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Potassium Carbonate Supported on γ-Alumina Sorbent Regeneration in Fluidized Bed Reactor for Carbon Dioxide Capture Technology

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Abstract. Nowadays, the world is facing severe climate change due to the rapid increase in the world population and the continuing growth of the economy and industry. These lead to substantial greenhouse gas emissions into the atmosphere, especially carbon dioxide, which causes global warming. Thus, carbon dioxide (CO₂) capture becomes an essential technology for mitigating adverse effects on the atmosphere. The solid sorbent is an appropriate alternative for CO₂ capture because it is cheap, environmentally benign, and recyclable. In this study, solid-sorbent regeneration using potassium carbonate supported on gamma-alumina in a fluidized bed reactor was investigated. The effects of operating variables of solid sorbent regeneration were studied by varying the temperatures of 100, 200, and 300 degrees Celsius and pressures in the range from 0 to 1 atmospheric pressure. The results showed that regeneration temperature had a positive effect and initial pressure had a negative effect on the sorbent regeneration, respectively. The sorbent regeneration can be enhanced by increasing the regeneration temperature and decreasing the initial pressure. The optimal condition for sorbent regeneration was at the temperature of 300 degrees Celsius and initial pressures of 0.35 bar. Kinetic studies of the sorbent regeneration were also conducted, and obtained a pseudo-second-order model to be the best-fit model.

Keywords: Carbon dioxide capture, regeneration, potassium carbonate, gamma-alumina, fluidized bed reactor.
1. Introduction

Climate change is one of the world’s most pressing challenges. Human activities are responsible for almost all of the increase in greenhouse gases in the atmosphere over the last 150 years. For the significant greenhouse gas, the global average concentration of carbon dioxide (CO$_2$) reaches 407.8 parts per million in 2018, up from 405.5 parts per million (ppm) in 2017. Therefore, this motivates many countries to turn their attention and be aware of the greenhouse gas effects in various fields. Since the United Nations Framework Convention on Climate Change (UNFCCC) has become the most recent and vital international convention to regulate greenhouse gas emission country by country [1], this convention reflects the urgency and high priority for solving climate change by reducing the CO$_2$ emission including prevention of the adverse effects to human beings.

CO$_2$ capture technologies are those to separate CO$_2$ from gases produced in electricity generation and industrial processes. These technologies can be classified into three groups, which consist of pre-combustion, oxyfuel combustion, and post-combustion technologies. The post-combustion technologies are the appropriate alternative since it has an excellent performance without the need to modify the considered process [2]. A variety of post-combustion CO$_2$ separation technologies are commercially available, for instance, liquid absorption, membrane separation, and dry solid adsorption. Among these, amine liquid absorption is the technology that has been widely implemented in industries. However, the amines have weaknesses in thermodynamic properties, corrosivity, and toxicity [3]. The membrane separation is expensive. Thus, dry solid adsorption becomes an attractive alternative for CO$_2$ capture since it is inexpensive and environmentally benign.

Potassium carbonate supported on gamma-alumina (K$_2$CO$_3$/γ-Al$_2$O$_3$) solid sorbent is an outstanding alkali metal comparing to the other alkali and alkali earth metals. The gamma-alumina enhances the adsorption of CO$_2$ on the sorbent by increasing specific surface areas to accommodate distributed active metal and improves the physical properties of the sorbent [4]. The adsorptive reaction of CO$_2$ by K$_2$CO$_3$/γ-Al$_2$O$_3$ is reversibly exothermic and occurs under atmospheric pressure, as shown in Eq. (1)

$$K_2CO_3(s) + H_2O(g) + CO_2(g) ⇌ 2KHCO_3(s) + ΔH \quad (1)$$

Sorbent regeneration can be performed by a temperature swing method or pressure swing method where the change of the process condition shifts the equilibrium backward, as shown in Eq. (1). The application of heat to raise the temperature is the conventional method to convert potassium bicarbonate (KHCO$_3$) to K$_2$CO$_3$, but this is an intensive energy-consuming process. On the other hand, the application of pressure reduction is a low energy-consuming process. When the pressure decreases, the reaction shifts backward to increase the mole of CO$_2$ and H$_2$O [5]. The spent sorbents then become active again. In reality, since the sorbent has alumina as a support material, the metal carbonate also reacts with the support materials and forms a complex compound. In this case, it was potassium dawsonite (KAl(CO$_3$)$_2$(OH)$_2$). The potassium dawsonite is a non-CO$_2$ adsorbing compound, and it is high thermal stability. Thus, to decompose the compound, it requires an even higher amount of energy to convert the spent K$_2$CO$_3$ sorbent back to the active K$_2$CO$_3$.

The prepared adsorbent, K$_2$CO$_3$ support on γ-Al$_2$O$_3$, was employed to adsorb CO$_2$ in the flue gas. The adsorption of CO$_2$ produced KHCO$_3$ and the complex compound or potassium dawsonite compound as the other product on the sorbent. Therefore, to fully recover spent solid sorbents with low input energy, the adsorption process has to be operated so that KHCO$_3$ is the only component formed. It is necessary to restrict the dawsonite formation in the CO$_2$ adsorption process [6].

The fluidized bed reactor was the system employed in this study for the adsorption reaction since it provides a high mixing rate, which causes the adsorbent particles and CO$_2$ to be more exposed and provides a constant temperature distribution throughout the reactor. The regeneration of the spent K$_2$CO$_3$/γ-Al$_2$O$_3$ sorbent via conventional heat regeneration and depressurization in a fluidized bed reactor has not yet been studied in detail.

The scope of this study was to investigate the effect of the regeneration temperature and initial regeneration pressure on the spent sorbent (K$_2$CO$_3$/γ-Al$_2$O$_3$) regeneration to determine the optimal condition for solid sorbent regeneration and to develop the kinetic model for the solid sorbent regeneration in the fluidized bed reactor.

2. Experimental Section

This experiment consisted of three parts. In the first part, the K$_2$CO$_3$/γ-Al$_2$O$_3$ adsorbents were synthesized by impregnation. Then, the 12% (v/v) CO$_2$ balanced with nitrogen (N$_2$) was passed through the steam generator and then entered the fluidized bed reactor where the CO$_2$ was adsorbed in a fluidized bed reactor. The second part involved the characterization of the fresh and spent K$_2$CO$_3$/γ-Al$_2$O$_3$ adsorbents. The last part was the in situ conventional heat regeneration and depressurized regeneration of the solid sorbents in the reactor.

2.1. Preparation of the K$_2$CO$_3$/γ-Al$_2$O$_3$ Adsorbents by Impregnation

The potassium-based solid sorbents used in this study were prepared by the conventional impregnation of K$_2$CO$_3$ onto γ-Al$_2$O$_3$ porous support as shown in Fig. 1. First, 5g of γ-Al$_2$O$_3$ were added to an aqueous solution containing 5g of K$_2$CO$_3$ in 25mL of deionized water and mixed using a solution shaker at room temperature and a rotational speed of 230 rpm for 24h. Then, the mixture was dried at 105 °C for 24 h in an oven. The dried sample
was grained and sieved for collecting different sizes of solid sorbent particles. The samples were calcined in a furnace at 200 °C with the temperature ramping rate at 3 °C/min for 4 h. At this stage, the solid adsorbents were ready for adsorption.

2.2. Characterization of the Fresh and Spent \( \text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3 \) Adsorbents

The nitrogen adsorption−desorption method was used to determine the Brunauer−Emmett−Teller (BET) surface area and total pore volume of the adsorbents using a Micromeritics ASAP 2020 apparatus. Before the measurement, the samples were degassed at 200 °C under vacuum for at least 2 h. Pore size distribution was calculated by a Barrett-Joyner-Halenda (BJH) method.

The amount of alkali metal impregnated on the \( \gamma\text{-Al}_2\text{O}_3 \) support was determined by X-ray fluorescence (XRF).

The chemical bonding of materials was examined using Fourier transform infrared spectroscopy (FTIR) over the range of 4000−500 cm\(^{-1}\).

The XRD analysis was performed to identify phases presented in the spent and regenerated adsorbents using X-ray diffraction (XRD) using Cu−K\( \alpha \) radiation at room temperature. The analysis was performed at a scanning rate of 0.02 °C/min in 20 range 10°−80°.

2.3. \( \text{CO}_2 \) Adsorption and Regeneration in the Fluidized Bed Reactor

Figure 2 shows a schematic diagram of the adsorption and regeneration processes used in this study. The 99.99 % \( \text{N}_2 \) (A) was fed for removing \( \text{CO}_2 \) that remained in the system. For the adsorption process, mixed gas with 12 ± 1% (v/v) \( \text{CO}_2 \) balanced by nitrogen (B) was fed and controlled by a mass flow controller (C). The mixed gas was first entered into the steamer (E) and then passed through the adsorbent in the glass column (H) with a flow rate of 0.8 L/min, maintained at a temperature of 60 °C and total pressure 1 atm. The regeneration process using conventional heat and depressurization was investigated as follows. The mass flow controller was closed, and the three-way valve was twisted to connect to a vacuum pump (D). The pressure of the glass column, which contained the spent sorbent, was reduced below 1 atm by the vacuum pump. After that, a circulating pump (G) was started. Finally, the heat was supplied to raise the temperature in the column. The amount of \( \text{CO}_2 \) in the exiting gas, temperature, and pressure which was released from the glass column, was then detected in real-time by an (I) \( \text{CO}_2 \) sensor, (J) temperature sensor, and (K) pressure sensor at a sampling rate of 10 samples/min. These data were collected by LabVIEW System Design Software (National Instruments) and recorded in the computer (L). The \( \text{CO}_2 \) concentration profile was recorded as a breakthrough curve and regeneration curve (M).

3. Results and discussion

3.1. Characterization of Adsorbents

Table 1 shows the BET surface area, pore-volume, pore size, and \( \text{K}_2\text{CO}_3 \) loading of the \( \text{K}_2\text{CO}_3 \), \( \gamma\text{-Al}_2\text{O}_3 \) and \( \text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3 \). The fresh \( \gamma\text{-Al}_2\text{O}_3 \) showed a surface area of 122.2 m\(^2\)/g, a pore volume of 0.225 cm\(^3\)/g, and pore size of 7.4 nm. The surface area and pore volume of the \( \text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3 \) decreased with an increase in the \( \text{K}_2\text{CO}_3 \) loading. The \( \text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3 \) showed a surface area of 41.5 m\(^2\)/g, a pore volume of 0.092 cm\(^3\)/g, and pore size of 6.4 nm. As a result, the adsorbents with support had higher surface area and porosity than those without.
support. That is because γ-Al2O3 has a high surface area and porosity, and it enhanced the distribution of K2CO3 on the support. The spent K2CO3/γ-Al2O3 showed a surface area of 37.1 m²/g, a pore volume of 0.085 cm³/g, and pore size of 6.4 nm. It indicates that surface area and pore volume slightly decreased compared with fresh K2CO3/γ-Al2O3 because the molecule of CO2 and H2O covered the adsorbent surface.

The potassium-based γ-alumina sorbents were analyzed with X-ray fluorescence analysis (XRF) to measure K2CO3 loadings.

It was found that the K2CO3 loading on the K2CO3/γ-Al2O3 was 40.83 wt%.

For spent K2CO3/γ-Al2O3 after regenerated at three different temperatures, viz., 100, 200, and 300 °C, the K2CO3 loadings on the adsorbent were 39.56, 38.54 and 38.19 wt%, respectively. From the experimental results, the weight of K2CO3 on the sorbent slightly changed when compared with the fresh K2CO3/γ-Al2O3. It indicates that the amount of K2CO3 in the adsorbent is not leached or lost during the operation.

Fig. 2. Schematic diagram of CO2 fluidization adsorption system and conventional heat - depressurized regeneration system used in this study for (A) N2 vessel, (B) Mixed CO2 vessel, (C) Mass flow controller, (D) Vacuum pump (E) Steamer, (F) Vessel (G) Circulating pump, (H) Glass column, (I) CO2 sensor, (J) Temperature sensor, (K) Pressure sensor, (L) Computer and (M) CO2 Concentration profile.

Table 1. The physicochemical properties of the solid sorbent.

| Sample                             | SBETa (m² g⁻¹) | Pore volumeb (cm³g⁻¹) | Pore sizec (nm) | Sextd (m²g⁻¹) | K2CO3 loadinge (wt%) |
|------------------------------------|----------------|-----------------------|-----------------|---------------|---------------------|
| K2CO3                             | 2.5            | 0.001                 | 2.0             | n.d.*         | 100                 |
| γ-Al2O3                            | 122.2          | 0.225                 | 7.4             | 45.8          | n.d.*               |
| K2CO3/γ-Al2O3-Fresh                | 41.5           | 0.092                 | 6.4             | 40.2          | 40.83               |
| K2CO3/γ-Al2O3-Spent                | 37.1           | 0.085                 | 6.4             | 35.9          | 40.41               |
| K2CO3/γ-Al2O3-Regen-100 °C         | 38.0           | 0.086                 | 6.5             | 36.4          | 39.56               |
| K2CO3/γ-Al2O3-Regen-200 °C         | 37.8           | 0.085                 | 6.4             | 36.3          | 38.54               |
| K2CO3/γ-Al2O3-Regen-300 °C         | 38.7           | 0.087                 | 6.5             | 37.4          | 38.19               |

*a n.d. = Not determined  
*b BET surface area  
*c Total pore volume  
*d Pore diameter calculated using the BJH method  
*e External surface area determined from t-plot curves  
*f X-ray Fluorescence  

N2 adsorption-desorption isotherm is shown in Fig. 3. The formation of the hysteresis loop of mesopore type
H3 was observed. Thus, all sorbents were mesopore type IV according to the International Union of Pure and Applied Chemist (IUPAC). Mesopores are compatible with the size of CO2 molecules, enhancing the physical sorption on its support framework. The fresh K2CO3-impregnated on the γ-Al2O3 support sorbent and the spent sorbents did not change the pore type. Hence, the change in the CO2 adsorption capacity was not likely to be caused by the change in surface area or pore type. The adsorption-desorption isotherms of the regenerated sorbents were similar to the fresh one and had only a slightly lower surface area than the fresh adsorbent [7].

The XRD patterns of fresh, spent, and regenerated adsorbents are shown in Fig. 4. Both K2CO3 and KAl(CO3)2(OH)2 phases were presented in the fresh adsorbents. For the fresh K2CO3-based adsorbents, the major diffraction peaks shown at 20 of 26.2, 30.0, 31.6, 31.6, 32.0, 34.0, 37.7, 38.8, 42.8, and 48.9 were assigned to K2CO3 of the monoclinic crystalline phase. While the peaks at 20 of 16.0, 21.8, 28.2, 29.7, 32.5, 35.9, and 41.5 were assigned to KAl(CO3)2(OH)2. Additional peaks at 2θ of 12.9, 24.9, 30.2, 31.5, 39.0, and 40.8 were assigned to KHCO3 [8].

The XRD peaks of spent and regenerated adsorbents confirmed the presence of KHCO3 and K2CO3 along with KAl(CO3)2(OH)2, respectively. The XRD pattern of sorbents after being regenerated at 100 °C had the peaks at 2θ of 34.26, 37.64, 39.49, 43.10, and 49.46, which were assigned to K2CO3, while peaks at 2θ of 16.45, 21.89, 28.16, 36.11, and 41.78 were assigned to KAl(CO3)2(OH)2.

After the regeneration at 200 °C, the major peaks of the XRD pattern shown at 2θ of 26.17, 29.96, 31.93, 33.96, 37.68, 42.89, and 49.09. They were assigned to K2CO3 while the peaks at 2θ of 16.37, 22.18, 28.24, 36.38, and 41.31 were assigned to KAl(CO3)2(OH)2 [9].

K2CO3/γ-Al2O3 after regenerated at 100 and 200 °C showed the presence of the same peak position of K2CO3 and KAl(CO3)2(OH)2, indicating that only KHCO3 was converted entirely to the K2CO3 and the bicarbonate commences decomposition temperature at 364 K [10]. After the regeneration at 300 °C only the K2CO3 peaks were observed in the XRD patterns [4]. Since KAl(CO3)2(OH)2 is a side product in the adsorption and preparation of adsorbent. The complex compound or Potassium dawsonite compound is produced by potassium aluminum oxide (KAlO2), potassium carbonate (K2CO3), and H2O, which consists of potassium (K), aluminum (Al), carbon (C), oxygen (O) and hydrogen (H) [9]. Also, the high thermal stability of dawsonite, high input energy are required for the regeneration process. The temperature to decompose the KAl(CO3)2(OH)2 is in the range of 270 - 350 degrees Celsius [6]. Furthermore, it is necessary to restrict the dawsonite formation.

The solid-state FTIR study was conducted for fresh, adsorbed, and regenerated sorbents, as shown in Fig. 5. The peaks that appeared between 1060 and 1506 cm⁻¹ were attributed to the C=O bond. For K2CO3, KHCO3, and KAl(CO3)2(OH)2 the peak appearing between the 740, 865 and 1101 cm⁻¹ region indicated the presence of CO3²⁻ ions. The peaks appearing between 995 cm⁻¹ indicated the presence of Al–OH tension. The peak that
appeared at 525 cm\(^{-1}\) reported the presence of the Al–O group. The peaks observed between 3404 cm\(^{-1}\) correspond to the O–H bond stretching band for all of these [11].

![FTIR spectra of different samples](image)

**Fig. 5.** FTIR spectra of (a) K\(_2\)CO\(_3\)/γ-Al\(_2\)O\(_3\)-Fresh, (b) K\(_2\)CO\(_3\)/γ-Al\(_2\)O\(_3\)-Spent, (c) K\(_2\)CO\(_3\)/γ-Al\(_2\)O\(_3\)-Regen-100 °C, (d) K\(_2\)CO\(_3\)/γ-Al\(_2\)O\(_3\)-Regen-200 °C and (e) K\(_2\)CO\(_3\)/γ-Al\(_2\)O\(_3\)-Regen-300 °C [V, γ-Al\(_2\)O\(_3\); ●, K\(_2\)CO\(_3\); ●, KHCO\(_3\); ■, KAl(3CO\(_3\)(OH)\(_2\))].

### 3.2. \(\text{CO}_2\) Adsorption Studies of K\(_2\)CO\(_3\)/γ-Al\(_2\)O\(_3\) Sorbents

A breakthrough curve was plotted in the term of \(\text{CO}_2\) concentration (%Volume) concerning time in the riser column, as shown in **Fig. 6**. The area under the curve could then be integrated to determine the \(\text{CO}_2\) capture capacity as mg-\text{CO}_2/g-K\(_2\)CO\(_3\) sorbent (or mg-\text{CO}_2/g-sorbent) using Eq. (2):

\[
q = \frac{MW_{\text{CO}_2}P_F}{RT m_{\text{adsorbent}}} \text{(area \% CO}_2) \quad (2)
\]

where \(q\) is the \(\text{CO}_2\) capture capacity (mg-\text{CO}_2/g-sorbent), \(MW_{\text{CO}_2}\) is the molecular weight of \(\text{CO}_2\), \(P_F\) is the total pressure, \(F\) is the inlet gas flow rate (L/min), \(R\) is the gas constant, \(T\) is the adsorption temperature and \(m_{\text{adsorbent}}\) is the mass of active sites on the sorbent (g), respectively.

In this study, the adsorption capacity was found to be 90.46 mg-\text{CO}_2/g-adsorbent. The result gave a similar \(\text{CO}_2\) capture capacity at about 84-92 mg \(\text{CO}_2/g\)-adsorbent of Jaiboon et al. [12]. Focusing on the 500 seconds of adsorption time, the \(\text{CO}_2\) concentration at the outlet of the column had returned to its initial feed concentration since the \(\text{CO}_2\) capture capacity of solid sorbent was entirely adsorption [13].

![Breakthrough curve](image)

**Fig. 6.** The breakthrough curve of \(\text{CO}_2\) adsorption.

### 3.3. Sorbent Regeneration Studies of K\(_2\)CO\(_3\)/γ-Al\(_2\)O\(_3\) Sorbents

The regeneration of spent sorbents is common practice in various industries where many sorbents are used, and they are easy to regenerate so that the costs due to process operation and waste disposal are reduced. In this research, two sorbent regeneration methods were employed, which were thermal regeneration and depressurization.

Thermal regeneration is a conventional method of sorbent recovery. Temperature swing adsorption is one technology that has been developed based on this approach. The technique gains heat from the adsorption process and then transfers heat to utilize in the regeneration process.[13] The heat treatment can reverse the reaction equilibrium, as shown in Eq. (1) and can bring back the reactants to the original form.

On the other hand, an application of pressure reduction is an alternative method for regeneration. This method consumes less energy, requires shorter regeneration time, and provides high homogeneity to the regenerated sorbent [14]. The % sorbent regeneration is calculated by Eq. (3):

\[
\% \text{Sorbent regeneration} = \frac{m_{\text{released CO}_2}}{m_{\text{adsorbed CO}_2}} \times 100 \quad (3)
\]

where \(m_{\text{released CO}_2}\) is the mass of \(\text{CO}_2\) desorption (mg-\text{CO}_2/g-sorbent) and \(m_{\text{adsorbed CO}_2}\) is the mass of \(\text{CO}_2\) adsorption (mg-\text{CO}_2/g-sorbent), respectively.

To study the effect of regeneration temperature on the sorbent regeneration, the spent sorbents were heated at three different temperatures, viz., 100, 200, and 300 °C. Figure 7 displays the % sorbent regeneration at these three different temperatures in the fluidized-bed adsorption-regeneration process.
As shown in the figure, as the temperature for the regeneration increases, the % sorbent regeneration also increases from 43.91% to 67.91%. This is due to the easier decomposition of KHCO₃ (saturated adsorbent) at a higher temperature. It is interesting to note that even at 100 °C, appreciable regeneration of the sorbent (43.91%) occurred and that the % sorbent regeneration increased to 57.14% and 67.91% at higher temperatures (200 and 300 °C), respectively.

It was also found that the sorbent was almost completely regenerated at 350 °C, as displayed by the XRD analysis. For the regeneration at 200 °C, the phases of K₂CO₃ and KAl(CO₃)₂(OH)₂ were still observed. It indicated that only KHCO₃ was entirely converted to the K₂CO₃. However, when the regeneration was conducted at 300 °C, only the peaks of K₂CO₃ were observed in the XRD patterns. It is indicated that KAl(CO₃)₂(OH)₂ was decomposed completely. This confirms that the spent sorbent in this study was completely regenerated [15].

To study the effect of pressure on the sorbent regeneration, the spent sorbents were regenerated at three different pressures, viz., 0.35, 0.61, and 0.88 bar. As shown in Fig. 8, the increase of regeneration initial pressure from 0.35 bar to 0.88 bar reduced the sorbent regeneration from 83.29% to 31.85%. At the 0.61 bar, the regeneration was found at 53.80%. Due to the unequal moles of the gas phase between the reactant and product, as shown in Eq. (1). When the system pressure was reduced, the reaction equilibrium would be shifted backward to increase the moles of gas species (CO₂(g) and H₂O(g)) and the pressure in the system [15]. The pressure reduction will initially cause a pressure gradient between the inside and outside of the sorbent pores. The external pressure is less than the internal pressure within the pores. This pressure difference led to the release of unreacted H₂O on the inner surface and then the CO₂ adsorbed on the sorbent surface. When the initial regeneration pressure was 0.35 bar, the pressure driving force between the outer and inner pores was higher than that when the initial regeneration pressure at 0.88 bar.

Consequently, the water in the pores and carbon dioxide would be pulled out of the pores with a stronger force (with greater pressure differential). Whereas initial regeneration pressure at 0.88 bar resulted in the water, carbon dioxide, or products in the pores would be pulled out of the pores with a weaker force. So, the sorbent regeneration at 0.88 bar is less than the sorbent regeneration at 0.35 bar [14].

Consider the effects of regeneration temperatures and pressures on % sorbent regeneration, as shown in Figs. 7 and 8. It can be noted that the regeneration temperature shows a positive influence on the % sorbent regeneration, while the regeneration pressure shows a negative impact. Due to the physical phenomenon, the increase in temperature will raise the kinetic energy of the gas molecules. The high kinetic energy molecules can easily escape from the pores of the sorbent; then, the spent sorbents become active again [16].

3.4. Optimal Condition of K₂CO₃/γ-Al₂O₃ Sorbents Regeneration

The response surface method was implemented to determine the optimal condition of the operating sorbent regeneration process. The method uses a statistical model and explores the relationships between several input variables and one or more response variables. Typically the response variables will be plotted against several independent variables. The contour of the response surface corresponds to the height of the response surface, which can relate to the operating parameters [17]. Figure 9 shows the response surface where % solid sorbent regeneration (Y) was plotted as a function of the regeneration temperatures and initial regeneration pressures. The maximum solid sorbent regeneration was
found at a high regeneration temperature (300 °C) and initial regeneration pressures. (0.35 bar). Due to the curvature of the response surface, the solid sorbent regeneration was improved by increasing regeneration temperature and the decrease of initial regeneration pressures. The regeneration process is an endothermic reaction. The energy is absorbed to break down the bonds of the adsorbed species. The products convert to reactants. In this reaction, the reactants have lower energy than the products when increasing the temperature for regeneration [18]. Resulting in gas molecules had higher kinetic energy. Then, the water or impurities inside the structure of the porous can easily exit from the pores. While the initial regeneration pressure decreases, the reaction can shift backward to increase the moles of CO₂, H₂O, and K₂CO₃ [19].

\[ q_t = q_e[1 - \exp^{-k_1t}] \]  
\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]

where \( q_e \) is the quantity regeneration at equilibrium (mg/g), and \( q_t \) is the quantity regeneration at time \( t \) (mg/g). \( k_1 \) is the rate constant for the pseudo-first-order sorption (min⁻¹). A linear graph with a negative slope is expected from the plot of \( \ln(q_e - q_t) \) against \( t \) at different concentrations, \( k_1 \) and \( q_e \) can then be obtained from the slope and intercept, respectively.

The pseudo-second-order kinetic model [21], presented in Eq. (6) and (7):

\[ q_t = \frac{k_2q_e^2t}{1 + k_2q_e t} \]  
\[ \frac{t}{q_t} = \frac{1}{k_2q_e} + \frac{t}{q_e} \]

where \( k_2 \) is the rate constant of the pseudo-second-order kinetic equation in mg/g min⁻¹, \( q_e \) is the maximum regeneration capacity in mg/g, and \( q_t \) (mg/g) is the amount of regeneration at time \( t \). A plot of \( t/q_t \) against \( t \) was depicted. Then \( q_t \) and \( k_2 \) can be calculated from the slope and intercepts of the plot.

Equations (8) and (9) express the nonlinear and linear forms of the Avrami kinetic model, respectively [22].

\[ q_e[1 - \exp^{-K_{AV}AV}] \]  
\[ \ln[\ln(1 - \alpha)] = n_{AV}K_{AV} + n_{AV} \ln t \]

\( K_{AV} \) is the Avrami constant and \( n_{AV} \) is the Avrami model exponent of time related to the change in the mechanism of adsorption. \( K_{AV} \) and \( n_{AV} \) can be obtained from the intercept and slope of the plot of \( \ln[\ln(1 - \alpha)] \) against \( \ln t \).

Calculated parameters of various kinetics models and the validation results were reported in Table 3. This table shows the corresponding kinetic parameters of sorbent regeneration at a regeneration temperature of 300 °C and regeneration initial pressure of 0.35 bar. The best-fit kinetic studies of the sorbent regeneration were considered from the correlation coefficient \( (R^2) \) and % error. The equilibrium rate constant of the pseudo-first-order sorption \( (k_1) \) was observed to be 0.0096 min⁻¹. The equilibrium rate constant of the pseudo-second-order model \( (k_2) \) was 0.000075 mgCO₂/gₐₐ₃ min⁻¹, and 0.010225 min⁻¹ were assigned to the rate constant of the Avrami model.

In the case of the pseudo-first-order model, the \( R^2 \) value was found as 0.9813. While the \( R^2 \) value of the pseudo-second-order model was 0.9911, and the \( R^2 \) value for the Avrami model was 0.9606. The value of % error of the pseudo-first-order model, the pseudo-second-order model, and the Avrami model were 2.26, 1.60, and 4.41%, respectively.
It was observed that among the three models, the pseudo-second-order equation gave the best fit to the experimental data since its correlation coefficient ($R^2$) was very close to unity [23]. The value of % error was also lower than those of the pseudo-first-order model and Avrami model.

These results are suggested that the pseudo-second-order kinetic model provides the best-fit model on sorbent regeneration at regeneration temperature 300 °C and regeneration initial pressure 0.35 bar. This model represents adsorption at high adsorbate loadings [24]. The adequacy of the pseudo-second-order kinetic model can be used to describe the behavior of chemisorption or CO$_2$ adsorption on potassium carbonate supported on gamma-alumina (K$_2$CO$_3$/$\gamma$-Al$_2$O$_3$) [25]. Besides, this model can be used to describe the chemical reaction backward to the reactant.

4. Conclusions

In this study, solid-sorbent regeneration using potassium carbonate supported on gamma-alumina (K$_2$CO$_3$/$\gamma$-Al$_2$O$_3$) in a fluidized bed reactor was investigated. The spent adsorbent after CO$_2$ adsorption can be regenerated by heat treatment and depressurization. However, for the prepared adsorbent, the exothermic equilibrium reaction was not only converted K$_2$CO$_3$ to KHCO$_3$, but it also produced the byproduct potassium dawsonite compound (KAl(CO$_3$)$_2$(OH)$_2$), which was the drawback for the regeneration. The high input energy is required in the regeneration process with KAl(CO$_3$)$_2$(OH)$_2$. It thus was necessary to restrict the dawsonite formation. The XRD analysis confirmed only the K$_2$CO$_3$ peaks with the regeneration temperature of 300 °C. Focusing on the main effect of operating parameters, regeneration temperature promoted a positive trend to sorbent regeneration.

In contrast, the initial regeneration pressure shows a negative trend. The initial regeneration pressure expressed a higher impact on the regeneration than the regeneration temperature. However, at high temperatures, the dawsonite complex would be completely decomposed, and the sorbent returned to the original form. Therefore, the optimal condition for sorbent regeneration in this study was at a temperature of 300 degrees Celsius and initial pressures of 0.35 bar. Kinetic studies of the sorbent regeneration were also conducted and obtained a pseudo-second-order model as the best-fit model.

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