

Fuel

Study of natural zeolites for hydrogen purification: CO₂ adsorption capacity and kinetic mechanism

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Abstract:	Hydrogen is considered a promising alternative fuel. However, in order to be used, it is necessary to achieve a high degree of purity through purification processes. Adsorption is considered one of the most important techniques for purification. In this research, the CO₂ adsorption capacity and kinetic mechanism of natural zeolite were investigated with the aim to understand the carbon dioxide adsorption behaviour under different operating conditions. Multicomponent breakthrough curves of a mixture of H₂/CO/CH₄/CO₂ were obtained at different pressures and gas flow rates. Moreover, the analysis of CO₂ adsorption equilibrium and kinetics were carried out. The obtained adsorption isotherm data were fitted with different model equations. Freundlich, Sips and Toth models showed the best fit for the experimental data, indicating the heterogeneous nature of the adsorbent surfaces. The carbon dioxide adsorption kinetic was analysed using different kinetic models, obtaining that the adsorption process is both physical and chemical and that the limiting step of the diffusion process is intraparticle diffusion, although other processes are also involved such as diffusion through the boundary layer.
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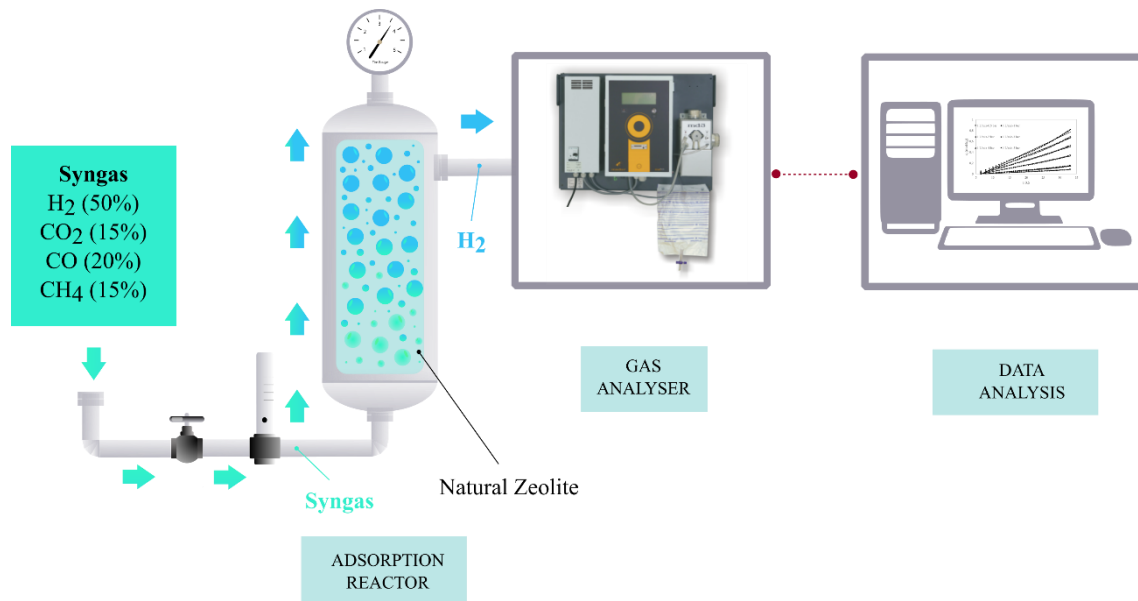
Enhanced understanding of CO₂ adsorption behavior under various operating conditions.

Multicomponent breakthrough curves for H₂/CO/CH₄/CO₂ mixtures were obtained.

Detailed analysis of CO₂ adsorption equilibrium and kinetics on natural zeolite.

Isotherm data correlated with pressure using various model equations.

Comprehensive kinetic analysis of CO₂ adsorption using different kinetic models.



1 **Study of natural zeolites for hydrogen purification: CO₂ adsorption capacity and kinetic**
2 **mechanism**

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8

9 **Abstract**

10 Hydrogen is considered a promising alternative fuel. However, its use requires a high degree of
11 purity achieved through purification processes. Adsorption is considered one of the most
12 important techniques for purification. This study investigates the CO₂ adsorption capacity and
13 kinetic mechanism of natural zeolite to understand carbon dioxide adsorption behavior under
14 various operating conditions. Multicomponent breakthrough curves of a mixture of
15 H₂/CO/CH₄/CO₂ were obtained at different pressures and gas flow rates. Additionally,
16 comprehensive analyses of CO₂ adsorption equilibrium and kinetics were conducted. The
17 adsorption isotherm data were fitted with different model equations. Freundlich, Sips and Toth
18 models providing the best fit, indicating the heterogeneous nature of the adsorbent surfaces. The
19 carbon dioxide adsorption kinetic was analysed using different kinetic models, obtaining that the
20 adsorption process involves both physical and chemical interactions. The limiting step of the
21 diffusion process is intraparticle diffusion, although a sequence of linear sections observed in the
22 qt vs. $t^{1/2}$ plots indicates the presence of multiple mass transfer mechanisms, such as diffusion
23 through the boundary layer.

24 **Keywords:** natural zeolites, kinetic mechanism, carbon dioxide adsorption, hydrogen purification

25 **1. Introduction**

26 Hydrogen is a clean fuel considered an alternative to fossil fuels to enable the transition to a clean,
27 low-carbon energy system, reducing the negative impact of carbon emissions on the climate and
28 improving air quality [1]. This energy vector can be obtained from a wide range of methods (water
29 electrolysis, steam reforming, coal or biomass gasification) [2] and energy sources (natural gas,
30 coal, biomass, or ethanol) [3], being the steam reforming the main production method. Among
31 these, steam reforming emerges as the predominant production technique, wherein hydrocarbons
32 undergo conversion to hydrogen, carbon monoxide, and, to a lesser extent, carbon dioxide and
33 other impurities like methane, facilitated by catalysts [4].

34 Hydrogen purification is a very important step to link hydrogen production with hydrogen
35 utilization and to be a low-carbon energy carrier [5]. Carbon dioxide, a byproduct of several
36 hydrogen production processes, necessitates mitigation to prevent atmospheric emissions through

concentration, capture, or sequestration, thereby enhancing hydrogen quality. Various methods for hydrogen purification, including adsorption, absorption, low-temperature separation, and metal hydride separation, have been explored [6].

Adsorption is one of the most widely used technologies to remove carbon dioxide. The advantages of adsorption are simplicity, cost-effectiveness [7], lower regeneration energy requirements and minimum pressure drop [8]. The efficacy of this process in the capacity to sequester CO₂ from a medium has already been demonstrated in previous studies, where different adsorbents have been used, such as zeolites[9], activated carbon [10], alkali metal adsorbents [11], 5A or 13X molecular sieves [12], metal-organic frameworks (MOFs) [13]. Notably, pure silica zeolites, especially those with small pores, have garnered attention for carbon dioxide adsorption [14].

Compared to conventional CO₂ adsorbents, synthetic and natural zeolites have been used as adsorbent of hydrogen [15,16] or other gases [12,17] due to their properties (porous structure, adsorption ability, cation exchange or thermal stability) [18] that allow them to discriminate between molecules. They have been applied in many industrial processes to separate different compounds and have a potential applicability in process under development [19–22]. Natural zeolites offer cost-effective alternatives to synthetic zeolites, with comparable adsorption performance [23]. Environmentally, natural zeolites require less energy for extraction and processing, resulting in lower greenhouse gas emissions compared to the energy-intensive production of synthetic zeolites, which involves high-temperature and high-pressure processes [24]. Moreover, natural zeolites involve minimal chemical treatment, reducing the environmental impact associated with hazardous chemical waste [25]. Economically, natural zeolites are more cost-effective due to their abundance and lower extraction and processing costs [26]. This makes them viable for large-scale industrial applications, including CO₂ adsorption in hydrogen purification, where cost-efficiency is very important. Additionally, the use of natural zeolites promotes a more sustainable supply chain by reducing dependence on complex manufacturing and international supply chains required for synthetic zeolites [27]. According to Pérez-Botella et al. [28], natural zeolites have shown promising results in adsorption applications due to their abundance and low cost. In order to choose a suitable material for the adsorption process, it is

very important to know equilibrium data and kinetic properties, because they provide information on the adsorption rate at controlled conditions [10]. Moreover, other parameters of CO₂ (single-component and multicomponent equilibrium and kinetic adsorption) are necessary to obtain a mathematical adsorption model that describes the dynamic adsorption phenomena in a fixed bed. Li et al. [29] conducted an investigation on a specific commercial zeolite for the purpose of separating CO₂ from CH₄. Their study aimed to assess the efficiency of this zeolite in selectively adsorbing CO₂ over CH₄ and found a physical adsorption process on CO₂ on zeolites. Majchrzak-Kuceba et al. [30] explored the adsorption of CO₂ on zeolites derived from fly ash, revealing a notable preference for CO₂ adsorption over other gases. Furthermore, the research highlighted the structural and surface characteristics of these zeolites as influential factors in their CO₂ adsorption performance. Siriwardane et al. [31] evaluated CO₂ adsorption levels on two zeolite types (13X and WE-G 592) using thermogravimetric analysis. Furthermore, it has been observed that adsorption on zeolites is a dynamic process involving various steps, including diffusion within pores and surface reactions. In their research, Shikuku et al. [32] investigated the adsorption equilibrium and kinetics of natural zeolite. They found that the equilibrium sorption data could be accurately described by both the Langmuir and Freundlich models. Moreover, the adsorption kinetics followed the pseudo-second-order kinetic law, suggesting a complex adsorption mechanism where pore diffusion was not the sole determining step in the process.

The aim of this study is to assess the carbon dioxide adsorption of a commercially available natural zeolite (ZEOPOL) within multicomponent gas mixtures (H₂, CO, CH₄, CO₂), closely mimicking industrial conditions. While prior research has extensively studied single-component adsorption [22,33,34], understanding the behaviour of multicomponent mixtures during carbon dioxide adsorption and evaluating their adsorption properties assumes great significance in hydrogen purification outcomes. It provides an in-depth analysis of adsorption kinetics using various models to elucidate the mechanisms involved and evaluates different isotherm models to represent adsorption equilibrium accurately. Moreover, experiments conducted in a fixed-bed reactor offer practical insights into the zeolite's performance under continuous flow conditions, demonstrating its potential as a cost-effective and efficient alternative for hydrogen purification.

It is expected that the obtained results can provide a better understanding of carbon dioxide adsorption in a mixture of gas for hydrogen purification.

2. Materials and methods

2.1 Adsorbent used in this study

The material used for carbon dioxide adsorption was natural zeolite ZEOPOL (with a particle size ranging between 1-3 mm). Before adsorption process, the natural zeolite was dried in an oven at 105 °C for 4 hours to reduce the moisture content. The physical and chemical properties provided by the supplier are summarized in Table 1.

Table 1. Physical and chemical properties of natural zeolite.

Properties		Values
Chemical composition	SiO ₂ %	68.15
	Al ₂ O ₃ %	12.3
	K ₂ O %	2.8
	CaO %	3.95
	Na ₂ O %	0.75
	MgO %	0.9
	Fe ₂ O ₃ %	1.3
	TiO ₂ %	0.2
BET surface area	m ² /g	25-50
Porosity	%	30
Apparent density	g/cm ³	0.7
MOHS Hardness		3-3.5
Cation exchange capacity (CEC)	Ca ²⁺ meq/g	1.2-1.96
	NH ₄ ⁺ meq/g	1.2-1.5
Thermal stability	°C	<450
Chemical stability	Ph	3-11

2.1.1 Characterization

The following properties were determined to characterize the natural zeolite:

Mineral phase characterization was detected by X-ray diffraction using a Philips X'Pert Bragg Brentano X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV (generator voltage), 30 mA (tube current), with 0.02° scan step size, 200 s/step of counting time, and data angle range (2 θ) of 5–80°.

Microstructure, morphology, and chemical composition were studied by environmental scanning electron microscopy (ESEM) and energy dispersive X-ray spectroscopy (EDX) using an FEI ESEM Quanta 200 microscope equipped with an EDAX EDX detector.

The thermal behaviour of the zeolite was determined using a thermogravimetry–differential scanning calorimeter (TG-DSC, Labys Evo 1180). The measurements were made in duplicate, in an N₂ atmosphere, and heating the samples from 30 to 900 °C using a heating ramp of 10 °C/min. The specific surface area, in the range of relative pressure p/p_0 from 0.06 to 0.2, was calculated both by the Brunauer–Emmett–Teller (BET) and Langmuir techniques using an ASAP 2020 volumetric adsorption analyzer (Micromeritics). For this purpose, N₂ adsorption–desorption measurements were carried out at 77 K. The total pore volume and the average pore-size were calculated from the desorption branch of the isotherm using BJH (Barrett–Joyner–Halenda) method. The pore size distribution was calculated from the absorption branch of the isotherm using BJM model. The micropore volume was calculated by the t-plot method.

2.2. CO₂ adsorption experiments

The adsorption test and kinetic mechanism were carried out in a fixed-bed cylindric reactor (6.35 cm of diameter and 34 cm of length), in which the amount of zeolite used by weight was kept constant at 300±10 g in each test (Figure 1). A mixture of the main components of syngas was introduced in the system at six different pressures (0.5, 1, 2, 3, 4 and 5 bar) and two gas flow rates (0.5 and 1 L/min). The syngas composition in volume was: 50% hydrogen, 15% carbon dioxide, 15% methane and 20% carbon monoxide. The gas outlet was measured continuously with a modular stationary gas analyser (maMoS IP55, Madur), which can measure the volume fraction of each gas in percentage. From these data, the breakthrough curves are obtained, for each of the gases analysed and operating conditions applied, to estimate the adsorption capacity. These curves were plotted as the CO₂ concentration in the outlet stream and as a plot of C/C_0 versus time, in both cases, where C and C_0 are the volumetric CO₂ concentrations in the outlet and inlet stream, respectively.

At the end of the adsorption measurement, the natural zeolite was replaced by a new one to carry out the following test. A total of 3 tests were performed under the same conditions of pressure and gas flow rate.

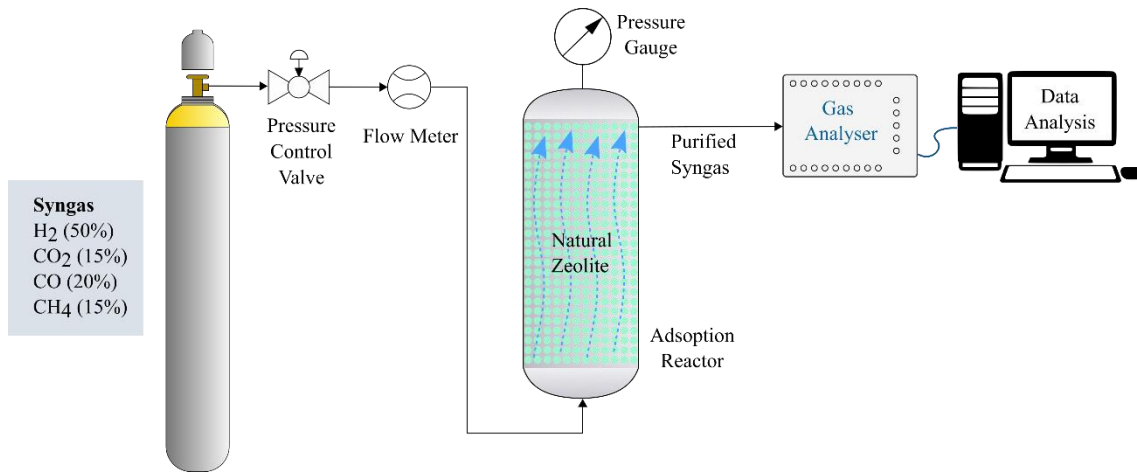


Figure 1. Schematic diagram of the experimental set-up used.

During the experiments, the composition of the outlet gas was recorded every second with the gas analyser until a constant value is reached. The CO₂ adsorption capacity of natural zeolite, per unit mass of adsorbent, was determined by integrating the breakthrough curves using the following mass balance equation (expression used in previous studies [35,36]):

$$Q = \frac{1}{m} \int_0^t (F_{in} - F_{out}) dt \quad (1)$$

where Q is the CO₂ adsorption capacity (mol/kg), m is the amount of adsorbent in the fixed bed reactor (kg), F_{in} and F_{out} are the inlet or outlet CO₂ molar flow rate (mol/s) respectively, and t is the time (s).

2.3 Adsorption isotherms models

The adsorption of single components has been studied for many authors since offers a description of adsorption behaviour, such as adsorption mechanism, surface properties or adsorbent affinity. However, in the hydrogen purification results crucial to know the behaviour of the mixtures during the carbon dioxide adsorption. For that reason, some isotherm models were used to analyse the adsorption process and investigate the most suitable one. Currently, there are many isotherm models for describing the adsorption process on solid adsorbents, being the two parameters model the most popular one [37]. In this research, nine models, among one to five parameters, were applied to fit and analyse the experimental data: Henry, Langmuir, Freundlich, Sips, Toth, Temkin, Dubinin-Radushkevich, Harkins-Jura and Virial. Linear and nonlinear regression analysis was carried out to obtain the model parameters for natural zeolite. To evaluate the best model, two

error factors were used: the R^2 determination coefficient, which allow evaluating the suitability of the fit, being higher when its value is close to unity, and the root-mean-square error (RMSE) that shows the difference between the theoretical and experimental values, resulting in the best model that which shows the lowest value of RMSE.

2.3.1 One Parameter Isotherm Model

- Henry isotherm

The Henry's isotherm uses a linear expression to describe the adsorption equilibrium state of secluded adsorbates at relatively low concentration in constant temperature, in which the amount of surface adsorbate is proportional to the equilibrium gas pressure (2).

$$q_e = K_{He}P_e \quad (2)$$

where q_e represents the equilibrium amount of adsorbate (mol/kg), K_{He} is Henry's adsorption constant, and P_e is the equilibrium gas pressure of the adsorbate on the adsorbent (bar). Any isotherm can be used for correlation if the equation has a definite slope at the origin, Henry's constant.

2.3.2 Two Parameter Isotherm Models

- Langmuir isotherm model

Langmuir model uses a simplified model of the surface of a solid to obtain the adsorption equation, which supports monolayer adsorption. It assumes that the solid has an energetically homogeneous surface, that there is no interaction between the different adsorbed molecules, and that the adsorbed molecules are located in specific positions, i.e., when all the sites are occupied, adsorption cannot continue, and the system becomes saturated. The Langmuir equation is given as follows [38]:

$$q = \frac{q_{max} \cdot b_0 \cdot P}{1 + b_0 \cdot P} \quad (3)$$

where q_{max} is the maximum-monolayer adsorbed amount (mol/kg), b_0 is Langmuir constant, and P is the experimental gas pressure (bar).

- Freundlich isotherm model

This model is based on multilayer adsorption on an energetically heterogeneous surface. This model assumes an exponential decrease in adsorption energy as the number of available adsorption sites decreases, which occurs with increasing surface coverage [39]. According to this model, the adsorption capacity of the adsorbent is related to the pressure, as stated in the following equation [38]:

$$q = K_F P^{1/n} \quad (4)$$

where K_F and n are constants related to the adsorption capacity and the type of the adsorption process respectively (value of n greater than 1 indicates a physical process and less than 1 indicates a chemical process [40] and P is the experimental gas pressure (bar). The Freundlich adsorption intensity parameter, given by the ratio $1/n$, is a measure of the binding energy between adsorbate and adsorbent and of the surface heterogeneity. Values of $1/n$ lower than 1 represent a favourable adsorption [41].

- Temkin isotherm model

The Temkin isotherm model considers that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface due to adsorbent–adsorbate interactions [37]. According to this model, there is a uniform distribution of binding energies during the adsorption, until a maximum binding energy. The Temkin isotherm model has the following linear expression [38]:

$$q = b_T \cdot \ln(K_T) + b_T \cdot \ln(P) \quad (5)$$

where q is the adsorbed amount (mol/kg), K_T represents equilibrium binding constant at the maximum binding energy, b_T is related to the adsorption heat and P is the experimental gas pressure (bar).

- Dubinin-Radushkevich isotherm model

This model assumes that adsorbent size is similar to the micropore size. In that case, the adsorption equilibrium between adsorbate-adsorbent can be defined using the adsorption potential, ε , without independence of temperature.

$$\varepsilon = RT \cdot \ln \left(1 + \frac{1}{P} \right) \quad (6)$$

This isotherm represents the adsorption process on surface sites with a Gaussian-type distribution. It is suitable for physical adsorption, since represents the adsorption for microporous adsorbent with gasses [42], implying a multilayer nature. The model can be described by the following equation [38].

$$\ln q = \ln Q_{DR} - K_{DR} \varepsilon^2 \quad (7)$$

where q is the adsorbed amount (mol/kg), Q_{DR} is the Dubinin-Radushkevich constant and K_{DR} represents the mean sorption free energy per molecule of sorbate when it is transferred to the solid surface.

- Harkins-Jura isotherm model

The Harkins-Jura adsorption isotherm is typical for multilayer adsorption on the surface of adsorbents with heterogeneous pore spreading [42]. This model is defined by the following equation [38]:

$$\frac{1}{q^2} = \frac{B}{A} - \frac{1}{A} \cdot \log P \quad (8)$$

where q is the adsorbed amount (mol/kg), A y B are constants and P is the experimental gas pressure (bar).

2.3.3 Three Parameter Isotherm Models

- Sips (Langmuir –Freundlich) isotherm model

The Sips isotherm model combines Langmuir and Freundlich models for predicting the adsorption in heterogeneous systems [43]. Thus, when the adsorbate concentration is low, it is equivalent to the Freundlich isotherm; whereas at higher concentrations this model predicts a monolayer adsorption characteristic of the Langmuir isotherm. It can be expressed as follows [38]:

$$q = q_{max} \cdot \frac{(kP)^{1/n}}{(1+k \cdot P)^{1/n}} \quad (9)$$

where q_{max} is the maximum adsorbed amount (mol/kg), k and n are constants, and P is the experimental gas pressure (bar). The constant n is the intensity factor; if n is greater than 1 the process is heterogeneous and is related to a cooperative interaction between molecules, i.e., the absorption of one molecule increases the absorption of more molecules, whereas if the value of n is less than 1, it is rather related to a Gaussian distribution of sorption/energy binding sites. When

the value of n is close to or equal to 1, this model is equivalent to Langmuir model (homogeneous adsorption process) [44].

- Toth isotherm model

This model can be applied to systems with heterogeneous surfaces and multilayer adsorption.

This model is particularly effective for systems where the adsorption process involves a wide range of energy sites and describes many systems that have not yet reached the full capacity of the monolayer [45,46]. The expression of Toth model is given in the following equation [38].

$$q = q_{max} \cdot \frac{kP}{((1+(kP)^n)^{1/n}} \quad (10)$$

where q_{max} is the maximum adsorbed amount (mol/kg), k and n are specific constants for each adsorbent-adsorbate pair, and P is the experimental gas pressure (bar). The constant n is different than 1 in heterogeneous process; if n is equal to 1 this model is equivalent to Langmuir model [12], which could mean that the system behaves homogeneously or that the adsorbent sites are energetically equal for adsorption.

2.3.4 Five Parameter Isotherm Models

- Virial isotherm model

This model is mathematically very versatile (11), as it can represent any isotherm and defines Henry's constant (12) [47].

$$\ln\left(\frac{P}{q}\right) = A_0 + A_1 \cdot q + A_2 \cdot q^2 + A_3 \cdot q^3 + A_4 \cdot q^4 \quad (11)$$

$$K_{He} = \exp(-A_0) \quad (12)$$

where q is the adsorbed amount (mol/kg), K_{He} is Henry's adsorption constant, P is the experimental gas pressure (bar), A_0 is related with Henry constant and A_1 , A_2 and A_3 are the Virial coefficient for the interactions between two, three and four molecules.

2.4. Adsorption kinetic models

Adsorption kinetics is a vital parameter to consider when designing an adsorption process as it infers the limiting step of the process. Kinetic models provide information about the adsorption pathways and mechanism involved, as well as the adsorption rate, which indicates the time required to reach the equilibrium of the adsorption process.

There are three main steps in an adsorption process. a) the external mass transfer of the adsorbate from the bulk solution to the external surface of the adsorbent; b) the internal diffusion of the adsorbate to the adsorption sites; c) the adsorption of the adsorbate on active adsorbent sites. Some models are based on the fact that the adsorption is the rate limiting step in the process, while others consider the diffusion as the rate limiting step. In this study five different adsorption kinetic models were used to analyse the breakthrough curves of carbon dioxide, to predict the behaviour of natural zeolite during hydrogen purification. In particular, three adsorption kinetic models and two diffusion kinetic models were used.

2.4.1. Adsorption-based kinetic models

In the adsorption kinetic models, the adsorption is considered to be the slowest process. In this study the following adsorption-based kinetic models were used:

- Pseudo-first order kinetic model (PFO)

Pseudo-first kinetic model is usually used to analyse physical gas-solid adsorption process (i.e., to represent reversible interactions between adsorbent and adsorbate), in which the adsorbate attaches to the surface of the adsorbent through diffusion. The experimental carbon dioxide adsorbed amount was fitted using the following equation proposed by Lagergren [48], which assumes that the adsorption rate is proportional to the number of available free active sites on the adsorbent surface.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (13)$$

The slope and y-intercept of $\ln(q_e - q_t)$ versus t were used to calculate the K_1 constant and the maximum quantity of carbon dioxide adsorbed (q_e).

- Pseudo-second order kinetic model (PSO)

A pseudo-second order kinetic model considers that the chemical adsorption on the gas-solid interface is the control step of the adsorption process [49]. It is suitable when the process is controlled by chemical adsorption and follows Langmuir isotherm model. The following expression was used to fit the obtained data, which assumes that the adsorption rate is proportional to the square of the number of available adsorption sites on the adsorbent surface.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} - \frac{t}{q_e} \quad (14)$$

The slope and y-intercept of t/q_t versus t were used to calculate the K_2 constant and the maximum quantity of carbon dioxide adsorbed (q_e).

Both models (i.e., PFO and PSO) consider the following assumptions [50] 1) Adsorption occurs on localized sites and involves no interaction between the adsorbates. 2) The adsorption energy is independent of the surface coverage. 3) Maximum adsorption corresponds to a saturated monolayer of adsorbates on the adsorbent surface. 4) The concentration of the adsorbate is constant. 5) The adsorption is governed by either PFO and PSO rate equations.

- Elovich kinetic model

The Elovich kinetic model is suitable for multilayer adsorption, is more compatible with chemisorption, and is based on Temkin adsorption isotherm. This model is based on the number of adsorbent surfaces grows rapidly with the adsorption process [42]. The following expression was used to fit the experimental data:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (15)$$

The slope and y-intercept of q_t versus $\ln t$ were used to calculate the α and β constants.

This model considers the following assumptions [50] 1) adsorption only occurs on localized sites and there is interaction between the adsorbates. 2) The energy of adsorption increases linearly with the surface coverage. 3) The concentration of the adsorbate is constant.

2.4.2. Diffusion-based kinetic models

Diffusional models assume that diffusion is the rate limiting step, dividing this process into two parts, external mass transfer between the adsorbate and the solid surface of the adsorbent and internal diffusion characterized by intraparticle diffusion [51]. In this study were used the following diffusion-based kinetic models.

- Weber kinetic model

Weber kinetic model refers to the gas diffusion in the pores of solid adsorbent during the process (i.e., intraparticle diffusion) [52]. This model is not suitable when the surface diffusion is the

control step. The experimental carbon dioxide adsorbed amount was fitted using the following equation:

$$q_t = K_w t^{1/2} + X \quad (16)$$

The slope and y-intercept of q_t versus $t^{1/2}$ were used to calculate the K_w (intraparticle diffusion rate constant) and X (the thickness of the boundary layer) constants. When the plot is linear, can be considered that intraparticle diffusion plays an important role in the adsorption rate. Furthermore, if the plot goes through to the origin ($X=0$), intraparticle diffusion mechanism is considered as the only rate-limiting step for the adsorption process. If this does not occur, other kinetic parameter slows down the adsorption capacity, since the presence of the term X is related with external mass transfer to the solid surface. As stated Raganati et al. [35], usually the adsorption mechanism involved in the process is composed of several phases whose effect on the overall adsorption rate cannot be neglected, so the weber plot is usually multilinear.

- Boyd kinetic model

Boyd's model allows to identify if the control step of mass transfer during adsorption is diffusion in the fluid film (i.e. film diffusion) or diffusion in the particle (intraparticle diffusion). This model assumes that the diffusion resistance surrounding the particle boundary layer is the control step [53]. Boyd model can be defined as follows: [54]

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{(-n^2 Bt)} \quad (17)$$

where F is the ratio of CO_2 adsorbed at equilibrium and at time t (q_t/q_e), and Bt mathematical function of F , which is estimated in a different way for short and long adsorption times as follows:

$$\text{If } F < 0.85: Bt = 2\pi - \frac{F\pi^2}{3} - \left(1 - \frac{\pi F}{3}\right)^{1/2} \quad (18)$$

$$\text{If } F > 0.85: Bt = \ln\left(\frac{6}{\pi^2}\right) - \ln(1 - F) \quad (19)$$

The experimental CO_2 adsorbed amount was fitted using the following equation:

$$-\ln(1 - F) = K_b \cdot t \quad (20)$$

where K_b is the kinetic constant of Boyd. This model is applied to predict the stages involved in the adsorption process plotting $-\ln(1-F)$ versus time. If the representation is a straight line passing through the origin, pore diffusion controls the rate of adsorption. If the representation is not a

straight line or does not pass through the origin, it can be said that the adsorption is controlled by the transport of the adsorbate through the boundary layer (i.e. film diffusion).

3. Results and discussion

3.1. Adsorbent characterization

X-ray diffraction analysis confirms the presence of heulandite-Ca ($(\text{Ca},\text{Na},\text{K})_5(\text{Si}_{27}\text{Al}_9)\text{O}_{72}\cdot 26\text{H}_2\text{O}$) heulandite-K ($(\text{K},\text{Ca},\text{Na})_5(\text{Si}_{27}\text{Al}_9)\text{O}_{72}\cdot 26\text{H}_2\text{O}$) and stellerite ($\text{Ca}_4(\text{Si}_{28}\text{Al}_8)\text{O}_{72}\cdot 28\text{H}_2\text{O}$) as the main components of the natural zeolite used (Figure 2), which is in accordance with the composition provided by the supplier (Table 1). The same result can be seen in the analysis obtained by SEM (Figure 3), where the presence of Si and Al as fundamental elements and Ca, K, Na and Mg as exchangeable cations can be noted by EDX analysis. As reported by [55,56], the presence of these alkali and alkaline earth cations increases the adsorption capacity of the zeolite in the following order $\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$.

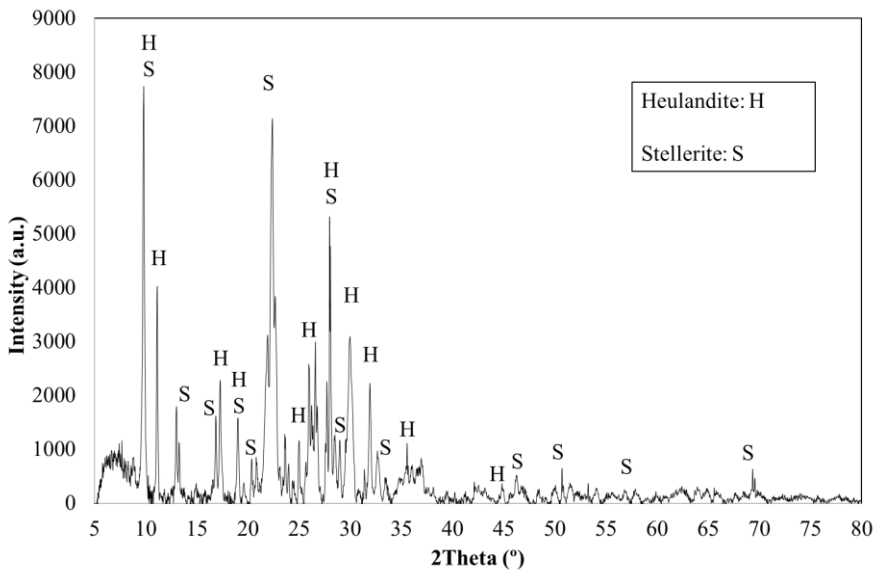


Figure 2. XRD pattern showing the main minerals of the natural zeolite

Taking into account the Si/Al ratio detected by EDX (a value of 5.25), and also that supplied by the manufacturer (in this case a ratio of 5.5), this natural zeolite can be classified as clinoptilolite as this ratio is higher than 4 [57], and also as a high-silica zeolite, since the Si/Al ratio is higher than 5 [58,59] which gives it a higher hydrophobicity than that achieved by other zeolites with a lower ratio.

The morphology detected by SEM (Figure 3) shows that the zeolite crystals present a laminar structure typical of this kind of zeolite [57,60].

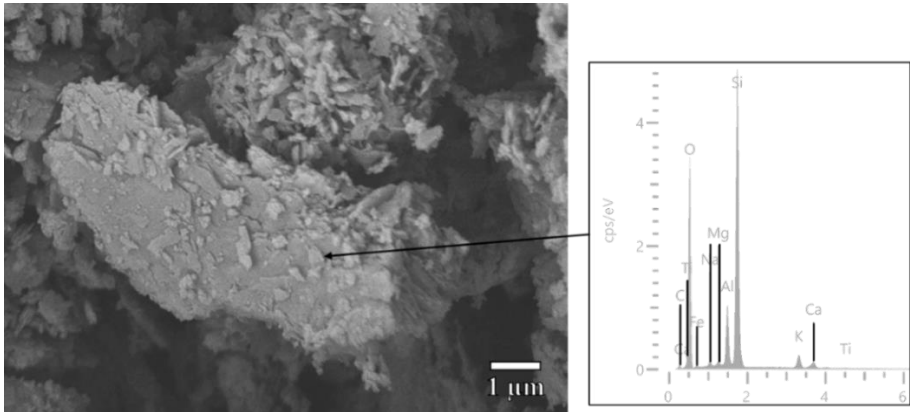


Figure 3. SEM microphotograph and EDX analyses of clinoptilolite crystals.

As shown in the thermogram (Figure 4), the weight loss suffered by the zeolite is continuous throughout the entire heating process, reaching a total loss of 8% associated with dehydration and dehydroxylation process of the sample. Three zones of fall can be appreciated, a first sharp fall corresponding to the linear section up to 200 °C, due to the loss of the hygroscopic water and loosely bonded water [61]. A second fall of 3.3%, slower than the previous one (between 400 and 600°C), and a third fall of 1.44% (for $T > 400^{\circ}\text{C}$) corresponding to the elimination of hydroxyl groups [62].

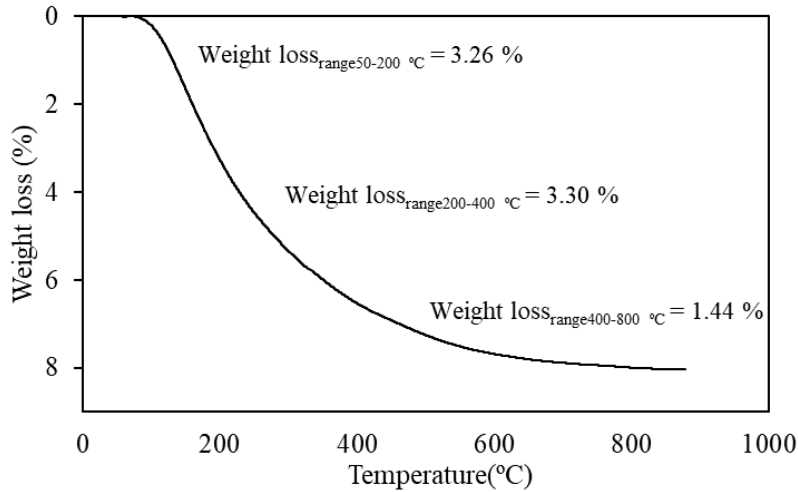


Figure 4. Thermogram of the zeolite assessed showing the average percentage weight loss (n = 2) at different temperatures.

The specific surface area calculated by BET, model that considers multilayer formation, was 25 m²/g approximately, which is also in accordance with the data provided by the supplier. According to Langmuir model, which considers that only a monolayer adsorbate can be formed on the top of the surface, the surface area was 34 m²/g approximately. The average pore size using the BJH method during the desorption phase was 17 nm, and the total pore volume using the same method was 0.115 cm³/g, of which 2.9% corresponds to the volume of micropores.

Table 2. Surface area and pore volume of the used zeolite.

Property	
BET surface area (m ² g ⁻¹)	25.53 ± 0.04
Langmuir surface area (m ² g ⁻¹)	34.11 ± 0.47
Total pore volume (cm ³ g ⁻¹)	0.1146
Total micropore volume (cm ³ g ⁻¹)	0.0033
Average pore size diameter (nm)	17.13

Figure 5 shows the nitrogen adsorption–desorption isotherms obtained results. According to the IUPAC classification, the adsorption curve of this natural zeolite is a type IV adsorption isotherm. This type of isotherm is characterized by: i) a monolayer adsorption at low relative pressure (below 0.2), ii) a multilayer adsorption at medium relative pressure (between 0.2 and 0.4 approximately), and iii) a process of mesopore filling marked by the appearance of a hysteresis loop at high relative pressure (between 0.45-0.9 approximately). At relative pressures close to 1, complete filling of the pores does not occur, so the process will continue in the macropores of the material.

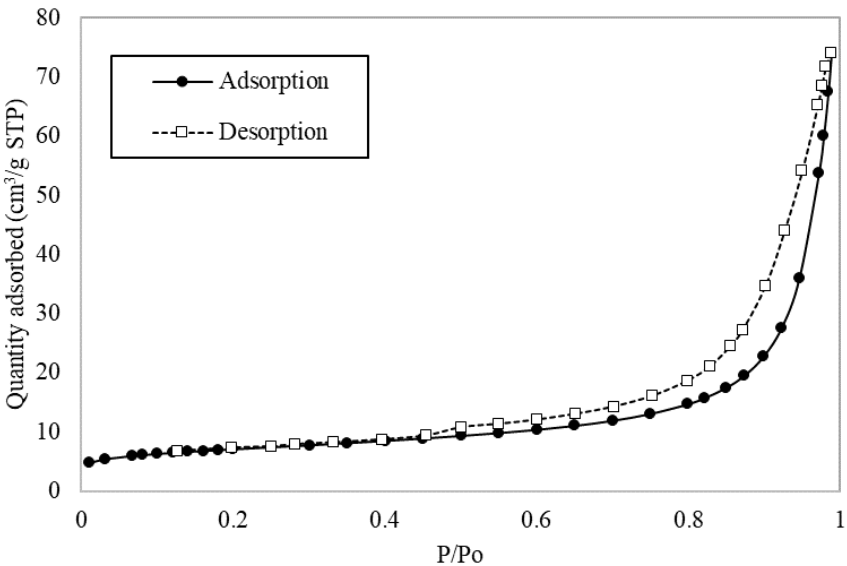


Figure 5. Nitrogen adsorption-desorption isotherms on natural zeolite at 77 K.

In summary, the shape of the Type IV isotherm indicates that this zeolite has a predominance of non-microporous surface (mesopores, macropores and external surface), where adsorption occurs as a multilayer. This does not mean that the natural zeolite does not present microporosity, since in the low-relative pressure range ($P/P_0 < 0.45$), adsorption is related to the micropore filling mechanism. Furthermore, this kind of zeolite exhibit a hysteresis loop of H3-type, in the range 0.45-0.99 P/P_0 , which is typical of materials with laminar type porosity such as clinoptilolite [60,62,63]. This fact agrees with the morphology observed in the SEM images (Figure 3). The pore size distribution (Figure 6) shows that this material is characterized by a unimodal pore size distribution ranged from 5.5 to 120 nm, peaking at 23 nm. Practically the entire pore volume (approximately 65%) falls within the mesopore size range established by IUPAC, between 2 and 50 nm. Only about 3% corresponds to micropores. The volume corresponding to macropores corresponds to the rest, although a large part of them cannot be detected with this technique since they are above the detection limit of the equipment.

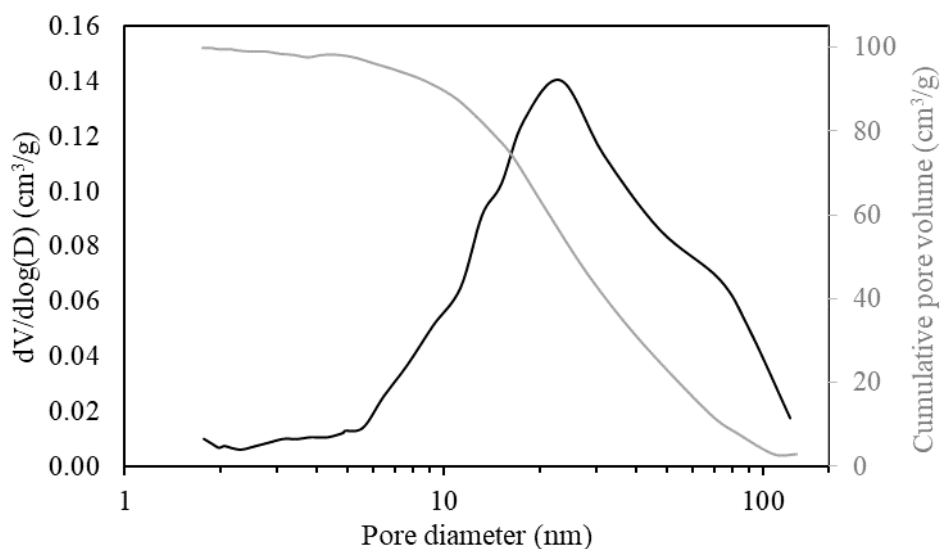


Figure 6. Pore size distribution of zeolite from the adsorption branch by the BJH model. Data shows the incremental pore volume and the cumulative volume, both in cm^3/g .

3.2. Multicomponent breakthrough curves

Experimental multicomponent breakthrough curves for hydrogen, methane, carbon monoxide and carbon dioxide have been obtained for natural zeolite at different pressures and gas flow rates.

Figure 7 shows an example of the obtained breakthrough curves, showing the composition of the outlet gas, at a constant pressure of 1 bar and two different flow rates (a) and also at a constant flow rate of 0.5 L/min and two different pressures (b).

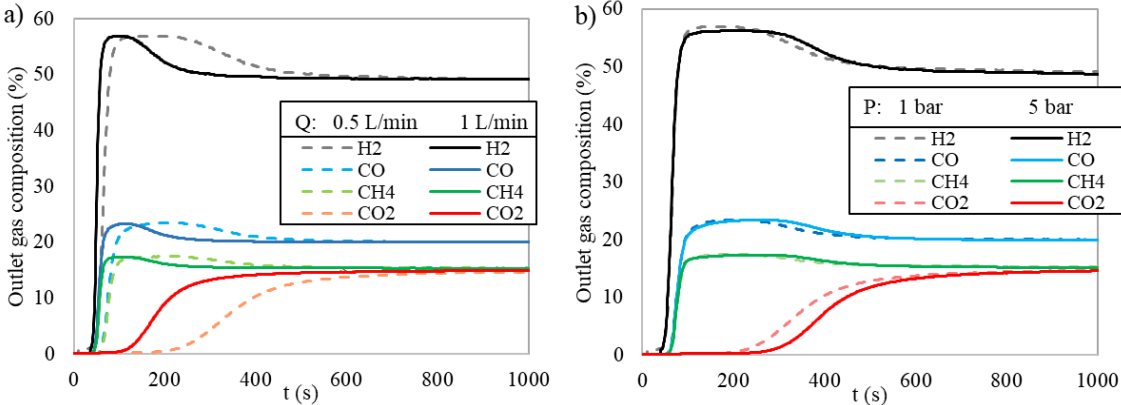


Figure 7. Experimental multicomponent breakthrough curves in natural zeolite; a) at constant pressure (1 bar) and two different gas inlet flow rates: 0.5 L/min (dash line) and 1 L/min (continuous line), and b) at constant flow rate (0.5 L/min) and two different pressures: 1 bar (dash line) and 5 bar (continuous line).

In general, regardless of the conditions evaluated, both pressure and flow rate, clinoptilolite presents a high selectivity in terms of CO₂ adsorption with respect to the other gases of the mixture such as CH₄, CO and H₂, which agrees with what has been reported in previous studies [64]. In practically all the cases analysed, during the first 200 seconds the zeolite adsorbs CO₂, which causes an increase in the percentage of the other gases present in the mixture with respect to its original proportion (Figure 7). This fact shows that zeolite allows purifying the syngas to obtain H₂ by reducing the CO₂ content of the mixture. However, it does not reduce the content of other impurities such as CH₄ and CO, whose separation is almost negligible as shown in Figure 8.

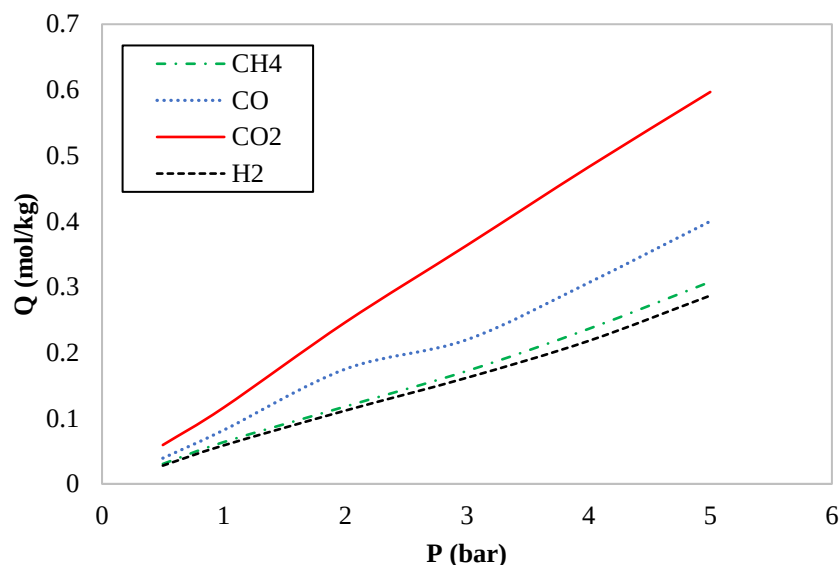


Figure 8. Adsorption isotherm of CO₂, CO, CH₄ and H₂ obtained at 25°C.

This strong affinity for CO₂ is related to 1) its smaller kinetic diameter (3.3 Å) compared to that of the other gases present (CH₄:3.8 Å, CO: 3.6 Å), except for hydrogen (2.9 Å), allows a more efficient diffusion through the zeolite pores [65,66]: 2) the large quadrupole moment of carbon dioxide, which is higher than other gas molecules [67], leads a strong interaction with the electric field gradient generated inside the pores of the zeolite [9]. As stated in [68], the quadrupole moment of the gases used in this study varies as follows: CO₂>CO>H₂>CH₄; 3) acid gases, such as CO₂, tend to be adsorbed on the basic sites occupied by alkaline metal oxides (such as Na₂O and K₂O) and alkaline earth oxides (such as CaO and MgO) and also in those occupied by metal oxides of weak acidity such as alumina [64].

Despite this high selectivity, it can be seen that this zeolite saturates very quickly in terms of CO₂ adsorption, this is due to the fact that 1) the higher the Si/Al ratio, the lower the acidity of the zeolite and the lower its adsorption capacity [31,58,69], and 2) the Ca-clinoptilolite adsorbs less than other clinoptilolite such as those enriched with Na or K. This is mainly due to the position of these cations within the zeolite structure [60].

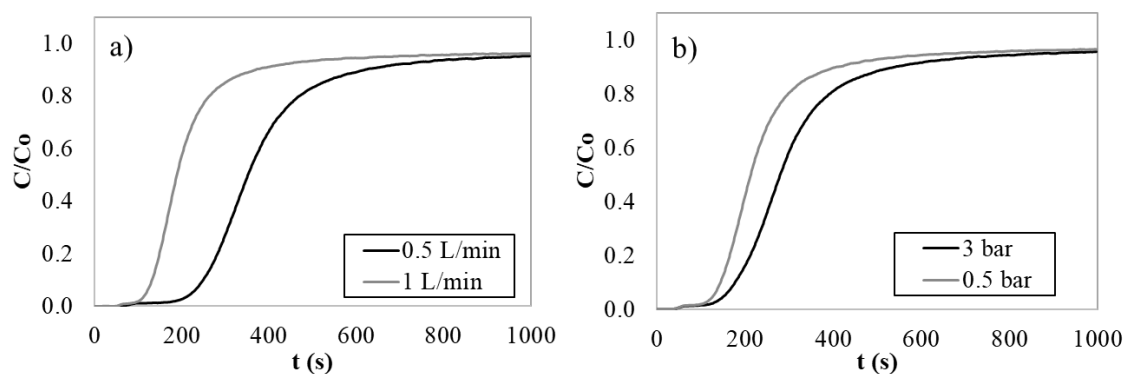


Figure 9. Effect of flow rate at 1 bar (a) and pressure at 1 L/min (b) on the adsorption breakthrough curves where C is the outlet CO_2 concentration and C_0 is the inlet CO_2 concentration.

A detailed analysis of the influence of each of the parameters evaluated on the volumetric fraction of CO_2 shows that:

1) the lower the flow rate supplied the higher the adsorption time (Figure 9a), possibly due to the fact that a smaller amount of CO_2 is supplied (specifically, half of the molar flow rate), and the diffusion process through the porous structure of the material is favoured [70]. In this way at a flow rate of 0.5 L/min the carbon dioxide begins to be released after approximately 200 seconds and the saturation of the zeolite is not reached until after 1000 seconds. While at 1 L/min the release of CO_2 begins at 120 seconds and the saturation of the zeolite with this compound occurs at approximately 800 seconds. In addition to promoting the diffusion, as stated in [71], the higher the feed flow rate, the higher the degree of turbulence of the delivered gas flow, which accelerates the breakthrough time due to the smaller mass transfer zone in the fixed bed column.

2) The higher the pressure, the higher the adsorption capacity of the zeolite (Figure 9b), which agrees with previous studies [72]. This fact is due to the gas circulation is forced through all the pores of the material, including the micropores or those pores that are less well communicated, favouring a greater mass transfer [73]. Furthermore, as established in previous studies [74,75], at low pressures the adsorbed molecules tend to occupy the most favourable positions from an energetic point of view, corresponding to adsorbate-pore interactions, while at high pressures the adsorbed molecules occupy the central region of the pores and the increase in their packing leads to a greater density.

3.3. Adsorption isotherms

Figure 10 shows the quantity of CO₂ adsorbed at the different pressures applied for each of the inlet flow rates assessed, indicating that the higher the flow rate, the greater the amount of CO₂ adsorbed. From the experimental data, Henry's isotherm fits the process perfectly, indicating the same idea that the amount of adsorbate is proportional to the partial pressure of the adsorptive gas (Figure 10 and Table 2).

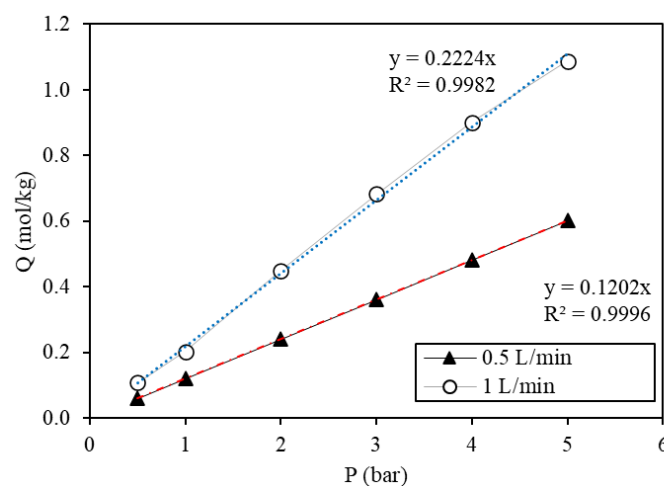


Figure 10. Effect of pressure and gas inlet flow rate on CO₂ adsorption. The Henry's isotherm adjustment is also shown for each flow rate.

Regarding the two-parameter models (Figure 11 and Table 2), both the Langmuir and Freundlich isotherms achieve good process fits with high R^2 and low errors, similar result to that achieved by Shikuku et al. [32]. Among both isotherms the Freundlich isotherm is the best fit to the experimental data. This means that the adsorption process mainly occurred on a heterogeneous surface instead of on discrete adsorption centres as suggested by Langmuir isotherm. In this model, the higher the value of K_F the larger the capacity of the adsorption, indicating that adsorption should be higher at higher feed flow rates (in this case at 1L/min). This fact agrees with what was previously observed during the tests (see Figure 9 experimental data). Considering the value of the n parameter, which is close to 1, the adsorption process is both physical and chemical. In addition, considering the adsorption intensity parameter ($1/n$), which lower than 1, the adsorption process is favourable [76].

The other 2 parameters models used (Temkin, Harkins-Jura and Dubinin-Radushkevich) exhibit values for R^2 about 0.92-0.95, which could be considered reasonable. However, they present high

error values and therefore are not able to correctly represent the experimental data. In these models a micropore filling mechanism is considered. Therefore, the adsorbed amount depends on the pore volume (mainly the mesopores) and the adsorbate molar volume [28].

Table 2. Equilibrium isotherm models parameters of CO₂ adsorption on natural zeolite at different syngas flow rates.

	Isotherm	Parameters	0.5 L/Min	1 L/min
1 Parameter	Henry	K_{He}	0.1202	0.2217
		R^2	0.9996	0.9982
		RMSE	0.0036	0.0149
2 Parameters	Langmuir	q_{max} (mol/kg)	12.943	17.522
		B_o	0.0096	0.0133
		R^2	0.9667	0.9530
		RMSE	0.0036	0.0315
	Freundlich	K_F	0.1189	0.2147
		n	1.0108	1.0271
		$1/n$	0.9893	0.9736
		R^2	0.9996	0.9985
		RMSE	0.0045	0.0176
	Temkin	b_T	0.2280	0.4233
		K_T	1.9744	1.9514
		R^2	0.9208	0.9243
		RMSE	0.0498	0.0902
	Dubinin-Radushkevich	Q_{DR}	0.6655	1.2314
		K_{DR}	$9.81 \cdot 10^{-7}$	$9.86 \cdot 10^{-7}$
		R^2	0.9533	0.9612
		RMSE	0.04489	0.0757
	Harkins-Jura	A	0.0287	0.0989
		B	0.7735	0.7756
		R^2	0.9160	0.9061
		RMSE	0.0602	0.1178
3 Parameters	Toth	q_{max} (mol/kg)	4.9874	4.9660
		K	0.0241	0.0446
		n	4.9714	5.0192
		R^2	0.9997	0.9987
		RMSE	0.0074	0.0119
	Sips	q_{max} (mol/kg)	5.5309	4.8916
		K	0.0285	0.0826
		n	0.9344	0.8202
		R^2	0.9999	0.9997
		RMSE	0.0018	0.0064
5 Parameters	Virial	A_0	2.097	1.407
		A_1	1.104	1.892
		A_2	-8.291	-6.623
		A_3	19.996	7.895
		A_4	-15.205	-3.048
		R^2	0.7309	0.8669
		RMSE	0.0026	0.0073

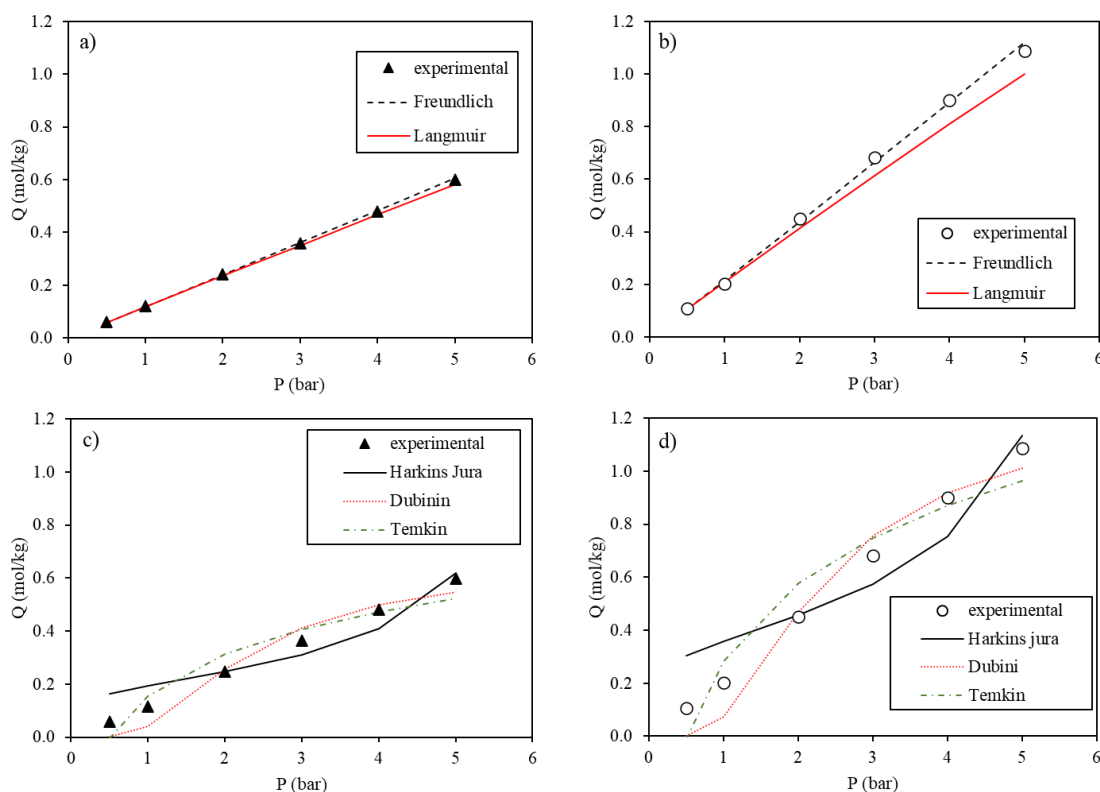


Figure 11. Experimental (marker points) and predicted (dashed lines) data of CO₂ adsorption on natural zeolite at different syngas flow rates: 0.5 L/min (left) and 1 L/min (right) using the following 2 parameters models: Freundlich and Langmuir (a and b) and Harkins-Jura, Dubinin and Temkin (c and d).

Regarding the 3 parameters models used (Figure 12 and Table 2), both Toth and Sips models fit the experimental data very well with R^2 values of 0.999 and low errors, which demonstrates the heterogeneous nature of the adsorbent surfaces. Between the two models, the one with the lowest error rate is the Sips model. The value of n obtained using the Sips model was close to 1, which is indicative that this natural zeolite presents relatively homogeneous binding sites [77], which is consistent with that shown by Freundlich's model.

Toth model allows to obtain a value of Henry's constant similar to the one obtained by Henry's model using the following expression: $K_{He} = q_{max} \cdot k$. These values obtained using this expression were 0.120 and 0.221 for 0.5L/min and 1 L/min respectively.

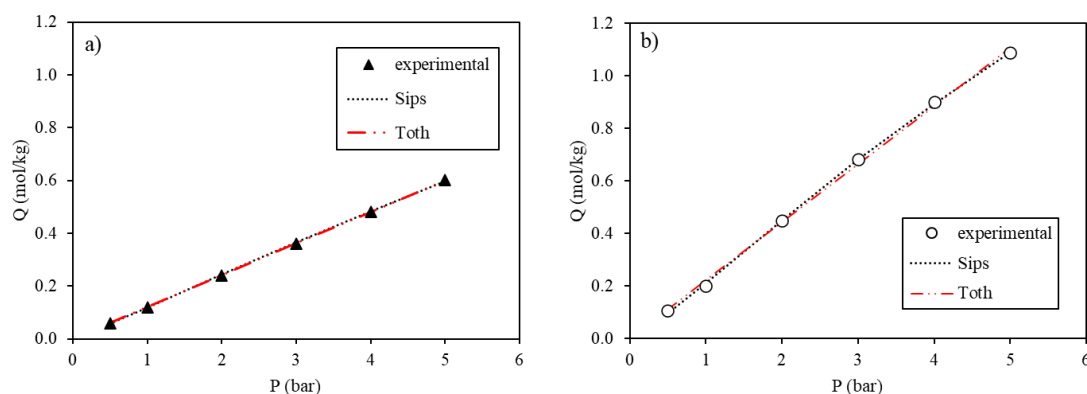


Figure 12. Experimental (marker points) and predicted (dashed lines) data of CO₂ adsorption on natural zeolite at different syngas flow rates: 0.5 L/min (a) and 1 L/min (b) using the following 3 parameters models: Sips and Toth.

The fit achieved following Virial's polynomial model was not very good since the R^2 value was lower than 0.9, despite the fact that the data predicted using the model fit the experimental data (Figure 13). The Henry's constant values obtained from A_0 were 0.123 mol/kg·bar (at 0.5 L/min) and 0.245 mol/kg·bar (at 1 L/min), very similar to those obtained by Henry's isotherm model.

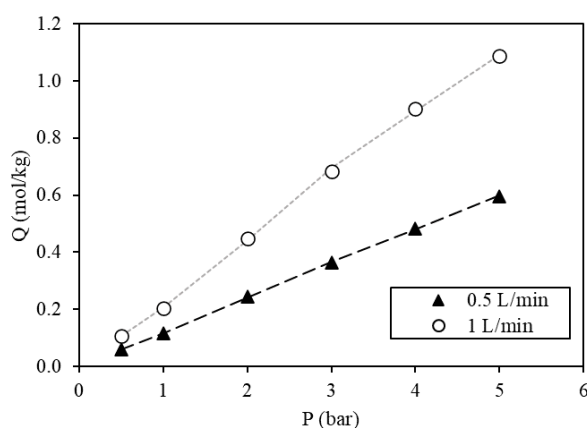


Figure 13. Experimental (marker points) and predicted (dashed lines) data of CO₂ adsorption on natural zeolite at different syngas flow rates: 0.5 L/min (triangles) and 1 L/min (dots) using the 5-parameter model of Virial.

According to obtained results, it can be said that the models that use three parameters (Toth and Sips) and the Freundlich model were found to fit the data well because they account for the heterogeneous nature of natural zeolite surfaces. The Freundlich model's ability to describe multilayer adsorption and its non-uniform distribution of heat of adsorption makes it well-suited

for data of this research. The Sips model, with its hybrid nature, effectively bridges the gap between Langmuir and Freundlich isotherms, providing a comprehensive description across different pressure ranges and is particularly useful for describing adsorption on zeolites heterogeneous surfaces. The Toth model introduces a corrective parameter that enhances its accuracy for non-uniform surfaces, reflecting the intrinsic heterogeneity of natural zeolite.

3.4. Adsorption kinetics study

Table 3 collects the parameters for all studied kinetics models for two gas flow rates and the correlation coefficient (R^2).

According to the calculated results both pseudo-first and the pseudo-second order kinetic models have a correlation coefficient greater than 0.95 (showing an average value of 0.98 for PFO and 0.95 for PSO), indicating that both models can be used to simulate the adsorption mechanism (Figure 14). This fact means that the adsorption of CO_2 is controlled by both physical and chemical adsorption. Similar results were found by Shikuku et al. [32]. Considering that the correlation coefficients (R^2) achieved were higher using PFO, and that the q_e calculated with PFO is closer to the experimental q_e than that obtained with PSO, it could be said that physical adsorption is dominant in the process. The possible chemical adsorption occurring in this process can be attributed, as indicated by previous studies [78], to two mechanisms: 1) the formation of carbonates and bicarbonates with different degrees of hydration, which happens when the zeolite contains water.; 2) the formation of carbonates due to the interaction of CO_2 with the oxygen bridging aluminium and silicon atoms in the zeolite structure. Given the prior drying of the zeolite in this study, which effectively removes water, the second mechanism is more likely to be the dominant process.

The existence of a possible chemisorption process supporting the main physisorption process is also supported by the good fit obtained with the Elovich model (Figure 15), which shows correlation coefficients above 0.90.

Analysing the fitting parameters, it can be seen that the constant k_1 , of the PFO model, remains constant regardless of pressure and flow rate. While the constant k_2 , of the PSO model, decreases with increasing pressure and flow rate. This fact indicates that by increasing either of these

parameters less time is needed to reach equilibrium and promotes higher adsorption (q_e), which is in agreement with what is observed in Figure 9.

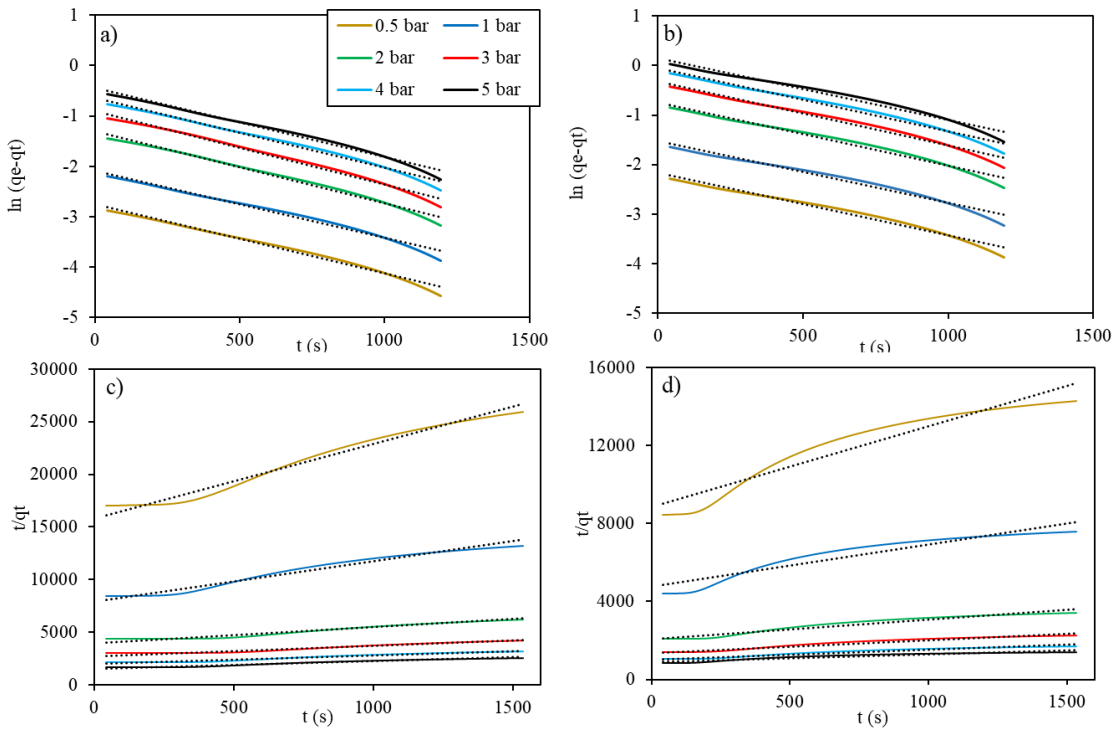


Figure 14. Fitting results of pseudo-first order (a and b) and pseudo-second order reaction kinetic model (c and d) at different gas inlet flow rates: 0.5 L/min (a and c) and 1 L/min (b and d).

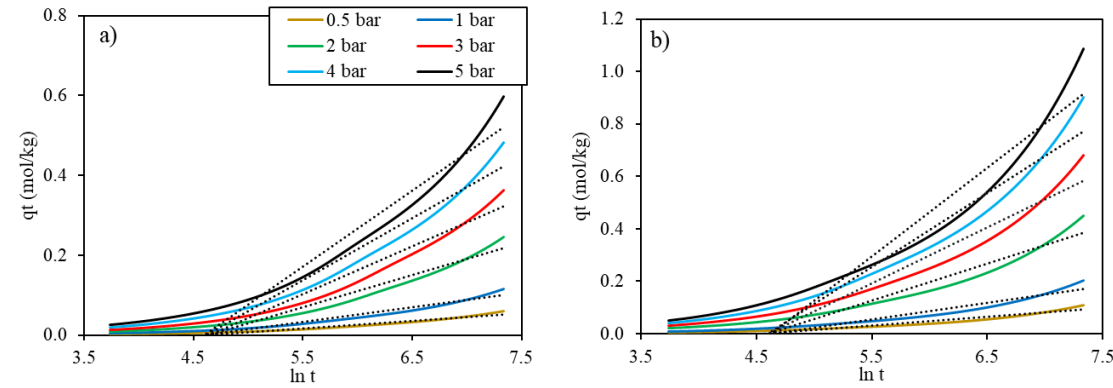


Figure 15. Fitting results of Elovich kinetic model using a gas inlet flow rate of 0.5 L/min (a) and 1 L/min (b).

564 Table 3. Kinetic model parameters of CO₂ adsorption on natural zeolite at different pressures and gas flow rates.

Pressure (bar)	Flow rate (L/min)	Experiment	Pseudo-First Order (PFO)				Pseudo-Second Order (PSO)			Elovich			
		qe (mol/kg)	qe (mol/kg)	K ₁ (s ⁻¹)	R ²	qe (mol/kg)	K ₂ (kg/mol·s)	R ²	qe (mol/kg)	α (mol/kg·s)	β (kg/mol)	R ²	
0.5	0.5	0.0592	0.0641	0.0014	0.9884	0.141	0.0032	0.9807	0.0521	1.92·10 ⁻⁴	52.632	0.9294	
	1	0.1076	0.1148	0.0014	0.9781	0.2401	0.0020	0.9156	0.0789	3.41·10 ⁻⁴	20.243	0.9274	
1	0.5	0.1163	0.1243	0.0013	0.986	0.263	0.0018	0.9724	0.1004	3.69·10 ⁻⁴	27.248	0.9244	
	1	0.2029	0.2172	0.0012	0.976	0.4607	0.0010	0.9442	0.1475	6.37·10 ⁻⁴	20.243	0.9213	
2	0.5	0.2461	0.2719	0.0014	0.9906	0.658	0.0006	0.9656	0.2171	7.80·10 ⁻⁴	12.438	0.9335	
	1	0.4498	0.4792	0.0013	0.9807	0.9936	0.0005	0.9738	0.3364	1.45·10 ⁻³	8.881	0.9355	
3	0.5	0.3634	0.4054	0.0015	0.9909	1.0143	0.0004	0.9591	0.3219	1.15·10 ⁻³	8.361	0.9334	
	1	0.682	0.7276	0.0013	0.9821	1.5209	0.0003	0.9538	0.5132	2.21·10 ⁻³	5.804	0.9375	
4	0.5	0.4825	0.5244	0.0014	0.9892	1.1973	0.0004	0.9746	0.4225	1.53·10 ⁻³	6.435	0.9311	
	1	0.9013	0.9591	0.0013	0.9816	1.9806	0.0002	0.9488	0.6765	2.92·10 ⁻³	4.415	0.9374	
5	0.5	0.5968	0.6426	0.0014	0.9884	1.4013	0.0003	0.9766	0.5209	1.91·10 ⁻³	5.249	0.9303	
	1	1.0879	1.1628	0.0012	0.976	2.4588	0.0002	0.9449	0.7885	3.41·10 ⁻³	3.788	0.9218	

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3.5. Adsorption diffusion study

The intraparticle diffusion model of Weber suggests that the adsorption of CO₂ by zeolite is not linear during the entire adsorption time (Figure 16), especially if it is observed the adjustment made by the model in the first instants of the process. Therefore, it is necessary to adjust the process using multilinear plots. This fact indicates the existence of different steps involved in the adsorption process. In the literature, it is common to present a sequence of linear sections when plotting qt as a function of $t^{1/2}$ to analyse the multilinearity. Some works associate the initial linear section with resistance to external mass transfer [79], followed by a second step where intraparticle diffusion becomes rate limiting, and concluding with a slower step due to approaching equilibrium [80].

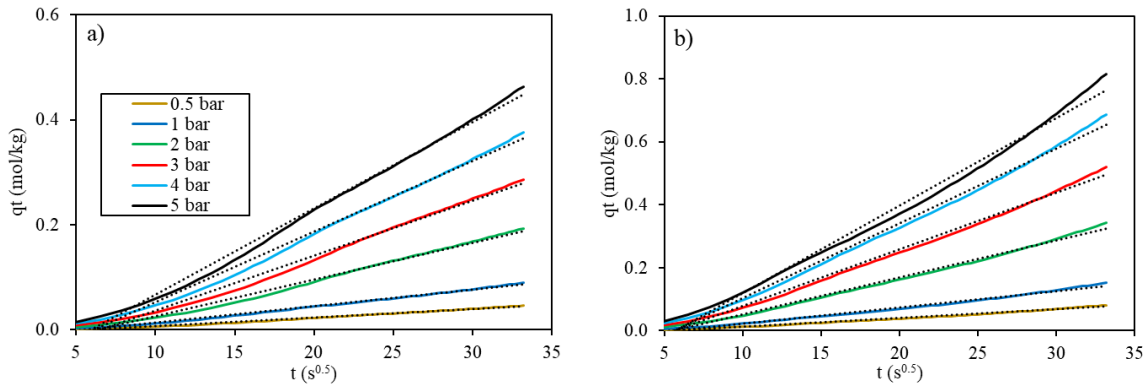
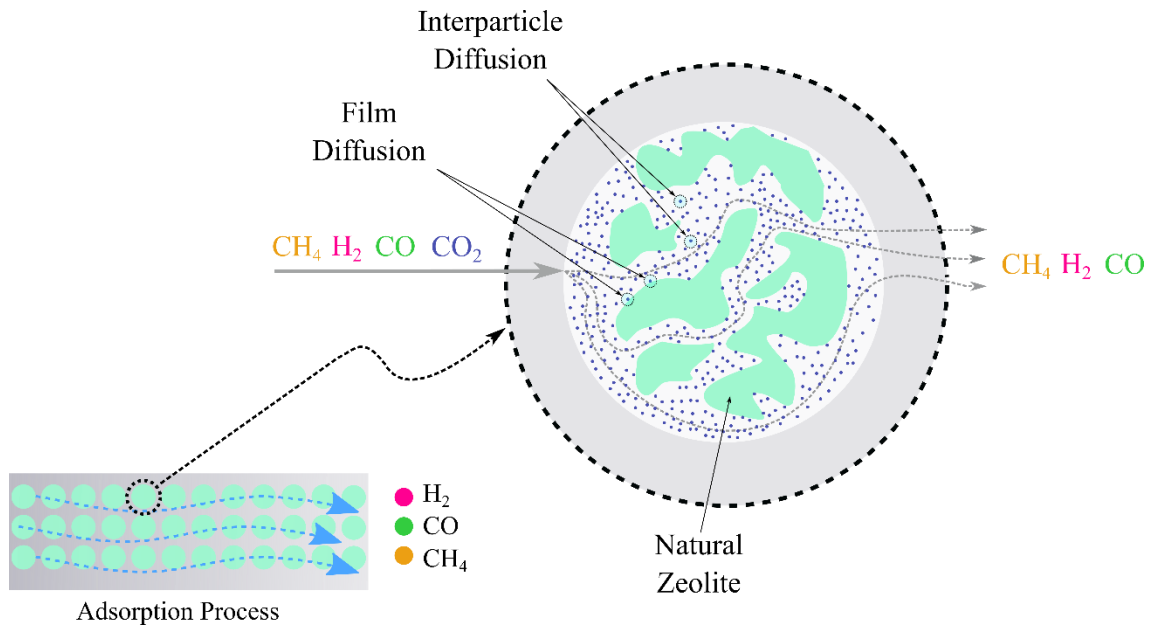


Figure 16. Fitting results of Weber kinetic model (solid lines) of experimental data (marker points): gas inlet flow rate of 0.5 L/min (left) and 1 L/min (right).

Frequently, Weber kinetic model identify three main steps (Figure 17): (1) film diffusion where occurs the mass transfer of the species to be adsorbed by diffusion from the bulk fluid phase to the solid external surface, (2) intraparticle diffusion where occurs the adsorbate mass transfer by diffusion into both the adsorbed phase and adsorbent pores, and (3) surface adsorption at equilibrium where happens the adsorption of the bulk fluid on the solid's active sites [81].



Adsorption Process

Figure 17. Adsorption mechanisms of CO₂ adsorption during H₂ purification on natural zeolite.

Figure 18 shows the existence of these three main steps, mentioned in the previous paragraph (i.e., external film diffusion, intraparticle diffusion, and the surface adsorption at equilibrium), in the adsorption process.

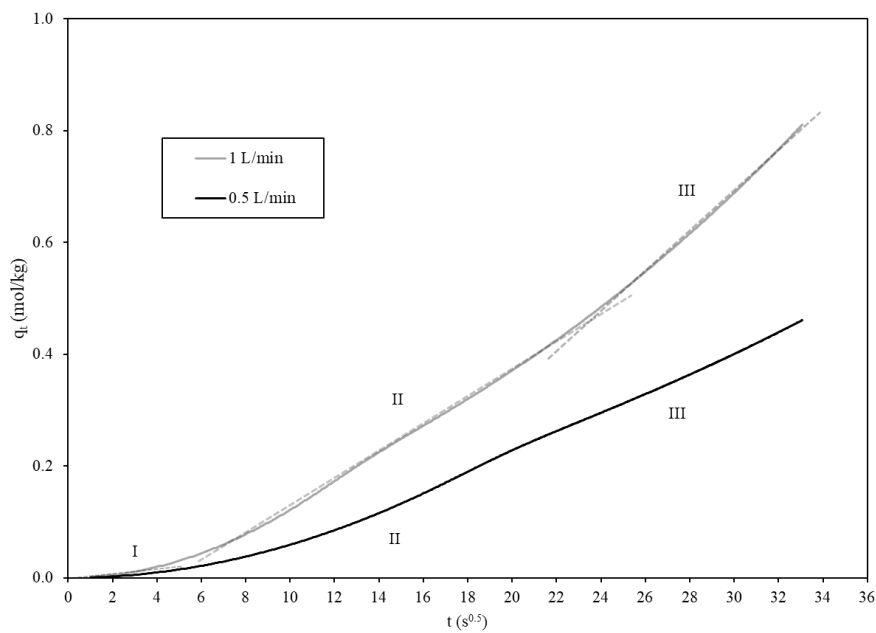


Figure 18. Fitting results of the Weber kinetic model for different gas flow rates (0.5 and 1 L/min) at 5 bar. The three stages in one of the branches that can be observed during the process are shown in dashed line.

The first step, regardless of the inlet flow rate, is a straight line that crosses the origin, indicating that at this step the intraparticle diffusion is the only rate controlling step [82]. The time of this step ranges from 7.3 to 14.4 seconds, depending on the inlet flow rate (the higher the inlet flow, the shorter the time). This step shows the lowest kinetic constants (K_{w1}) of the whole adsorption process.

Both the second step, which takes the longest time in the process (454 s for 1L/min and 331 s for 0.5 L/min) so there is a longer contact time between the adsorbate and the adsorbent, and the third step are characterized by presenting a straight line but not crossing through the origin, indicating that the intraparticle diffusion exists but is not the only rate controlling step, coexisting other processes such as the adsorption of the adsorbate on active adsorbent sites [82] and the surface boundary adsorption (i.e., external diffusion).

The slope of the third step is greater than that of previous steps, indicative that the process is faster than the previous ones. It is usually admitted that the adsorption on active sites is so fast that is cannot be the rate-determining step [21]. The interception of this step is higher, which results in a thicker boundary layer. This fact indicates that CO₂ also diffuses through the boundary layer on the outer surface of the adsorbent. This step last lasts 81 s for 1 L/min and 121 for 0.5 L/min.

The presence of different steps in the adsorption process can be attributed to the heterogeneous nature of the zeolite surfaces and the distribution of pore sizes, as confirmed by porosimetric analysis. Mesopores and macropores facilitate multilayer adsorption on heterogeneous surfaces, enhancing CO₂ uptake efficiency. This multi-step process involves both physical and chemical adsorption mechanisms, with the chemical adsorption being evidenced by the interaction of CO₂ molecules with specific sites within the zeolite framework [72]

617 Table 4. Diffusion model parameters of CO₂ adsorption on natural zeolite at different pressures and gas flow rates.

Pressure (bar)	Flow rate (L/min)	Weber									Boyd (F<0.85)	
		K _{w,1} (mol/kg·s ^{0.5})	X (mol/kg)	R ²	K _{w,2} (mol/kg·s ^{0.5})	X (mol/kg)	R ²	K _{w,3} (mol/kg·s ^{0.5})	X (mol/kg)	R ²	K _B (s ⁻¹)	R ²
0.5	0.5	0.0005	-0.0011	0.9810	0.0016	-0.0096	0.9891	0.0018	-0.0133	0.9993	0.013	0.9770
	1	0.0011	-0.0022	0.9810	0.0025	0.0129	0.9990	0.0033	-0.0304	0.9967	0.012	0.9669
1	0.5	0.0011	-0.0022	0.9810	0.0031	-0.0187	0.9918	0.0034	-0.0262	0.9981	0.013	0.9757
	1	0.0020	-0.0021	0.9810	0.0046	-0.0222	0.9995	0.0063	-0.0606	0.9965	0.012	0.9640
2	0.5	0.0021	-0.0042	0.9810	0.0063	-0.0398	0.9850	0.0075	-0.0575	0.9996	0.013	0.9766
	1	0.0043	-0.0088	0.9810	0.0112	-0.0616	0.9975	0.0137	-0.1180	0.9971	0.012	0.9701
3	0.5	0.0030	-0.0061	0.9810	0.0091	-0.0578	0.9849	0.1140	-0.0907	0.9992	0.013	0.9757
	1	0.0065	-0.0132	0.9810	0.0171	-0.0972	0.9965	0.0206	-0.1737	0.9974	0.012	0.9714
4	0.5	0.0042	-0.0085	0.9810	0.0126	-0.0798	0.9858	0.0144	-0.1054	0.9993	0.013	0.9771
	1	0.0087	-0.0176	0.9810	0.0226	-0.1265	0.9971	0.0273	-0.2302	0.9972	0.012	0.9712
5	0.5	0.0053	-0.0108	0.9810	0.0159	0.0995	0.9877	0.0176	-0.1272	0.9989	0.013	0.9775
	1	0.0109	-0.0222	0.9810	0.0244	-0.1189	0.9995	0.0338	-0.3218	0.9972	0.012	0.9641

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Finally, the initial step of adsorption was examined also using the Boyd model. The obtained result, plotted up to an F value below 0.85 (Figure 19), indicates that the process cannot be represented by a single adsorption phase even though the R^2 values obtained are above 0.95. Two steps can be seen in this model, a first one corresponding to a straight line passing through the origin indicating that intraparticle diffusion is taking place, followed by a second step where the fit is not linear, confirming that film diffusion processes are also involved, similar result to that showed by Weber. The transition time between the two steps involved changes as a function of the inlet flow rate, finding the transition at 480s approximately at 0.5L/min and at 210 s at 1L/min. This fact makes sense if we take into account that the higher the flow rate the adsorbent saturation is reached much faster (Figure 7a).

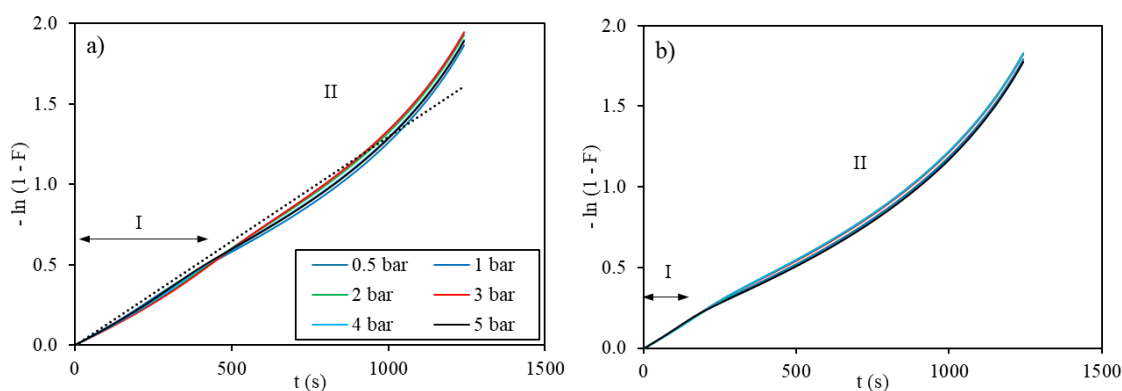


Figure 19. Fitting results of Boyd model, for a lower F value of 0.85, at different inlet flow rates: 0.5 L/min (a) and 1 L/min (b). Also, the two steps detected as well as the linear fit of one of the sections are represented.

According the obtained results, the adsorption process in natural zeolites involves multiple steps, which can be attributed to their unique microstructure, which significantly influences their adsorption dynamics. Natural zeolites have a highly porous framework with channels and cavities of varying sizes, which influence the adsorption dynamics. The initial adsorption step is typically rapid due to the availability of high-energy sites on the external surface and the larger pores. Subsequent steps involve slower intraparticle diffusion into smaller pores and deeper cavities, where the kinetics are controlled by the microporous structure of the zeolite. The multiple steps observed in the adsorption process of natural zeolites are closely linked to their heterogeneous

microstructure, which includes a mix of macropores, mesopores, and micropores, as evidenced by porosimetric analysis. These larger pores allow for the adsorption of multiple layers of CO₂ molecules, improving the overall adsorption capacity of the zeolite [83].

Some researches [84,85] have demonstrated that the porosity and surface area of natural zeolites play an important role in their adsorption behaviour. For instance, studies [86,87] have indicated that natural zeolites exhibit a combination of mesopores and micropores, which facilitate different stages of the adsorption process. The mesopores provide rapid initial adsorption, while the micropores contribute to the slower, more controlled uptake of adsorbates. The presence of these multiple pore sizes enhances the zeolite's ability to capture and retain gases [88], making them highly effective for applications such as CO₂ adsorption and hydrogen purification.

Various materials have been explored for CO₂ adsorption with distinct properties and advantages [89]. Activated carbons have been widely used due to their high surface area and pore volume, which contribute to significant CO₂ adsorption capacity. For example, Lua and Yang [90] demonstrated that activated carbons derived from pistachio-nut shells exhibit notable CO₂ adsorption capabilities due to their extensive porosity and surface area. Metal-organic frameworks (MOFs) [91,92] have gained attention for their tunable pore sizes and high surface areas. Studies by Millward and Yaghi [93] revealed that MOFs like MOF-177 have exceptional CO₂ uptake due to their large pore volumes and specific surface chemistry. However, their stability and cost remain challenges for large-scale applications. Synthetic zeolites, such as Zeolite 13X, have also been extensively studied [12,64]. Their uniform pore structures and high ion-exchange capacities make them effective for CO₂ adsorption. Research by Wang et al. [94] indicated that Zeolite 13X can achieve high CO₂ adsorption capacities under various conditions, highlighting its potential for industrial use. Studies [95,96] have shown that the adsorption behavior of zeolites, such as NaY and 13X, often involves initial rapid uptake followed by a slower diffusion process into the microporous structure. This is consistent with the behavior observed in our study, where the unique structural properties of natural zeolite contributed to its CO₂ adsorption capacity.

In comparison with other adsorbent, natural zeolites offer a cost-effective and environmentally friendly alternative. Despite their slightly lower surface areas compared to activated carbons and

MOFs, natural zeolites exhibit favorable adsorption dynamics due to their hierarchical pore structure, which includes a combination of micropores and mesopores. This structural diversity allows for efficient initial adsorption at high-energy sites, followed by slower intraparticle diffusion into smaller pores.

4. Conclusions

This study reports on the carbon dioxide adsorption capacity and kinetic mechanism of a natural zeolite rich in calcium and potassium, with a high Si/Al ratio and a predominance of mesopores and macropores in its pore structure, for hydrogen purification. The SEM images revealed that zeolite crystals present a laminar structure. Adsorption experiments were conducted at flow rates of 0.5 and 1 L/min and pressures ranging from 0.5 to 5 bar. The results demonstrated that increasing the gas flow rate and pressure enhances CO₂ adsorption and reduces residence time.

The adsorption isotherms were fitted with eight models, obtaining the best fits with the Freundlich, Sips and Toth isotherms. These fits indicated that the used zeolite is characterized by a heterogeneous adsorption process combining monolayer and multilayer adsorption.

Different kinetic models were applied to study and analyse the adsorption kinetics, revealing that carbon dioxide adsorption by the natural zeolite is primarily controlled by physical and chemical adsorption, with physical adsorption being dominant. Moreover, the CO₂ adsorption mechanism was further analysed using Weber and Boyd models, showing that intraparticle diffusion governs the early stages of adsorption, being this process faster the higher the gas flow rate supplied. As adsorption progresses, the process is governed also by other mechanisms such as external film diffusion.

Natural zeolite (clinoptilolite) used in this research exhibited high CO₂ selectivity compared to other gases present in the mixture (CO, CH₄ and H₂). This makes it a suitable material for a first stage of H₂ purification since it is capable of capturing CO₂ in the presence of other gases. The findings of this research contribute to our understanding of the dynamic interactions between carbon dioxide and zeolite surfaces, providing valuable insights for the optimization of hydrogen purification processes and have significant implications for industrial hydrogen purification processes. The demonstrated CO₂ adsorption capacity and kinetics of natural zeolite suggest it is

an effective, economical, and environmentally friendly adsorbent for hydrogen purification. Its wide availability and low cost make it an attractive alternative to synthetic adsorbents, reducing operational costs and enhancing the economic feasibility of industrial hydrogen purification. Furthermore, effective CO₂ removal from syngas streams ensures high hydrogen purity, which is essential for applications in fuel cells and other hydrogen-based technologies. The use of natural zeolite leverages a sustainable resource, aligning with environmentally conscious practices.

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.

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