Oxygen Adsorption Kinetics Study used Pressure Swing Adsorber (PSA) for Nitrogen Production

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Abstract. One of the methods for air separation to get nitrogen gas is using the Pressure Swing Adsorption (PSA). Adsorption is a separation process to adsorb oxygen and release nitrogen as a product. This research aims to study the equilibrium and kinetics that occur in the oxygen adsorption using carbon sieve molecular (CMS) as an adsorbent. Air flowed through the compressor to PSA, air pressure (4 - 7 bar) and absorption time (3 - 9 minutes) were observed. The results showed that the higher pressure, the lower nitrogen purity. The highest nitrogen purity is 96.2% that produced at 4 bar pressure in 7 minutes. The adsorption equilibrium fits well to Temkin isotherm with $R^2 = 0.9938$, Temkin isotherm constant $(b) = 63.203 \times 10^3$, Temkin isotherm equilibrium binding constant $(A) = 1.00 \text{ L/g}$, and Constant related to heat of sorption $(B) = 0.03 92 \text{ J/mol}$. First order pseudo model kinetics is suitable for oxygen adsorption processes. The value of adsorption rate constants are vary around (4, 5, 6 and 7 bar pressure) : 0.8089 min$^{-1}$, 0.203 min$^{-1}$, 0.3476 min$^{-1}$, and 0.6668 min$^{-1}$ with $R^2 = 1$.

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1. Introduction
Air contains oxygen (20.9476%), nitrogen (78.084%), argon (0.934%), carbon dioxide (0.0314%), and water vapor [1]. Nitrogen is an element that can make various kinds of proteins and amino acids [2]. Nitrogen gas is widely used as an insulator for a system, especially from material contact with oxygen [3]. This can be found in metallurgical industries such as steel, iron, oil refinery, ammonia industry.

One of the technologies for separating nitrogen and oxygen from the air is adsorbing it with Pressure Swing Adsorber (PSA). PSA operates based on the physical adsorption of oxygen through adsorbents. Adsorbents used usually are activated carbon, alumina, and zeolite. The advantages of this process are more economical than cryogenic processes, and this separation process is very fast [3] with 99% nitrogen purity [4].

The adsorbent material is specially made as a molecular sieve which is intended to adsorb the target gas at high pressure which then slowly becomes low in pressure by readsorbing the adsorbent material. Materials that can be used as molecular sieves include zeolite and carbon. Molecular sieve from carbon (CMS) is produced through special manufacturing procedures so that it has a selectivity and very narrow pore size. Raw materials can be in the form of chemicals such as polyvinylidene dichloride and a phenolic resin or using natural materials in the form of anthracite coal and coconut shells. The surface of CMS is non-polar and often used in nitrogen production processes with high purity by the PSA method [5].
2. Experimental procedure

2.1. Materials and equipments
Air with a flow rate of 41.16 m/s which is pumped using a compressor to mini nitrogen production equipment. A mini nitrogen production equipment consisting of the cooler, air tank, PSA column, and buffer column. 7000 grams carbon molecular sieve 0.3 – 0.6 nm were into PSA column.

2.2. Methods
Air is pumped using a compressor with observed pressure and flow rate, then its cooled in the cooler. The cooled air is put into the PSA which already inserted 7000 grams CMS. Oxygen adsorption is observed every 3 -9 minutes with using nitrogen analyzer. The study continued by observing the pressure variables (4 - 7 bar).

3. Results and discussion

3.1. The pressure effect in oxygen adsorption
In the adsorption process, the separation process occurs due to differences in molecular size, or polarity because some molecules bind more strongly to the surface of the adsorber compared to other molecules or due to pores that are too small to accept larger molecules [6]. In this case, the size of the oxygen molecule is smaller when compared to nitrogen, i.e. 0.29Å and 0.30Å. While the pore size of CMS is 0.3Å
Pressure has an important role in oxygen adsorption by Carbon Molecular Sieve in the PSA column. The concentration of oxygen adsorption can be seen in figure 1.

![Figure 1. The Pressure Effect in O₂ Adsorption (oxygen adsorbed vs adsorption time in several pressure)](image)
From figure 1 show that the lower pressure, the higher CMS adsorb the oxygen. That is indicated the purity of nitrogen is higher too. In 7 minutes, the adsorption of oxygen has equilibrium in several pressure, because in the 9 minutes oxygen is saturated on the surface of the adsorbent pores so that the CMS cannot absorb again (see in the figure: decreasing adsorption of oxygen value from 7 minutes to 9 minutes).

3.2. Isotherms adsorption
Isotherm adsorption models are used to describe the adsorption capacity of the adsorbent used. Adsorption modeling is made for the adsorption approach. Various adsorption models are presented based on literature to describe research data from isotherm adsorption [7].

3.2.1. Langmuir isotherm adsorption
Langmuir developed a quantitative model to explain the phenomenon of adsorption isotherms with a kinetics approach. Analogous to the decrease in the adsorption equation in gas, Langmuir assumes that on the surface of the adsorbent there are active sites that are proportional to the surface area. The Langmuir equation model is stated as follows [8]

\[ q_e = \frac{Qo c_e}{1+bc_e} \]  
\[ \frac{1}{q_e} = \frac{1}{Qo} + \frac{1}{b} \]

Where,
- \( q_e \) = adsorbate which adsorbed per adsorbent weight (mg/g)
- \( c_e \) = adsorbate concentration in equilibrium (mg/L)
- \( b \) = Langmuir constants
- \( Qo \) obtained from the intercept and \( b \) obtained from the slope in plotting graph 1/qe versus 1/C_e. From this research work, the maximum monolayer coverage capacity (Qo) from Langmuir Isotherm model was determined to be 0.08787 mg/g, \( b \) is 0.07014 L/mg, and the \( R^2 \) value is 0.9594.

3.2.2. Freundlich isotherm adsorption
Freundlich isotherm adsorption is used for the adsorption kinetics model on heterogeneous adsorbent surfaces. Freundlich equation is stated in the following equation [8,16]

\[ q_e = K_F C_e^{1/n} \]  
\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]

\( K_F \) and \( n \) constants are adsorption capacity and adsorption intensity. The \( K_F \) value and \( n \) are obtained from the intercept and slope of the graph plot between the \( q_e \) versus \( \ln C_e \). From the data in table 1, that value of \( 1/n = 0.3345 \) while \( n = 2.9895 \) and the \( R^2 \) value is 0.9891.

3.2.3. Temkin isotherm adsorption
Temkin isotherm adsorption describes explicitly the interaction between adsorbent and adsorbate. Ignoring very low and large concentrations, this model assumed that the molecules adsorption heat in layer will decrease. The Temkin equation [9] is
where, 
\( A_T = \text{Equilibrium constant of Temkin adsorption isotherm (L/g)} \)
\( b_T = \text{Temkin Isotherm Constant} \)
\( R = \text{ideal gas constant (8,314 J/mol/K)} \)
\( T = \text{Temperature at 298K} \)
\( B = \text{absorption heat constant (J/mol)} \)

The values were determined: \( A_T = 1.00 \text{ L/g, } B = 0.0392 \text{ J/mol, } b_T = 63.203 \times 10^3 \), which is an indication of the heat of sorption indicating a physical adsorption process and the \( R^2=0.9938 \) proving that the sorption data fits well to Temkin Isotherm model.

### 3.2.4. Dubinin–Radushkevich isotherm

Dubinin-Radushkevich isotherms are generally used to describe the mechanism of adsorption with energy distribution to heterogeneous surfaces [10, 11]. This model often succeeds in entering the high solute activity and medium data concentration range well [12, 13].

\[
q_e = \left( q_s \right) \exp \left( -K_{ad} \varepsilon^2 \right).
\]

Where,
\( q_e = \text{the amount of adsorbate in the adsorbent in equilibrium (mg / g)} \); \( q_s = \text{theoretical isotherm saturation capacity (mg / g)} \); \( K_{ad} = \text{an activity coefficient constant related to sorption energy (mol}^2/\text{J}) \) and \( \varepsilon \) is Polanyi potential. This approach is usually applied to distinguish the physical and chemical adsorption of metal ions with average free energy, \( E \) per adsorbate molecule (to remove molecules from its location in the absorption chamber to infinity) can be calculated by the equation [12, 13]:

\[
E = \frac{1}{\sqrt{2B_{DR}}} \tag{7}
\]

Where \( B_{DR} \) is denoted as an isothermic constant. Meanwhile, the parameter \( \varepsilon \) can be calculated as:

\[
\varepsilon = RTln\left[ 1 + \frac{1}{C_e} \right] \tag{8}
\]

Where,
\( R = \text{ideal gas constant (8.314 J/mol.K)} \)
\( T = \text{absolute temperature in Kelvin} \)
\( C_e = \text{concentration adsorbate in equilibrium (mg/L)} \)

The value of \( E \) is \( >8 \text{ J/mol} \) that reveals the sorption process follows chemical sorption.
From the linear plot of DRK model, \( q_s = 0.0991 \) mg/g, the mean free energy, \( E = 75.5928 \) J/mol and the \( R^2 = 0.9423 \) lower than Temkin.

**Table 1.** Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm constants for the adsorption of oxygen in PSA.

| Materials     | Isotherms Adsorption | Langmuir          | Freundlich      | Temkin          | DRK                |
|---------------|----------------------|-------------------|-----------------|-----------------|--------------------|
| Oxygen adsorption | Qo = 0.08787 mg/g  | \( \frac{1}{n} = 0.3345 \) | B = 0.0392 J/mol | \( q_s = 0.0991 \) mg/g |
| by CMS        | b = 0.07014 L/g     | \( n = 2.9895 \)  | b = 63.203 x 10^3 J/mol | Kad = 8.7561 x 10^{-5} mol^2/J^2 |
|               | R^2 = 0.9594        | K_F = 0.4580 mg/g | A = 1.00 L/g    | E = 75.5928 J/mol |
|               |                      | R^2 = 0.9938      | R^2 = 0.9423    |                 |

### 3.3. Kinetics model

A fairly simple model to describe the adsorption kinetics is a pseudo first order rate model and a pseudo second order rate model [14]. As for some equations of the adsorption kinetics model proposed as follows [15]:

**Pseudo first order model**

\[
\frac{dQ}{dt} = k_1 (Q_e - Q) \tag{9}
\]

The pseudo second order model

\[
\frac{dQ}{dt} = k_2 (Q_e - Q)^2 \tag{10}
\]

**Figure 2.** Pseudo First Orde Model for Oxygen Adsorption.
From figure 2 and 3 we get the linear equation that shows us which model is suitable for this research. $R^2$ in pseudo first order is 1 and $R^2$ in pseudo second order is 0.999. These two models match in this research, but we also must see the k value of these models. From Table 2, $k_2$ is greater than $k_1$. This indicates that the adsorption speed runs spontaneously so that adsorption is rather difficult to measure.

### Table 2. Data of constant adsorption speed (k) on pressure variations

|        | $k_1$ (min⁻¹) | $k_2$ (g/mg.min) |
|--------|---------------|------------------|
| 4 bar  | 0.8089        | 0.203            |
| 5 bar  | 0.3476        | 0.6668           |
| 6 bar  | 20.3155       | 30.5224          |
| 7 bar  | 30.5224       | 48.6522          |
|        | $R^2 = 1$     | $R^2 = 1$        |

4. Conclusion

From this research, we can conclude that high pressure causes a decrease in oxygen concentration which results in nitrogen purity decreasing. The best oxygen adsorption in the PSA is 4 bar for 7 minutes, obtained by nitrogen purity of 96.2%. The isotherm adsorption model that is suitable for oxygen is Temkin isotherm adsorption, and the pseudo first order is suitable to describe the adsorption of kinetics that occurred.

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