

High-Pressure CO₂ Adsorption onto NaX Zeolite: Effect of Li⁺, K⁺, Mg²⁺, and Zn²⁺ and Equilibrium Isotherms Study

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ABSTRACT: Due to the adverse effects of Carbon dioxide (CO₂) emissions on the environment; various mitigation is regulated to control its emissions. In this study, CO₂ adsorption isotherms on NaX or Faujasite X and exchanged zeolites with Li⁺ (LiX), Zn⁺ (ZnX), Mg²⁺ (MgX) and K⁺ (KX) at different temperatures (298, 308, 323, 353, and 362 K) were investigated, using high pressure (3 MPa (30 bar)) thermogravimetric analyzer. The experimental results were then validated using numerous isotherm kinetics models namely Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Elovich, Toth, and Sips. From the study, it was found that the CO₂ adsorption isotherms are characterized by a strong increase in low-pressure adsorption and a trend towards a high-pressure limit value Q_{max} . Specific surface area and pore volume revealed the most significant influent parameters for this study. These findings revealed that both experimental and modeling well correlated with Toth and Sips, gave the best results regardless of the material used.

KEYWORDS: NaX zeolite; Exchange cations; LiX, KX, MgX and ZnX; CO₂ adsorption; Isotherme study.

INTRODUCTION

Greenhouse gases, such as carbon dioxide, methane, nitrous oxide, are naturally present in the atmosphere, and at the same time play the role of a thermal regulator for our

planet. Since the industrial revolution, human actions and activities, have caused an artificial increase of these gases and translates by the formation of a denser layer

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in the atmosphere, causing global warming [1]. Scientists predict an increase of 5°C by 2100; which multiplies extreme weather: cyclones, hurricanes, droughts, heatwaves, and overwhelming torrential rains [2].

For years, many authors have been concerned about materials to be used for the storage of greenhouse gases, in order to reduce their quantity present in the atmosphere, or emitted by the industry principally work on CO₂. That represents 60% of the greenhouse effect of anthropogenic origin and may reach 80% in industrialized countries. Several methods have been used to such separation and adsorption, which are supposed to play a fundamental role in CO₂ capture [3-4]. Microporous materials such as active charcoal [5-6] and zeolites [3-4], gave encouraging and remarkable results but not enough, which has led researchers and scientists to find alternatives to enhance their adsorption capacity. Among these chemical doping onto zeolites materials (HZSM-5, M-ZSM-5, 13X, and NaX) claimed among the most higher adsorption capacity of CO₂ [5-7].

NaX or Faujasite X (Na_xAl_xSi_{192-x}O₃₈₄) has great commercial use, due to its crystal structure stability and large voluminous pores. The Si/Al ratio of NaX depends mainly on the initial composition of the starting hydrogel and varies between 1 and 1.5 [8-9]. The structure of the NaX consists of 24 TO₄ tetrahedra, which forms a cube-octahedron called cage β or sodalite, with a diameter of 7 Å and a volume around 160 Å³. Together, these components contain a large multi-surface cavity called supercage, which constitutes the basic unit of the microporosity of the NaX zeolite [11]. The super cages are assimilated to pseudo-spheres of 13 Å in diameter and about 850 Å³ in volume and communicate with each other through openings with 12 oxygen atoms (7.4 Å in diameter), which allows access to many molecules [11]. The cage β is connected to the cage α by openings, with 6 oxygen atoms of approximately 3 Å in diameter. The exchange of ions of zeolites is done with compensation cations such as Na⁺, Li⁺, Rb⁺, K⁺, H⁺, Cs⁺, Ca²⁺, Mg²⁺, and Ba²⁺, which is reversible [12-14].

The size of the exchanged cation has a direct induction on the adsorption capacity, and on the interaction energy between the cationic sites and the CO₂ molecules. Walton *et al.* [3], have shown that the size of the exchanged cation is inversely proportional to the adsorption capacity. Khelifa *et al.* [4], have shown that the size of the exchanged

cations is inversely proportional to the interaction energy, between the cationic sites and the CO₂ molecules.

Stacey *et al.* [15], have demonstrated that under the effect of cationic interactions, the adsorption of CO₂ in BaX and LaX is low; in contrast to KX, and the adsorption of CO₂ in KX is made in the form of bidentate carbonate.

Ahn *et al.* [16], studied the adsorption type on zeolite 4A and CaX, and found that the diffusion in the zeolite 4A is controlled by the diffusion of the micropore; on the other hand, in the CaX zeolite, the diffusion was controlled by microporous and macroporous diffusion. Park *et al.* [6], studied the adsorption of CO₂, CO, N₂, and CH₄ on a LiX zeolite, and they showed that the addition of Li⁺ ions increases the CO₂ adsorption capacity of NaX.

However, there are limited studies of high-pressure adsorption for KX, MgX, and ZnX, except LiX. It is postulated that exchange zeolites, and also the inexistence of studies on the influence of nature, and the charge of added ions on the validity of the widely used isothermal models in the other listed zeolites, may have similar results with LiX.

Therefore, in this study, two types of monovalent Li⁺ and K⁺ cations, and divalent Mg²⁺ and Zn²⁺ cations, were investigated for exchanged NaX. The adsorption capacities measurement of these materials were performed at high pressure of about 3 MPa (30 bar), and at several temperatures (298, 308, 323, 353, and 362 K). The analyses of a specific surface area and the pore volumes by BET technique were also carried on each obtained sample using the 2020-M porosity analyzer. The experimental results were then validated using isothermal modeling, with Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Elovich, Toth, and Sips models; by calculating the regression coefficients and a relative error of all exchanged NaX samples. It is expected that the significantly influenced variables can be determined and validated by appropriate model, for each material sample.

EXPERIMENTAL SECTION

Material and methods

The materials used for our experiments are synthetic NaX zeolites, with a Si/Al ratio of about 1.1, and a pore diameter of 7.4 Å. The exchange of ions of NaX zeolites was carried out with nitrate or cationic oxide salt solutions of Li⁺, K⁺, Zn²⁺, and Mg²⁺, as reported by Nibou *et al.* [10, 14]. In a 200 mL beaker of the solution, containing the cation to

exchange, 1 g of NaX sample was mixed; the whole mixture was stirred about 36 hours at room temperature, then the solution was filtered; the obtained powder was washed with demineralized water and dried in an oven at 323 K for 30 hours. The exchange rates after the mass percentages exploitation of different cations were monitored by Induced Coupled Plasma Emission Spectroscopy (ICP-OES). The Si/Al ratios of exchanged NaX with Li⁺, K⁺, Zn²⁺, and Mg²⁺ cations, were also determined by the same technique. The obtained results are shown in Table 1.

The determination of the specific surface and the pore volumes

The 2020-M porosity analyzer instrument was used to determine the pore volumes and BET of zeolites NaX and exchanged NaX with Li⁺ (LiX), Zn²⁺ (ZnX), Mg²⁺ (MgX), and K⁺ (KX), with relative pressure (p/p_0) varying from 0.01 to 0.99.

Adsorption of CO₂ at high pressure

The adsorption tests were carried out using a gravimetric device, consisting of a magnetic suspension balance brand Rubotherm (Bochum, Germany) (Fig1). The balance is linked with the control and acquisition instruments data on one side; and on the other side, it is linked with the elements necessary for the control and regulation of pressure, as illustrated in Figure 2. Adsorption tests were carried out on 1 g samples, under high pressure and at different temperatures (298, 308, 323, 353, and 362 K).

RESULT AND DISCUSSION

Adsorption isotherms

The curves of Fig.3 to Fig.5 represent the adsorption isotherms of CO₂ onto NaX, LiX, KX, ZnX, and MgX, at high pressure and at different temperatures (298, 308, 323, 353, and 362 K). These curves are of type I, according to the IUPAC classification and characteristic of the microporous materials. They correspond to monolayer adsorption, where the filling of the micropores is done with saturation when the available volume is totally filled.

These curves are characterized by a strong increase of adsorption at low pressure and a tendency to a limit value. The characteristic of these curves, is a strong increase of

Table 1: The cation exchange rates and the Si/Al ratios of exchanged NaX by induced coupled plasma emission spectroscopy (ICP-OES).

Cation	Exchange rate (%)	Si/Al ratio
Na ⁺	-	1.10
Li ⁺	72.80	1.11
K ⁺	87.36	1.13
Zn ²⁺	99.10	1.42
Mg ²⁺	96.20	1.39

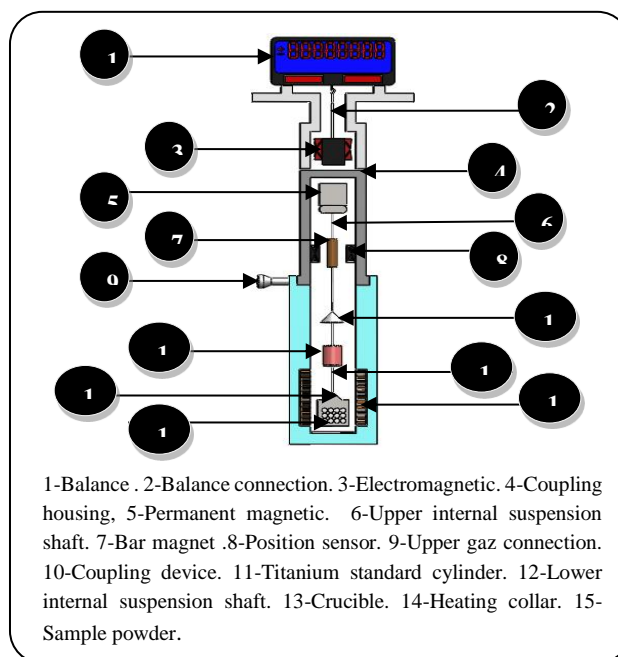


Fig. 1: The magnetic suspension scale.

adsorption at low pressure, and a tendency to a limit value Q_{max} at high pressure. In general, the zeolites' adsorption capacity increases with the pressure of CO₂, and decreases with the increase of temperature. This is caused by, the increase of temperature providing more internal energy to the CO₂ molecules; which allows the gaseous molecules to diffuse faster; but at the same time, it reduces the possibility of capturing or trapping CO₂, by fixed energy adsorption sites on the surface of the adsorbent. These observations are in an agreement with other researchers [6-7, 17-19]. Table 2 shows the CO₂ adsorption capacities, onto the material samples used at different temperatures. The CO₂ adsorption capacities, onto NaX, ZnX, and MgX, at 298 K are 7.56, 6.73, 6.91 mol/kg respectively.

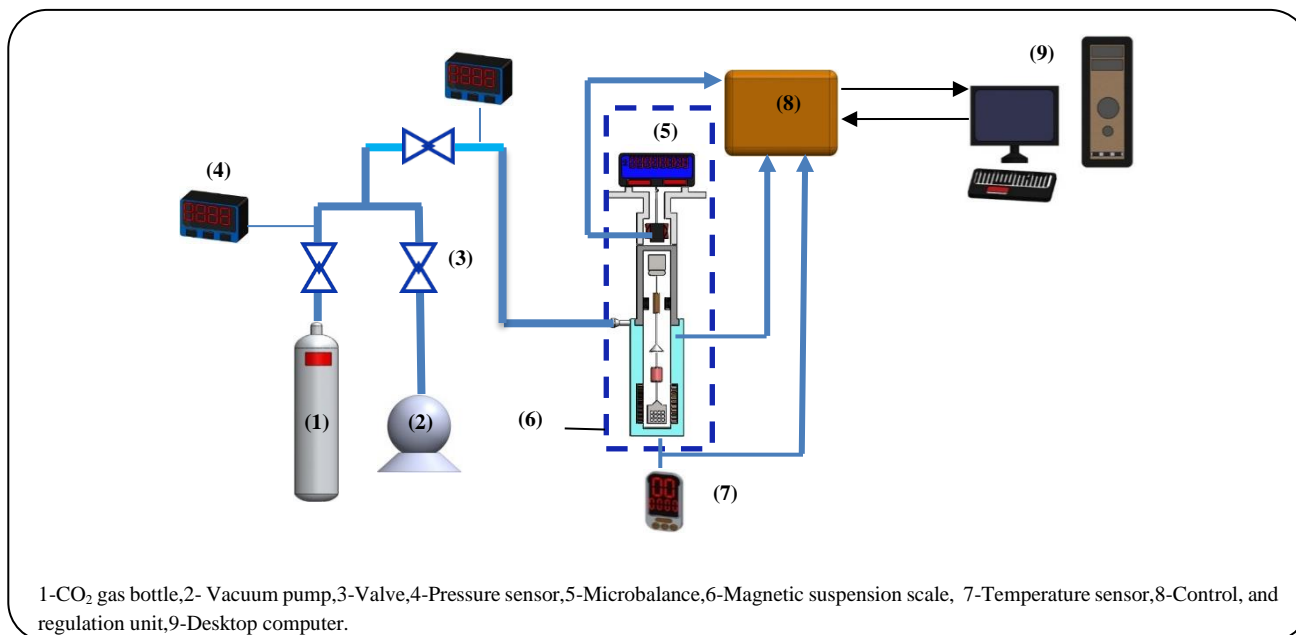


Fig. 2: Used gravimetric devices diagram.

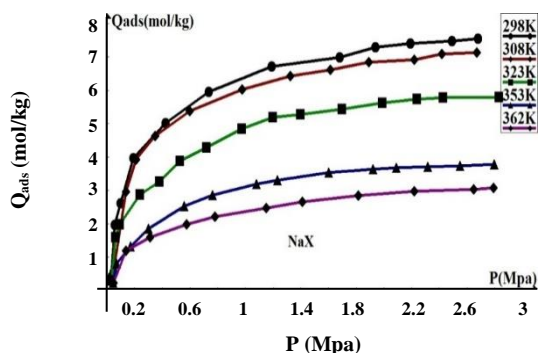


Fig. 3: Adsorption isotherms of CO₂ onto NaX at high pressure and at different temperatures (298, 308, 323, 353, and 362 K).

Table 3 summarizes only, a comparison of adsorption capacities of CO₂ onto NaX and LiX, with those found in the literature; because there is no previous work onto KX, ZnX and MgX, under our current conditions of pressure and temperature

From this comparison, it seems that our results are very close to the results found previously [3,15-17]; the different values of CO₂ adsorption capacities onto these samples, seem to be fine

BET and pore volume

The specific surface values and pore volumes, obtained from the different materials, are grouped in Table 4.

From the obtained results, in Table 4, we notice a significant increase in the specific surfaces and the pore volumes of the exchanged zeolites, except for LiX, which can be explained by the loss of the specific surfaces, and the pore volume. This increase is probably related to the size of the exchanged ions Na⁺, by smaller monovalent Li⁺ in NaX samples. In the case of the exchanged ions, Na⁺ by larger monovalent K⁺, the effect of the substitution is reverse and decreasing in pore volume and specific surface area of KX sample is observed.

On the other hand, the loss of specific surfaces and pore volumes regarding ZnX and MgX zeolites, is mainly due to the decrease of the cations density in the super cages, since the divalent ions have a tendency to fill the inaccessible sites in the sodalite cages (sites I' and II'), and the hexagonal prism (site I), which leads to a decrease in cationic sites (site III) [20]. There are also other factors responsible for this loss, such as the partial collapse of the zeolite structure, and the clogging of the porosity [21].

Effect of anionic radius and electronegativity of cations

The addition of cations decreases the amount of CO₂ adsorbed onto zeolites, except the cation Li⁺. For monovalent cations, the adsorption of CO₂ is influenced by the anionic radius r (K⁺ (1.33 Å) > (Na⁺ (0.97 Å)) > (Li⁺ (0.68 Å)), as shown in Table 5. The obtained results are in agreement with those of Walton *et al.* [3].

Table 2: Adsorption capacity of CO₂ onto NaX, LiX, KX, ZnX, and MgX at high pressure, and at different temperatures (298, 308, 323, 353, and 362 K).

	Q _{max} (mol/kg)				
	298 (K)	308	323	353	362
NaX	7.56	7.14	5.79	3.77	3.09
LiX	9.16	8.56	6.10	4.38	3.92
MgX	6.91	6.11	3.7	1.42	1.02
ZnX	6.73	4.72	2.68	1.31	0.99
KX	4.18	3.74	3.26	2.33	2.09

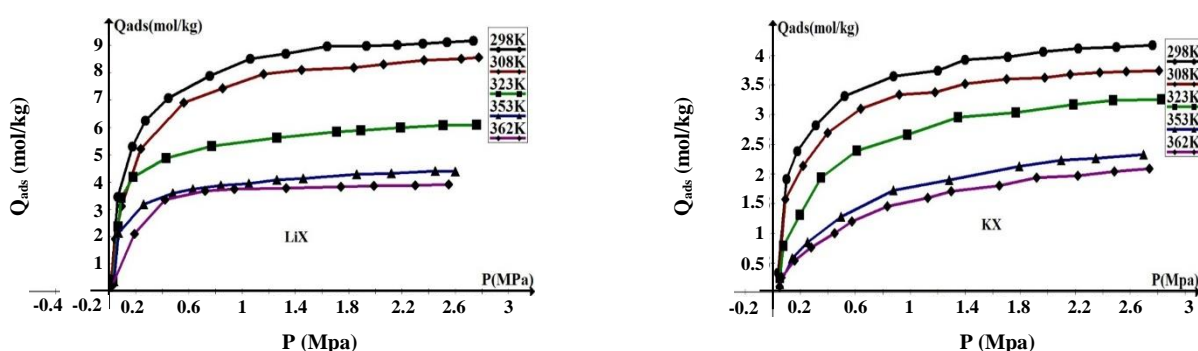


Fig. 4: Adsorption isotherms of CO₂ onto LiX and KX at high pressure and at different temperatures (298, 308, 323, 353, and 362 K).

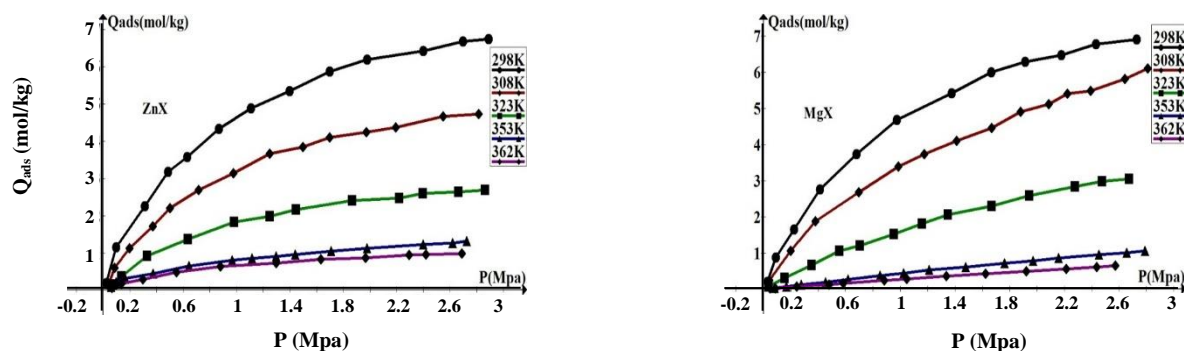


Fig. 5: Adsorption isotherms of CO₂ onto ZnX and MgX at high pressure and at different temperatures (298, 308, 323, 353, and 362 K).

The substitution of Na⁺ by larger atoms, in our case K⁺, leads to the decrease of pore volume and the specific surface area (table4), which implies a capacity decrease of adsorbed CO₂ by the material; on the other hand, the substitution of Na⁺ by smaller atoms, in our case Li⁺, increases the pore volume and specific surface area, which leads to an increase in the capacity of adsorbed CO₂

by the material; thus it can be concluded that in doping with the monovalent ions, the increase of anionic radius causes the decrease of pore volume and the specific surface area, which implies a decrease in CO₂ adsorption capacity; on the other hand, the decrease in ionic radius increases the microporous volume and the specific surface; which implies the increase of the adsorption capacity of CO₂.

Table 1: Comparison of adsorption capacities of CO₂ onto NaX and LiX with those of the literature.

	T(K)	P(Mpa)	Reference		This work
			Q _{max} (mol/kg)		Q _{max} (mol/kg)
NaX	298	2.66	7.22	[16]	7.50
	308	2.50	6.63	[16]	7.00
	323	2.69	5.62	[16]	5.90
	353	1	4.10	[17]	2.4
LiX	298	0.1	5.5	[3]	3.50
	308	0.8	5.30	[18]	7.50
	323	0.8	4.60	[18]	5.50

Table 4: Specific surface and pore volume of NaX, LiX, ZnX, MgX and KX samples.

Material sample	Specific surface(m ² /g)	Pore volume (cm ³ /g)
NaX	624,059	0,323
LiX	653,046	0,412
ZnX	550,884	0,302
MgX	570,978	0,313
KX	405,198	0,252

Table 5: Anionic radius and electronegativity of Na⁺, Li⁺, K⁺, Zn²⁺ and Mg²⁺ cations.

Cation	Anionic radius(Å)	Electronegativity
Na ⁺	0.97	
Li ⁺	0.68	0.98
K ⁺	1.33	0.82
Zn ²⁺	0.74	1.65
Mg ²⁺	0.66	1.31

In divalent ions, the increase of the ionic charge causes the decrease of the adsorption capacity. These results are in agreement with the results obtained by *Erten et al.* [19].

This phenomenon is due to the adsorbate/adsorbent interactions, and which have the greatest influence on the adsorption phenomenon, mainly of electrostatic origin related to the distribution of charges. However, studies have confirmed that the addition of bivalent ions, decreases the basicity of the zeolite [13]; the cationic density in the supercage [20], and promotes the formation of oxides (MgO and ZnO in our case), which play the role of a barrier in the pores of the NaX zeolite structure, this considerably reduces the amount of CO₂ adsorbed, and explains the decrease in the CO₂ retention capacity of

MgX and ZnX [22]. MgX has an adsorption capacity greater than ZnX, this phenomenon is related to several factors; such as the difference in anionic radius between Zn²⁺(0.74 Å) and Mg²⁺(0.66 Å), because the difference in size has a direct impact on the pore volumes; as shown in Table4; where the volume pore of MgX is greater than ZnX.

This size effect is also found on the oxide forms, so; the ZnO has a greater size than MgO, knowing that these oxides play a role of barriers in the micropore, the increase in the size of these oxides increases the size of the barriers, leading to a decrease in adsorption capacity of CO₂.

Also, the quantity of the formed oxides is an added factor, influencing the adsorption capacity effectively.

The ZnO oxide is formed more quickly than MgO, due to the difference in their electronegativity (Table 5), this leads to an increase in the number of barriers in ZnX compared to MgX, and explains the increase in the adsorption capacity of CO₂ onto MgX compared to ZnX samples.

The nature of the oxides formed also influences the adsorption capacity of CO₂, the MgO is known as a good CO₂ adsorber unlike ZnO; its presence in the zeolite structure of MgX increases the adsorption capacity of MgX, compared with ZnX.

Equilibrium isotherms

The equilibrium isotherms study is elemental in contributing the necessary information for the design of the adsorption process. In the present work, Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Elovich, Toth, and Sips isotherm models, were used to explore the equilibrium data by means of NaX, LiX, KX, ZnX, and MgX zeolites.

Langmuir model

The isothermal model of Langmuir is generally used, to describe the physical adsorption (gas/solid) and is based on the assumption that, the adsorption is localized and there is no interaction between adsorbed molecules, so the surface is uniform [23]. The model is expressed as follows:

$$n = \frac{n_m B P}{1 + B P} \quad (1)$$

Where P is the pressure at equilibrium (Mpa), n : the amount of CO₂ adsorbed (mol/kg), n_m : maximum adsorption of single-layer coverage (mol/kg), and B : Langmuir constant (Mpa⁻¹)

The linearization of the model gives the following equation:

$$\frac{P}{n} = \frac{1}{K_e} \left(\frac{1}{n_m} \right) + \frac{P}{n_m} \quad (2)$$

The separation factor RL is a dimensionless constant and one of the essential features of the Langmuir isotherm and is defined by:

$$R_L = \frac{1}{1 + B P} \quad (3)$$

With p is the initial pressure (Mpa) and B Langmuir constant (Mpa⁻¹),

When the separation factor $RL > 0$, it indicates that the adsorption is favorable, if $RL = 1$, the adsorption is supposed to be linear, and if $RL > 1$, the adsorption is considered unfavorable [23-24].

Freundlich model

The Freundlich model is applicable to adsorption processes, that occur on heterogeneous surfaces and are expressed by [25-26]:

$$n = K_f P^{\frac{1}{m}} \quad (4)$$

Where n : the amount of adsorbed gas (mol/kg), P : pressure at equilibrium (Mpa), K_f (mol/kg), and m : constant.

The linearization of the model gives the following equation:

$$\ln n = \ln K_f + \left(\frac{1}{m} \right) \ln P \quad (5)$$

Temkin model

The Temkin model assumes that the heat of adsorption of all the molecules in the layer would, decrease linearly rather than logarithmically; with coverage due to adsorbate/adsorbent interactions, which implies that the adsorption is characterized by a uniform distribution of binding energies [27]. This model is expressed by:

$$\frac{n}{n_m} = \frac{RT}{Q} \ln (K_0 P) \quad (6)$$

$$\frac{n}{n_m} = \left(\frac{RT}{Q} \right) \ln K_0 + \left(\frac{RT}{Q} \right) \ln P \quad (7)$$

Where K_0 : Temkin binding constant, Q : isothermal constant of Temkin which is related to adsorption heat, R : perfect gas constant (8.314J/mol/K), T : temperature (K) and B is an isothermal constant with $B = RT/Q$;

Dubinin-Radushkevich (DR) model

The DR model is applied to express the adsorptive mechanism, with a Gaussian energy distribution on a heterogeneous surface [24, 28], and the adsorption follows a mechanism to fill the pores, it generally applies to the

difference between chemical and physical adsorption of metal ions. It is expressed by:

$$n = n_s e^{-K_{ad} \varepsilon^2} \quad (8)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{P} \right) \quad (9)$$

Where n : the amount of adsorbed gas (mol/kg), n_s : the amount of gas adsorbed at saturation (mol/kg), K_{ad} , ε : isothermal constants of Dubinin-Radushkevich, P : pressure at equilibrium (Mpa) and T : temperature (K).

The average free energy E is calculated from the following relation:

$$E = \frac{1}{\sqrt{K_{ad}}} \quad (10)$$

Elovich model

This model was developed to describe the kinetics of the chemical sorption of gases on solids, it supposes that the adsorption is multilayer adsorption, where the adsorption sites increase exponentially with the adsorption [29].

$$\frac{n}{n_m} = K_E P e^{-\frac{n}{n_m}} \quad (11)$$

The linear form is:

$$\ln \left(\frac{n}{P} \right) = \ln (K_E n_m) - \frac{n}{n_m} \quad (12)$$

Where n : the amount of adsorbed gas (mol/kg), n_m : the amount of gas adsorbed at equilibrium (mol/kg), P : pressure at equilibrium (Mpa), and K_E : Elovich constant.

Toth model

The Toth isotherm is proposed to reduce computational errors between the experimental data and the predicted equilibrium values, caused by the Langmuir equation, it is generally used to describe adsorptions in low and high heterogeneous systems pressure, as well as systems with underlay cover [30]. It is expressed by:

$$\frac{n}{n_s} = \theta = \frac{K_L P}{\left[1 + (K_L P)^m \right]^{\frac{1}{m}}} \quad (13)$$

Where n : amount of adsorbed gas (mol/kg), n_s : amount of adsorbed gas at equilibrium (mol/kg), P : pressure at equilibrium (Mpa), K_L and m are the equation constants.

The parameter m characterizes the heterogeneity of the system, with $0 < m < 1$, and for $m = 1$ the equation is reduced to Langmuir [23].

The adsorbate/adsorbent interactions is described by the constant Henry's law slope K_h ($K_h = n_s K_L$).

The linear form of the isotherm of Toth is:

$$\ln \left(\frac{n^m}{n_s^m - n^m} \right) = m \ln K_L + m \ln P \quad (14)$$

A computer program has been done to solve this equation.

Sips model

The Sips model, is used for adsorptions on heterogeneous surfaces, this model is a combination between Langmuir and Freundlich isotherms, limited to low pressure or it is reduced to the Freundlich model [31] but very specified at high pressure compared to the model of Freundlich, with isothermal parameters as a function of temperature. It is expressed by:

$$n = \frac{n_s (BP)^{\frac{1}{m}}}{1 + (BP)^{\frac{1}{m}}} \quad (15)$$

Where n : amount of adsorbed gas (mol/kg), n_s : amount of adsorbed gas at equilibrium (mol/kg), P : pressure at equilibrium (Mpa), m : isothermal constant is always greater than or equal to 1 and B : isothermal affinity constant;

A computer program has been done to solve this equation.

The results obtained from each model are grouped in Tables 6, 7, 8, 9. Each table represents the values, and the constants of each model, its linearization, and the regression coefficient for all the materials used, and at different temperatures.

The Langmuir constant B or affinity constant is a measure of the attraction force of the adsorbed molecule to the surface. Based on these results (Table 6), the Langmuir constant is influenced by the indicated temperature [23, 24]. The attraction force between the adsorbed molecules and the surface is influenced by the temperature, so

Table 6: Isothermal constants, linear equations and regression coefficients obtained by the Langmuir and Freundlich isothermal models of CO₂ adsorption onto NaX, LiX, MgX, ZnX and KX at different temperatures (298, 308, 323, 353 and 362 K).

Langmuir						
	T(K)	Model constants			Linear form	R ²
		n _s (mol/kg)	B (Mpa ⁻¹)	R _L		
NaX	298	8.4459	3.1914	0.3923995	y = 0.1184x + 0.0371	0.9840529
	308	8.0321	3.0292	0.34660744	y = 0.1245x + 0.0411	0.97446098
	323	6.6445	2.6923	0.39178363	y = 0.1505x + 0.0559	0.98368311
	353	4.4783	2.1368	0.40094354	y = 0.2233x + 0.1045	0.99442391
	362	3.5894	2.1106	0.39438841	y = 0.2786x + 0.132	0.98231504
LiX	298	9.8619	5.1472	0.27739445	y = 0.1014x + 0.0197	0.98486753
	308	9.3023	4.2829	0.33014556	y = 0.1075x + 0.0251	0.99481331
	323	6.4977	5.5161	0.31308424	y = 0.1539x + 0.0279	0.93471391
	353	4.7596	4.8299	0.27329723	y = 0.2101x + 0.0435	0.92969614
	362	4.3103	4.6123	0.2721538	y = 0.232x + 0.0503	0.96870122
MgX	298	9.803921569	0.91152815	0.56185655	y = 0.102x + 0.1119	0.9992782
	308	9.208103131	0.618803419	0.57634282	y = 0.1086x + 0.1755	0.996385473
	323	8.326394671	0.307318321	0.7486848	y = 0.1201x + 0.3908	0.999236788
	353	8.110300081	0.075914296	0.91172424	y = 0.1233x + 1.6242	0.999431616
	362	7.407407407	0.061697363	0.9338652	y = 0.135x + 2.1881	0.999691174
ZnX	298	8.92853	1.09268293	0.51282515	y = 0.112x + 0.1025	0.99835455
	308	6.60501982	0.9288	0.55768094	y = 0.1514x + 0.163	0.99846573
	323	3.98565165	0.78161994	0.5515227	y = 0.2509x + 0.321	0.97695752
	353	1.4781966	1.27042254	0.48338212	y = 0.6765x + 0.5325	0.97580385
	362	1.37400385	0.92114922	0.57326734	y = 0.7278x + 0.7901	0.99752924
KX	298	4.5413	4.2924	0.29781298	y = 0.2202x + 0.0513	0.96653707
	308	4.14075	3.71538462	0.2913427	y = 0.2458x + 0.0612	0.96691612
	323	3.78214826	2.3971	0.41147834	y = 0.2644x + 0.1103	0.98957659
	353	2.9744	1.3985	0.48899008	y = 0.3362x + 0.2404	0.99595398
	362	2.6810	1.3060	0.5142782	y = 0.373x + 0.2856	0.99729428

Table 6: (Continued)

Freundlich					
	T(K)	Model constants		Linear form	R ²
		K _f (mol/kg)	m		
NaX	298	5.7632	2.0367	$y = 0.491x + 1.7518$	0.9001
	308	5.4948	2.0708	$y = 0.4829x + 1.7038$	0.8605
	323	4.5512	1.9120	$y = 0.523x + 1.5154$	0.9021
	353	2.7020	1.806	$y = 0.5537x + 0.994$	0.9014
	362	2.1756	1.8681	$y = 0.5353x + 0.7773$	0.9074
LiX	298	7.4715	2.1734	$y = 0.4601x + 2.0111$	0.8145
	308	6.6953	1.7912	$y = 0.5583x + 1.9014$	0.8379
	323	5.0612	2.5233	$y = 0.3963x + 1.6216$	0.7167
	353	3.6840	2.3579	$y = 0.4241x + 1.304$	0.7559
	362	3.2201	1.7343	$y = 0.5766x + 1.1694$	0.6665
MgX	298	4.1400	1.3738	$y = 0.7279x + 1.4207$	0.9575
	308	3.1277	1.3714	$y = 0.7292x + 1.1403$	0.9886
	323	1.8244891	1.16225012	$y = 0.8604x + 0.6013$	0.9861
	353	1.79391431	1.0545	$y = 0.9483x - 0.5844$	0.9980
	362	0.42176795	1.03455411	$y = 0.9666x - 0.8633$	0.9986
ZnX	298	4.1235	1.4335	$y = 0.6976x + 1.4167$	0.9398
	308	2.8594	1.4138	$y = 0.7073x + 1.0506$	0.9495
	323	1.5331	1.3931	$y = 0.7178x + 0.4273$	0.9398
	353	0.7598	1.5946	$y = 0.6271x - 0.2747$	0.9836
	362	0.5833	1.4832	$y = 0.6742x - 0.539$	0.9714
KX	298	3.3656	2.3052	$y = 0.4338x + 1.2136$	0.8277
	308	2.9268	2.2331	$y = 0.4478x + 1.0739$	0.8204
	323	0.5466	5.5371	$y = 0.1806x - 0.604$	0.8877
	353	1.5428	1.5865	$y = 0.6303x + 0.4336$	0.9344
	362	1.3685	1.5526	$y = 0.6441x + 0.3137$	0.9372

the attraction force has an influence on the adsorption capacity. We also notice that $B > 0$ for all the zeolites, implying that the separation factor $R_L = 1/(1+BP)$ is always $0 < R_L < 1$, which means that the adsorption is favorable [32-36]. In general, the Langmuir model (Table 6), has a better description of the CO₂ adsorption data onto NaX, LiX, KX, ZnX, and MgX zeolites, with a high R² correlation factor.

The Freundlich K_f constant is an approximate indicator of the adsorption capacity, while m is a function of the adsorption force [25-26], whose adsorption cases vary according to 3 values: $m > 1$, indicates physical adsorption, $m < 1$ reveals chemical adsorption, and $m = 1$ indicates linear adsorption. The obtained values of m (Table 6), are all greater than 1, showing that the adsorption is favorable and of a physical type. We note that the two constants K_f and m are influenced by the temperature, the increase of the temperature causes the decrease of the constant K_f, which follows an exponential variation law ($K_f = Ae^{B/T}$), A and B constants which may be determined graphically or analytically.

From these results, we note that the Freundlich model is valid in general for exchanged zeolite samples with divalent cations (Zn²⁺ and Mg²⁺), and is not valid for exchanged zeolites with monovalent cations. The results can be explained by the addition of divalent cations, leading to the formation of oxides, in our case MgO and ZnO; the latter remain on the surface and cluster to form oxide-rich surfaces, which increases the heterogeneity of the surface, and ultimately increases the validity of the Freundlich model, which is already designed to model heterogeneous surfaces.

Comparing the values of R², obtained by the two models, it is noted that R² of Langmuir model of NaX, LiX, and ZnX zeolites are better than those of Freundlich model. We also note that Freundlich model has a better description of the adsorption data of MgX and ZnX samples. These results give us a preview of the type of adsorption, but the transition to the Sips model is essential to confirm the type of adsorption.

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms, which is used to describe heterogeneous adsorption systems; when m is always near or equal to 1, the model tends towards the Langmuir model. The maximum adsorption capacities are shown in Table 7. It can be observed that the Sips model describes

better the adsorption data, with R² values close to 1. This indicates and confirms that the dominant adsorption of CO₂ onto NaX, LiX, MgX, ZnX, and KX zeolites is heterogeneous.

The K_d, n_s, E, and regression coefficient R² values of DR model are classified in Table 8. The obtained regression coefficients R² of NaX are good; on the other side, we note a decrease of R² for the exchanged zeolites, suggesting that the DR model is valid for the NaX zeolite but not for the exchanged zeolite (LiX, KX, MgX, ZnX). n_s is inversely proportional to the temperature for all materials used. The obtained free energy E values increase with the increase of temperature and are between 4.08 and 6.75 kJ/mol, the free energy E is used to define the type of adsorption [37-42], if the value of E is greater than 6 kJ/mol, the adsorption is dominated by intra-particle diffusion, if E is between 8 and 16 kJ/mol, the adsorption process is chemisorption, where ion exchange is the dominant factor, while values of E are below 8 kJ/mol, the dominant process is physical adsorption. The obtained values (Table 8) of the free energy by the DR isothermal model of adsorption of CO₂ onto NaX, LiX, ZnX, MgX, KX samples, at different temperatures, are less than 8 kJ/mole, which means that the adsorption of CO₂ follows a physical adsorption process.

The isothermal constant K_E and n_m of the CO₂ adsorption Elovich model onto NaX, LiX, MgX, ZnX, and KX zeolites are also given in Table 8. From these results, it seems that the regression coefficient R² values are low, compared to those of Langmuir, Freundlich, Sips, and DR. This means that, the adsorption of CO₂ on used zeolites is not multilayer adsorption, and the adsorption sites do not increase exponentially. Therefore, the Elovich model cannot describe the isothermal adsorption of CO₂ on the NaX, MgX, ZnX, LiX, and KX zeolites.

The value of the equilibrium constant of Temkin K₀ is related to the adsorption affinity of CO₂; the increase of the K₀ value implies an improvement of the affinity. The results of Table 9 show that NaX, LiX, ZnX, MgX, and KX zeolites, have high K₀ values with acceptable regression coefficient R², from which they have a good affinity for CO₂.

From Table 10, the Toth model gives a good value of regression coefficient R², especially for MgX and ZnX samples where R² is greater than 0.99. The average value of m is related to the heterogeneity of the surface,

Table 7: Isothermal constants, linear equations, and regression coefficients obtained by the Sips isothermal models of CO₂ adsorption onto NaX, LiX, MgX, ZnX, and KX at different temperatures (298, 308, 323, 353, and 362 K).

Sips						
	T(K)	Model constants			Linear form	R ²
		ns mol.kg ⁻¹	B Mpa ⁻¹	m		
NaX	298	8.2256	4.2109	1.0525	$y = 0.0755x + 0.0103$	0.9901
	308	7.6964	4.1352	1	$y = 0.0733x + 0.0584$	0.9868
	323	7.0853	2.5308	1.2228	$y = 0.1645x - 0.0291$	0.9866
	353	4.358	2.5115	1	$y = 0.1645x - 0.0291$	0.9961
	362	3.7202	2.1347	1.1735	$y = 0.2945x + 0.0618$	0.988
LiX	298	9.6364	5.6669	1	$y = 0.0388x + 0.055$	0.9926
	308	9.0635	4.2829	1.052	$y = 0.0605x - 0.0056$	0.9997
	323	6.2503	9.2483	1	$y = 0.0604x + 0.039$	0.968
	353	4.5433	7.9407	1	$y = 0.0833x + 0.1201$	0.9513
	362	4.2555	6.2165	1	$y = 0.1025x + 0.1473$	0.9833
MgX	298	9.7114	0.9408	1.0084	$y = 0.1384x + 0.0397$	0.9993
	308	16.559	0.1737	1.2814	$y = 0.3327x - 0.032$	0.9972
	323	8.13	0.3194	1	$y = 0.4086x + 0.0906$	0.9993
	353	7.2	0.0872	1	$y = 1.6413x + 0.1083$	0.9995
	362	6.5908	0.0703	1	$y = 2.2188x + 0.0919$	0.9997
ZnX	298	9.4578	0.9622	1.0871	$y = 0.1742x - 0.0005$	0.9984
	308	6.4216	1.0114	1.0089	$y = 0.2207x + 0.0334$	0.9989
	323	3.6919	0.9556	1	$y = 0.3845x + 0.1623$	0.9987
	353	3.2294	0.2085	1.4169	$y = 1.177x - 0.0282$	0.995
	362	1.4287	0.8483	1.0632	$y = 1.0969x + 0.2273$	0.9977
KX	298	4.3848	6.0429	1	$y = 0.0974x + 0.1126$	0.9805
	308	4.0083	5.1254	1	$y = 0.1246x + 0.1281$	0.9785
	323	3.6619	2.9535	1	$y = 0.1637x + 0.136$	0.9936
	353	2.8432	1.6702	1	$y = 0.3348x + 0.1406$	0.998
	362	2.6245	1.4306	1.0199	$y = 0.3901x + 0.158$	0.998

Table 8: Isothermal constants, linear equations, and regression coefficients obtained by the DR and Elovich isothermal models of CO₂ adsorption onto NaX, LiX, MgX, ZnX, and KX at different temperatures (298, 308, 323, 353, and 362 K)

Dubinin–Radushkevich							
	T (K)	Model constants				Linear form	R ²
		K _d (Kg ⁻² .mol ⁻²)	n _s (mol/kg)	ε (KJ ² .mol ⁻²)	E (KJ.mol)		
NaX	298	0.034	7.628	3.146	5.423	y = -0.0344x + 2.0318	0.9953
	308	0.038	7.281	2.662	5.1299	y = -0.0383x + 1.9853	0.9961
	323	0.03	5.632	3.097	5.7735	y = -0.0303x + 1.7285	0.9785
	353	0.03	3.663	3.08	5.7735	y = -0.0297x + 1.2982	0.9848
	362	0.028	2.916	3.028	5.9761	y = -0.0284x + 1.0703	0.9797
LiX	298	0.029	9.460	2.782	5.8722	y = -0.0291x + 2.2471	0.9977
	308	0.025	8.537	3.315	6.3245	y = -0.0254x + 2.1444	0.9839
	323	0.025	5.632	3.397	6.3245	y = -0.0252x + 1.8804	0.9562
	353	0.022	4.562	3.099	6.7429	y = -0.0221x + 1.5177	0.9494
	362	0.022	4.107	3.217	6.7419	y = -0.0219x + 1.4127	0.9761
MgX	298	0.044	5.654	2.709	4.740	y = -0.0445x + 1.7323	0.906
	308	0.046	4.628	2.14	4.647	y = -0.0463x + 1.5321	0.8291
	323	0.046	2,566389378	2.563	4.657	y = -0.0461x + 0.9495	0.7897
	353	0.060	0.930717021	2.538	4.082	y = -0.06x - 0.0718	0.7966
	362	0.045	0.629	3.075	4.73	y = -0.0447x - 0.4636	0.7606
ZnX	298	0.041	5.532	2.563	4.933	y = -0.0411x + 1.7106	0.8811
	308	0.047	3.972	2.651	4.588	y = -0.0475x + 1.3792	0.9204
	323	0.05	2.361	2.445	4.481	y = -0.0498x + 0.8592	0.8830
	353	0.033	1.066	2.886	5.471	y = -0.0334x - 0.0563	0.881
	362	0.038	0.860	3.276	5.116	y = -0.0382x - 0.1503	0.8964
KX	298	0.034	4.325	2.657	5.423	y = -0.034x + 1.4645	0.9720
	308	0.035	3.874	2.496	5.368	y = -0.0347x + 1.3542	0.9746
	323	0.035	3.207	3.059	5.33	y = -0.0352x + 1.1654	0.8916
	353	0.035	2.159	3.132	5.33	y = -0.0352x + 0.7697	0.8683
	362	0.032	1.838	3.341	5.617	y = -0.0317x + 0.6088	0.8656

Table 8: (Continued)

Elovich					
	T (K)	Model constants		Linear form	R ²
		K _E (Mpa ⁻¹)	n _m (mol/kg)		
NaX	298	12.7198	3.214	y = -0.3111x + 3.7108	0.8491
	308	10.4031	3.269	y = -0.3059x + 3.5266	0.7783
	323	10.6407	2.597	y = -0.385x + 3.3192	0.8578
	353	6.1046	2.003	y = -0.4993x + 2.5036	0.8377
	362	7.1155	1.507	y = -0.6637x + 2.3722	0.8956
LiX	298	22.469	3.442	y = -0.2905x + 4.3483	0.6707
	308	15.0135	3.530	y = -0.2833x + 3.9702	0.7432
	323	26.9161	2.224	y = -0.4497x + 4.0919	0.6335
	353	17.3113	1.838	y = -0.5442x + 3.4598	0.5668
	362	7.0907	2.238	y = -0.4469x + 2.7642	0.5016
MgX	298	3.6354	2.205	y = -0.4534x + 2.0817	0.5133
	308	1.1927	5.397	y = -0.1853x + 1.862	0.9944
	323	7.0798	2.029	y = -0.4929x + 2.6672	0.8673
	353	0.0827	7.457	y = -0.1341x - 0.4831	0.9992
	362	0.0658	6.949	y = -0.1439x - 0.7821	0.9995
ZnX	298	2.4753	4.662	y = -0.2145x + 2.4458	0.9677
	308	6.7958	2.046	y = -0.4888x + 2.6368	0.9611
	323	1.3915	2.407	y = -0.4154x + 1.2089	0.9531
	353	2.5016	0.853	y = -1.1725x + 0.7578	0.9887
	362	1.8706	0.767	y = -1.3038x + 0.361	0.9277
KX	298	9.7394	1.186	y = -0.8428x + 2.4472	0.5962
	308	13.3927	1.607	y = -0.6222x + 3.0692	0.6674
	323	7.0726	1.657	y = -0.6034x + 2.4614	0.8276
	353	3.1715	1.530	y = -0.6537x + 1.5793	0.9361
	362	3.0029	1.383	y = -0.7228x + 1.4242	0.9495

Table 9: Isothermal constants, linear equations, and regression coefficients obtained by the Temkin isothermal model of CO₂ adsorption onto NaX, LiX, MgX, ZnX, and KX at different temperatures (298, 308, 323, 353, and 362 K).

Temkin model						
	T(K)	Model constants			Linear form	R ²
		B	Q (J.mol ⁻¹)	K ₀ (Mpa ⁻¹)		
NaX	298	0.2061	12.004	54.890	y = 0.206x + 0.826	0.9918
	308	0.2163	11.877	46.352	y = 0.216x + 0.827	0.9784
	323	0.214	12.566	45.811	y = 0.214x + 0.817	0.9905
	353	0.233	12.607	31.049	y = 0.233x + 0.799	0.9931
	362	0.225	13.376	31.39	y = 0.225x + 0.779	0.996
LiX	298	0.192	12.931	100.7074	y = 0.192x + 0.884	0.9745
	308	0.183	14.008	108.36	y = 0.183x + 0.856	0.9843
	323	0.177	15.189	138.203	y = 0.177x + 0.874	0.9214
	353	0.186	15.745	114.357	y = 0.186x + 0.883	0.9117
	362	0.242	12.421	92.293	y = 0.242x + 1.096	0.9347
MgX	298	0.234	10.583	21.178	y = 0.234x + 0.715	0.9483
	308	0.225	11.381	15.625	y = 0.225x + 0.618	0.9173
	323	0.239	11.245	12.693	y = 0.239x + 0.607	0.868
	353	0.271	10.834	6.743	y = 0.271x + 0.517	0.8729
	362	0.211	14.234	10.984	y = 0.211x + 0.507	0.8294
ZnX	298	0.222	11.16	25.182	y = 0.222x + 0.716	0.9498
	308	0.239	10.696	18.177	y = 0.239x + 0.694	0.9685
	323	0.264	10.172	14.3	y = 0.264x + 0.702	0.9798
	353	0.212	13.831	19.197	y = 0.212x + 0.627	0.963
	362	0.255	11.793	15.351	y = 0.255x + 0.697	0.9826
KX	298	0.195	12.705	80.744	y = 0.195x + 0.856	0.9581
	308	0.212	12.09	58.357	y = 0.212x + 0.861	0.9532
	323	0.230	11.711	33.4139	y = 0.23x + 0.805	0.9908
	353	0.249	11.791	20.733	y = 0.249x + 0.755	0.9936
	362	0.263	12.737	21.915	y = 0.263x + 0.729	0.9865

Table 10: Isothermal constants, linear equations, and regression coefficients obtained by the Toth isothermal model of CO₂ adsorption onto NaX, LiX, MgX, ZnX, and KX at different temperatures (298, 308, 323, 353, and 362 K).

Toth model							
	T(K)	Model constants				Linear form	R ²
		ns (mol.kg ⁻¹)	K _L (Mpa ⁻¹)	m	K _h (mol.kg ⁻¹ Mpa ⁻¹)		
NaX	298	8.4395	4.9799	0.8642	42.0279	y = 0.9493x + 1.3873	0.9901
	308	7.6966	4.1348	1	31.8239	y = 1.119x + 1.4107	0.9868
	323	7.4885	4.6466	0.6809	34.7961	y = 0.74x + 1.0412	0.9868
	353	4.3583	2.5107	1	10.9424	y = 1.0533x + 0.9049	0.9961
	362	3.9652	3.4677	0.7084	13.7501	y = 0.7853x + 0.8658	0.988
LiX	298	9.6843	7.0062	0.9759	67.8501	y = 1.0784x + 1.8924	0.9927
	308	9.0663	5.6739	0.9986	51.4413	y = 1.0933x + 1.7269	0.9993
	323	6.2503	9.2483	1	57.8046	y = 1.1109x + 2.1841	0.9640
	353	4.1559	7.8967	1	32.8179	y = 1.1645x + 2.1096	0.9511
	362	4.2555	6.2165	1	26.4543	y = 1.1198x + 1.7351	0.9833
MgX	298	9.6407	0.9574	0.9993	9.23	y = 1.0183x - 0.0449	0.9993
	308	35.0138	0.3205	0.4062	11.2219	y = 0.4258x - 0.4697	0.9989
	323	8.13	0.3194	1	2.5967	y = 1.0094x - 1.144	0.9993
	353	8.7114	0.0729	0.9147	0.6350	y = 0.9269x - 2.4011	0.9995
	362	9.0726	0.0519	0.8737	0.4708	y = 0.8835x - 2.5884	0.9997
ZnX	298	9.7881	1.1834	0.8389	11.5832	y = 0.8718x + 0.1364	0.9984
	308	6.4543	1.0321	0.9786	6.6615	y = 1.0169x + 0.0247	0.9989
	323	3.6917	0.9558	1	3.5285	y = 1.063x - 0.0731	0.9987
	353	7.2661	0.7753	1	5.6334	y = 0.352x - 0.0892	0.993
	362	1.5305	0.9891	0.8268	1.5138	y = 0.8572x - 0.0165	0.9978
KX	298	4.3848	6.0429	1	26.4969	y = 1.1216x + 1.8025	0.9805
	308	4.008	5.1254	1	20.5426	y = 1.0998x + 1.6009	0.9785
	323	3.6619	2.9535	1	10.8154	y = 1.0708x + 1.0675	0.9936
	353	2.8432	1.6702	1	4.7487	y = 1.0678x + 0.4997	0.998
	362	2.6705	1.5083	0.9399	4.0279	y = 0.9828x + 0.3804	0.998

with m between 0 and 1; If m is equal to 1, the surface is very homogeneous, and if m is equal to 0, the surface is very heterogeneous [30]. When m tends to 1, the Toth equation is reduced to that of Langmuir. For NaX the average value of m is around 0.8507, with m varying between 0.68 and 1, while for ZnX, the mean value of $m = 0.9289$, with m varying between 0.8268 and 1, which indicates that the dominant surface in these zeolites is the homogeneous

surface, with a presence of small heterogeneous areas. The average value of m decreases in MgX, where the average value of m is 0.8388, with m varying between 0.4062 and 1, this decrease indicates, an increase in heterogeneous regions in the MgX zeolite sample, compared to the NaX and ZnX zeolite samples.

As for Zeolite LiX, the Average value of m is equal to 0.9949, with m varying between 0.9759 and 1, while for KX,

Table 11: Relative average error of used models onto NaX, LiX, MgX, ZnX, and KX at different temperatures.

	T(K)	Relative Average Error Models						
		Langmuir	Freundlich	Temkin	DR	Elovich	Toth	Sips
	298	14.8267	29.3656	8.3527	28.738	37.4577	8.7404	9.1606
	308	10.1597	26.0112	8.6608	22.6763	37.3074	7.3457	7.3457
NaX	323	13.0093	25.5981	7.98	26.3753	27.6869	10.358	8.9714
	353	8.7380	24.2306	8.8158	26.1841	30.4652	6.1779	6.1779
	362	9.3221	25.5217	8.7874	26.1982	25.1147	9.8588	8.1619
	298	9.1019	30.4895	9.0259	20.0677	45.151	6.3128	6.3426
	308	9.5745	37.8533	20.4781	24.4405	40.3874	5.5583	7.6079
LiX	323	17.0828	58.3966	13.8414	21.6811	68.7785	10.0598	10.223
	353	13.9016	28.1404	12.5156	19.0096	56.8159	17.5862	9.5822
	362	10.4971	37.0105	14.1419	19.4101	53.6156	10.5370	10.5370
	298	4.4139	17.4079	21.5381	20.2726	416.4377	4.4111	4.4776
	308	3.7984	8.8033	22.9966	22.5976	2.8099	3.2475	3.5595
MgX	323	1.9692	8.8067	27.4634	32.2372	69.8613	2.0471	2.047
	353	1.4308	73.8288	34.5903	35.2714	1.6646	1.6292	1.4817
	362	1.3187	2.8911	70.7302	39.3486	1.5639	1.6606	1.4016
	298	5.2888	20.4650	19.0911	17.2284	11.9853	5.4208	5.6709
	308	5.7091	17.4919	21.2165	15.4635	25.2843	4.8823	4.8914
ZnX	323	36.7175	16.2569	26.4958	35.2553	12.7802	4.9356	4.9406
	353	54.2714	13.6779	16.9483	38.0423	9.3775	77.7657	46.2436
	362	7.6875	15.5004	121.9325	41.4162	42.7864	6.6081	6.9395
	298	10.8163	9.1126	10.3482	26.6121	573.183	7.5551	7.5544
	308	10.7593	9.6974	10.5611	25.4671	43.0863	6.9054	6.9026
KX	323	10.4562	32.2758	7.9437	25.3488	31.2533	7.7435	7.7436
	353	7.7902	36.0313	41.0148	22.5591	19.2618	5.7590	5.7590
	362	7.6827	36.7305	34.6097	19.6760	16.1001	5.9028	5.8737

the average value of m is 0.9880, with m varying between 0.9399 and 1. These values of m are very close to 1, convert the equation of Toth into the Langmuir equation, and it shows that LiX and KX have very homogeneous surfaces; therefore the predominant adsorption is monolayer adsorption.

The constant K_H , is the product of Toth parameters n s and k , it represents the slope of the Henry law, it is directly related to the interaction of the adsorbate with the surface. A large value of K_H implies a strong adsorbate interaction/adsorbent [30, 35-36]. From the results of Table 10, the constant K_H has high values for NaX, LiX, and KX, and has low values for MgX and ZnX samples.

These results; show that the adsorbate/adsorbent interactions in NaX, LiX, and KX are strong and low in the MgX and ZnX. Hence, the addition of divalent ions considerably reduces the adsorbate/adsorbent interactions.

Average relative error

The average relative error was expressed by:

$$\varepsilon = \frac{100}{n} \sum_{i=1}^n \left| \frac{n_{\text{calcule}} - n_{\text{modele}}}{n_{\text{modele}}} \right| \quad (16)$$

Table 11 shows the average relative error values of each model for NaX, LiX, MgX, ZnX, and KX zeolites samples, and at different temperatures. In order to facilitate

Table 12: Regression coefficient R² of used models onto NaX, LiX, MgX, ZnX, and KX at different temperatures (298, 308, 323, 353 and 362 K).

	T(K)	Coefficient of Regression						
		Langmuir	Freundlich	Temkin	DR	Elovich	Toth	Sips
NaX	298	0,9840	0,9002	0,9918	0,9486	0,7479	0,9901	0,9901
	308	0,9745	0,8605	0,975	0,9822	0,6869	0,9868	0,9864
	323	0,9837	0,9021	0,9905	0,9381	0,7608	0,9866	0,9868
	353	0,9944	0,9014	0,9831	0,9696	0,7992	0,9961	0,9965
	362	0,9823	0,9074	0,991	0,9807	0,7842	0,9877	0,9880
LiX	298	0,9849	0,7714	0,9745	0,972	0,7027	0,9927	0,9926
	308	0,9948	0,8411	0,9842	0,991	0,7719	0,9993	0,9997
	323	0,9347	0,9716	0,9214	0,894	0,5793	0,9640	0,9680
	353	0,9297	0,6964	0,9101	0,8793	0,5297	0,9511	0,9515
	362	0,9687	0,8344	0,9347	0,991	0,5238	0,9833	0,9831
MgX	298	0,9992	0,9575	0,9482	0,906	0,5132	0,9993	0,9993
	308	0,9964	0,9886	0,9173	0,8291	0,9944	0,9989	0,9972
	323	0,9992	0,9861	0,868	0,7897	0,8673	0,9993	0,9993
	353	0,9994	0,9980	0,8718	0,7966	0,9992	0,9995	0,9995
	362	0,9997	0,9986	0,8294	0,7606	0,9995	0,9997	0,9997
ZnX	298	0,9983	0,9534	0,9498	0,8811	0,9679	0,9984	0,9984
	308	0,9985	0,9695	0,9685	0,9204	0,9611	0,9988	0,9988
	323	0,9769	0,9618	0,9798	0,883	0,9531	0,9987	0,9987
	353	0,9758	0,9836	0,963	0,881	0,9887	0,9930	0,995
	362	0,9975	0,9714	0,9825	0,8964	0,9276	0,9978	0,9977
KX	298	0,9765	0,7440	0,9581	0,9720	0,5962	0,9874	0,9805
	308	0,9831	0,7507	0,9532	0,9746	0,6674	0,9755	0,9785
	323	0,9885	0,8587	0,9908	0,9750	0,8276	0,9916	0,9936
	353	0,9939	0,9178	0,9965	0,9887	0,9361	0,9980	0,9980
	362	0,9953	0,9257	0,9865	0,9670	0,9495	0,9945	0,9980

the comparisons between the models, a calculation of the regression coefficients, and the mean average error corresponding to each model has been performed. The results are summarized in Table 12. The choice of the appropriate model for each zeolite sample is based on the regression coefficient value R^2 , and the average relative error. The accuracy of the model increases with increasing of R^2 , and decreasing of the average relative error. On this basis, these models are ranked in Table 13,

in descending order of the averages of the regression coefficients and increasing of an average of relative errors.

From these results, on the basis of a classification of R^2 (decreasing), and average error coefficients (increasing), we can notice that at high pressure, the Toth and Sips models gave the best results, regardless of the material used in these experiments. We also note that the order of the model's validity, is the same for exchanged zeolite samples with monovalent, ions (Li^+ and K^+), and divalent

Table 13: Average of regression coefficients R² and relative errors of used models onto NaX, LiX, MgX, ZnX, and KX at different temperatures (298, 308, 323, 353, and 362 K)

	Average value of the regression coefficients						
	Lang	Freu	Tem	DR	Elov	Toth	Sips
NAX	0.984	0.894	0.986	0.963	0.844	0.989	0.99
LiX	0.963	0.823	0.946	0.945	0.621	0.978	0.979
MgX	0.998	0.986	0.887	0.816	0.875	0.999	0.999
ZnX	0.989	0.970	0.969	0.892	0.960	0.997	0.998
KX	0.987	0.839	0.976	0.975	0.794	0.989	0.990
	Average value of average relative errors						
	Lang	Freu	Temk	DR	Elov	Toth	Sips
NAX	11.211	26.145	8.519	26.034	31.606	8.496	7.964
LiX	12.032	38.378	14.001	20.922	52.95	10.011	8.859
MgX	2.606	22.348	35.464	29.945	98.467	2.599	2.593
ZnX	21.935	16.678	41.137	29.481	20.443	19.922	13.73
KX	9.501	24.77	20.859	23.933	136.577	6.773	6.767

Table 14: Ranking of the models in descending order of R² average and increasing relative error averages.

	Ranking of models in descending order of average R ²						
	Sips	Toth	Temk	Lang	DR	Freun	Elov
NAX	Sips	Toth	Temk	Lang	DR	Freun	Elov
LiX	Sips	Toth	Lang	Temk	DR	Freun	Elov
MgX	Sips	Toth	Lang n	Freu	Temk	Elov	DR
ZnX	Sips	Toth	Lang	Freu	Temk n	Elov	DR
KX	Sips	Toth	Lang	Temk	DR	Freun	Elov
	Classification of models in ascending order of relative error averages						
	Sips	Toth	Temk	Lang	Freu	DR	Elov
NAX	Sips	Toth	Temk	Lang	Freu	DR	Elov
LiX	Sips	Toth	Lang	Temk	DR	Freun	Elov
MgX	Sips	Toth	Lang	Freun	DR	Temk	Elov
ZnX	Sips	Freun	Toth	Elov	Lang	DR	Temk
KX	Sips	Toth	Lang	Temk	DR	Freu	Elov n

ions (Mg²⁺ and Zn²⁺). Consequently, we can conclude that the models of Toth and Sips give the best results, whatever the material used, and their precision is not influenced by the exchange ions and its nature. On the other hand, the validity of two or one parameter models is influenced by the doping and by the nature of the ions added, either monovalent or divalent.

CONCLUSIONS

The following most important conclusions can be inferred based on the above study:

- The adsorption of CO₂ at high pressure of about 3 MPa (30 bar) was carried out onto NaX and exchanged NaX with Li⁺ (LiX), K⁺ (KX), Zn²⁺ (ZnX), and Mg²⁺ (MgX), and at different temperatures 298, 308, 323, 353 and 362 K.

- The CO₂ adsorption isotherms onto the zeolite samples NaX, LiX, KX, ZnX, and MgX are characterized by a strong increase in adsorption at low pressure and a tendency to a limit value Q_{max} at high pressure.

- The exchange of ions of NaX zeolite with divalent cations Zn²⁺, Mg²⁺, and large ionic radius monovalent cation K⁺, decreases the pore volumes, the specific surface areas, and the adsorption capacities of CO₂ onto KX, ZnX, and MgX.

- The exchange of ions of NaX with small ionic radius monovalent cation Li⁺, increases the pore volume, surface area, and adsorption capacity of CO₂ onto LiX.

- The increase in the size of the MgO and ZnO oxides increases the size of the barriers, leading to a decrease in the adsorption capacity of CO₂.

- Increasing the electronegativity of divalent cations Mg²⁺ and Zn²⁺, causes the decrease of the adsorption capacity of CO₂.

- The experimental results have been analyzed by Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Elovich, Toth, and Sips isotherm adsorption models. Toth and Sips isotherms at high pressure have a better fitting model than Langmuir, Freundlich, DR, and Elovich, as the previous have a higher correlation regression coefficients R².

- The two models give the best results in the present study, regardless of the material used, and their accuracy is not influenced by the zeolite exchange ions and the nature of the substitution cations.

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