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Continuous Adsorption of CO_2 With Zeolite 5A In a Micro-Scale Fixed-Bed Column

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Abstracts

CO_2 is the primary greenhouse gas which mainly stems from human activities. Increased CO_2 emission in the atmosphere promotes global warming, which adversely affects human health and the environment. Adsorption is proposed as one of the practical and economical methods for CO_2 removal. Zeolite 5A is an adsorbent that can be employed in CO_2 adsorption due to its high porosity and adsorption capacity. In this study, we investigate the CO_2 adsorption behavior by zeolite 5A adsorbent in a continuous, micro-scale fixed-bed column at different bed heights. Gas chromatography was utilized to determine CO_2 exit concentrations. The column pressure drop was calculated using Ergun's equation. The obtained data were analyzed in the form of breakthrough curves, then fitted to Thomas and Yoon-Nelson's mathematical model to obtain adsorption rate coefficient in the column. The experimental data of CO_2 adsorption by zeolite 5A shows the good correspondence with both Thomas's and Yoon-Nelson's mathematical models. At a flow rate of 30 mL/min and bed height variations of 10 and 12 cm, the CO_2 adsorption capacities (q_0) were 0.0071 and 0.0099 mol/g, respectively. While the Thomas's adsorption rate coefficient, k_{TH}, for the same conditions were 0.4164 min^{-1} and 0.4342 min^{-1}.

Keywords: Adsorption, fixed bed, zeolite 5A, CO_2 reduction, Thomas's model

Introduction

CO_2 emissions are one of the main greenhouse gases generated from human activities. According to the International Energy Agency (IEA), global carbon dioxide emissions from energy combustion and industrial processes grew 0.9% or 321 Mt in 2022 to an all-time high of 36.8 Gt. Several factors drove the increase in global CO_2 emissions—first, dependence on fossil fuel power plants. Second, global CO_2 emissions from oil production grew by 2.5% or 268 Mt to 11.2 Gt in 2022. Third, total global CO_2 emissions from transportation increased by 2.1% or 137 Mt [1]. Increased carbon dioxide emissions can have an impact on global warming. Global warming is the gradual increase of the average temperature of the earth. Global warming can have negative impacts such as climate instability, melting polar ice that causes sea level rise, ecological disturbances, and others [2].

Several methods can be applied to reduce CO_2 emissions, such as adsorption, absorption, cryogenics, and membranes. In 2005, the Intergovernmental Panel on Climate Change (IPCC) stated that adsorption process is promising for CO_2 gas separation by selecting suitable adsorbents [2]. Adsorption is the separation of gas or liquid components, where in the process the absorbed substance is called adsorbate and the absorbing substance is called adsorbent [3]. The adsorbent is a material that supports the adsorption process because it has a small priority inside the structure, a high surface area, and a high pore volume [4]. In CO_2 adsorption, there are many adsorbents that can be used. In several previous studies, CO_2

adsorption research was carried out using a continuous fixed bed column. In CO_2 adsorption using 13X molecular sieve adsorbent, an adsorption capacity of 0.0021 mol/g was obtained [5]. In CO_2 adsorption using 13X zeolite adsorbent and 4X zeolite, each received a capacity of 0.0042 mol/g and 0.0026 mol/g [6]. In CO_2 adsorption using nitrogen-doped adsorbents, an adsorption capacity of 0.0035 mol/g was obtained [7]. In CO_2 adsorption using Norit R2030 commercial adsorbent, an adsorption capacity of 0.0022 mol/g was obtained [8]. In CO_2 adsorption using 5A zeolite adsorbent, an adsorption capacity of 0.0072 mol/gram was obtained [4]. It can be concluded that zeolite 5A has a higher CO_2 adsorption capacity.

Zeolite is a porous crystalline alumina silicate composed of SiO_4 and AlO_4 tetrahedral assemblies [9]. Zeolite 5A is one of the solid adsorbents with a sodalite-shaped cubic lattice that has been used in various adsorption and separation processes. This absorbent has a pore size of 0.49 nm to absorb gas adsorbate molecules with a kinetic diameter of less than 0.49 nm. 5A zeolite has a high potential to absorb CO_2 molecular gas due to the interaction between cations in 5A zeolite and the CO_2 quadrupole moment [4].

The adsorption system consists of two types: batch and continuous systems. Continuous system offers some advantages compared to batch due to its ability for large-scale operation and efficiency. Fixed bed columns are widely used in various chemical industries to separate molecules that want to be removed [10]. The fixed bed column used in this study is a micro-scale fixed bed column. Micro-columns can produce faster results while needing lower cost because there are not many adsorbents used. Micro fixed bed columns can be used as transitions or preliminary studies before going to the industrial stage [11] [12].

Overall, the design and performance of the fixed bed column system are influenced by several parameters such as flow direction, bed height, flow rate, and pressure drop. The direction of flow entry can be divided into two: from bottom to top (down-flow) and from top to bottom (up-flow). The use of down-flow leads to lower adsorption capacity than up-flow flow. This is due to channeling so that the distribution of fluid flow to the adsorbent is uneven [13]. The breakthrough time is influenced by the height of the bed; the more the height of the bed is used, the longer the breakthrough time and saturation time will be. It causes the absorbent in the column to increase so that the mass transfer zone increases [11]. The flow rate influences the breakthrough time; the higher the flow rate used, the more it will accelerate the breakthrough time and saturation time. Also, the higher the flow rate used, the contact time of the adsorbent and adsorbate becomes faster, so the adsorbent will become saturated quickly [11]. At the same time, the effect of pressure drop can cause column regeneration ability and adsorption ability to decrease [14].

The breakthrough curve is a curve that describes the performance of a fixed bed column. The breakthrough curve is defined as the ratio of the effluent concentration (C_t) and the influent concentration (C_0) as a function of time [15]. Breakthrough is also called the condition when the adsorbate concentration is first detected as an effluent concentration (Ct) [16]. The breakthrough curve can be used to determine the effectiveness of the adsorption column, the capacity of the adsorption column, and increase (scale up) the size of the fixed bed column. This curve can be known as the breakthrough point and exhaust point. The breakthrough point is the starting point of the adsorbate going out with effluent (the start of the mass-transfer zone). In contrast, the exhaust point is the point where the ratio between effluent and feed is almost the same (end of mass-transfer zone) [10].

Mathematical modelling is also used in the design and behavioral processes of fixed bed column dynamics on an industrial scale. The mathematical model of the adsorption column aims to determine the efficiency and application capability of the adsorption column. There are several mathematical models commonly used to model fixed bed adsorption columns, including the Thomas, Yoon-Nelson, Adam-Bohart, and Bed Depth Service Time (BDST) models. These models have different assumptions when determining the kinetic parameter corresponding to the adsorption process studied.

In this study, the experimental data of continuous adsorption experiments are fitted against Thomas's and Yoon-Nelson's model to obtain mass transfer or adsorption rate coefficient in the column. The Thomas model assumption is developed from the equation of conservation of mass in the flow system assuming adsorption-desorption kinetics following Langmuir kinetics. Adsorption occurs in a monolayer and under isothermal and isobaric conditions. Thomas's model aims to determine the maximum adsorption capacity (q_m) and Thomas's rate constant (k_{TH}) according to this relation:

$$\frac{C_t}{C_0} = \frac{1}{1+exp\left((\frac{K_{TH}}{Q})(q_{TH}m - C_0Qt\right)} \quad (1)$$

The parameters of the constants k_{TH} and q_{TH} are obtained by plotting a linear form of Thomas's model as follows[17].

$$ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{TH}q_{TH}m}{Q} - k_{TH}C_0t \quad (2)$$

On the other hand, Yoon-Nelson's model is used to predict the adsorption rate and column working time before regeneration, k_{YN} and τ, according to this relation:

$$\frac{C_t}{C_0 - C_t} = exp(k_{YN}t - \tau k_{YN}) \quad (3)$$

The parameters of the constants k_{YN} an τ are obtained by plotting a linear form of Yoon-Nelson's model as follows[17]:

$$ln\frac{C_t}{C_0 - C_t} = k_{YN}t - \tau k_{YN} \quad (4)$$

Material and Methods

The materials used in this study were *glass wool*, zeolite 5A (PinXiang XINGFENG Chemical), and CO_2-Ar gas mixture with a composition of 20% CO_2 and 80% Argon (Sinergi Berkat Gasindo). The specifications of zeolite 5A are displayed in Table 1.

Table 1. Zeolite 5A adsorbent specification

Specification	Value
Density	1100 kg/m^3
Porosity	0.2-0.5
Surface area	200-600 m^2/g
Pore size	2-10 A
Bulk density	640 kg/m^3

Fixed-bed column assembly

In this study, a fixed-bed adsorption micro-column prototype was made. The column specification can be seen in Figure 1 and Table 2.

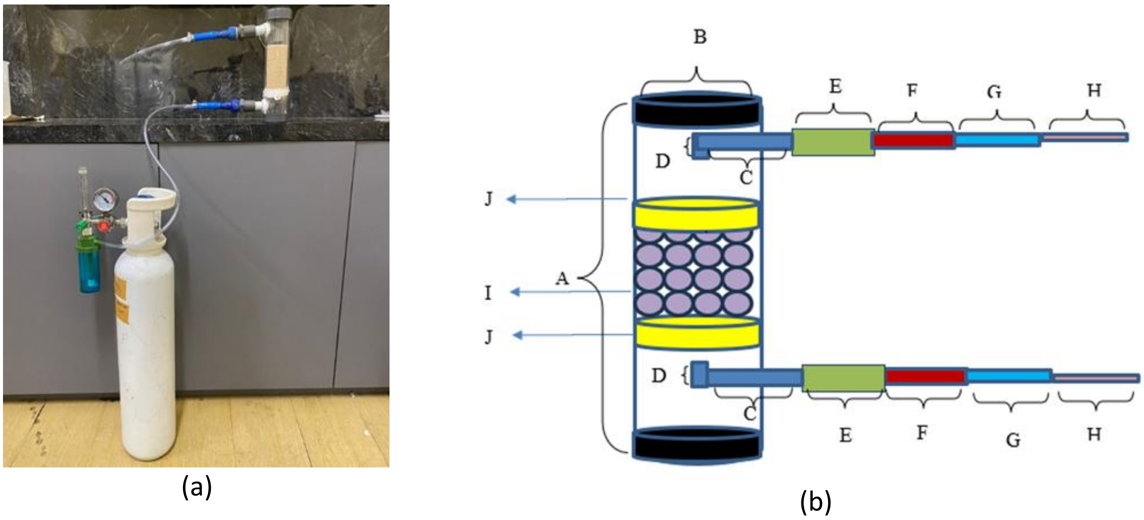


Figure 1. Adsorption column prototype: (a) as a whole, and (b) schematic

Table 2. Specifications of fixed-bed micro-column.

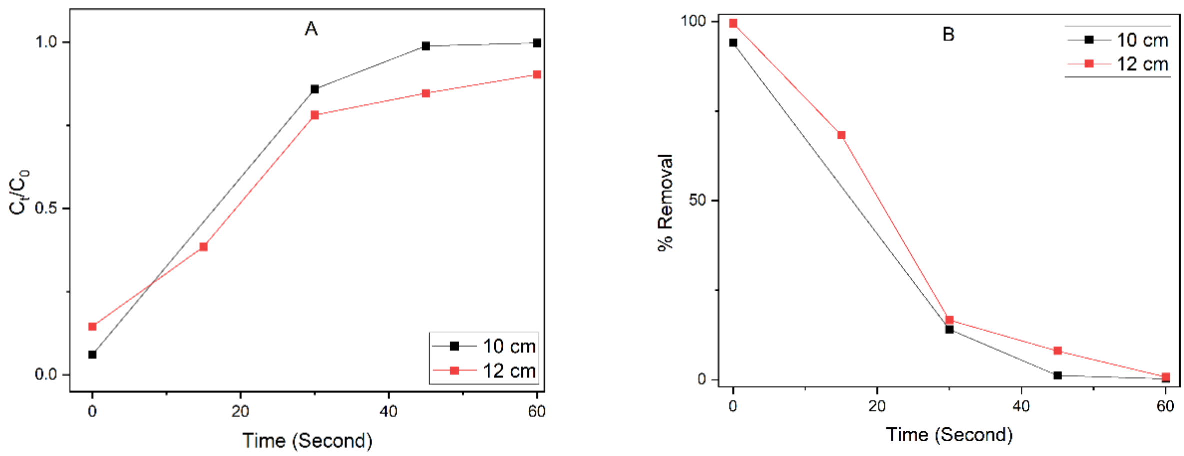
Acrylic pipe length	(A)	25 cm
Acrylic pipe diameter	(B)	2 inches
PVC pipe 0.5" length	(C)	5 cm
Elbow pipe 0.5" length	(D)	2 cm
Shock drats 0.5" length	(E)	10 cm
Pipe-to-hose connection	(F)	5 cm
Hose 0.5"	(G)	5 cm
Hose 0.25"	(H)	5 cm
Adsorbent	(I)	150 grams
Glass wool	(J)	

Adsorbent preparation and fixed-bed adsorption measurements

The preparation of adsorbent was carried out by heating zeolite 5A at a temperature of 378 K for 60 minutes to remove the water content inside the matrix. The total height of the column was 25 cm with an inner diameter of 4.8 cm. Glass wool was installed at the top and the bottom of the column so that fluidization did not occur. The column was filled with zeolite 5A adsorbent as high as 10 cm and 12 cm (150 g and 160 g). 30 mL/min CO_2-Ar gas mixture was then flowed into the column with down-flow configuration. The adsorption experiment was carried out at room temperature conditions of 25°C and 1 atm. The column effluents were analyzed at 0; 15; 30; 45; and 60 s using Agilent 8890 gas chromatograph with TCD detector (GC-TCD).

Results and Discussion

To analyze the performance of the fixed-bed column, breakthrough curves were constructed at adsorbent height variations of 10 and 12 cm as can be seen in Figure 2. Over time, adsorbents in the column will reach saturation so that the concentration of effluent (C_t) approaches the concentration of influent (C_0). It can be observed that a bed height of 10 cm has a steep graph so that breakthrough time (t_B) and exhaustion time (t_E) are achieved faster. A bed height of 12 cm has a sloping graph, which means that the breakthrough time (t_B) and exhaustion time (t_E) are longer. As the height of the bed increases, the available adsorption sites also increase, which causes breakthrough time, exhaustion time and removal percentage to increase. The 12 cm column has a better performance in terms of its % removal due to similar reasons.



(a) (b)

Figure 2. (a) Breakthrough curves and (b) % removal for different bed heights

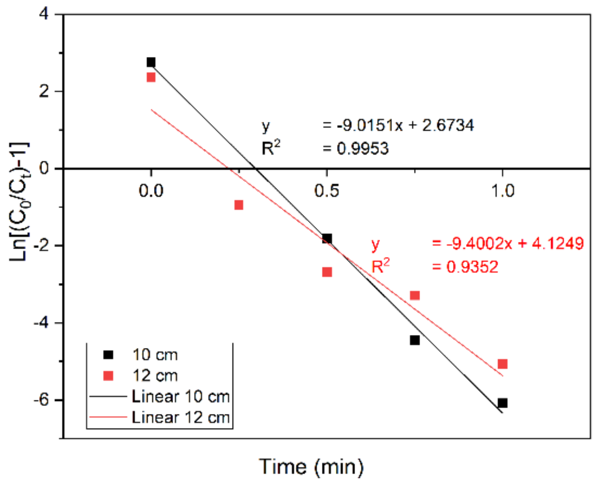


Figure 3. Thomas's model data fitting

The experimental data is plotted to fit against Thomas's model linear equation as displayed in Figure 3. The calculated model parameters are tabulated in Table 2. As shown by their correlation coefficient values (R^2), experimental data at different bed heights, especially at 10 cm, are in good accordance with Thomas's model. The value of Thomas's rate constant (k_{TH}) decreases with an increase in bed height. This is in accordance with Thomas's mathematical model theory. Higher k_{TH} means that the mass transfer rate is faster so that the time for the adsorbate to diffuse towards the adsorbent decreases [18]. On the other hand, the column adsorption capacity (q_{TH}) increases along the increase in bed height. In this experiment, q_{TH} are 0.0071 and 0.0099 mol/g at bed heights of 10 and 12 cm, respectively. These values are higher than previously reported [4][5][6][7][8].

Table 3. Parameters of Thomas's adsorption model

Flow rate, Q (mL/minute)	Bed height (cm)	k_{TH} (min^{-1})	q_{TH} (mol/g)	R^2
30	10	0.4164	0.0071	0.9976
	12	0.4342	0.0099	0.9352

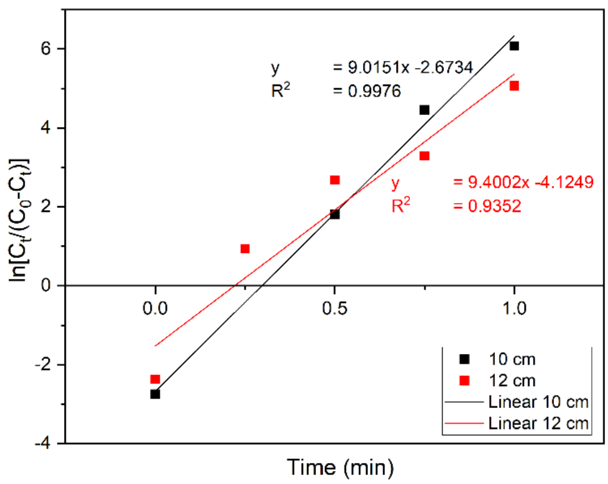


Figure 4. Yoon-Nelson's model data fitting

As can be seen in Table 3, the value of the rate constant k_{YN} decreases with an increase in bed height. While the constant τ, which predicts 50% breakthrough time, increases when there is a decrease in bed height. The predicted 50% breakthrough time (τ) for 10 and 12 cm are 0.2970 and 0.4388 min, respectively. These results are in an agreement with Yoon-Nelson's mathematical model, as also supported by the value of their linear correlation coefficient (R^2) which are close to 1 [18].

Table 4. Parameters of Yoon-Nelson’s adsorption model

Flow rate, Q (mL/min)	Bed height (cm)	k_{YN} (min^{-1})	τ (min)	R^2
30	10	9.0015	0.2970	0.9976
	12	9.4002	0.4388	0.9352

Analysis of pressure drop parameters is determined using Ergun's equation, which combines Kozeny, Burke, and Plummer's equations. The pressure drop calculated from Ergun's equation can be seen in Table 4.

Table 5. Calculated column pressure drops

Flow rate, Q (mL/menit)	Bed height (cm)	Δp (Pa)	K_{TH} ($Minute^{-1}$)	K_{YH} ($Minute^{-1}$)
30	10	34.4163	0.4164	9.0151
	12	41.2996	0.4342	9.4002

Based on the results, pressure drop increases with the increase of bed height. With increasing bed height, the bed resistance to the flow increases so that the adsorbate is not evenly adsorbed on the adsorbent surface. A significant pressure drop can lead to lower bed adsorption capacity and quicker breakthrough time compared to what are predicted by Thomas’s model [14]. Thomas’s model is built under the assumption of isothermal and isobaric condition. Even though the calculated pressure drop in this experiment is relatively insignificant, the correlation coefficient (R^2) values decrease with increasing pressure drop.

Conclusion

This study shows that CO_2 adsorption with zeolite 5A at both adsorbent height variations of 10 and 12 cm are in accordance with the mathematical model of Thomas and Yoon-Nelson. The results of adsorption capacities (q_0) obtained at a variation in bed height of 12 cm were 0.0092 mol/g, which is higher than the previous research. This shows the potential application of zeolite 5A for CO_2 adsorption in a large-scale operation. In the next step, the effect of other variables such as CO_2 gas flow rate, composition, temperature, adsorbent size, and pH on the adsorption performance of the column needs to be investigated to find the optimum operating condition.

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