that the LDF equation underestimated the adsorption uptake at the beginning of adsorption due to consideration of equilibrium uptake. Despite this, the LDF equation was used to obtain a constant diffusion time that fit the experimental data.

7.2. Comparison between CFD model simulated and experimental data

The time variation of volume averaged CO₂ uptakes for different adsorbent bed thicknesses, and pressures are shown in Fig. 8. In this figure, solid lines and symbols correspond to simulated and experimental uptakes, respectively. It is noted that there are considered the comparison results only for the lowest ($T_{ads} = 30$ °C) and highest ($T_{ads} = 70$ °C) adsorption temperatures. As can be seen from Fig. 8, there is a reasonable agreement between simulated and experimental uptakes for different adsorbent bed thicknesses and pressures, which means that the CFD model is capable of predicting the adsorbed mass of CO₂. From Fig. 8, it can be seen that there are two types of mismatch between the simulated and experimental data. The first one is related to the mismatch between simulated and experimental final uptake values inherited from fitting experimental equilibrium data by a modified D-A equation. The second one is seen at earlier adsorption times and sourced from the LDF model, which is used to obtain diffusion time constant by fitting to the experimental data. The fitting of the experimental data is carried out considering constant adsorption temperature, although it changes during the adsorption. Any other indirect potential sources of discrepancies between experimental and simulated data may be related to the model assumptions that a) the CFD model uses constant temperature condition instead of convection heat transfer condition; b) there is local thermal equilibrium between the adsorbate and adsorbent particle

**Fig. 7.** Fitting of the LDF equation (solid lines) to the experimental data (symbols) for an adsorbent bed thickness of 0.9 (left), 5 (middle), and 25 (right) mm at 30 °C.

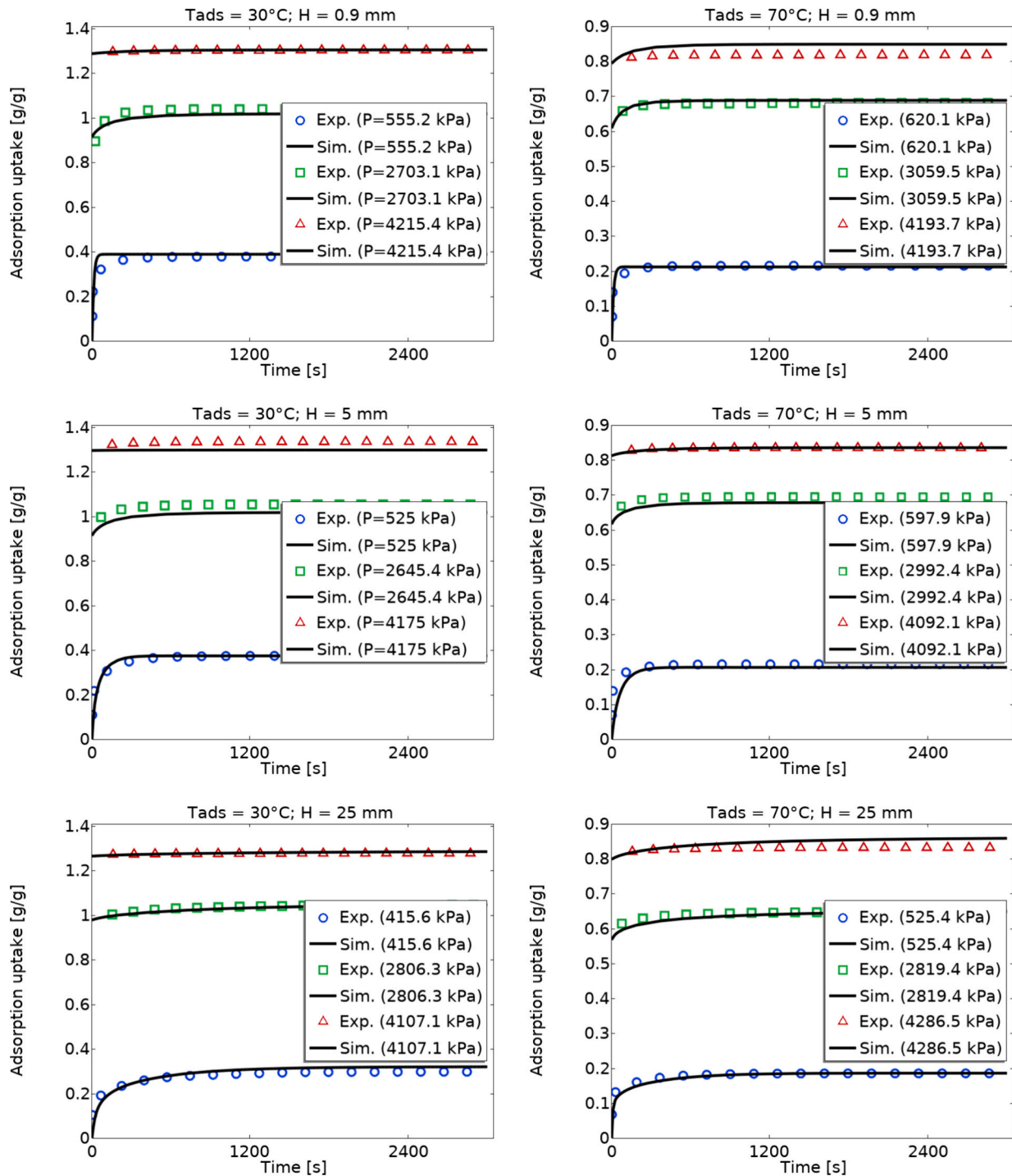


Fig. 8. Simulated using CFD model (solid lines) uptakes in comparison to the experimental uptakes (symbols).

and c) CFD model defines the flow characteristics (velocity, pressure, temperature, etc.) over the Darcy scale that is sufficiently large compared to the adsorbent particle (or interparticle void) size and sufficiently small compared to the size of the simulation domain. The former assumption was made due to the lack of information about the flow condition of CO_2 around the cooling side of the basket. The last two assumptions were made to reduce the whole computation time and due to the lack of information about the real pore structure of the adsorbent bed. The knowledge of the real pore structure of the adsorbent bed allows us to conduct pore-scale simulations instead of Darcy scale simulations that help to consider more real flow regimes of the adsorbate at a

smaller scale. Despite this, it should be noted that the maximum error of simulated uptake does not exceed 3–5%.

7.3. Effect of adsorbent bed thickness on diffusion time constant

The diffusion time constant $\left(\frac{D_s}{R_p^2}\right)$ is the important parameter in the LDF model (Eq. 6) that influences the kinetics of adsorption onto adsorbents. The detailed understanding of diffusion time constants and their dependence on operating conditions and adsorbent bed design enables significant optimization opportunities for adsorption-based

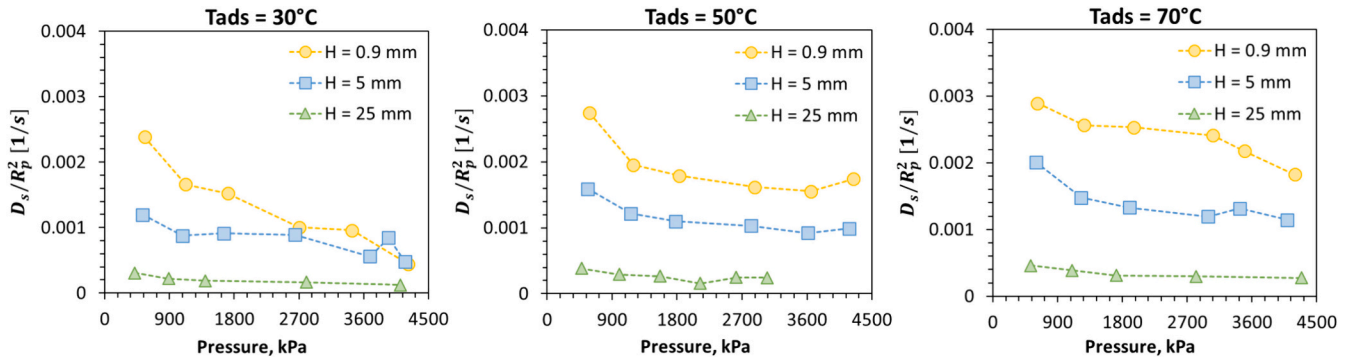


Fig. 9. Diffusion time constant vs. equilibrium pressure for different adsorbent bed thickness and adsorption temperature.

Table 2

Parameters of adsorption kinetics.

Bed thickness, H [mm]	Adsorption temperature [°C]					
	30		50		70	
	P_{eq} [kPa]	D_s/R_p^2 [s ⁻¹]	P_{eq} [kPa]	D_s/R_p^2 [s ⁻¹]	P_{eq} [kPa]	D_s/R_p^2 [s ⁻¹]
0.9	555.2	2.38×10^{-3}	586.5	2.74×10^{-3}	620.1	2.89×10^{-3}
	1126.0	1.66×10^{-3}	1193.8	1.95×10^{-3}	1269.1	2.57×10^{-3}
	1712.5	1.52×10^{-3}	1828.4	1.79×10^{-3}	1956.8	2.53×10^{-3}
	2703.1	1.01×10^{-3}	2878.0	1.62×10^{-3}	3059.5	2.41×10^{-3}
	3436.6	9.58×10^{-4}	3655.9	1.56×10^{-3}	3496.1	2.18×10^{-3}
	4215.4	4.44×10^{-4}	4239.7	1.74×10^{-3}	4193.7	1.82×10^{-3}
	525.0	1.20×10^{-3}	563.0	1.59×10^{-3}	597.9	2.01×10^{-3}
	1077.4	8.75×10^{-4}	1154.4	1.22×10^{-3}	1227.6	1.48×10^{-3}
5	1651.0	9.11×10^{-4}	1776.0	1.10×10^{-3}	1895.7	1.33×10^{-3}
	2645.4	8.89×10^{-4}	2826.7	1.03×10^{-3}	2992.4	1.19×10^{-3}
	3686.3	5.61×10^{-4}	3610.7	9.19×10^{-4}	3429.2	1.31×10^{-3}
	3946.6	8.45×10^{-4}	4185.4	9.90×10^{-4}	4092.1	1.14×10^{-3}
	4175.3	4.82×10^{-4}				
	415.6	3.09×10^{-4}	474.1	3.83×10^{-4}	525.4	4.61×10^{-4}
	887.7	2.20×10^{-4}	998.0	2.93×10^{-4}	1097.8	3.86×10^{-4}
	1400.3	1.87×10^{-4}	1564.7	2.67×10^{-4}	1716.9	3.11×10^{-4}
25	2806.3	1.67×10^{-4}	2122.8	1.58×10^{-4}	2819.0	2.99×10^{-4}
	4107.1	1.26×10^{-4}	2618.4	2.47×10^{-4}	4286.5	2.75×10^{-4}
			3050.0	2.42×10^{-4}		

heating and cooling technologies. By leveraging these insights, engineers can design systems that are more efficient, cost-effective, and tailored to specific applications. This optimization leads to enhanced performance, reduced energy consumption, and improved sustainability of ACHS. Fig. 9 depicts the change of the diffusion time constant versus equilibrium pressure of adsorption stages, which is obtained by fitting experimental data with the LDF model for different adsorbent bed thicknesses and adsorption temperatures. From this figure, it can be seen that there is a decreasing trend in diffusion time constant as pressure increases for all considered adsorbent bed thicknesses and adsorption temperatures. This might be due to the fact that it is hard to reach more and more adsorption rates for high pressures due to quick saturation. It shows that the pressure-dependence nature of the diffusion time constant has to be considered when assessing the performance of the fixed bed adsorbent layer.

Fig. 9 also shows that the diffusion time constant (D_s/R_p^2) for CO₂ adsorption onto activated carbon of type Maxsorb-III is higher for thinner adsorbent beds than thicker ones for a certain value of adsorption temperature and, especially, for lower adsorption pressures. It means thinner adsorbent beds have more adsorptive capability for CO₂ than thicker beds for a given adsorption temperature and pressure. Additionally, it can be observed from Fig. 9 that the effect of adsorption temperature on diffusion time constant is bigger for high temperatures compared to low temperatures for a fixed bed thickness and a given pressure (see Fig. 9 and Table 2). This coincides with the dependence of D_s/R_p^2 on temperature according to the Arrhenius equation (Eq. 7).

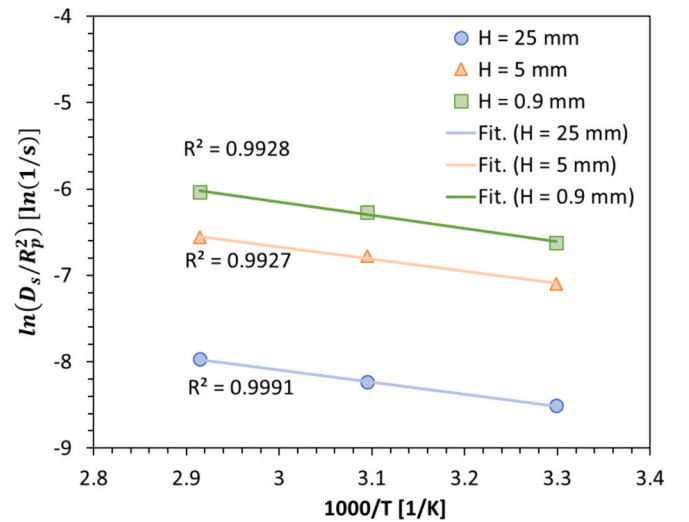


Fig. 10. Plot of linearized Arrhenius equation for different adsorbent bed thicknesses.

Table 3

Parameters of Arrhenius equation.

Bed thickness, H [mm]	D_{s0}/R_p^2 [s ⁻¹]	E_a [kJ kg ⁻¹]
0.9	2.18×10^{-1}	291.4
5	8.64×10^{-2}	265.8
25	2.05×10^{-2}	264.9
Average	1.08×10^{-1}	279.6

Table 2 consists of fitted values of D_s/R_p^2 for a pressure from about 500 kPa to pressures >4000 kPa. It is noted that the coefficient of determination R^2 for the fitting of experimental uptake data using the LDF equation ranges from 0.8174 to 0.9995, and prediction is improved with increasing equilibrium pressure. This data can be used to interpolate the values of the diffusion time constant for pressure levels that are not considered in this study.

The average values of diffusion time constant at each adsorption temperature are calculated and fitted with the Arrhenius equation (Eq. 7). Its plot versus the inverse of adsorption temperature is shown in Fig. 10 for different adsorbent bed thicknesses. It can be seen from Fig. 10 that the plots of the relationship between $\ln(D_{s0}/R_p^2)$ and $1/T$ for different adsorbent bed thicknesses are almost collinear. This could mean that the same plot but for the other adsorbent bed thicknesses, which are not considered in this study, can be derived by interpolating or extrapolating these data, at least for the pressure range considered in this study. The fitting parameters of the Arrhenius equation are given in Table 3. Table 3 shows that the activation energy E_a for larger adsorbent bed thicknesses by almost 9% is less than those for lowest adsorbent bed

thicknesses. The reason for this could be the fact that the overall surface coverage of the adsorbent bed by CO₂ molecules is higher in the case of thinner adsorbent beds than in thicker ones. On the other hand, the limiting (or zero energy level) diffusion time constant D_{s0}/R_p^2 is reduced by 2.5 and 4.2 times, respectively, for the increase of adsorbent bed thickness by 5 times from 0.9 to 5 mm and from 5 to 25 mm, i.e., the linear increase in adsorbent bed thickness led to a faster nonlinear decrease in D_{s0}/R_p^2 . This may suggest that there exists a maximum adsorbent bed thickness, after which the diffusion time constant is almost zero.

7.4. Effect of adsorbent bed thickness on adsorption kinetics

Fig. 11 shows the evolution of simulated adsorption uptake (upper) and adsorbent bed temperature (lower) over adsorption time for different adsorbent bed thicknesses and $T_{ads} = 30^\circ\text{C}$. Here, the simulation results are displayed only for low (500 kPa) and high (4200 kPa) pressure levels since the behavior of uptake and temperature distribution over time for other pressure levels and adsorption temperatures is the same as for these pressures and temperatures. It is noticed that these pressures are not considered during experimental measurements but are very close to the pressures of the beginning and final adsorption steps. Initial uptake and pressure for these simulations are 0 (g/g), 1.0 kPa and 1.271 (g/g), 4000 kPa, respectively, for low and high-pressure cases. The main goal is to apply the same conditions for three adsorbent bed thicknesses in order to compare their adsorption kinetics.

Fig. 11 clearly shows that CO₂ adsorbed faster onto adsorbent beds with lower thicknesses than higher thicknesses. For 500 kPa, adsorbent

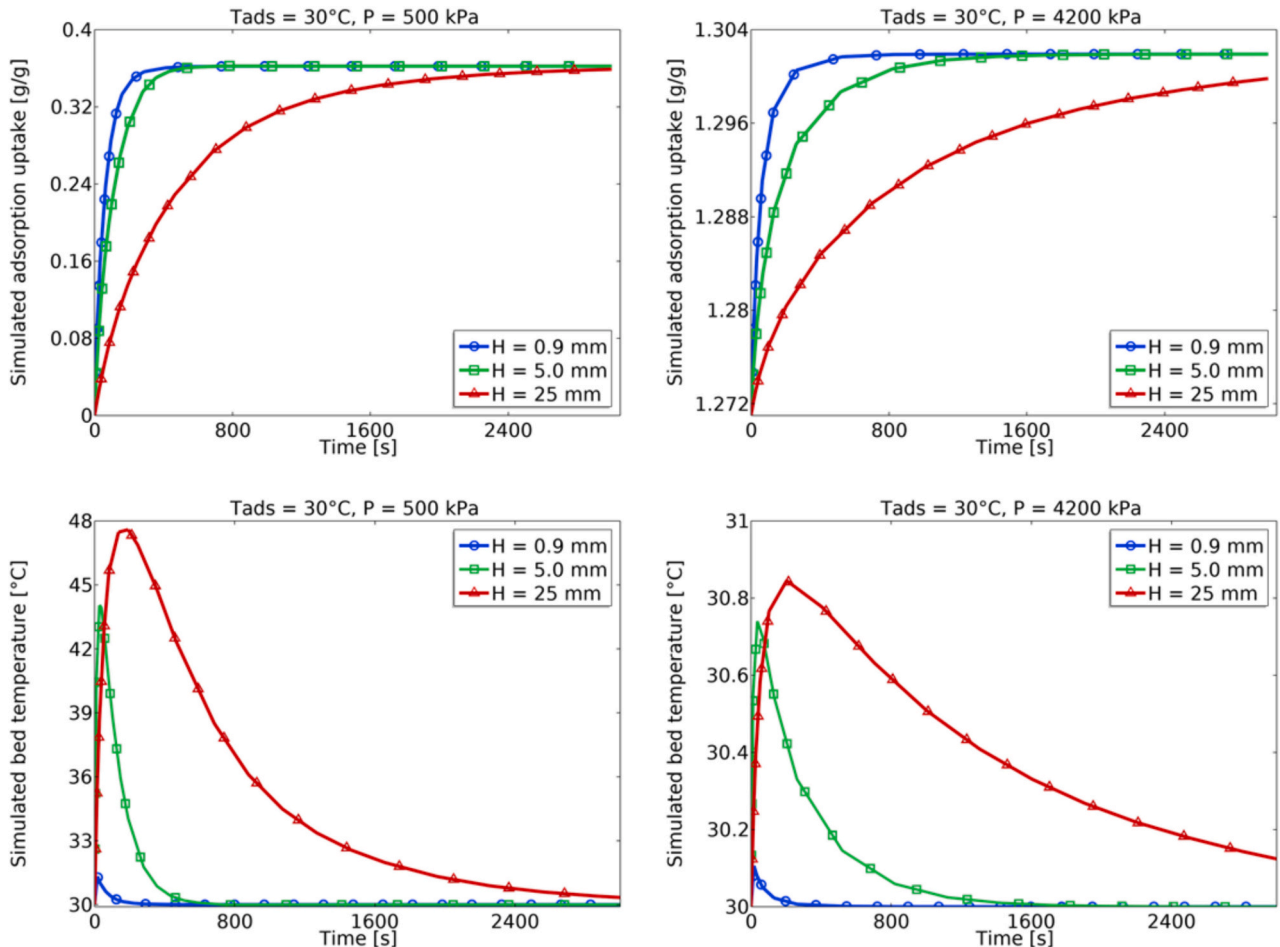


Fig. 11. Simulated adsorption uptake (upper) and bed temperature (lower) using CFD model for different adsorbent bed thicknesses and two pressures.

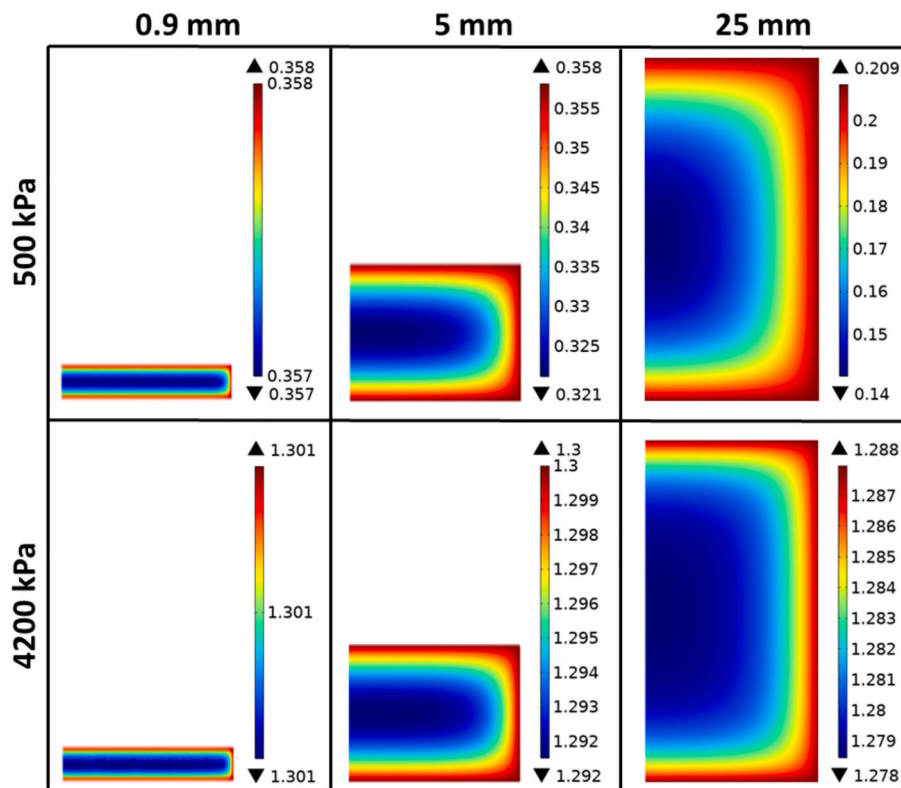


Fig. 12. Distribution of simulated adsorbed mass of CO₂ using CFD model for different adsorbent bed thicknesses and adsorption steps at 300 s.

beds with 0.9 and 5 mm thicknesses reach equilibrium conditions much faster than 25 mm adsorbent bed thickness. This is due to the faster cooling of thinner adsorbent beds. Adsorbent beds with higher thickness have poor cooling rates due to high thermal resistances. Fig. 10 also shows that the adsorbent bed thickness effect is more intensified in high-pressure cases, although the increase in adsorption uptake is much lower than in the case with 500 kPa. This also influences the cooling rate of adsorbent beds, although much lower adsorption heat is released in high-pressure cases due to high-pressure gradients.

Fig. 12 demonstrates the distribution of adsorption uptake for different adsorbent bed thicknesses and two pressure levels at 300 s. Fig. 12 depicts simulation results just for the adsorption temperature of $T_{ads} = 30^\circ\text{C}$ as before. Fig. 12 shows that the distribution behavior of adsorption uptake for any adsorbent bed thicknesses and adsorption pressures considered are the same. Only minimum and maximum values of adsorption uptake are changed from one case to another case. This possibly means that the equi-surfaces of adsorbate concentration can be described spatially by a unique formula for any adsorbent bed thicknesses, adsorption pressures, and temperatures with correction of initial and equilibrium uptakes. This allows us to reduce simulation time significantly.

Fig. 12 also shows that the difference between the minimum and maximum uptake values rises with the increase of adsorbent bed thickness for both values of adsorption pressure. This means that the whole part of thinner adsorbent beds efficiently works compared to adsorbent beds with higher thicknesses. The main reason for this is the poor cooling rate of adsorbent beds with higher thickness since the specific surface area (total surface area to the total volume of adsorbent bed) available for cooling decreases with the increase of adsorbent bed thickness. It can be concluded that the thinner adsorbent beds are more efficient for CO₂ adsorption onto Maxsorb-III. However, the efficiency of adsorbent beds with a higher thickness can be increased by the addition of fins.

8. Conclusions

The effects of adsorbent bed thickness on CO₂ adsorption equilibria and kinetics are studied using a magnetic suspension adsorption measurement unit and a transient heat and mass transfer CFD model. Three different mass amounts of Maxsorb-III have been employed in this study: 66 mg, 369 mg, and 1843 mg, which provide the adsorbent bed's thicknesses as 0.9 mm, 5 mm, and 25 mm, respectively. Adsorption kinetics and isotherms of CO₂ onto the Maxsorb-III (AC) are measured gravimetrically using a magnetic suspension measurement unit at three different temperatures of adsorption, viz. 30, 50, and 70 °C and pressure up to 4.5 MPa.

Adsorption equilibrium data of CO₂ for adsorption temperatures of 30, 50, and 70 °C and pressures up to 4.5 MPa are fitted well using modified Dubinin-Astakhov and Tóth equations, and the RMSD of fitting are respectively 2.46 and 1.73. Tóth equation is used for the estimation of averaged isosteric heat of adsorption, which is equal to 18,046.4 J/mol. This study shows the pressure dependence behavior of diffusion time constant, and it decreases with the increase of pressure for all adsorption temperatures considered. The pressure dependence behavior of diffusion time constant could be useful for designing adsorbent beds operating with the adsorption pressure from the range of about 0.5–4.5 MPa and adsorption temperatures of 30, 50, and 70 °C. The study also reveals the dependence of diffusion time constant on adsorbent bed thickness. Adsorbent beds with lower thicknesses have higher diffusion time constant and, consequently, faster kinetics. Averaged values of diffusion time constants corresponding to different adsorption pressures fit well with the Arrhenius equation, which allowed us to estimate the following values of limiting diffusion time constant of 2.18×10^{-1} , 8.64×10^{-2} and 2.05×10^{-2} 1/s, respectively for adsorbent bed thicknesses of 0.9, 5, and 25 mm. The adsorbent beds with higher thicknesses are poorly cooled due to their lower specific surface area subjected to external cooling. This study also shows that the provided CFD model can be a useful simulation tool for a comprehensive study of the adsorption

of CO₂ onto Maxsorb-III activated carbon powder adsorbent bed for adsorption temperatures of 30, 50 and 70 °C and pressures up to 4.5 MPa.

An adsorbent bed with a thickness of 0.9 mm has 9% higher activation energy than those for 5 and 25 mm, which is 291.4 kJ/kg. The estimated diffusion time constant and activation energy can be used to predict CO₂ adsorption kinetics onto activated carbon of type Maxsorb-III and are crucial for designing a CO₂-based adsorption heating/cooling system, considering temperatures of 30, 50, and 70 °C and pressures up to 4.5 MPa. This system can be optimized for adsorbent beds ranging from 0.9 to 25 mm thick by utilizing experimental isotherms data, kinetics data, and simulated data using the CFD model.

The findings from this study offer several significant applications and performance benefits for adsorption-based heating and cooling technologies. By understanding the influence of adsorbent bed thickness on adsorption kinetics, the study enables the design of optimized adsorption beds that achieve higher adsorption rates and faster cycle times, leading to increased overall efficiency and more effective cooling and heating cycles. Tailoring adsorbent bed thickness enhances adsorption kinetics and equilibria, minimizing energy consumption during regeneration phases and resulting in significant energy savings and lower operational costs. These comprehensive insights, derived from both experimental and numerical approaches, facilitate the development of more efficient, adaptable, and cost-effective ACHS, meeting industrial and environmental standards while offering significant energy savings and operational benefits.

To enhance the compactness of CO₂-based ACHS, it's suggested that carbon-based composite adsorbents with different innovative designs of heat exchangers be explored. In the future, the authors aim to widen this research by considering the pore-scale simulation technique to improve the CO₂ adsorption prediction onto the Maxsorb-III activated carbon powder adsorbent bed.

CRedit authorship contribution statement

Bakytzhan Assilbekov: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Animesh Pal:** Writing – original draft, Writing – review & editing, Methodology, Investigation, Formal analysis. **Md. Amirul Islam:** Writing – original draft, Investigation, Formal analysis. **Bidyut Baran Saha:** Writing – review & editing, Supervision, Resources, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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