

Modeling of CO₂ Adsorption on Activated Carbon and 13X Zeolite via Vacuum Swing Adsorption

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Abstract. Due to carbon dioxide role in global warming, low CO₂ emission limits have been established in recent years. This has led to a variety of studies on CO₂ removal approaches. In this study, a VSA cycle consisting of two packed beds is considered for CO₂ removal from flue gas. An atmospheric stream containing 20% CO₂ and 80% N₂ is fed to the beds at 50°C. Two adsorbents, namely Zeolite 13X and activated carbon were selected to compare their performance. Due to the monolayer adsorption of CO₂ and N₂ on these adsorbents, the Toth isotherm was used for equilibrium adsorption estimation. A quasi-second order model was considered for the mass transfer rate prediction due to low CO₂ concentration. The modeling results showed that the average absolute deviation for equilibrium adsorption capacity prediction was 2%, and the CO₂ breakthrough time curve was predicted with less than 2.5% deviation. Based on the results, the VSA cycle time for zeolite 13X bed will be 3.5 times of the activated carbon bed. Another advantage of Zeolite 13X is that in each process cycle, 80% of adsorbent will be used, while only 74% of activated carbon in beds is used. The advantage of activated carbon bed is its better regeneration capability, since the activated carbon will be regenerated 5% more than zeolite 13X at a vacuum pressure of 0.02bar.

1. Introduction

The increase in greenhouse gas emission has created many environmental problems. Carbon dioxide is one of the greenhouse gases with the greatest impact on global warming [1]. In recent years, the International Energy Agency has presented a roadmap to reduce CO₂ emission, develop sensible separation technologies and limit the increase in Earth's temperature to 2°C from 2013 to 2050. However; it is expected that the Earth's temperature will rise by 4°C during this period[2] due to industrial developments, the increase in fuel consumption and low CO₂ cost. Numerous studies have been conducted in recent years on trends and developments of CO₂ separation processes [3, 4] leading to suggested processes such as absorption, adsorption, membrane and refrigeration. The selection of each process depends on various factors such as operating pressure, feed gas temperature, product purity and feed gas impurities. The comparison of these processes has indicated that amine absorption is the most widely used process in industries. However; the application of this process is not recommended due to corrosion problems and high solvent regeneration cost. Similar problems in the refrigeration



process such as low life time, plastization problems, fouling in membranes and high energy requirements have attracted the researchers to the adsorption process in recent years.

In order to study the performance of adsorbents in CO₂ removal, experimental studies on different adsorbents such as activated carbon, zeolite 5A and zeolite 13X have been performed [5, 6]. Adsorbent capacity and selectivity are the most important factors in the process performance and efficiency. It should be noted that the application of very strong adsorbents will make the regeneration process more difficult. Adsorbent regeneration can be performed by heat in TSA [7], pressure in PSA [8], and electrical energy in ESA [9] processes. Vacuum can be used as the necessary driving force for regeneration when the gas feed pressure is near the atmospheric pressure. This process is known as vacuum swing adsorption (VSA). The required energy for regeneration in VSA process is 1-1.5 MJ/kg CO₂ [9]. This lower energy requirement for the VSA process compared to TSA process with 3-4 MJ/kg CO₂ [7] and PSA process with 2-3 MJ/kg CO₂ [10] has drawn the attention of researchers to the VSA process in recent years.

The aim of this study is to evaluate and compare the performance of zeolite 13X and activated carbon for CO₂ removal from a CO₂/N₂ mixture in an adsorption bed with VSA cycle. For this purpose, the experimental data of equilibrium isotherms and adsorption bed parameters of Dantas and her colleagues were used [11, 12]. Finally, in order to study the process limitations, a comprehensive review of the effective parameters such as feed conditions, vacuum pressure, purge to gas ratio and cycle time, and their effect on the recovery and performance of CO₂ productivity are studied.

2. Mathematical Modeling

Each VSA process cycle consists of four steps including bed pressurization, adsorption, blow-down and purging. To improve the process performance, blow-down and purging steps are carried out in the opposite direction of adsorption step [13]. Figure 1 shows an overview of the pressure profile in a VSA cycle. As can be seen, the flow in the adsorption step is downward to eliminate the possibility of adsorbent fluidization. Also, the pressure profile is assumed to be linear in the pressurization and blow-down steps.

The adsorption process mathematical modelling predicts the unsteady state behaviour of the adsorption bed. In order to achieve this goal, a set of partial differential equations including the mass, momentum and energy balance, along with one ordinary differential equation are considered and solved simultaneously to predict the mass transfer rate [14, 15].

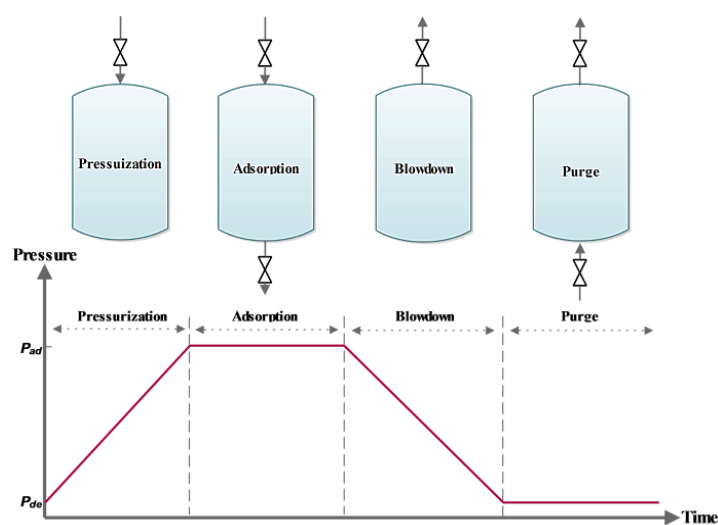


Figure 1. Pressure profile during a VSA cycle

In order to provide a mathematical model, the following assumptions are considered:

1. The adsorption bed operates under an isothermal condition.
2. The radial concentration gradients are negligible.
3. The pressure drop in the bed is calculated based on the Ergun equation.
4. The feed and purge gas conditions remain constant during the process.
5. The flow pattern is assumed to behave as an axially dispersed plug flow model.
6. The mass transfer rate is represented by a quasi-second order model.
7. The gas behaviour is considered to be ideal.

The flow model for the adsorption process is based on packed beds. The mass balance equation includes axial dispersion, convection, accumulation in gas phase, and rate of adsorption.

$$-D_{zi} \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial}{\partial z}(uC_i) + \frac{\partial C_i}{\partial t} + \left(\frac{1-\varepsilon_b}{\varepsilon_b} \right) \rho_p \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (1)$$

where C_i (mol.m^{-3}) is the adsorbate concentration of component i in the fluid phase, u (m.s^{-1}) is the fluid velocity, z (m) represents the distance along the bed, t (s) is time, ε_b is the bed void fraction, ρ_p (kg.m^{-3}) is the particle density and \bar{q}_i (mol.kg^{-1}) is the average concentration in adsorbent particle. The axial dispersion coefficient D_{zi} ($\text{m}^2.\text{s}^{-1}$) is defined by an empirical correlation as a function of Reynolds and Schmidt number.

$$\frac{\varepsilon_b D_{zi}}{D_{mi}} = 20 + 0.5 \text{Sc Re} \quad (2)$$

where D_{mi} ($\text{m}^2.\text{s}^{-1}$) is molecular diffusivity of component i and Sc and Re are the Schmidt and Reynolds numbers. The mass transfer rate is defined based on different adsorption kinetics. When the feed concentration is low, it is recommended to use a quasi-second order model[16]. Since CO_2 concentration in flue gas is 8 to 15 percent, it is recommended that a quasi-second order model be used to predict the mass transfer rate. The general form of this model is defined in Equation 3.

$$\frac{\partial \bar{q}_i}{\partial t} = K_{s,i} (q_i^* - \bar{q}_i)^2 \quad (3)$$

where $K_{s,i}$ ($\text{kg.mol}^{-1}.\text{s}^{-1}$) is the quasi-second order mass transfer coefficient and q_i^* (mol.kg^{-1}) is the adsorbed phase concentration in equilibrium with the fluid phase concentration. When the adsorption of all materials except component i is negligible, the equilibrium adsorption can be estimated with their pure isotherms at their partial pressure. Due to mono-layer adsorption of CO_2 and N_2 on zeolite 13X and activated carbon, the Toth isotherm is recommended for equilibrium adsorption prediction. This equation is defined as follows:

$$q_i^* = \frac{q_i^{\max} K_{eq} P}{\left[1 + (K_{eq} P)^n \right]^{1/n}} \quad (4)$$

where q_i^{\max} (mol.kg^{-1}) is the maximum amount adsorbed at equilibrium, K_{eq} (bar^{-1}) is an equilibrium constant, P (bar) is the total pressure and n is the Toth parameter. By passing the fluid through the empty spaces between adsorbent particles, a pressure drop may take place in the fluid. The Ergun equation was used to predict this pressure drop:

$$\frac{\partial P}{\partial z} = - \frac{150 \mu_g (1-\varepsilon_b)^2}{\varepsilon_b^3 d_p^2} u - \frac{1.75 (1-\varepsilon_b) \rho_g}{\varepsilon_b^3 d_p} u^2 \quad (5)$$

where μ_g (Pa.s^{-1}) is the gas viscosity, d_p (m) is the particle diameter and ρ_g (kg.m^{-3}) is the gas density. In order to evaluate the VSA cycle performance in CO_2 separation, it is necessary to calculate its emission to the atmosphere and the recovery. These two parameters are defined in Equations 6 and 7.

$$\text{CO}_2 \text{ Emmission} = \int_0^{t_{\text{adsorption}}} (1 - \text{purge/feed ratio}) \cdot \text{Flow}_{\text{CO}_2} dt \quad (6)$$

$$\text{CO}_2 \text{ Recovery} = \frac{\text{CO}_2 \text{ obtained in adsorption} - \text{CO}_2 \text{ used in purging}}{\text{CO}_2 \text{ fed during pressurization \& adsorption}} \quad (7)$$

In order to predict the VSA cycle behaviour, the above equations must be solved simultaneously. The set of partial differential equations are discretized in the length direction and solved by MATLAB with the ODE15s method.

To evaluate the VSA performance in CO_2 reduction, the experimental data by Dantas et.al was used [11, 12]. Therefore, an atmospheric mixture of 20% CO_2 and 80% N_2 is introduced to the cycle at 50°C with a flow rate of 3 L.min^{-1} . The adsorbent properties and bed parameters are reported in Tables 1 and 2.

Table 1. Zeolite 13X and activated carbon properties

| Zeolite 13X | | Activated Carbon | |
|---|-------|---|-------|
| Surface area [m^2/g] | 585.5 | Surface area [m^2/g] | 1053 |
| Micropore volume [cm^3/g] | 0.172 | Micropore volume [cm^3/g] | 0.097 |
| Particle density [g/cm^3] | 1.23 | Particle density [g/cm^3] | 1.14 |
| Particle porosity | 0.37 | Particle porosity | 0.46 |
| Particle diameter [mm] | 2.9 | Particle diameter [mm] | 3.8 |

Table 2. Adsorption bed parameters

| | |
|--|-------|
| Bed Length [cm] | 83 |
| Bed Diameter [cm] | 2 |
| Bed void fraction | 0.52 |
| Column wall thickness [mm] | 1.5 |
| Column wall density [kg.m^{-3}] | 7280 |
| Bed weight [kg] | 0.158 |

3. Results and Discussion

The adsorption equilibrium determination is one of the major problems in predicting the VSA process behaviour. Figure 2 shows the results of CO_2 and N_2 equilibrium adsorption prediction with the Toth model. The results indicate that the maximum deviation error for equilibrium adsorption capacity prediction is 2.5% for CO_2 and 2% for N_2 . As can be seen, the selection of Zeolite 13X is much better due to its higher capacity at low pressures.

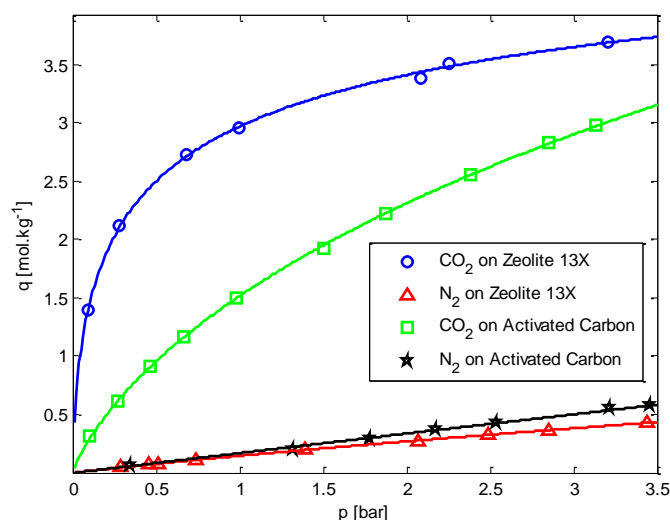


Figure 2. CO₂ and N₂ adsorption equilibrium on Zeolite 13X and activated carbon at 50°C; the solid lines represent the results of the Toth model.

Figure 3 shows breakthrough curve which is plotted to determine the proper time to carry out the adsorption cycle. Additionally, figure 3 indicates the results for modeling the VSA process in packed activated carbon and zeolite 13X beds. According to this figure; N₂ is adsorbed in the bed at first, and then the CO₂ molecules will replace N₂ due to the competitive adsorption nature of CO₂ and N₂. This phenomenon causes an overshooting peak on the N₂ breakthrough curve. The breakthrough time for zeolite 13X bed is 3.5 times greater than the one for activated carbon bed. An increase in breakthrough time reduces the necessary times for bed regeneration and improves the recovery. The results show that the average deviation error for breakthrough time prediction curve is 2.5%.

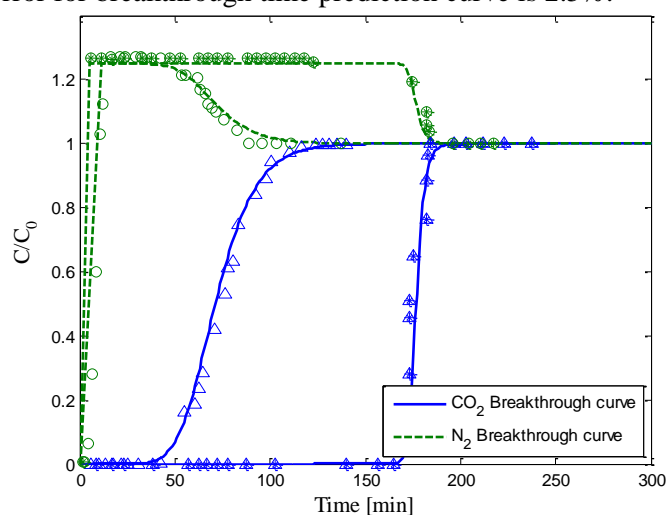


Figure 3. Breakthrough curve of CO₂/N₂ mixture on zeolite 13X(N₂: \odot , CO₂: \triangle) and activated carbon(N₂: \odot , CO₂: \triangle); lines are obtained by a quasi-second order model.

As an additional advantage, more parts of zeolite 13X adsorbent are consumed in each cycle of the process. Figure 4 demonstrates the available area in a VSA cycle for two adsorbents. In the adsorption step, the process should be stopped at break point time due to CO₂ emission limitation. At this time, the mass transfer zone reaches the bottom of the bed. The shorter the length of mass transfer zone, the greater the amount of consumed adsorbent. The mass transfer zone in the activated carbon bed is 2.5 times of zeolite 13X bed. The results show that at the end of the adsorption step, 93% of zeolite 13X

adsorbent is saturated, but only 85% of activated carbon is saturated at break point time. If the process is continued to saturate more activated carbons, the CO₂ emission to atmosphere will increase significantly. The advantage of activated carbon is the simplicity of its regeneration. At the end of blow-down to 0.1 bar and purging 15% of N₂, 89% of adsorbent will be regenerated. However, at the end of this step only 87% of zeolite 13X is regenerated. The reason is related to the strong interaction between CO₂ molecules and zeolite 13X adsorbent. This strong interaction causes a better and selective separation with more energy cost requirement for regeneration. As can be seen in figure 4, in each cycle of the process, 80% of zeolite 13X adsorbent will be consumed, as opposed to only 74% of adsorbent in the activated carbon beds.

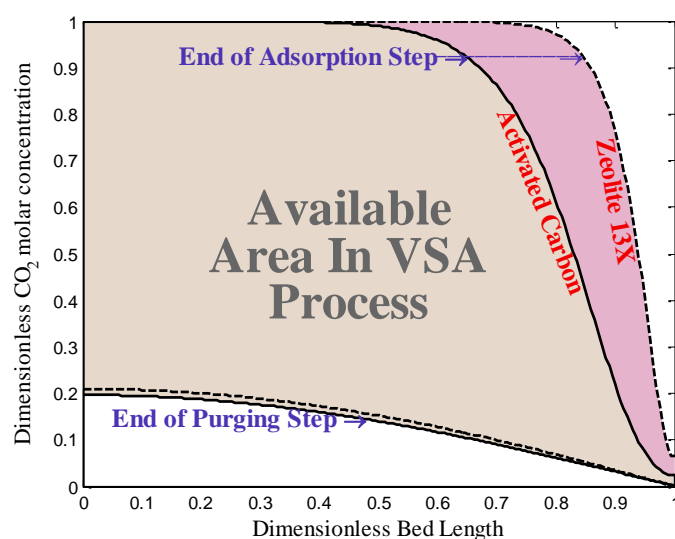


Figure 4. Adsorbent consumption in each cycle of VSA process for zeolite 13X and activated carbon; Solid line: activated carbon, Dash lines: zeolite 13X.

Since adsorption is an exothermic process, an increase in temperature will reduce the adsorbent capacity. Therefore, it is recommended to keep the temperature as low as possible in all adsorption processes to have the maximum available adsorbent capacity. Figure 5 shows the effect of temperature on the adsorption process. As can be seen, a rise of temperature from 50°C to 100°C will reduce the breakthrough time by 41% in a zeolite 13X bed and by 65% in an activated carbon bed.

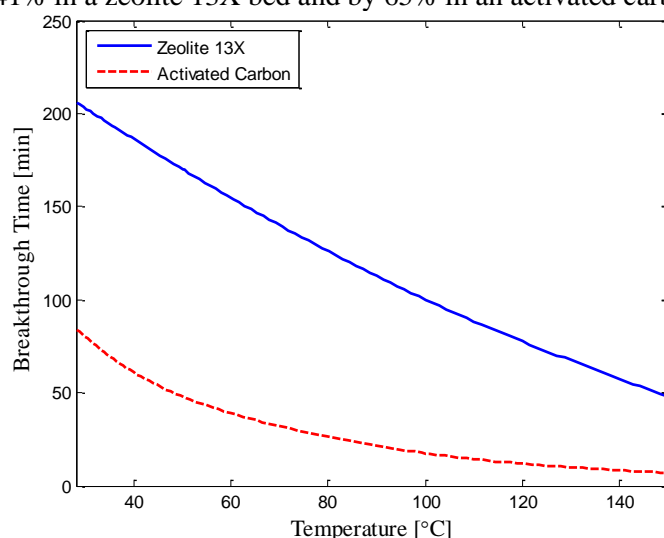


Figure 5. Temperature effects on breakthrough time of zeolite 13X and activated carbon beds.

As can be seen in Figure 6, a 33% increase in feed flow rate will decrease the breakthrough time by 25% in a zeolite 13X bed. However, this feed flow rate increase will reduce the break point time by 30% in an activated carbon bed.

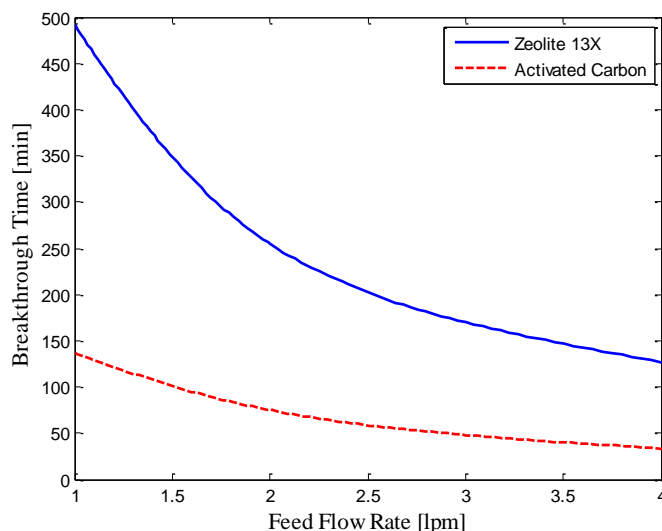


Figure 6. Feed flowrate effect on breakthrough time of zeolite 13X and activated carbon beds.

Figure 7 shows the effect of CO₂ feed concentration on the breakthrough time. An increase in CO₂ concentration will reduce the break point time and increase the number of regeneration times which will cause adsorbents' erosion and increase the pressure drop. A 15% increase in CO₂ concentration will reduce the break point time by 55% in a zeolite 13X bed, whereas this will only decrease the break point time by 26% in an activated carbon bed. Therefore, the feed concentration effect on activated carbon is less than the effect on a zeolite 13X bed.

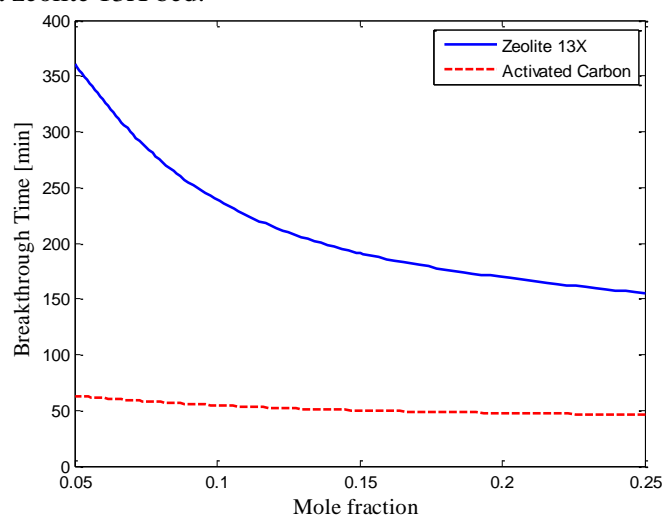


Figure 7. CO₂ feed concentration effect on breakthrough time of zeolite 13X and activated carbon beds.

One of the most important points in the design of a VSA process is its cycle time. Figure 8 shows the effect of cycle time on CO₂ emission and its recovery. In this process, 40% of cycle time is considered for the adsorption step. A reduction in cycle time increases the amount of CO₂ emission to atmosphere. The maximum cycle time is determined by the CO₂ emission limit. If the process is designed to minimize CO₂ emission, the maximum cycle time will become 280 minutes for zeolite 13X beds. However, the maximum cycle time in activated carbon beds will be only 110 minutes.

Another advantage of zeolite 13X is its higher CO₂ recovery. For a zeolite 13X bed with 280 minutes cycle time the recovery is 98%, whereas the CO₂ recovery for an activated carbon bed with a cycle time of 110 minutes is 95%.

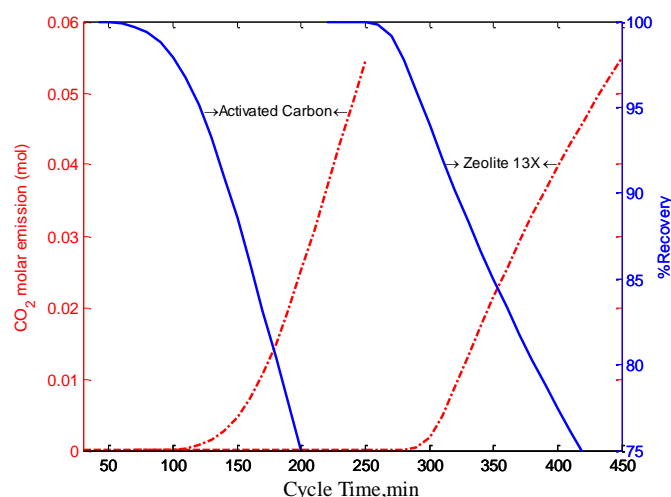


Figure 8. Cycle time effect on CO₂ emission to atmosphere and its recovery; Solid line: CO₂ recovery, Dash line: CO₂ molar emission.

A vacuum pump creates the required driving force for adsorbent regeneration in all VSA processes. Since the vacuum pump consumes energy, it is necessary to determine the required vacuum pressure. Figure 9 shows the effect of vacuum pressure in a bed regeneration process. As can be seen, any reduction of vacuum pressure increases the bed regeneration. It should be noted that both the zeolite 13X and activated carbon beds regenerated completely at 1mmHg vacuum pressure even though reaching this degree of vacuum is not cost effective. The regeneration behaviour of zeolite 13X showed that most of adsorbent regenerates at a very low pressure. The regeneration of 90% of zeolite 13X adsorbent required a vacuum pressure less than 0.01 bar. However, this amount of regeneration is possible with vacuum pressure equal to 0.06 bar in activated carbon beds.

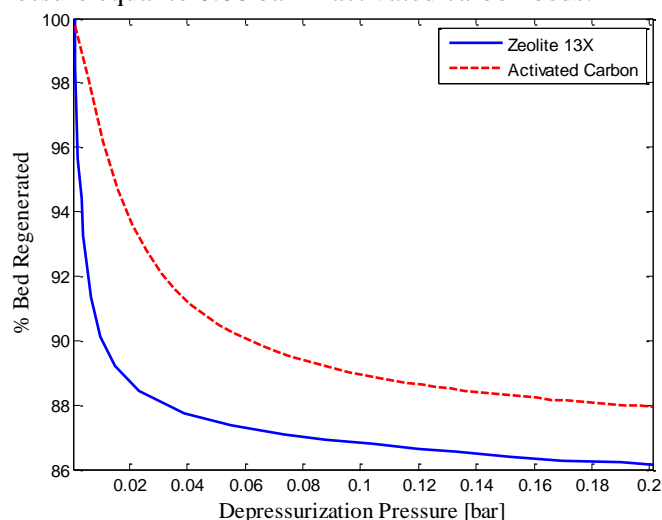


Figure 9. Vacuum pressure effect on CO₂ emission and bed regeneration.

The application of purge gas at the end of bed regeneration is another important factor in determining the process performance. As is shown in figure 10, increasing the purge to feed ratio improves the bed regeneration with little effect on CO₂ recovery. It should be noted that an increase in purge to feed ratio

will reduce the quality of CO₂ product at the end of the process. In the case where the N₂ product is important, an increase in purge to feed ratio will decrease N₂ productivity and its recovery.

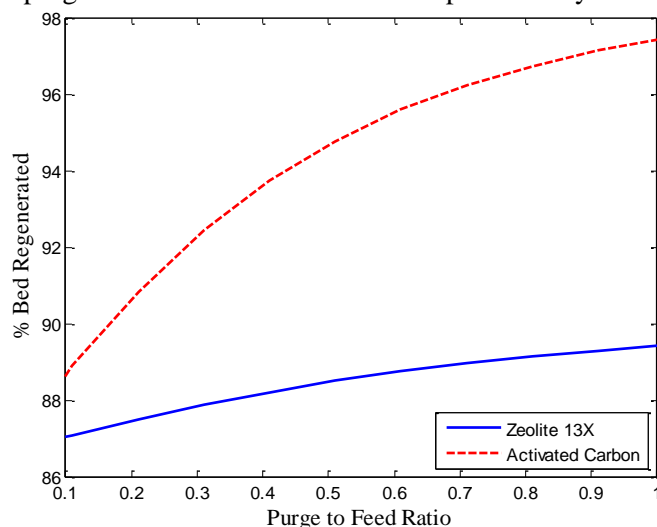


Figure 10. Purge to feed ratio effect on bed regeneration.

4. Conclusions

In order to evaluate the VSA performance in CO₂ removal, a process consisting of two adsorption beds was modelled. The equilibrium adsorptions were predicted by Toth isotherm. The comparison of the experimental results and the model showed that the maximum deviation errors for equilibrium adsorption capacity prediction are 2.5% for CO₂ and 2% for N₂. Then the beds were modelled with a quasi-second order model and the results showed that the average deviation error for breakthrough time prediction curves was 2.5%.

The results of the analysis for effective parameters can be summarized as follows:

- The breakthrough time for the zeolite 13X bed is 3.5 times greater than the time for activated carbon bed. This will reduce the necessary times for bed regeneration and improve the recovery.
- In each cycle of the process, 93% of zeolite 13X is saturated at the end of the adsorption step. Additionally, at the end of blow-down to 0.1 bar and purging 15% of product N₂, 87% of them will be regenerated. In fact 80% of adsorbent are used in each cycle. However, 85% of adsorbent are saturated at the end of adsorption step in an activated carbon bed and 89% of them will be regenerated at the end of purging. This phenomenon showed that only 74% of adsorbers are used in each cycle.
- A temperature rise of 50°C will reduce the break point time by 60% in the activated carbon bed. However, this will decrease the time by 40% in a zeolite 13X bed.
- Doubling the feed flow rate will decrease the break point time in the zeolite 13X bed by 50%, whereas this will reduce the time by 56% in an activated carbon bed.
- A 15% increase in CO₂ feed concentration reduces the breakthrough time by 55% in a zeolite 13X bed. However, this concentration change will decrease the time by only 26% in an activated carbon bed. In the case of feeding the system by several sources with different concentration, if the process steps are changed based on a time schedule rather than the usual CO₂ breakthrough, then it is better to use an activated carbon bed rather than one with zeolite 13X.
- Due to the strong interaction between CO₂ and zeolite 13X molecules and more adsorption capacity at a low pressure, most of adsorbent will be regenerated at low pressure. The regeneration of 90% of adsorbent requires a vacuum pressure of 0.01bar in a zeolite 13X bed. However, this amount of regeneration requires a vacuum pressure of 0.06bar in an activated carbon bed.

- A 10% increase in purge gas will increase the bed regeneration by 2%. It is recommended that purge gas be used as little as possible. An increase in purge gas will reduce the CO₂ product purity and N₂ recovery.

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