

Experimental, Kinetic, and Isothermal Modeling of Carbon Dioxide Adsorption with 13X Zeolite in a Fixed Bed Column

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ABSTRACT

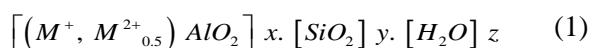
In this work, zeolite 13X with a porosity structure has been used as an adsorbent for adsorption of CO₂ flue gas. The effects of operating conditions, including pressure and time, on adsorption capacity were investigated. The experimental conditions include constant temperature, the range of pressure of 1-9 bars, and the registration of adsorption capacity with the passage of time. Experimental data were adjusted with adsorption isotherm models including two- and three-parameter isotherms. In addition, the process was studied in terms of kinetic models; after the implementation of the experimental data with kinetic models, the speed of the process equations was obtained. The first-order equation was selected as the best kinetic model for this process. The results showed that the adsorption capacity of 13X was 71.5 mg/g at a pressure of 8 bars. Also, the results indicate that 13X has a high capacity at low pressures. With regard to achieved results for adsorption isotherm modeling, the adsorption isotherm followed the three parameters and, among the three-parameter models, Toth isotherm can interpret the process. Also, the results of the fixed bed indicate very high adsorbent selectivity to carbon dioxide adsorption, and there is little oxygen and nitrogen adsorption.

1. Introduction

Due to porous crystalline and specific chemical structures of Zeolite, they have three characteristics: ion exchange, adsorption, and catalytic properties; almost all chemical processes will be done through one of these three channels. As a result, Zeolites are used in a wide range of industries. Concerning the adsorption by Zeolite, molecules that are small enough to penetrate the pores of the

Zeolite can bind tightly to Zeolite. Zeolites are composed mainly of alumino-silicate, and they are mostly used as adsorbents in industries commercially. Several studies have been conducted on the adsorption of gases by Zeolite. Due to different sizes and structures of the Zeolite pores, there are different types of Zeolites in industry. The structure of zeolites was determined by the following formula:

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where M⁺ is the alkaline metal cation, and M²⁺ is the alkaline earth cation. Various amounts of silica and aluminum are categorized as Y, A, X. More than 150 types of synthetic Zeolites are made, and more than 60 kinds of natural Zeolite are found such that only some of them are of industrial importance. Shiralkar found that the highest adsorption capacity of the Zeolite was replaced with sodium ions by reviewing Zeolite category of Y [1]. Kamiuto et al. (2001) used hexagon zeolite beds that are formed by combining the wall of the thin fibrous with approximately 80 % porosity of MS-13X and MS-4A Zeolites to adsorb carbon dioxide. The results showed that the recovery of carbon dioxide in the bed of MS-13X due to higher adsorption capacity was more than the bed including that of MS-4A [2]. Cavenati et al. (2004) found that 13X adsorbent seems a good option for purification of methane from natural gas and separation carbon dioxide from flue gas due to better adsorption capacity at high temperatures [3]. Sirivardane et al. (2005) found the adsorbent that has the highest pore diameter and the highest ratio of sodium to silicon, showing higher retention capacity [4]. Lano et al. examined the adsorption of carbon dioxide in the case of the Na-X adsorbent with 13X brand name in a 78-150 temperature range and in the 20-46 bar pressure range. It was observed that the adsorption capacity at a temperature of 273 K and pressure of 0.0001 bar was 3 and at 1 bar was 7 mmol/gram of adsorbent, respectively [5]. Araki et al. (2012) checked out the adsorption of carbon dioxide on RHO zeolite at 25 °C and 1 bar. RHO Zeolite can be built by the hydrothermal method from a mixture of silica, sodium and colloidal alumina, sodium hydroxide, cesium

hydroxide, and distilled water. The amount of adsorbed was obtained to be almost constant and equal to 1.3 mmol/g. This amount is more than that adsorbed by NaX. However, the selectivity of carbon dioxide over nitrogen for the adsorbent was evaluated more than NaX Zeolite [6]. The results of researches show that 13X adsorbent has the highest adsorption capacity to compare other adsorbents. In Table 1, it is clear that adsorption pressure is too low for 13X adsorbent.

This indicates that the cost of adsorption is lower for Zeolites adsorbent. In this study, kinetics, mechanism, adsorption isotherms of carbon dioxide adsorption regarding 13X Zeolite were investigated. A batch reactor and a fixed bed were used in the experiments. The experiments were carried out in different operational conditions to determine adsorbent behavior.

2. Process theory

2.1. Adsorption isotherm models

Isotherms show sorption mechanisms, i.e., how metal ions react with an adsorbent, and are used in a batch process to optimize required adsorbent dosage [7]. If q quantity of gas or vapor is adsorbed by the porous solid, a constant temperature and p partial pressure will be at steady-state equilibrium. In this case, function q (p) is adsorption isotherm. Isotherms can be a form shown in Figure 1.

Each of these types is practically adsorbed; however, so far, most common types are I, II, and IV. Isotherm of type I whose adsorption is limited to the completion of a separate monolayer is adsorbed on the adsorption surface. Adsorbents that have been widely distributed throughout the pore size form type II isotherms, and vapor adsorption occurs larger in these pores. Type-IV isotherms are similar to type-II isotherms except that the

adsorption results in near-unity surface pressure. Type-V isotherms at low partial pressure isotherms are similar to type-II ones, however, the inflection point is obtained later and is close to saturation with further increases in the partial pressure [8]. Several models have been presented based on this classification. These models include single-component isotherms and multi-component isotherms. In a single-component isotherm, adsorption of the soluble component is considered, and the single-component model is used to identify the adsorbed behavior. In a multi-component isotherm, the adsorption of multiple components is considered at the same time. In this adsorption, components impact each adsorption; therefore, the multi-component model is used for studying and identifying their adsorption behavior. These

types of models are shown in Table 2.

Langmuir adsorption isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent and, after that, no further adsorption takes place. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate on the plane of the surface. Freundlich adsorption isotherm is commonly used to describe the adsorption characteristics for a heterogeneous surface. Constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process [9].

Table 1

Researches in the case of gas adsorption using zeolites.

Researcher	Year	Adsorbent	Compound and gas type	Adsorption capacity of CO ₂ (mmole/g)	Pressure (bar)	Temperature (K)
Dan [2]	1996	H-ZSM-5, NaX, Na-ZSM-5, Zeolites	CO ₂	0.0872-4.62	0-0.028	305.8
Cavenati et al. [3]	2004	Zeolite 13X	CO ₂ , N ₂ , CH ₄	1.147-7.372	0.010-32	298, 308, 328
Siriwardan et al. [4]	2005	Sodium Alumina silicate zeolite	CO ₂ (15 %), N ₂ (82 %), O ₂ (3 %)	2.5-3	17.237-20.684	298
		Sodium Alumina silicate zeolite (4A)		1.2-1.4		
		Sodium, calcium, potassium Alumina silicate zeolite		0.7 -0.8		

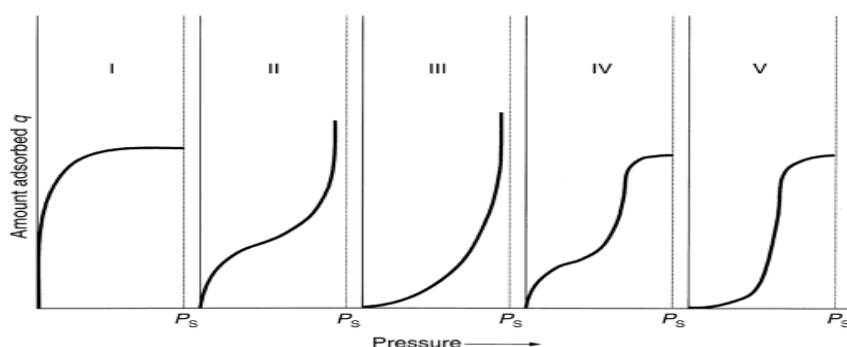


Figure 1. Types of adsorption isotherm.

Table 2

Adsorption isotherm models [8-13].

Model	Model equation
Two-parameter model	Langmuir $q_e = \frac{q_m k C_e}{1 + k C_e}$
	Freundlich $q_e = K_f C_e^n$
	Dubinin-Radukovich $q_e = \frac{RT}{b_T} \ln(A_T C_e)$
Three-parameter model	Redlich-Peterson $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$
	Toth $q_e = \frac{K_T C_e}{(a_R + C_e)^{1/t}}$
	Hill $q_e = \frac{q_{SH} C_e^{nH}}{K_D + C_e^{nH}}$
	Radke-Prausnitz $q_e = \frac{a_{RP} r_R C_e^{\beta_R}}{a_{RP} + r_R C_e^{\beta_R - 1}}$

Redlich-Paterson isotherm is the most used three-parameter isotherm model, which is a combination of the Langmuir and Freundlich models. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. The Toth isotherm model, which is similar to the Redlich-Peterson model, combines the characteristics of both the Langmuir and Freundlich isotherms. Toth equation possesses the correct Henry law type limit besides a parameter to describe the heterogeneities of the system [10].

Hill equation describes the binding of different species onto homogeneous substrates. It is assumed for the model that adsorption is a cooperative phenomenon with the ligand binding ability at one site on the macromolecule, which may influence different binding sites on the same macromolecule [13].

2.2. The sorption kinetics models

When adsorption occurs, theoretical thermodynamic and kinetic aspects, including performance details and review mechanism, should be checked. In addition to the adsorption capacity, the kinetic performance

of an adsorbent is very important. Kinetic analysis is performed according to solute adsorption rate, which determines the residence time required for a complete adsorption reaction. Kinetic data can be used to determine the dimensions of systems, fixed bed components, or any other streaming system. Several mathematical models have been proposed to describe the adsorption data, which generally have been classified as adsorption reaction models and adsorption diffusion models. The sorption kinetic models are made based on three consecutive stages spread throughout the film around the solid particles, diffusion in liquid in pores or along the walls of the cavity (internal influence), and adsorption and desorption of adsorbents and active surfaces. Common kinetic models are presented in Table 3 [14].

Lagergren (1898) presented a first-order-rate equation to describe the kinetic process of fluid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. In recent years, it has been widely used to describe the adsorption of pollutants

from wastewater in different fields. In 1995, Ho described a kinetic process of the adsorption of divalent metal ions onto peat based on the adsorption capacity of the concentration of solution. This equation has been successfully applied to the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions [14]. In 1977, Ritchie reported a model for the adsorption of gaseous systems. In this equation, n is the number of surface sites occupied by each molecule of the adsorbed gas. In recent years, the Ritchie equation has also been applied to solution/solid adsorption systems[16]. Elovich's equation is a kinetic equation of chemisorption established by Zeldowitsch (1934) and is used to describe the rate of adsorption of carbon monoxide on

manganese dioxide, which decreases exponentially with an increase in the amount of gas adsorbed. Elovich's equation has been widely used to describe the adsorption of gas onto solid systems. Weber-Morris found that, in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with contact time t . In this case, k_{int} is the intraparticle diffusion rate constant. For Weber-Morris model, it is essential for the $q_t \sim t^{1/2}$ plot to go through the origin if the intraparticle diffusion is the sole rate-limiting step. However, it is not always the case, and adsorption kinetic may be controlled by film diffusion and intraparticle diffusion simultaneously. Thus, the slope is not equal to zero[14].

Table 3
The adsorption kinetic models [14].

Models equations	Kinetic models
First Order Model	$q_t = q_e(1 - e^{-k_1 t})$
Second Order Model	$q_t = k_2 q_e^2 t(1 + k_2 q_e t)$
Ritchie equation	$q_t = q_e - q_e/(1 + k_2 t)$
Elovich equation	$q_t = \beta \ln(\alpha \beta) + \beta \ln(t)$
Weber-Morris model	$q_t = k_{int} t^{1/2}$

2.3. Numerical solution technique

In order to model, a nonlinear regression method was used in the calculation of model parameters. This type of regression is a method for finding a non-linear model characterized by a relationship between complex independent and the dependent variables. The counter model of traditional linear regression methods, i.e., non-linear regression model, can be assessed as in voluntary relationships between independent variables and the dependent, and using this based on the estimates algorithm is completed. The parameters are in fact part of

the model that fulfill nonlinear regression to achieve appropriate options. This parameter can be a mathematical constant value, or common factor, coefficient or values to be used in the evaluation. The advantages of this method reside in its quick and accurate calculation of the values of model parameters. In the non-linear regression method, basic parameter values in the model are required. In the case of disadvantages of this method, if the initial guess is not appropriate, it may not respond; therefore, to prevent this problem, it is necessary to guess the initial values of the parameters based on

the estimate of experimental data. To calculate the error of the models, the correlation coefficient was considered. The correlation coefficient error equation is used below (Equation (2)):

$$R^2 = \frac{(q_{meas} - \bar{q}_{calc})^2}{\sum_{i=1}^n (q_{meas} - \bar{q}_{calc})^2 + (q_{meas} - q_{calc})^2} \quad (2)$$

3. Experimental

3.1. Adsorption setup

To obtain experimental data for adsorption kinetics, a batch adsorption system was used on a laboratory scale. The system includes a sealed container for the adsorption process

that includes input and output paths for the passage of gas from the adsorbent surface and pressure, and the flow rate of gas inlet is adjustable with a valve and a pressure gauge. This enclosure's door is designed in a way that is completely isolated environmentally and, during the process, the waste gas is as low as possible. The adsorbent is inside a mesh container in an embedded place inside the enclosure. Due to the display of the temperature and pressure inside the chamber, a control panel is attached during the process, as shown in Figure 2.

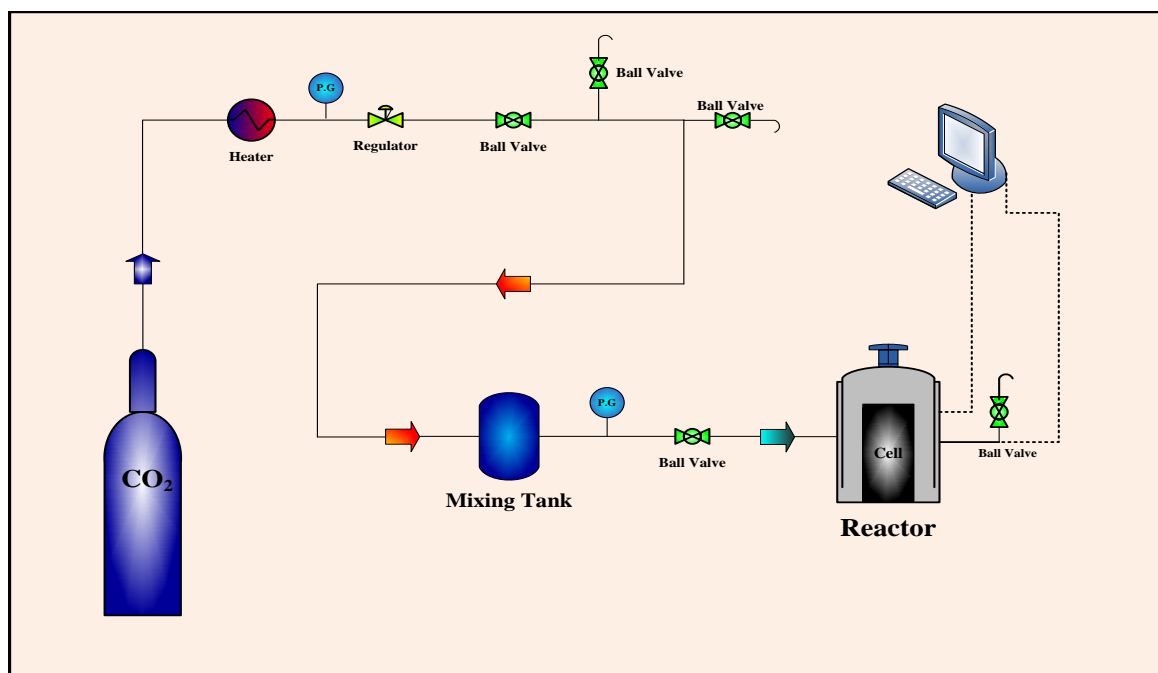


Figure 2. Schematic overall adsorption process gases.

Also, carbon dioxide adsorption experiments with zeolite X13 were performed in a fixed bed pilot. The used prototype schematic is shown in Figure 3. Usually, the ratio of the length to the diameter of the adsorption columns is greater than 1.5. To minimize the problem of a large MTZ area, more L/D values are needed. The break curve width directly affects the adsorption of a fixed bed. By increasing the curve width to the bed

length, the efficiency of the bed in each cycle of adsorption decreases, and more adsorbent will be required for a particular feed flow. In order to minimize the pressure drop in the adsorbent, a horizontal or sloping unit may be required. Therefore, a fixed bed of 1-meter high that has four beds with 25 cm height and 10 cm diameter was prepared. The experiments were carried out in the first stage with 15 cm and with 1 m of adsorbent height

in the second stage. The adsorption column is made of steel and an air filter is used in the adsorbent input path to block particles entry into bed. For analyzing carbon dioxide, an AX-350 L analyzer is installed on the inlet and outlet of the bed. The AX-350L is a life-safety device that measures the concentration of carbon dioxide (CO₂) in ambient air. It offers protection for people working in proximity to high CO₂ concentration sources and raises the alarm if the gas reaches

unhealthy levels. The AX-350L CO₂ gas sensor is a field-deployable, real-time, ambient gas analyzer that measures atmospheric levels of carbon dioxide with parts per billion (ppb) sensitivity while maintaining high linearity, precision, and accuracy over changing environmental conditions with minimal calibration required [15]. To remove moisture from the air, a dewatering device is used at the bed gas inlet.

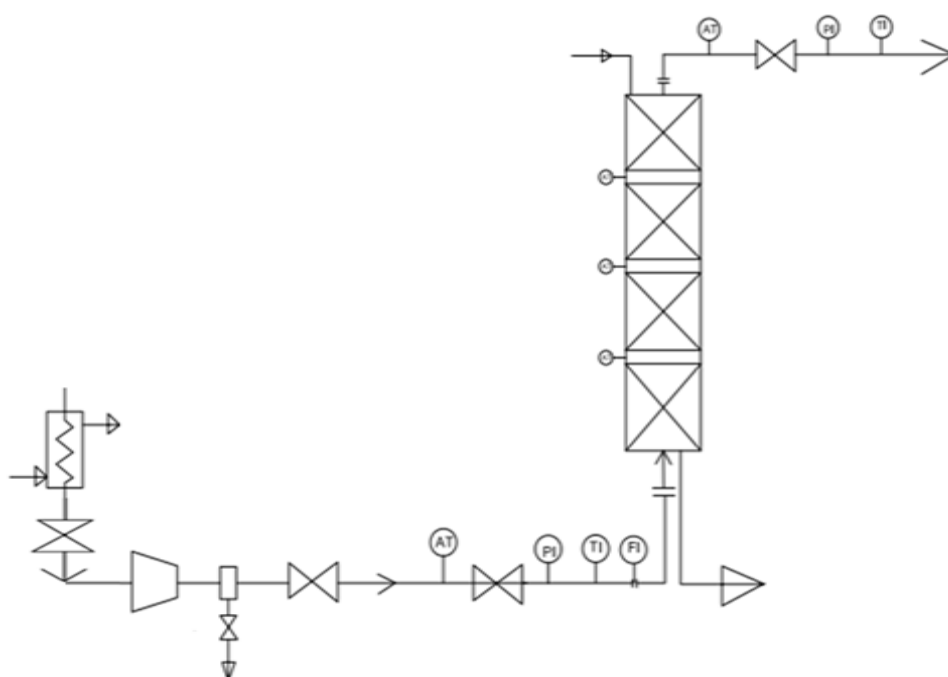


Figure 3. Adsorption fixed bed.

3.2. Experiments

13X zeolite adsorbent was purchased from Merck Company in the form of bulk grains. The gas phase consists of CO₂ and air supplied by Hamtagas Mehrabad Co. cylinder (99.99 % purity) and air compressor (Mahak, AP-301, 300 L capacity), respectively. After weighing adsorbent placed in special mesh, a solid container door was closed. After setting inlet gas pressure on the target value using a pressure gauge and reaching the pressure inside the enclosure to the pressure, all entry and exit gas valves were closed and allowed,

respectively. The adsorption process occurs slowly over time. Internal pressure recording at different times continued until the pressure reached an almost constant amount. No change in pressure indicates that the adsorption process is over. Therefore, the gas outlet valves remain open to release carbon dioxide of the enclosure; then, the compartment door should be open to let the consumed adsorbent out. This process is repeated for different stages, and each time the same amount of adsorbent is put at different initial pressures. In the experiments,

the initial pressure was set 1 to 9 bars. The experiments were performed in a constant-temperature environment (298 K).

The continuous adsorption experiments were carried out in a fixed bed with 1 m height and 10 cm diameter. The adsorption experiments were applied to investigate adsorption operating parameters including temperature, pressure, gas flow rate, and adsorbent amount.

4. Results and discussion

4.1. Characterization of 13X zeolite adsorbent

13X Zeolite was selected as the adsorbent tested due to its high adsorption capacity and selectivity, chemical and thermal stability, suitable recovery conditions, and also availability and reasonable prices. The XRF results of the chemical analysis of 13X zeolite and the percentage of the components in the adsorbent are presented in Table 4. Analytical results of the composition of zeolite percentages show that the molar ratio of SiO_2 to Al_2O_3 is about 2.5 (This ratio is usually between 2 and 3), which is suitable for zeolite, according to reports.

Table 4
Chemical analysis of 13X zeolite.

Compound	Weight percentage (%)
SiO_2	37.90
Al_2O_3	25.80
Na_2O	13.70
CaO	0.80
Fe_2O_3	1.80
MgO	0.09
TiO_2	3.02
K_2O	0.09
The other	13.50

4.2. The effect of time on the adsorption process

As mentioned, the process was performed with different initial pressures, and pressure loss occurred along the progress of adsorption. In Figure 4, the pressure variation with time shows that, in each stage, pressure reduction continues until equilibrium pressure and, after 1000 seconds, the pressure becomes almost constant. This shows that the adsorption process almost stops from somewhere, and adsorption capacity reaches its equilibrium amount.

In an area where pressure variation is

almost constant, the maximum amount of adsorption was selected as the adsorption isotherm equilibrium point. As seen in Figure 5, by increasing the pressure at a constant temperature, the adsorption capacity increases. Due to the resultant pressure increase, the chance of the interaction of gas particles on the adsorbent surface increases, while an adsorbent at low pressures has also a high adsorption capacity. Based on these presented values and models, modeling has been done and process behavior with any of the models has been investigated.

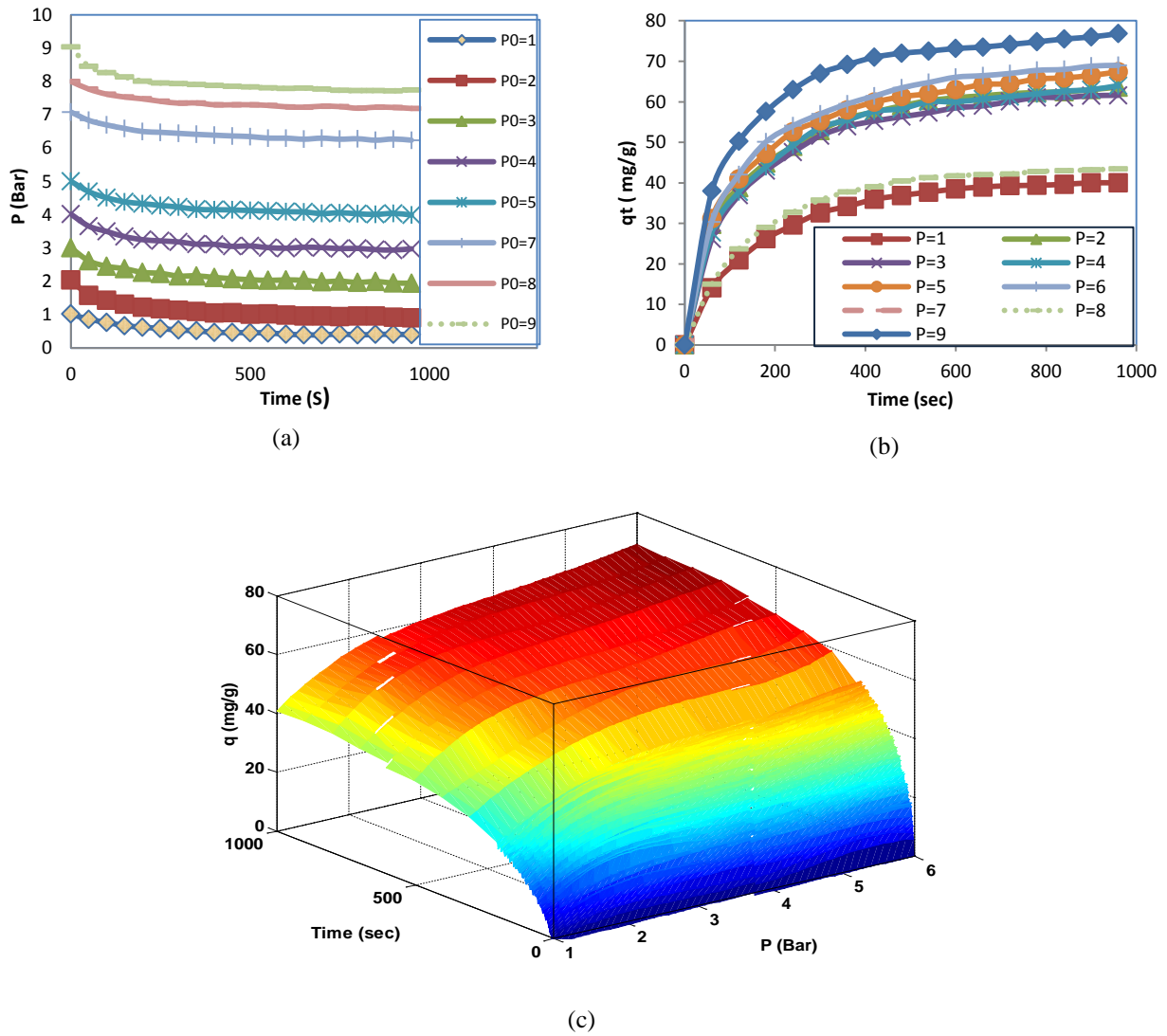


Figure 4. Time changes in the adsorption rate of carbon dioxide adsorption method with zeolite 13X adsorbent at a constant temperature of 298 K, a) Pressure, b) adsorption rate, and c) Pressure, adsorption capacity.

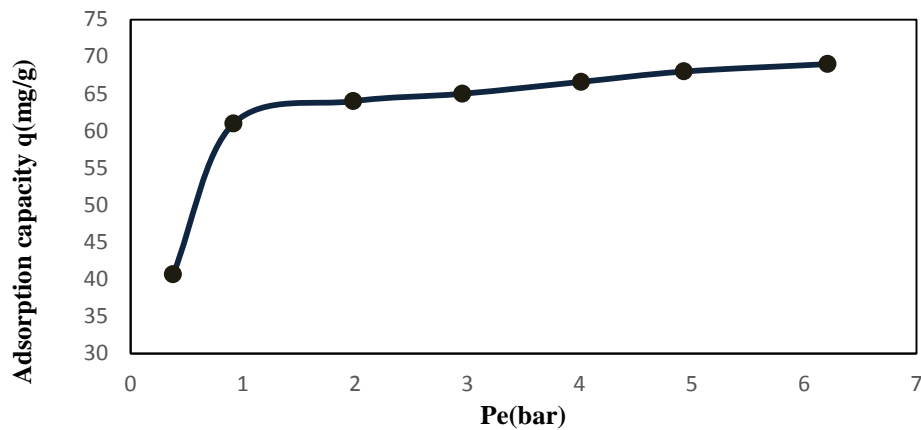


Figure 5. Adsorption isotherms of carbon dioxide with the zeolite 13X adsorbent at a constant temperature of 298 K.

4.3. Adsorption isotherms modeling

After adjusting the data model, carbon dioxide adsorption isotherm modeling results and two-parameter models are presented in Table 5, and the results of some of the models that have not received a proper interpretation of experimental results were ignored.

The adsorption data fit Langmuir, Freundlich, and Dubinin–Radushkevich isotherms out of which the Langmuir adsorption model was found to have the highest regression value and, hence, the best fit. Figure 6 shows the results of the two-parameter isotherm model.

Table 5

The result of two-parameter isotherm models for carbon dioxide with the zeolite 13X adsorbent at a temperature of 298 K.

Model	Parameters	values	R ²
Langmuir	qm	71.725	0.974
	KL	4.025	
Freundlich	K	6.926	0.894
	n	54.903	
Dubinin Radushkevich	qm	68.33	0.965
	Beta	0.044	
	E	3.376	

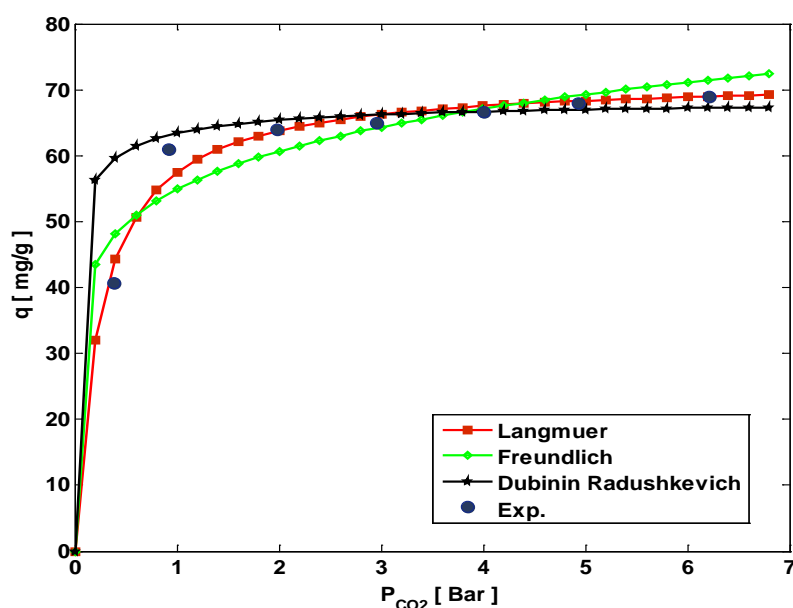


Figure 6. Isotherm model of carbon dioxide adsorption using zeolite 13X via two-parameter models.

As can be seen in the Freundlich model, n parameter is larger than 1; whenever the value of n is larger, the bond between the adsorbent and adsorbate is stronger and, thus, adsorption isotherm turns away from a linear mode. Larger amounts of K adsorbate can be separated from the adsorbent easily. Also, the

slope ranging between zero and one is the adsorption capacity size or surface heterogeneity, while the following amounts representing the chemical adsorption process where $1/n$ is greater than one indicates the equilibrium adsorption of the process [16].

By examining the behavior of the system

and matching it with three-parameter models, Table 6 shows the results of modeling carbon dioxide adsorption with 13X zeolite adsorbent

by three parameters models and values obtained for parameters of each model.

Table 6

The result of the three-parameter isotherm models for adsorption of carbon dioxide with zeolite 13X.

Model	Parameters	values	R ²
Hill	q _s	67.528	0.991
	K _D	0.108	
	n _H	1.854	
Toth	K _T	82.256	0.979
	a _T	0.372	
	t	0.931	
Redlich Peterson	K _R	220.162	0.981
	A _R	2.7848	
	g	1.066	

Toth isotherm model is a kind of experimental equations developed to improve the Langmuir equation and is useful for describing heterogeneous adsorption systems. In fact, the relation is Gaussian asymmetrical energy distribution by default in which many places have lower adsorbed energy than a peak (maximum) or a moderate amount. This model considers surface adsorbent as heterogeneous and multi-piece, and t parameter represents the heterogeneity level of the system. Whenever t is larger from 1, the amount of heterogeneous systems becomes greater. Thus, since the value obtained for this parameter is close to 1, it can be stated that the system is almost homogeneous. The Hill isotherm model has been used to express the bond between different components. In this model, it is assumed that the adsorption equilibrium phenomenon with the ability to link a ligand in one place has been over the macromolecule that may be affected by different bond's sites on the similar macromolecule. As mentioned, the Redlich Peterson model is a combined

isotherm model of both Langmuir and Freundlich isotherm models, in which three parameters form an empirical equation. In this model, linear dependence on the concentration in the numerator and an exponential function in the denominator exist to show the adsorbed balance throughout a wide range of concentrations, which can be applied to homogeneous or heterogeneous systems due to its versatility. For some, this model approaches the Freundlich isotherm model in high concentrations and, according to low viscosity limit, is ideal in terms of the Langmuir model [16]. According to the obtained value for parameters in the above table, this model can be close to the Freundlich isotherm model. In Figure 7, the results of the three-parameter models are presented, and observed that all the three-parameter models are consistent on the experimental data. Therefore, the result shows that the process of adsorption of carbon dioxide on 13X zeolite adsorbent follows the three-parameter models.

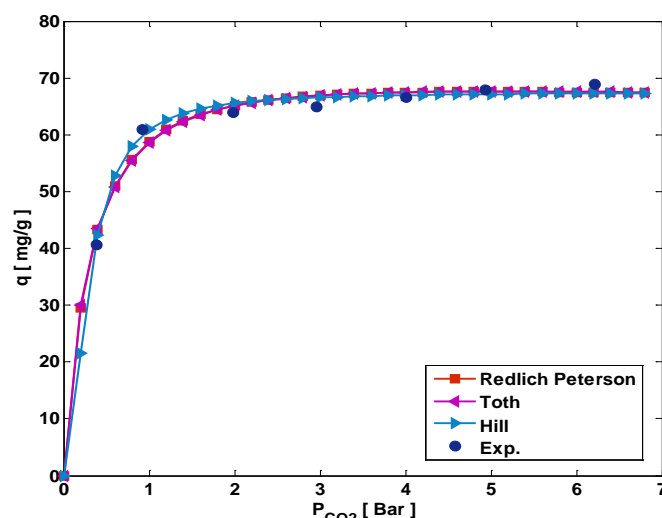


Figure 7. Isotherm modeling of carbon dioxide adsorption with zeolite 13X adsorbent via three-parameter models.

4.4. Kinetics modeling of adsorption

Adsorption experimental data fit at different pressures (the initial pressure of 1 to 9 bars), with models and average results for obtained

parameters presented in Table 7. Also, each model's error shows the deviation of the experimental results, too.

Table 7

The result of three-parameter isotherm models for adsorption of carbon dioxide with zeolite 13X.

Kinetics models	Parameter	P=3	P=5	P=7
First-Order	q_e	59.677	64.190	64.890
	k_1	0.007	0.008	0.008
	R^2	0.9938	0.9900	0.9870
Second-Order	q_e	68.361	72.814	73.407
	k_2	0.00014	0.00015	0.00016
	R^2	0.9997	0.9991	0.9986
Ritchie	q_e	68.361	72.815	73.407
	k_2	0.0.01	0.011	0.012
	R^2	0.9997	0.9991	0.9986
Elovich	α	0.009	0.009	0.009
	β	9.565	9.565	9.565
	R^2	0.9858	0.9858	0.9858
Weber-Morris	k_{int}	2.368	2.569	2.607
	R^2	0.9363	0.9324	0.9325
Experiment	$q_{e_{exp.}}$	61.789	67.04	70.456

In Table 7, the lowest error is achieved for the first-order model. The amount of adsorption capacity equilibrium, through this model, is achieved 358.59 mg/g, and this

amount is very close to the experimental data. As can be seen in Figure 8, the first-order equations could follow experimental data very well.

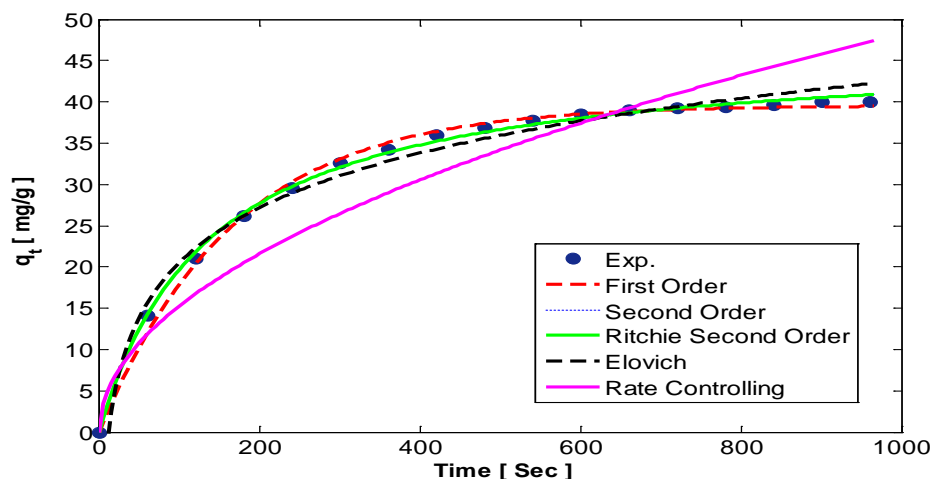


Figure 8. Kinetic modeling of carbon dioxide adsorption using 13X zeolite at a pressure of 1 bar.

Ritchie model also matches the experimental data very well. After that, the second-order and Ellovich models are located in some areas higher and some areas lower than the experimental plot, respectively. The Veber-Morris equation that is a controller and an adsorbed speed limiter has shown a large deviation from the data. This indicates that the intrusion has not been effective in the adsorption process [16].

4.5. Fixed bed experiments

Fixed bed adsorption experiments were carried out at first in 0.15 m adsorbent at various pressures of 1.5 to 6 bars. Figures 9 and 10 show the concentration of carbon

dioxide inside the bed and also the concentration of the adsorbed output as a function of time, while the bed is in homogeneous conditions. In Fig. 10, the experiments were carried out on a bed at a height of 1 m from the adsorbent and at various pressures of 1.5 to 6 bars; in addition, carbon dioxide concentration changes were presented. The results show that the selectivity of 13X zeolite in carbon dioxide adsorption is very high compared to Nitrogen and Oxygen. Adsorption results at different temperatures showed that an increase in gas temperature reduced the amount of adsorbent and, therefore, the adsorption was performed at 313 K.

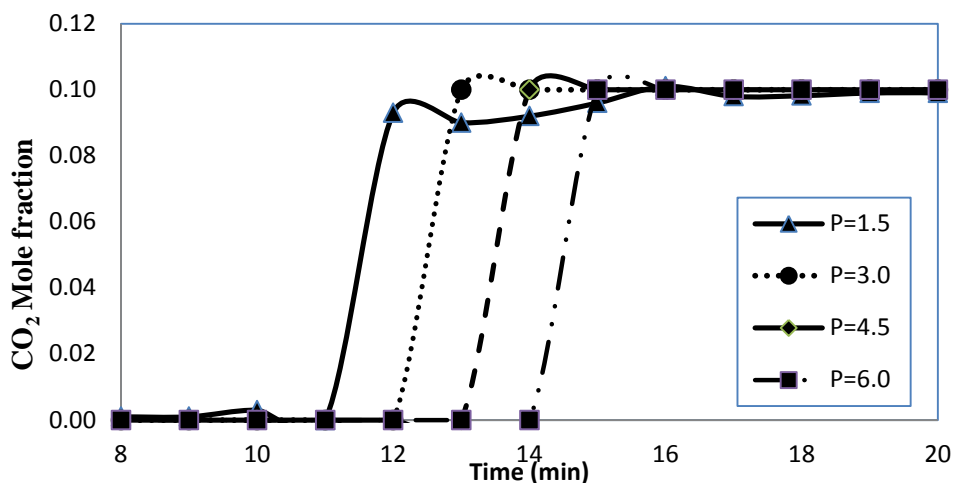


Figure 9. Comparison of adsorption at different pressures with 0.15 meters height.

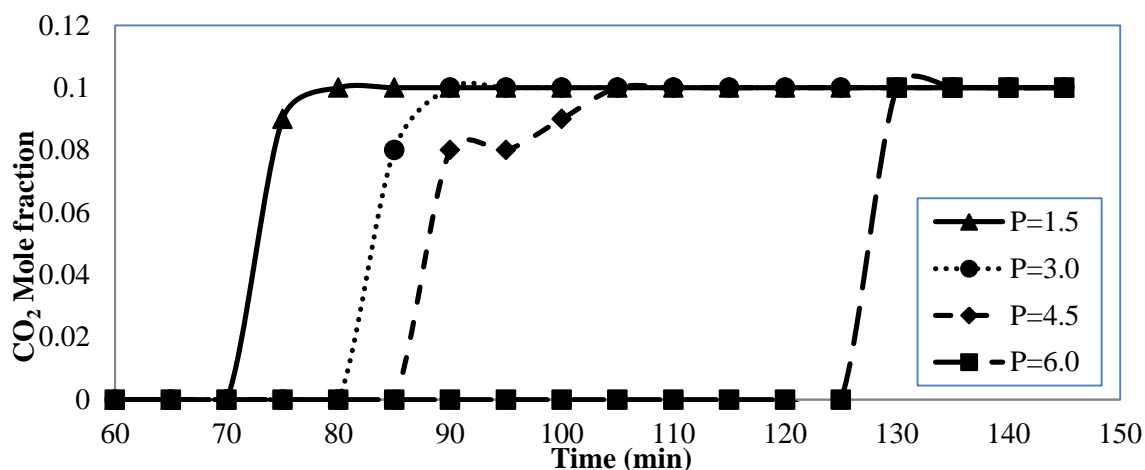


Figure 10. Comparison of adsorption at different pressures with 1 meter height.

As can be seen, as the pressure increases, the amount of carbon dioxide adsorption increases. Accordingly, the break point time increased and, at 6 bars, the break point time was the highest, indicating that adsorbent has been saturated later and that more carbon dioxide has been adsorbed. The results show that by increasing the pressure, the driving force of the adsorption process increases and overcomes the mass transfer resistance force; as a result, the adsorption capacity increases. Due to the carbon dioxide mass concentration, which is about 10 %, the adsorbent surface has reached saturation in a very short time; on the other hand, by appropriately distributing the gas mixture at

the bed inlet and preventing channelization, the whole of the solid has been saturated, causing a narrowing of the mass transfer region and increasing a sharp slope in the penetration curve. The break curves indicate that 13X adsorbent carbon dioxide adsorption capacities are not affected by other gases in the gas mixture [16]. The results of Figure 11 indicate very high adsorbent selectivity to carbon dioxide adsorption and there is little oxygen and nitrogen adsorption. The results show that the adsorbent is very selective to CO₂ than to oxygen and nitrogen gases. The molecular volume of CO₂ is larger than oxygen and nitrogen molecular volume; thus, the 13X pores can keep CO₂ molecules.

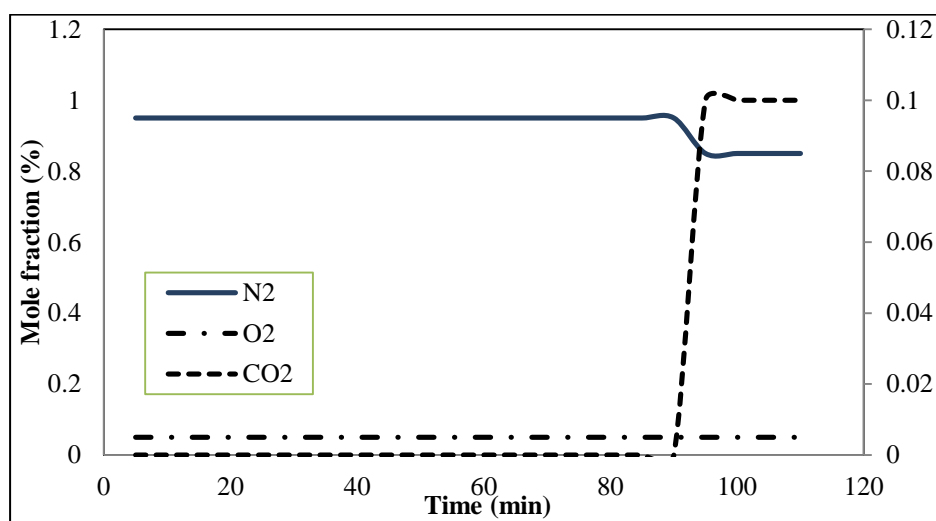


Figure 11. Carbon Dioxide/Nitrogen/Oxygen Selectivity.

5. Conclusions

In this work, adsorption of carbon dioxide was investigated experimentally in a batch reactor and a fixed bed column. The experimental results showed that the capacity of carbon dioxide adsorption by the 13X zeolite was 5.71 mg/g of adsorbent at about 8 bars. This amount of 13X zeolite adsorption capacity, at low pressures, shows a very good performance of the adsorbent in the process. The experimental result showed that the adsorption rate of carbon dioxide was increased by increasing pressure and bed height. The evaluation of adsorption isotherm data showed that CO₂ adsorption was physical and the adsorbent had high capacity. Also, the isotherm data were evaluated with different isotherm models, and the results showed that Hill model with a correlation coefficient of 0.99 is in good agreement with experimental data.

In the kinetic modeling, excellent results were obtained for the first-order models; in the case of error calculation, a slight deviation of the obtained amount of the model and the proximity of equilibrium adsorption capacity model from experimental data is visible. Therefore, it can be concluded that the process kinetics is of first order. In addition, the Veber-Morris model has the maximum deviation among the models. To continue research on 13X zeolite adsorbent, other factors that affect the adsorption capacity, such as temperature, structural impact, and changes in the type of gas, are highly recommended to be investigated.

References

- [1] Chang, F., Zhou, J., Chen, P., Chen, Y., Jia, H., Saad, S. M. I., Gao, Y., Cao, X. and Zhen, T, "Microporous and mesoporous materials for gas storage and separation: A review", *Asia-Pac. J. Chem. Eng.*, **8**, 618 (2013).
- [2] Kamiuto, K. and Ihara, E. K., "CO₂ adsorption equilibria of the honeycomb zeolite beds", *Appl. Energy*, **6**, 285 (2001).
- [3] Cavenati, S., Grande Carlos, A. and Rodrigues, A., "Adsorption equilibrium of methane, carbon dioxide and nitrogen on zeolite 13X at high pressures", *J. Chem. Eng. Data*, **49**, 1095 (2004).
- [4] Siriwardane, R. V., Shen, M. S. and Fisher, E. P., "Adsorption of CO₂ on zeolites at moderate temperatures", *Ener. Fuels*, **19** (3), 1153 (2005).
- [5] Llano-Restrepo, M., "Accurate correlation, structural interpretation and thermochemistry of equilibrium adsorption isotherms of carbon dioxide in zeolite NaX by means of the GSTA model", *Fluid Phase Equilib.*, **293**, 225 (2010).
- [6] Dantas, T. L. P., Luna, F. M. T., Silva, Jr. I. J., Torres, A. E. B. and de Azeved, D. C. S., "Modeling of the mixed-bed adsorption of CO₂ and CO₂/N₂ mixture on zeolite 13X", *Brazil J. Chem. Eng.*, **28**, 533 (2011).
- [7] Khambhaty, Y., Mody, K., Basha, S. and Jha, B., "Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*", *Chem. Eng. J.*, **145**, 489 (2009).
- [8] Dada, A. O., Olalekan, A. P., Olatunya, A. M., Dada, O., "Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ unto phosphoric acid modified rice husk", *IOSR-JAC*, **3** (1), 2278 (2012).

- [9] Seyed Hosseini, N. and Fatemi, Sh., "Experimental study and adsorption modeling of COD reduction by activated carbon for wastewater treatment of oil refinery", *Iran. J. Chem. Chem. Eng.*, **32** (3), 81 (2013).
- [10] Guixia, Z., Xilin, W., Xiaoli, T. and Xiangke, W., "Sorption of heavy metal ions from aqueous solutions", *T. O. Colloid S. J.*, **4**, 19 (2011).
- [11] Foo, K. Y. and Hameed, B. H., "Insights into the modeling of adsorption isotherm systems", *Chem. Eng. J.*, **156**, 2 (2010).
- [12] Tay, Ch., Liew, H. H., Yin, Ch. Y., Abdul-Talib, S., Surif, S., Suhaimi, A. A., Yong, S. K., "Biosorption of cadmium ions using *Pleurotus ostreatus*: Growth kinetics, isotherm study and biosorption mechanism", *Korean J. Chem. Eng.*, **28**, 825 (2011).
- [13] Modarress, H. and Allafkari, L., "Adsorption of bovine serum albumin onto hydroxylapatite: Theoretical modeling and measurements", *Iran. J. Chem. Chem. Eng.*, **29** (4), 125 (2010).
- [14] Qiu, H. L. v. L, Pan, B., Zhang, Q. -J., Zhang, W. -M. and Zhang, Q. -X., "Critical review in adsorption kinetic models", *J. Zhejiang Univ. Sci.*, **10** (5), 716 (2009).
- [15] AX carbon dioxide detector (user manual)-15 Ellerbeck Court, Stokelsey Business Park, North Yorkshire. TS9 5PT, UK, (www.analokes.net), (2015).
- [16] Yuh-Shan, H., "Review of second-order models for adsorption systems", *Journal of Hazardous Materials B136*, 681 (2006).