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Application and Comparison of MAF-66 with AC and CMS in Vacuum Swing Adsorption Process for CO₂ Capture from Flue Gas

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ABSTRACT

Vacuum swing adsorption (VSA) for CO₂ capture has been a focus of significant research efforts aimed at developing innovative CO2 adsorbent materials. In this study, three adsorbents (MAF-66, AC, and CMS) were utilized for capturing CO₂ from flue gas through the VSA process, and their performances were compared. The adsorption equilibrium and kinetics data were gathered from recent literature. A four-step VSA cycle was employed to assess the adsorbents' performance for CO₂ capture, with a molar feed composition of CO₂:N₂ at 15:85%. Simulations of two-colums VSA lab-scales with different adsorbents were conducted. The operating conditions such as total feed flowrate, feed composition, feed pressure, temperature, and vacuum pressure were kept constant, and the impact of the adsorbent mass on recovery and productivity was analyzed. The simulation results indicated that both recovery and productivity decreased with increasing adsorbent mass. Furthermore, the necessary amount of each adsorbent to achieve a purity of 99.5% was determined. The modeling outcomes suggested that the VSA process employing MAF-66, CMS, and AC adsorbents would require 1.25, 3.19, and 8.2 grams of the adsorbent, respectively, to achieve N₂ purity of 99.5%. Taking into account parameters such as recovery, productivity, and energy consumption, MAF-66 emerged as the most effective adsorbent in this study.

1. Introduction

With the growing concern of global warming, attention has shifted towards the capture of CO₂ from the flue gases emitted by power plants. These plants contribute significantly to the CO₂ emissions [1]. Vacuum swing

adsorption (VSA) is a promising method for separating CO_2 from flue gas due to its low energy consumption and low capital investment costs [2]. There are numerous potential adsorbent materials available for post-combustion CO_2 capture. Chunzhi Shen et al. [3] utilized activated carbon (AC) to separate carbon dioxide (CO_2) from flue gas in a vacuum swing adsorption (VSA) process. Carbon molecular sieve (CMS) is a commonly employed adsorbent in commercial adsorption processes [4]. Moreover, metal-organic frameworks like Mg-MOF-74 have also been employed in the VSA process to separate CO_2 from the flue gas [5]. Cho et al. [9] in 2004 used 13X zeolite adsorbent to separate a gas mixture containing 10.5% carbon dioxide. The PSA method was used and the final purity was equal to 99%, whereas the recovery of carbon dioxide was 80% and the amount of energy used for the process was 2300-2800 kj/kg CO_2. In 2012, Changzhi et al. [10] used activated carbon adsorbent and VSA process to separate a gas mixture containing 15% carbon dioxide and the rest of sulfur dioxide and nitrogen dioxide, which are flue gases from burning fossil fuels. Purity was equal to 95.3%, carbon dioxide recovery was 74.4%, productivity was equal to 0.035 kg of carbon dioxide per hour per kg of absorbent, and the amount of energy consumed was equal to 723.6 kJ/kg CO_2. In 2020, Nan et al. used laboratory-scale adsorption processes to capture CO_2 from dry flue gas to achieve carbon capture and storage (CCS) specifications (95% CO_2 purity,90% CO_2). By using 13X zeolite, various cyclic methods such as TSA, VTSA and VPSA were compared. The results showed that the CO_2 purity could reach to the the CCS specification, however these processes were different from the base of productivity and energy consumption. specificati In the VPSA process, productivity and energy consumption were determined 3.8 molCO2/kgads/h and 0.79

MJ/kgCO2, respectively. The TVSA exhibited best results in CO_2 purity and recovery with values of 97.27% and 97.66%,, respectively, while productivity was as low as 1.63 mol/kgads/h and energy consumption was as high as 3.22 MJ/kgCO2 [11]. In 2016, George et al. simulated the VSA and PSA processes for three adsorbents including activated carbon, zeolite and Mg-MOF-74. In terms of recovery and purity, zeolite was superior to the the others, but in terms of productivity, the Mg-MOF-74 adsorbent had a better performance. Both zeolite and Mg-MOF-74 had the same performance in terms of energy consumption [12].

Golmakani et al. designed the VSA unit for hydrogen purification. The purpose of this work was to carbon dioxide capture and storage (CCS). For this purpose, they used three adsorbents containing AC, zeolite 5A, and SAPO-34 and compared them with each other. According to the recovery, purity, and productivity, SAPO-34 had a better performance than zeolite 5A and AC. [14].

In this work, three different kinds of adsorbents (MAF-66, AC, CMS) would be investigated. These adsorbents are used to capture CO_2 by VSA process from the flue gas and their performances would be compared with each other, to find out the best adsorbent from the base of the lowest energy consumption. The required equilibrium and kinetic data are derived from the previous experimental studies, for MAF-66 [6], AC [7], and CMS [8].

The Aspen Adsorption™ software is employed to simulate the VSA process and breakthrough curves. The accuracy of the breakthrough model would be validated using the experimental data. The study of the amount of adsorbents' mass, as an economic factor, is studied in this work to reach to the purified flue gas with 99.5% N_2 .done

2. VSA process description

The feed of the unit is flue gas, which has a significant amount of carbon dioxide. The purpose of this unit is to separate CO_2 from flue gas and obtain high-purity nitrogen products. The numerical simulations of the VSA unit with two columns and 4 steps were carried out. As shown in Fig.1 each cycle contains 4 steps which are explained as follows:

Step (1): adsorption: the feed with specific operating conditions (1 bar,308K) entered to bed, and CO_2 molecules adsorbed in the solid phase. Then the puer nitrogen exited from the top of the bed. In this step, some of the produced product is separated from the product stream for use in the purge step. Step (2): vacuum: before appearing CO_2 molecules in the product, the feed was stopped and the pressure of the column was reduced to 0.1 bar by using the vacuum pump located under the bed. Step (3): Purge: to remove CO_2 from the

solid phase, a fraction of pure nitrogen product was introduced as the purge gas from top of the bed. This step was applied at relative vacuum pressure of 0.1 bar. Step (4): pressurization: the bed pressure was increased by opening the feed valve until the bed pressure was reached to the adsorption step. The flue gas feed flow rate was 10Nml/min with a composition of 85% N_2 and 15% CO_2. According to the timetable as shown in Fig.1, two beds are managed to work in parallel so that when the first bed is in the adsorption mode, the second one isis ing adjusted to be at the regeneration mode, with a fraction of the N_2 production product from the other bedof . Some operational conditions, such as the composition of feed, feed flowrate, purge-to-feed ratio, column temperature, the pressure of the adsorption stage and vacuum stage, and the time of the adsorption stage were considered fixed.
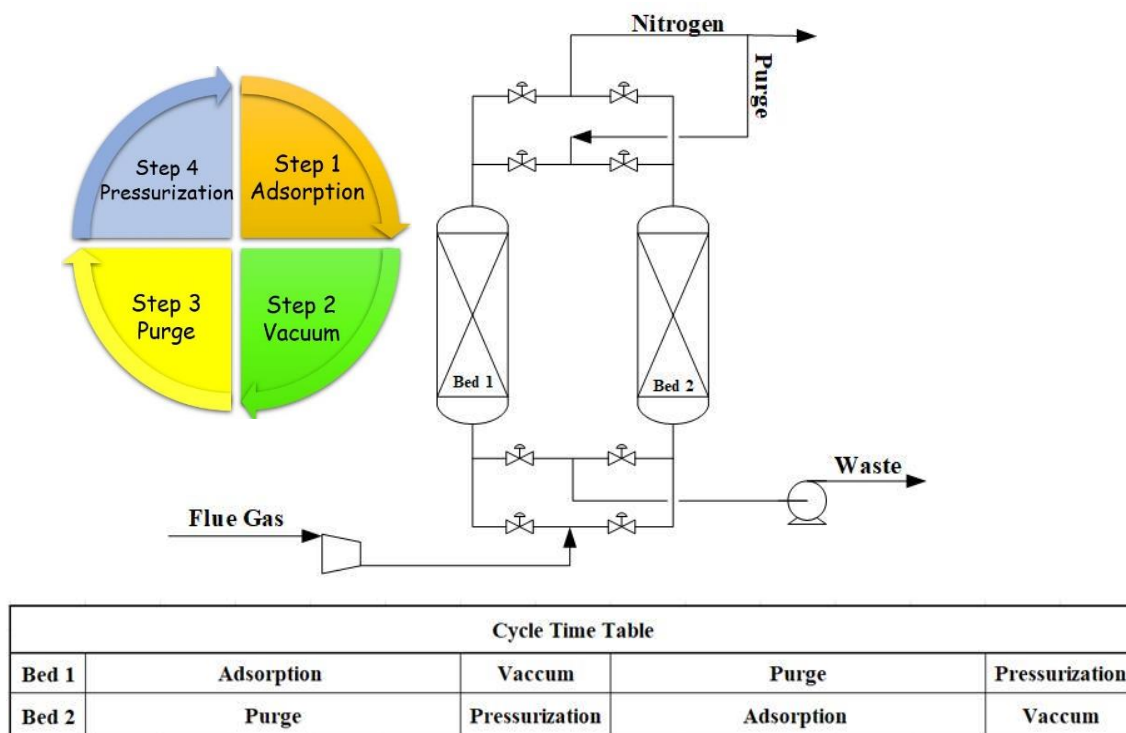

Cycle Time Table				
Bed 1	Adsorption	Vaccum	Purge	Pressurization
Bed 2	Purge	Pressurization	Adsorption	Vaccum

Figure 1. The schematic diagram time table of oVSA unit, withOperating steps of two-column four-step VSA process (adsorption, vacuum, purge, Pressurization)

3. Materials and methods

3.1. Materials

The performance of the VSA process depends on the characteristics and properties of the adsorbent used. These properties can be obtained from static and dynamic adsorption experiments. Through static experiments, it is possible to calculate the adsorption capacity at different pressures. Mass and heat transfer rates between solid and gas phases are obtained through breakthrough experiments. In this work, MAF-66 is proposed as the best adsorbent for separating carbon dioxide from flue gas by the VSA process. In the following, static and dynamic properties of MAF-66 are presented. Finally, the performance of two other common adsorbents AC and CMS was investigated in the VSA process to compare with MAF-66. The specifications and data related to AC were extracted from Shen [7] and CMS from Cavenati [8].

3.2. Experiments

Adsorbent MAF-66 was synthesized by sol-gel method and it was characterized by BET analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM) and fourier transform infrared spectroscopy (FTIR) was done based on our previous work [6]. Table 1 shows the specifications and features of the adsorbents.

Table 1. Specifications of adsorbents.

adsorbents	MAF-66	AC	CMS
Density (kg/m^3)	400	984	1059
Particle porosity (ε_p)	0.21	0.506	0.46
Bed porosity (ε)	0.42	0.32	0.33
Bulk solid density (kg/m^3)	232	669.12	709.53
Particle diameter (mm)	1	2	0.9

3.2.1. Measurment of the isotherms

The equilibrium absorption experimental data has been obtained from previous studies. The equilibrium isotherms were measured by a volumetric method at various temperatures. Fig.2 shows the general setup for equilibrium adsorption, which consists of an adsorption column and a reference tank column. Both columns are surrounded by a thermal jacket to keep the temperature constant during the experiment. The circulator is used to maintain the temperature of the columns. The pressure transducer is used to measure the internal pressure of the setup at the beginning and end of the experiment. The loading column is utilized as a reference point to measure the volume of connections and adsorption column, which is done using helium gas (an inert gas).

3.2.2. Dynamic measurements

The general schematic design used for dynamic adsorption is shown in Fig.3 The feed enters the bed with a certain composition, temperature, and pressure. The input flow to the bed is regulated by the mass flow controller. The output flow is entered into the Gas Chromatograph (GC) to display the composition of the output flow. Operating conditions (temperature, pressure, flow rate, and feed percentage composition) and bed characteristics are explained below in the graphs related to breakthrough curves.
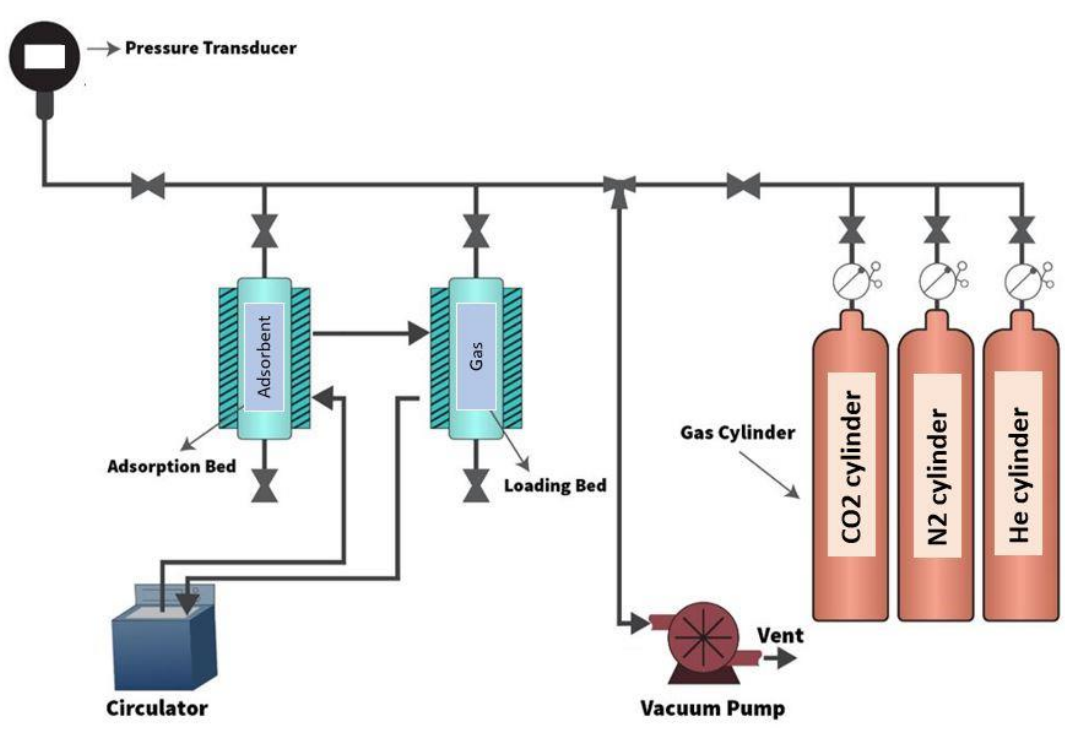
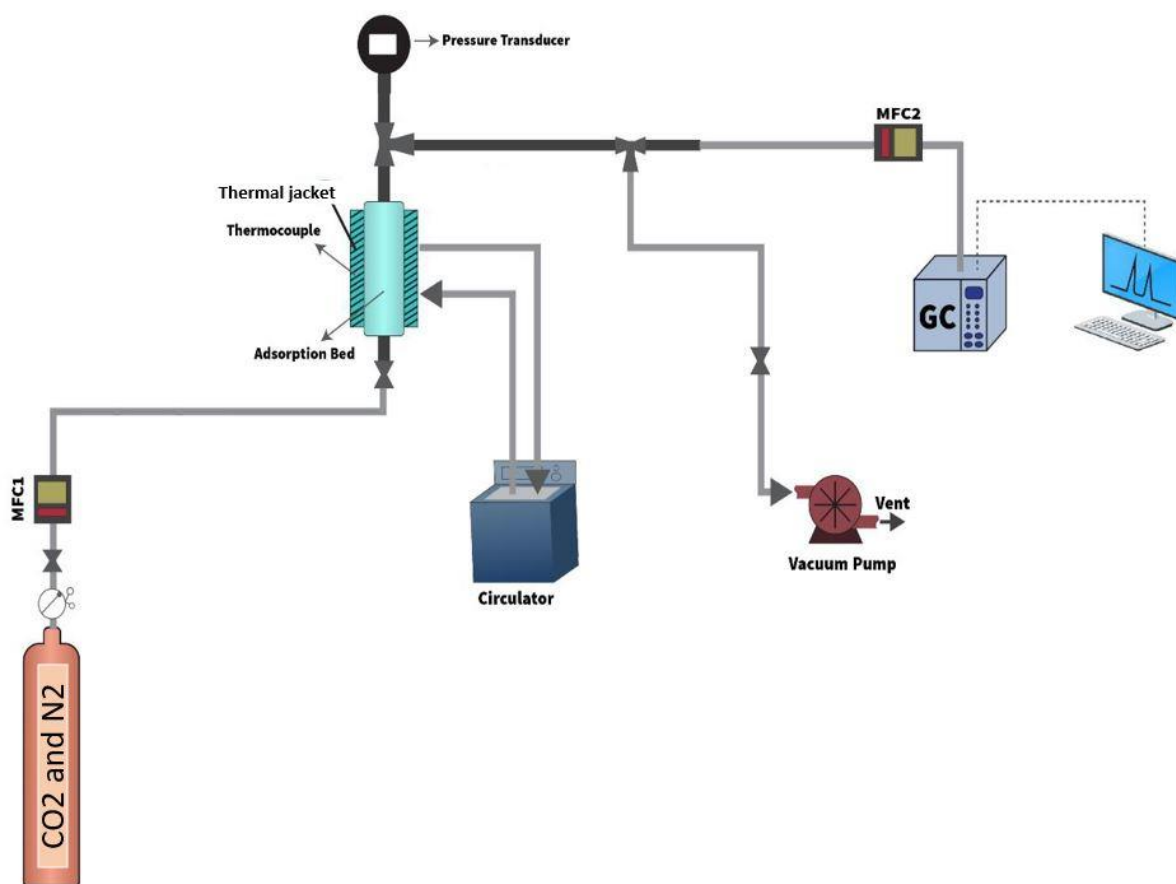**Figure 2.** Experimental setup for equilibrium adsorption.

Figure 3. Experimental setup for dynamic adsorption.

3.3. Mathematical model

Cyclic process simulation was performed based on the dynamic mathematical model of adsorption for a bed of adsorbents. A comprehensive mathematical model was used for the energy and momentum balance of the solid and gas phases. The model assumptions used are explained below:

1-The adsorbents used are assumed to be sphere particles whose characteristics, size, and bed porosity are constant and uniform.

2-The bed works in non-isothermal and adiabatic conditions.

3-The mass and energy balance in the bed is considered as a plug-flow model, and the axial dispersion along the bed is neglected.

4-The amount of drop in pressure of the bed is calculated from the Ergun equation. According to this equation, the amount of pressure at any point of the bed can be calculated.

5-The equilibrium adsorption capacity for adsorbents is obtained by Langmuir (for AC and MAF-66) and Langmuire-Freundlich (for CMS) isotherm equations.

6-The mass balance inside the particles is supposed lump kinetic model with the LDF (linear driving force) equation for the solid phase.

7-Due to the low pressure of flue gas and low operating pressure in the VSA process, the ideal state equation is considered to estimate fluid properties including density, concentration, etc.

8-Vant's Hoff equation is used to calculate the heat of adsorption for each of the adsorbents.

In cyclic processes, in initial cycles, the results obtained from each cycle are different from the next cycle because the process has not yet reached a stable condition. After the initial cycles, the obtained results, including the concentration and temperature profiles, reach the steady state, and the cyclic steady state is achieved. In this situation, the output results including recovery, purity, and productivity can be calculated and analyzed. The output product of this process is pure nitrogen, which is exited from the top of the bed during the adsorption step. The purpose of this research is to investigate the effect of increasing the mass of the adsorbent (by increasing the height of the bed) on the parameters of recovery, purity, and productivity. The calculation formula is shown below. In the second step, the purpose of the research is to compare the mentioned adsorbents (by calculation of the required mass of adsorbent) to reach a nitrogen concentration of 99.5% in the product.

According to equation (1), nitrogen purity is equal to the outlet molar flow of nitrogen to the outlet total molar flow from top of the bed, which includes the total moles of nitrogen and carbon dioxide.

$$Purity = \frac{\int_0^{t_{Ads}} u\, C_{N2}|_{Product}\, dt}{\int_0^{t_{Ads}} u\, C_{N2}|_{Product}\, dt + \int_0^{t_{Ads}} u\, C_{CO2}|_{Product}\, dt} \qquad (1)$$

Nitrogen recovery is defined as equation (2), according to which the recovery is equal to the molar flow of nitrogen of the product divided to the total input N_2 molar flow rates to the process.

$$Recovery = \frac{\int_0^{t_{Ads}} u\, C_{N2}|_{Product}\, dt}{\int_0^{t_{Ads}} u\, C_{N2}|_{Feed}\, dt + \int_0^{t_{Pres}} u\, C_{N2}|_{Feed}\, dt} \qquad (2)$$

Productivity of nitrogen is calculated according to equation (3). Productivity is qual to the molar flow of the nitrogen product on the base of unit time and unit adsorbent mass.

$$Productivity = \frac{\int_0^{t_{Ads}} u\, C_{N2}|_{Product}\, dt}{t_{cycle} W_{Adsorbent}} \qquad (3)$$

In the VSA process, to regenerate the bed and clean the adsorbent from carbon dioxide molecules, it is necessary to use a vacuum pump to bring the pressure below atmospheric pressure. The amount of electrical energy consumed in the vacuum pump is calculated using equation 4.

$$Energy - Consumption = \frac{\gamma}{\gamma-1} R_g T_{Feed} [(\frac{P_{high}}{P_{low}})^{\frac{\gamma}{\gamma-1}} - 1] \frac{B}{1000\eta} \qquad (4)$$

$\gamma = C_p/C_v$, Its value is equal to 1.5 for ideal gas. R_g: universal gas constant. P_{high} is the purge stream pressure (1 bar), P_{low} is the vacuum pressure (0.1 bar), B is the molar flowrate from the vacuum pump and η is the efficiency of the pump that supposed equal 0.8 in this work.

4. Results and discussion
4.1. Adsorption Isotherms
Many different theories have been stated about the phenomenon of surface adsorption, one of the most important theories is related to Langmuir, which states that the forces created by surface adsorption are very similar to the nature of the forces created by molecular bonding (van der waals forces). Langmuir adsorption theory considers the assumption of monolayer adsorption on a homogeneous surface with identical sites' enrgy. It has been obtained regardless of the mutual effects of the

adsorbed molecules. In this work, this model was employed to predict the equilibrium CO_2 adsorption capacity on the surface of MAF-66 and AC. According to this model, the loading amount is calculated according the equation (5), for the mixture adsorption, as the Extended Langmuir Eq., where K_i indicates the equilibrium parameter and q_{mi} indicates the maximum amount of the adsorption for component i.

$$Q_i^* = \frac{q_{mi} K_i P_i}{1 + \sum_{i=1}^{n} K_i P_i} \ , \ K_i = K_{0,i} \exp(\frac{k_{1,i}}{T}) \qquad (5)$$

The temperature dependence of the Extended Langmuir Equation can be shown as equation 6 :

$$Q_i^* = \frac{q_m K_{0,i} P_i \exp(\frac{K_{1,i}}{T})}{1 + \sum_{i=1}^{n} K_{0,i} P_i \exp(\frac{K_{1,i}}{T})} = \frac{A_{1,i} P_i \exp(\frac{A_{2,i}}{T})}{1 + \sum_{i=1}^{n} P_i A_{3,i} \exp(\frac{A_{4,i}}{T})} = \frac{\alpha_i P_i}{1 + \sum_{i=1}^{n} \beta_i P_i} \qquad (6)$$

According to equation 6, the temperature dependence of the parameters are shown by the Arrhenius relation: a $\alpha_i = A_{1,i} \exp(\frac{A_{2,i}}{T})$ and $\beta_i = A_{3,i} \exp(\frac{A_{4,i}}{T})$. The obtained parameters are presented in table2.

Table2. Langmuire isotherm parameter for CO_2 and N_2 on AC and MAF-66

Description		$-\Delta H_{ads}$ (kJ.mol^{-1})	$\alpha_i = A_{1,i} \exp(A_{2,i}/T)$		$\beta_i = A_{3,i} \exp(A_{4,i}/T)$	
			A_1 (kmol.kg^{-1}.bar^{-1})	A_2 (K)	A_3 (bar^{-1})	A_4 (K)
AC	CO_2	23.4	2.29E-06	2185	0.20817	316.13
	N_2	18.15	5.58E-07	1941.64	0.08873	310.49
MAF-66	CO_2	26	2.98E-08	3760.3	0.003	1632.4
	N_2	18	3.72E-06	1356.4	0.02267	418.22

According the tunned parameters, the model has been compared with experimental values in figs.4 and 5. They reveal that the CO_2 has a higher tendency to be captured in both MAF-66 and AC adsorbents than nitrogen. Also, the selectivity of CO_2 to N_2 in the MAF-66 is higher than AC.
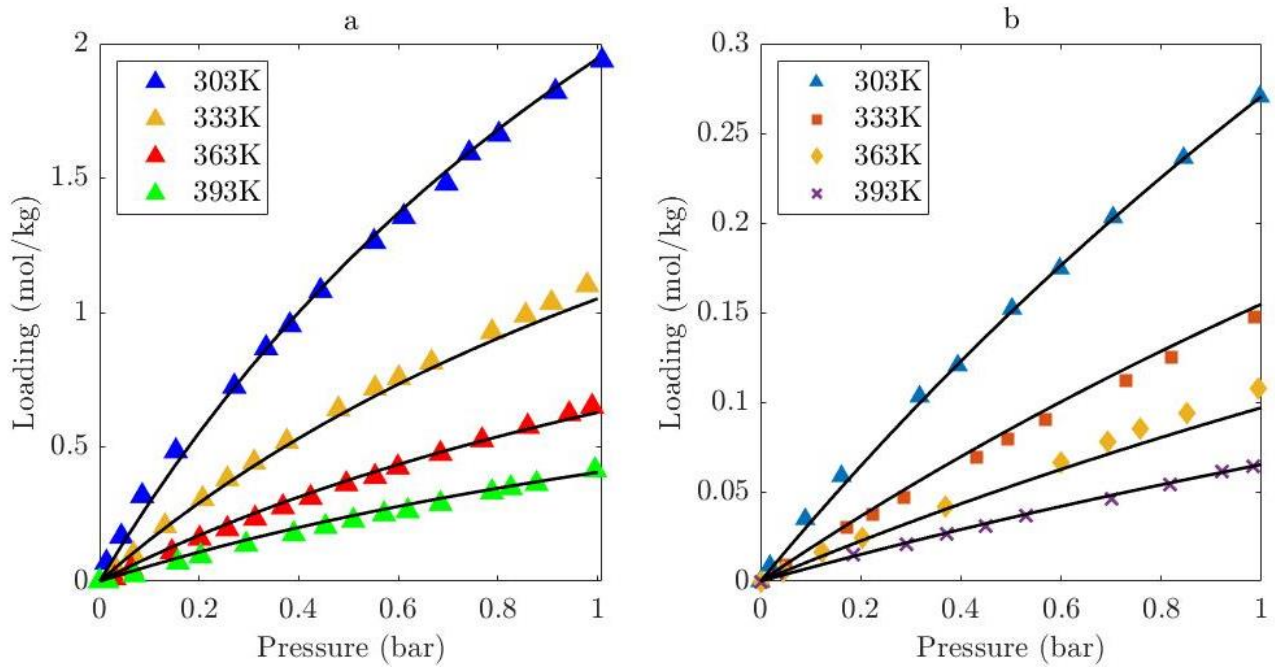

Figure 4. Langmuire model (solid lines) and experimental data (points) at 303K, 333K, 363K and 393K for AC on (a) CO_2 and (b) N_2
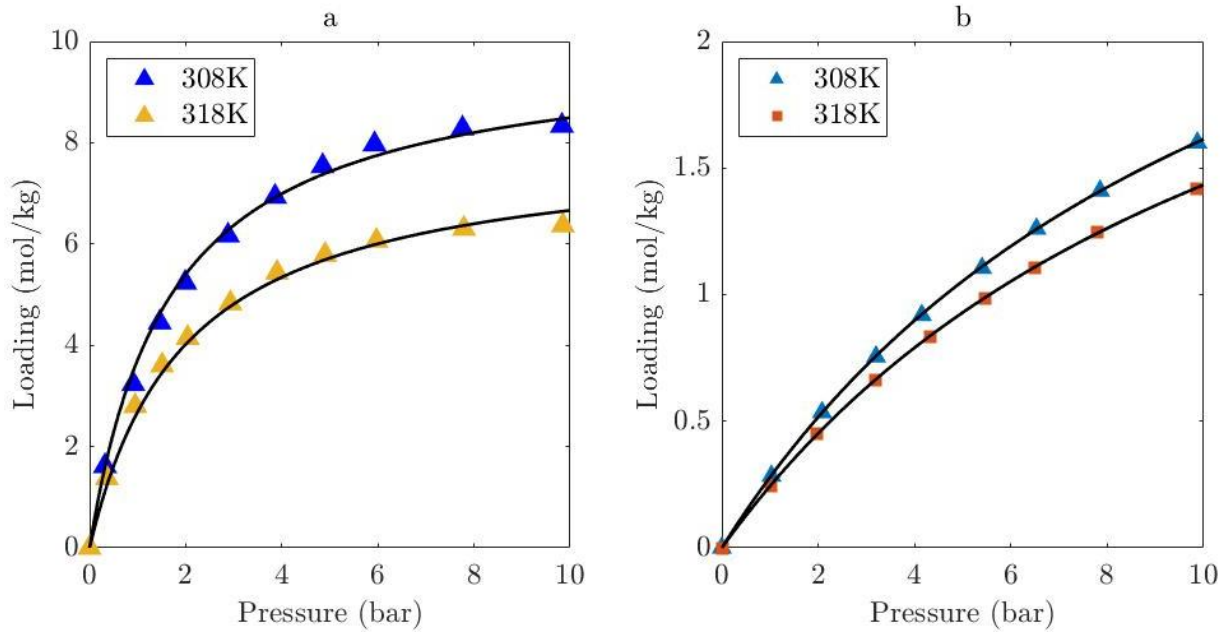
Figure 5. Langmuire madel (solid lines) and experimental data (points) at 308K and 318K for MAF-66 on (a) CO_2 and (b) N_2

In our study, the isotherms of CMS adsorbent followed the Langmuir-Freundlich model (LFM). This model, a combination of the Langmuir and Freundlich models, was presented by Yoon and Tornock [13] and is represented by equation 7.

$$Q_i^* = \frac{q_m K P_i^{(\frac{1}{n})}}{1 + K P_i^{(\frac{1}{n})}} \ , \ K_i = K_{0,i} \exp(\frac{k_{1,i}}{T}) \tag{7}$$

Therefore for the CO_2-N_2 mixture study, the extended Langmuir-freundlich Eq. is applied for the isotherms of the components as equation 8:

$$Q_i^* = \frac{q_m K_{0,i} p_i^{\frac{1}{n}} \exp(\frac{K_{1,i}}{T})}{1 + \sum_{i=1}^{n} K_{0,i} P_i^{\frac{1}{n}} \exp(\frac{K_{1,i}}{T})} = \frac{A_{1,i} A_{2,i} P_i^{A_{3,i}} \exp(\frac{A_{4,i}}{T})}{1 + \sum_{i=1}^{n} A_{5,i} P_i^{A_{3,i}} \exp(\frac{A_{6,i}}{T})} = \frac{\alpha_i P_i^{\beta_i}}{1 + \sum_{i=1}^{n} \gamma_i P_i^{\beta_i}} \tag{8}$$

According to equation 8, α_i and β_i are a function of temperature.

$$\alpha_i = A_{1,i} A_{2,i} \exp(\frac{A_{4,i}}{T}) \ , \ \gamma_i = A_{5,i} \exp(\frac{A_{6,i}}{T}) \text{ and}$$

$$\beta_i = A_{3,i}.$$

These parameters are presented in table3.

Table3. Langmuire-freunlich isotherm parameter for CO_2 and N_2 on CMS

Description		ΔH_{ads} (kJ.mol^{-1})	$\alpha_{i=}A_{1,i} A_{2,i} \exp (A_{4,i}/T)$				$\gamma_i = A_{5,i} \exp (A_{4,i}/T)$	
			A_1 (kmol.kg^{-1})	A_2 (bar^{-1})	A_3 (-)	A_4 (K)	A_5 (bar^{-1})	A_6 (K)
CMS	CO_2	-33.44	0.000116	0.00177	0.827	3040	2.38E-04	2670
	N_2	-16.62	2.29E-06	0.886	0.804	1580	0.00109	1450

According to the LF model, the model has been compared with the experimental value in Fig 6. The selectivity of CO_2 over N_2 is related to the ratio of adsorption capacities in each adsorbent. AccordingA to the isotherms shown in Figs. 5,6,7, the selectivity of CO_2 over N_2 for MAF-66 is higher than other adsorbents, and we expect that that MAF-66 would had greater performance in VSA processes for the separation of CO_2 from flue gas due to higher selectivity at the low pressure.
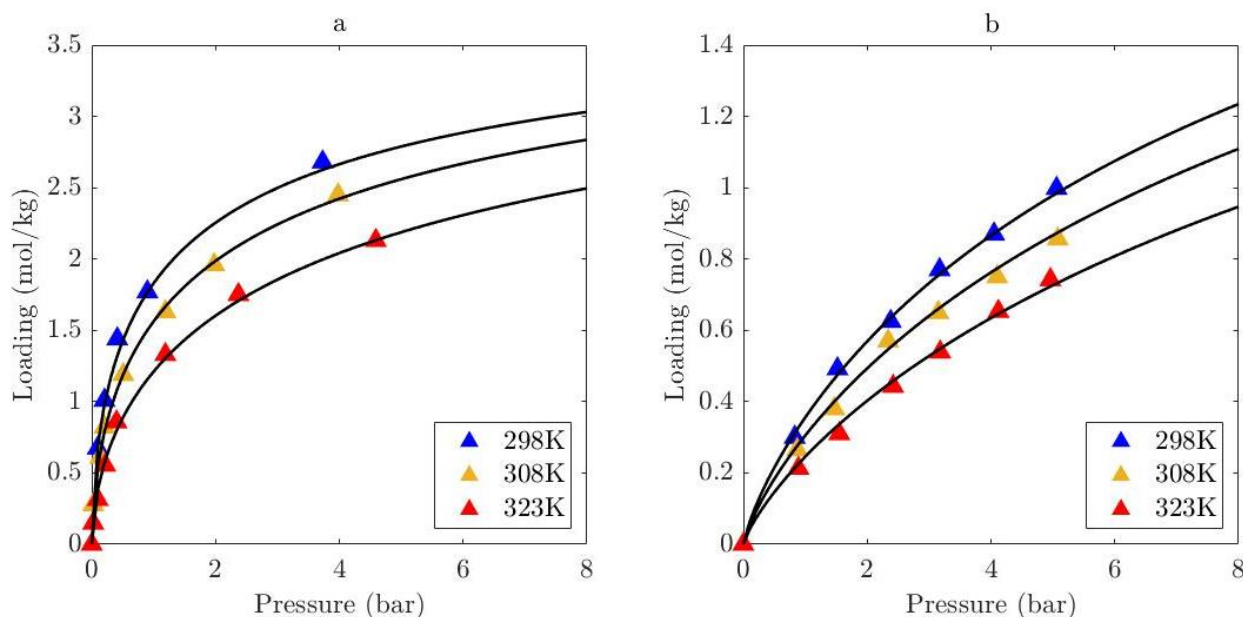

Figure 6. Langmuire-freundlich model (solid lines) and experimental data (points) at 298K, 308K and 323K for CMS on (a) CO_2 and (b) N_2

4.2. Dynamic adsorption
The breakthrough curves of gas mixtures containing CO_2 and N_2 were obtained from dynamic adsorption and detecting the outlet gas by gas chromatograph. The results are shown in Figs.7,8,9, respectively. The condition of each test such as dimensions of the bed, feed specifications, operating pressure, and temperature are explained in Table 6. The breakthrough curves were modeled and simulated by Aspen Adsorption software and the results were compared with the experiments. According to the breakthrough model, the mass transfer coefficients (MTC) of CO_2 and N_2 (between the gas and solid phase) were tunned to fit to

the experiments. The estimated MTCs are
presented in Table 4.

Table 4. Estimated MTCs of CO_2 and N_2 of to the three adsorbents.

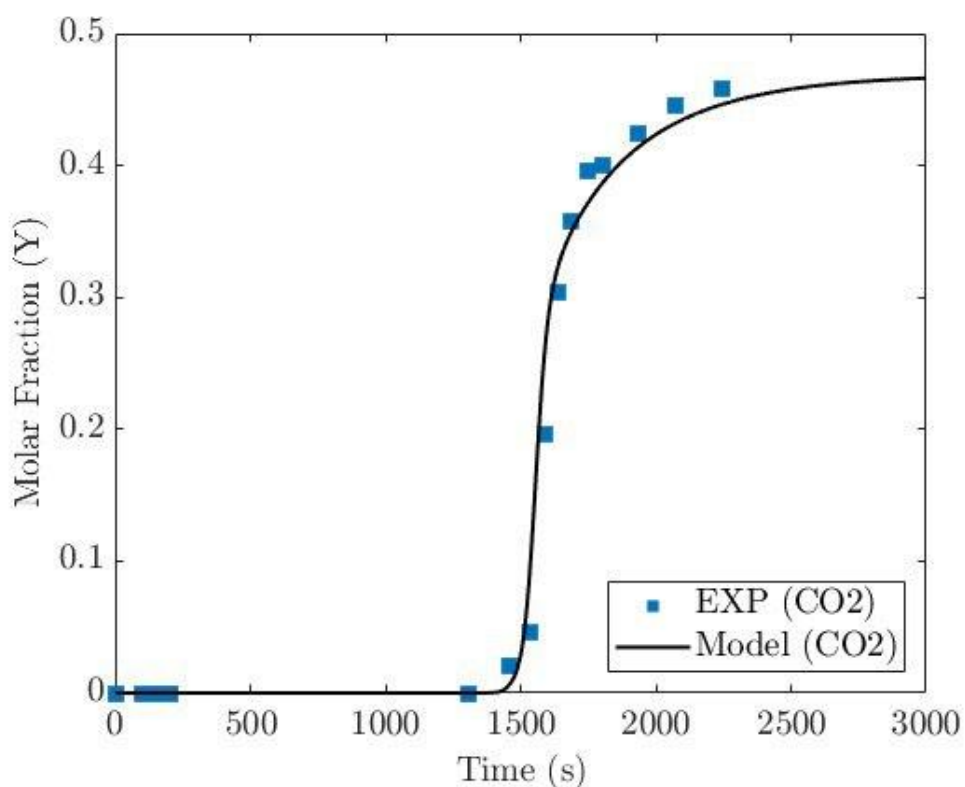| Description		K_{LDF} (s^{-1})
AC	CO_2	0.01058
	N_2	0.05
CMS	CO_2	0.0145
	N_2	0.00688
MAF-66	CO_2	0.085
	N_2	0.00075

Figure 7. Validation of breakthrough curve of CO_2 and on CMS with experimental data (feed gas mixture with CO_2 CO_2/ N_2 at 45:55% by volume, total gas flow rate of 1.5 SLPM at 303 K, height of CMS layer of 83 cm and column radius of 1.05cm)
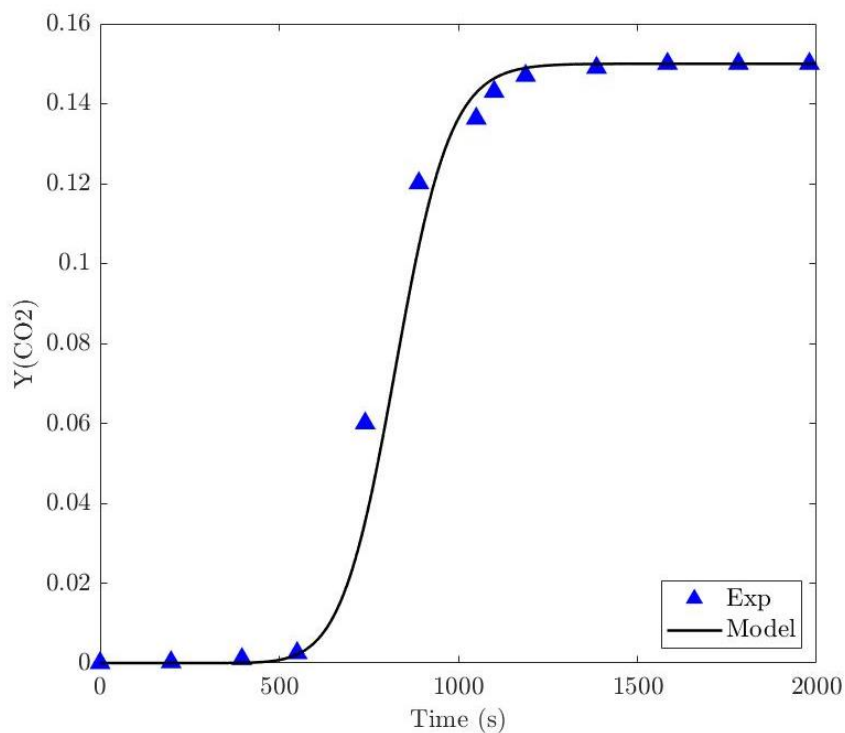
Figure 8. Validation of breakthrough curve of CO_2 on MAF-66 with experimental data (feed gas mixture with CO_2/ N_2 at 15:85% by volume, total gas flow rate of 10 Ncm^3/min at 308 K, height of MAF-66 layer of 5.6 cm and column radius of 0.725 cm)
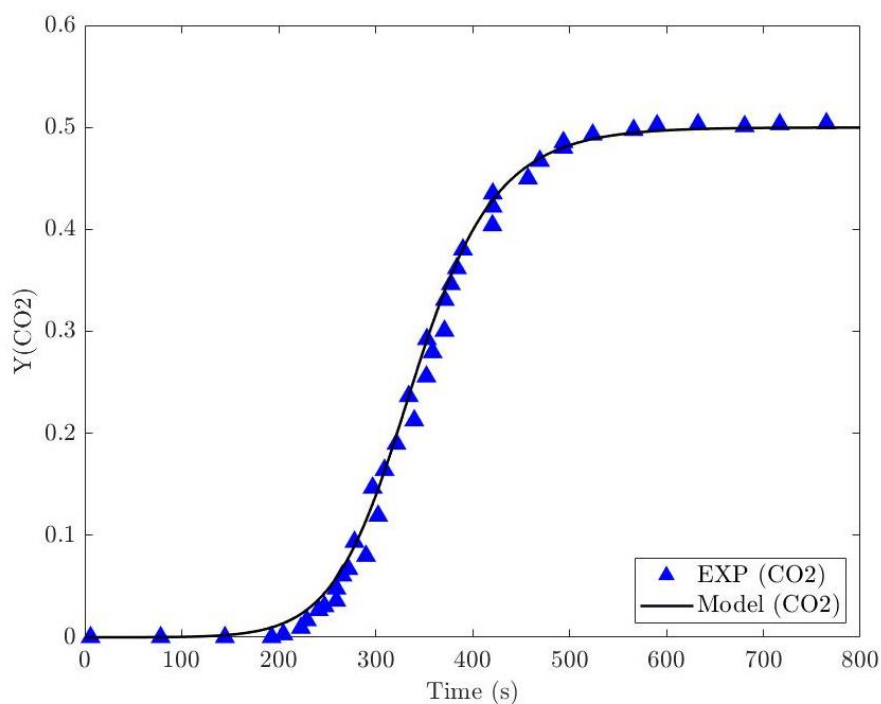

Figure 9. Validation of breakthrough curves of CO_2 and on AC with experimental data (feed gas mixture with CO_2/ N_2 at 50:50% by volume, total gas flow rate of 30 Ncm^3/min at 363 K, height of AC layer of 16.5 cm and column radius of 0.415 cm)

It is obvious that there is less difference between the experimental data and with model, so we can use the tuned MTCs in VSA simulation with a high confidence level.

4.3. Effect of adsorbent's mass on recovery and productivity

The amount of adsorbent used in the adsorption process can be one of the essential factors in discussing the economic efficiency of the process. Because if the adsorbent used in the process does not work properly, we have to prepare a larger amount of adsorbent to achieve the desired product purity. This can have a negative impact on the economic feasibility of the process from two points of view: First, a larger amount of adsorbent must be synthesized, which requires a lot of money and the costs of raw materials for the process multiply. Secondly, to put a larger amount of adsorbent in the process, the dimensions of the equipment should also be increased. For example, the dimensions of the bed should be bigger. This means that we need a more

powerful vacuum pump to vacuum a larger bed in a given amount of time.

So, the adsorbent is better from the economic point of view for the process of separating carbon dioxide from the flue gas, which will lead us to the desired product with the lowest amount of adsorbent in constant operating conditions.

That's why in this work, the effect of increasing the adsorbent mass on the important parameters of the VSA process (recovery, purity, energy consumption, and productivity) has been investigated. Fig. 10 shows the effect of increasing the adsorbent mass on the mentioned parameters. To change the adsorbent mass, we used the bed height parameter to avoid changes in modeling assumptions. Because changes in the diameter of the bed cause changes in the superficial velocity along the bed, and in this case, the assumptions used in the mass and energy balance must be changed. The specifications of process used in this part are presented in table 5.
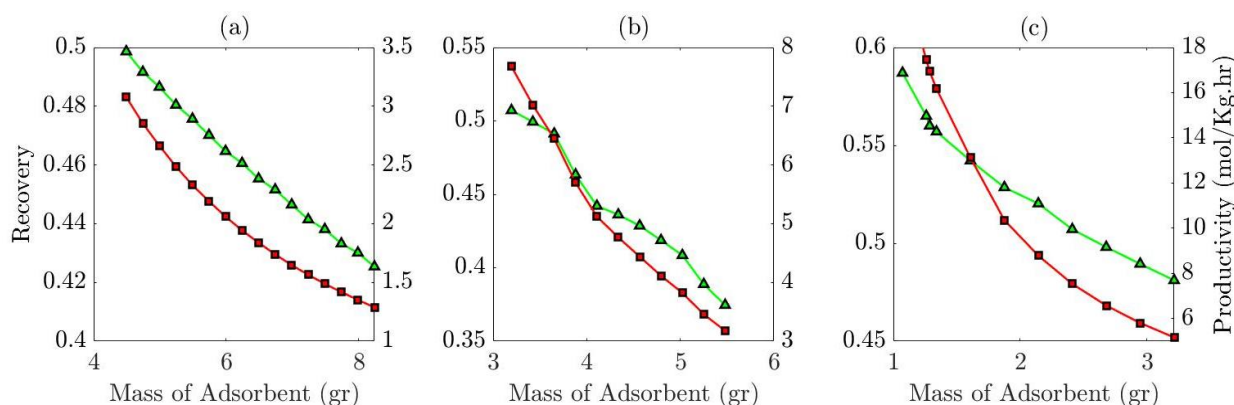

Figure 10. The effect of increasing adsorbent mass on recovery and productivity on (a) AC, (b) CMS and (c) MAF-66

According to Fig.10, the amount of recovery and productivity decreases with the increase of absorbent mass. As mentioned, to change the amount of absorbent inside the bed, the height of the bed has been changed. Increasing the

volume of the bed causes more moles of nitrogen to enter the bed during the pressurization stage to reach the desired pressure. According to equation 2, the amount of recovery will decrease with the increase of

the nitrogen moles entering the bed in the pressurization stage.

Because the feed flow is used for pressurization in this process, considering the constant flow for the feed, we must increase the time of the pressurization stage to reach from the vacuum pressure to the adsorption pressure. Because the mass of the adsorbent increases and the time of each cycle becomes

longer, then according to equation 3, the productivity will also decrease. As shown in Fig.10, the recovery value and productivity for MAF-66 at low masses have been investigated. According to Fig.11, this adsorbent can reach a purity of over 99% by consuming less amount of adsorbent and there is no need to check it at high masses of the adsorbent.
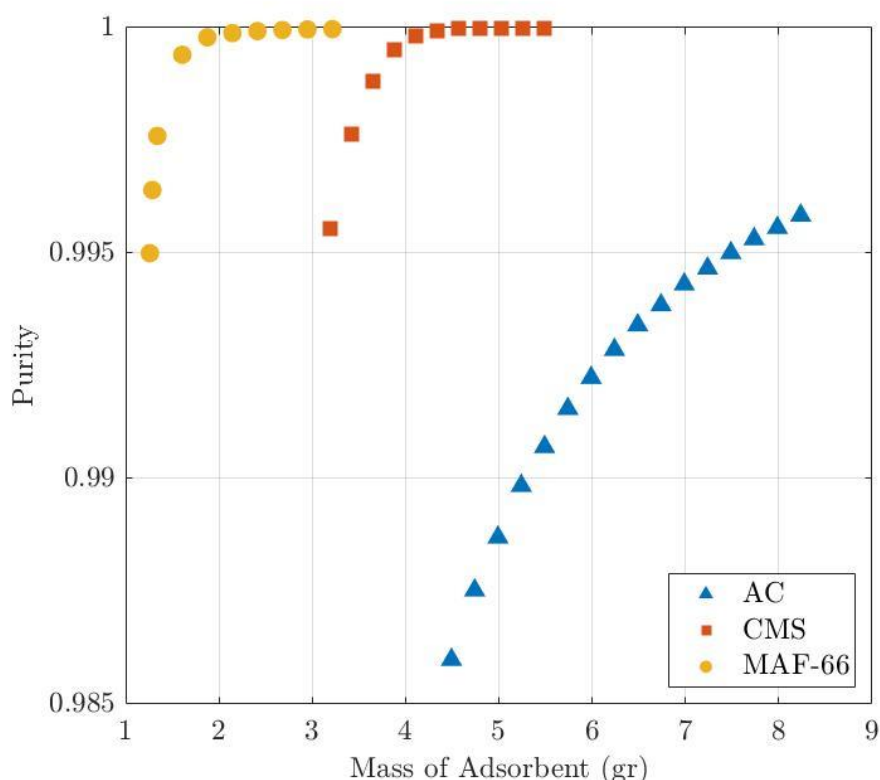

Figure 11. The effect of increasing mass of adsorbent in purity.

Table 5. Specifications of the process used to investigate the effect of increasing adsorbent mass

feed temperature (K)	308
feed pressure (Bar)	1
feed flowrate (ml/min)	10
bed diameter (cm)	1.45
P/F ratio (-)	0.25
vacuum pressure (Bar)	0.1
height of bed	variable

In the following, to better compare the performance of each adsorbent in VSA process of separating CO_2 from flue gas mixture, the required mass of each adsorbent was calculated. For this purpose, three identical VSA processes were considered, in each of which AC, MAF-66, and CMS were placed inside the bed. In these three cases, all operating conditions such as feed flow rate, temperature, pressure and bed diameter were considered constant. The operational conditions of the process are shown in Table 6.

for each of the cases, the required amount of absorbent (by changing the height of the bed) was calculated to reach the constant purity of the product (which is considered equal to 99.5% in this work). Also, in addition to the mass of the adsorbent, the amount of energy consumed, the recovery and the purity of the output product were calculated in a steady state cycle.

Table 6. Specifications of process used in constant product purity state

feed temperature (K)	308
feed pressure (Bar)	1
feed flowrate (ml/min)	10
bed diameter (cm)	1.45
P/F ratio (-)	0.25
vacuum pressure (Bar)	0.1
product purity (%)	99.5
height of bed	variable

According to Fig.12, only 1.25 grams of MAF-66 is needed to reach 99.5 percent purity of the product under the mentioned conditions. For AC and CMS, respectively, 3.19 and 8.2 grams of adsorbent should be consumed in the VSA process to reach 99.5% product purity.

The recovery value for MAF-66 is also higher than AC and CMS. Because in the same operating conditions, the adsorption capacity of MAF-66 is high as well as its selectivity. It means the proportions of carbon dioxide molecules to nitrogen inside the adsorbent is high, so when the adsorbent is regenerated in the vacuum step, fewer nitrogen molecules come out from the bottom of the bed, so according to equation 2, the recovery value of the MAF-66 increases.

Adjusting the mass of adsorbents to determine the required amount for achieving a specific product purity has involved varying the bed height. The calculated masses for AC and CMS were found to be higher than that of MAF-66, indicating that the bed height needed for AC and CMS adsorbents is greater compared to MAF-66. An increase in bed height results in a larger bed volume, necessitating the vacuum pump in the vacuum stage to extract more flow from the bed to achieve a pressure of 0.1 bar. So, according to equation 4, with the increase of the input flow rate from the vacuum pump, the amount of energy consumed will also increase.
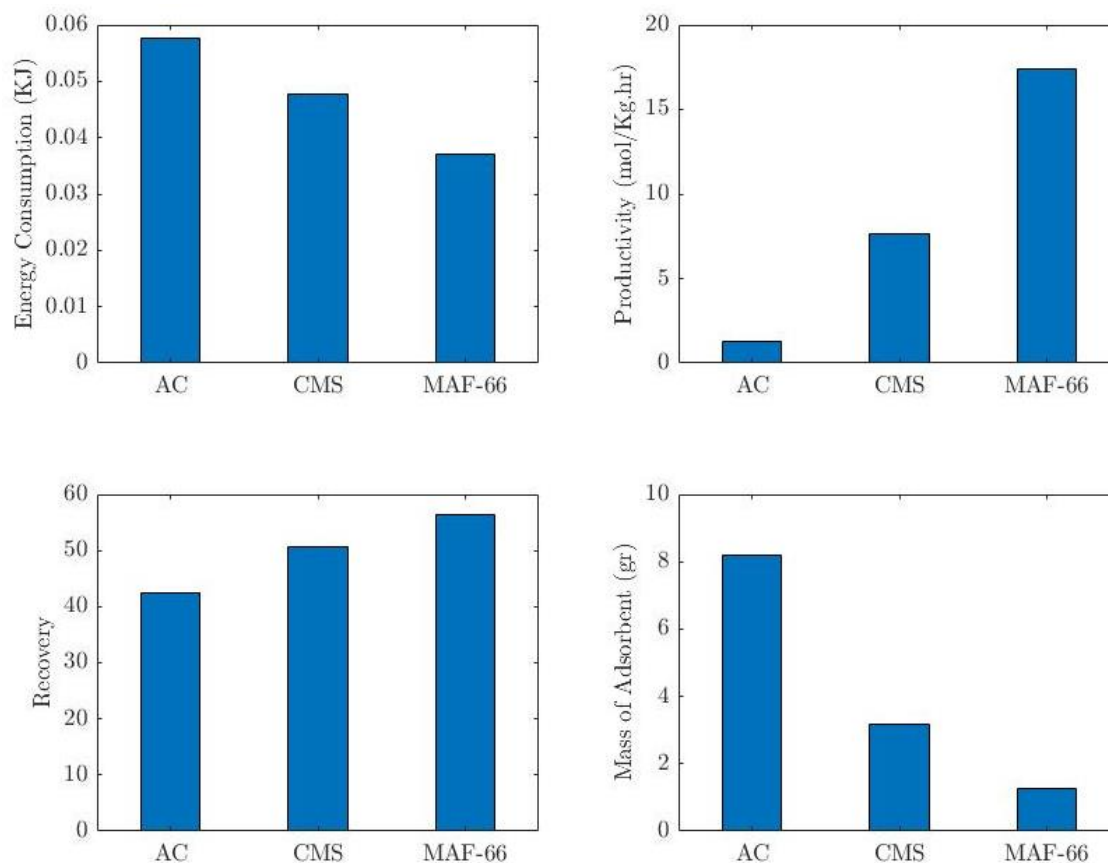
Figure 12. Comparison of recovery, productivity, energy consumption and mass of adsorbent for MAF-66, AC and CMS at fix output stream percentage (99.5% N_2)

5. Conclusions

The exhaust gas emitted from refinery plant chimneys typically contains high concentrations of carbon dioxide, necessitating the separation of CO_2 from the flue gas to meet environmental standards. To achieve this, a cyclic adsorption process utilizing three different adsorbents was proposed for comparative investigation. It was determined that, under the specified conditions, a VSA unit equipped with 1.25 grams of MAF-66 could elevate the nitrogen purity to above 99.5%.

Comparative analysis with the other adsorbents, AC and CMS, indicated that MAF-66 outperformed as the most effective adsorbent for the efficient separation of CO_2 from flue gases. The superior CO_2/N_2 selectivity of MAF-66 over the other adsorbents was identified as the primary factor facilitating the separation of carbon dioxide and the enrichment of nitrogen.

In assessing the feasibility of the VSA process, energy consumption, recovery, and productivity are crucial parameters. The calculated values for these metrics when utilizing MAF-66 to achieve a purity of 99.5% signify that this adsorbent stands out as the good choice for the VSA process.

A notable challenge not addressed in this study is the application of MAF-66 in long adsorption-desorption cycles. Furthermore, the stability of MAF-66 in the presence of water vapor should be considered, as the flue gas mixture may contain significant amounts of water vapor that could potentially diminish the CO_2 adsorption efficiency. These factors warrant further investigation to ensure the

effectiveness and reliability of MAF-66 in practical applications.

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