

Preliminary Study of Chitosan Coating Silica Derived from Geothermal Solid Waste

S. Silviana*, Annisya Noorpasha, Muhammad Miftahur Rahman

Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof. Sudarto SH Kampus Tembalang, 50275 Semarang, Indonesia

Received February 25, 2020; Revised May 20, 2020; Accepted May 29, 2020

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Abstract Purpose: The purposes of this research are to study preparation of chitosan coating silica aerogel derived from solid geothermal waste as adsorbent of CO₂ and CH₄ separation and to study CO₂ adsorption kinetics on chitosan coating silica aerogel by Pseudo First Order and Second Order methods. Methodology was conducted consisting of several steps. First, geothermal silica was leached with H₂SO₄ 20% 1: 5 w/v. Then, chitosan was added into silica with ratio of 1.3: 10, 1.5: 10, 1.9: 10, 2.2: 10, and 2.4: 10 w/v. Isopropyl alcohol was added to silica sol to form hydrogel and remained in gelation. The addition of n-hexane was carried out to occur the solvent exchange process. The gel was dried by ambient pressure drying method. CO₂ in biogas was removed of using 20 g of adsorbent chitosan coating silica aerogel. The experimental adsorption kinetics analyzed by both pseudo first and second order kinetics model. Results showed that impurities in geothermal silica required to be purified and it can be synthesized into silica aerogel. The remaining geothermal can act as adsorbents to silica aerogel coated with chitosan by using packed column. The data obtained was kinetics data from the pseudo first and second order method. The silica from solid geothermal waste has the potential as CO₂ adsorbent. Applications/ Originality/ Value: It was confirmed that silica from solid geothermal waste can be used as CO₂ adsorbent. Therefore, the improvement of innovation in the future of this research is to prepare chitosan coating silica aerogel as CO₂ adsorbent.

Keywords Chitosan, CH₄, CO₂, Geothermal Silica, Kinetics, Pseudo First Order, Pseudo Second Order

lower (BPPT, 2017). It is predicted that in 2025 - 2050 Indonesia will become an importer of oil and natural gas (BPPT, 2017). Nowadays, diversification of renewable energy has been strived, such as bioethanol (Melikoglu & Turkmen, 2019), biodiesel (Gozmen Şanlı, Uludamar, & Özcanlı, 2019), and biogas (Khalil, Berawi, Heryanto, & Rizalie, 2019). However, the process of utilizing these fuels still has limitations in the refining process, both in terms of separation efficiency and costs used, especially for the use of biogas.

Biogas produced from biomass fermentation has been widely used. However, the biogas calorific value is still below the standard (Al Mamun & Torii, 2017) and the carbon dioxide (CO₂) gas content in biogas is still 25-45% so that it can cause corrosion (Kusrini et al., 2017). In addition to reducing the calorific value, the presence of CO₂ gas also makes the biogas operation process uneconomical. Therefore the process of purifying biogas from CO₂ must be carried out to increase and maximize the use of biogas.

Several processes have been developed for biogas purification to achieve high biogas calorific values, such as absorption process using amine solvent (Hairul, Shariff, & Bustam, 2017), membranes (Kusworo, Qudratun, Utomo, Ramadhan, & Indriyanti, 2018), and adsorption using zeolites (Chen et al., 2017). The weaknesses of these processes are that they require high energy, expensive costs for the regeneration process, low adsorption capacity, and are corrosive (Kong, Shen, Cui, & Fan, 2015).

To cover up the existing process, research has been developed on polyethyleneimine (PEI) which has been synthesized and shows largest CO₂ adsorption capacity of 93.4 mg CO₂/g adsorbent at 1 atm pressure & 25-100°C temperature. However, aminated silica synthesis implicates toxic 3-aminopropyltriethoxycylcate reagents that can damage human mucous membranes and respiratory tracts, and toluene usage as solvent in an amount 100 times the dissolved silica mass. Exaggerated uses of aromatic

1. Introduction

The availability of oil and gas in Indonesia is getting

solvents and toxic reagents have to be evaded (Zhang et al., 2007). Several studies have covered this weakness by replacing amine compound with chitosan.

The use of chitosan as an adsorbent has been widely researched, one of which is Sneddon et al. (2015) which has coating chitosan into silica gel and has reached an adsorption capacity of $123 \text{ m}^2\text{g}^{-1}$ with chitosan composites of 19% w. Nevertheless, the low capacity is related to silica gel's surface area, which is only $186\text{m}^2\text{g}^{-1}$, too low for notable adsorption. To maximize chitosan's potential as CO_2 adsorbent, a much higher amount of supporting material is needed. Therefore, adsorbents such as silica aerogel can be used to overcome difficulties in terms of biogas purification, non-toxic, easily regenerated, and have higher porosity.

Silica aerogel is a material with a high specific surface area, high porosity, low density, and easily regenerated (de Fátima Júlio, Soares, Ilharco, Flores-Colen, & de Brito, 2016). In the study of Feng et al. (2018), silica aerogel has a surface area of $945.8\text{m}^2\text{g}^{-1}$ so it has potential to be an adsorbent for effective purification of CO_2 in biogas. However, the application of silica aerogel as an adsorbent for biogas purification is limited due to the high cost of manufacture so it is necessary to modify the porosity to maximize the use of silica aerogel.

Porosity is an important property for adsorbent. Distribution of pore size, surface area and pore volume can involve the dimensions and interactions of surface and gas. Therefore, porosity can play an important role in gas mixture separation (Yi et al., 2015). Modification of silica aerogel porosity has been carried out using 1N HCl volume variation and Cetyl trimethylammonium bromide (CTAB) surfactant to produce mesoporous silica aerogel with porosity of 12 nm and 2.9 nm (Lee et al., 2017; Vazquez, Gonzalez, Ferrari, & Castro, 2017). Silica aerogel's porosity can be engineered so silica aerogel can be more selective when it functions as adsorbent.

Thus, the innovation of this research is the development of chitosan coating silica aerogel adsorbent as a CO_2 purification adsorbent in biogas. Different from previous studies, chitosan coating silica aerogel has high selectivity, good thermal stability, and is easily regenerated. This is expected to increase the kinetics of adsorption on CO_2 so it can be used to reduce the level of CO_2 gas in biogas. In addition, with the modification of porosity and high surface area in silica aerogel coated with chitosan, the capacity to capture CO_2 will increase. This study also utilizes silica aerogel material made from silica from geothermal solid waste in Dieng. Geothermal silica as an effort to create products that have high economic value to waste utilization, it is expected that the coating of chitosan with silica aerogel and modified porosity with HCl can produce sustainable adsorbent for the purification of CO_2 in biogas that is effective, energy efficient, easily regenerated, and preserves the environment.

The purposes of this research are to study the synthesis

of chitosan coating silica aerogel made from solid geothermal waste in Dieng as adsorbent for separating CO_2 and CH_4 , and to study CO_2 adsorption kinetics on chitosan coating silica aerogel by Pseudo First Order and Pseudo Second Order methods.

2. Material and Method

Material

Geothermal solid waste from Dieng Indonesia, Sulfuric Acid (H_2SO_4), Sodium Hydroxide (NaOH) Hydrochloric Acid (HCl), n-Hexane and IPA were procured from p.a Merck, chitosan was delivered from CV Nura Jaya, Methane (CH_4) and Carbon Dioxide (CO_2) were supplied from PT Samator Surabaya (p.a Merck), and Aquadest.

Method

Adsorbent preparation

Dieng geothermal silica sample was dried at 110°C for 24 hours, followed by leaching process for 1 hour 45 minutes at 100°C with a ratio of silica and H_2SO_4 20% 1: 5 w/v. This was done to remove organic impurities and metals in Dieng geothermal silica. Second, washing geothermal silica solution using aquadest to pH 7. Drying of sample is carried out at a temperature of 105°C to a constant weight using a vacuum oven to purify silica powder. To make soles, 10 grams of fine granules from geothermal silica were extracted in 100 ml of NaOH 6N for 1 hour under 98°C heating. Then the mixture was cooled down to 30°C . Samples were filtered using filter paper (whatman 41), the results of this filter in the form of residues namely solid impurity and filtrate in the form of sodium silicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$). To form gelation, the filtrate that has been obtained is cooled to room temperature and stirred with magnetic stirrer for 30 minutes. The filtrate was titrated with HCl 1N to pH 7 to produce silica gel. The gel is aged for 18 hours at room temperature, then filtered. Then, chitosan was added with silica and chitosan ratio of 1.3: 10, 1.5: 10, 1.9: 10, 2.2: 10, and 2.4: 10 w/v (Sneddon, Ganin, & Yiu, 2015). Samples were washed with distilled water for 5 times and IPA (60 ml) was added to silica sol to form hydrogel and gelled for 10 seconds. After the formation of hydrogels, the addition of n-hexane is carried out to occur the solvent exchange process. This is done for surface modification of the hydrogel with the ratio of hydrogel and n-hexane 0.75 from a base of 60 ml water glass. Then it continued with aging for 3-5 hours (Lee et al., 2017). A mixture of solutions containing silane and solvent agents. The gel is dried by Ambient Pressure Drying method to evaporate the liquid in a vacuum oven at a temperature of 70°C for 1 hour and 150°C for 1 hour until dry to evaporate the liquid to produce chitosan coating silica aerogel (Lee et al., 2017).

Adsorbent Test

The chitosan coating silica aerogel was measured by weight before being put into the column. After that, put in 20 gram chitosan coating silica to packed column. Then, the flow of methane and carbon dioxide gas each flowed at a rate of 600ml/min. Then the gas that had been mixed was regulated its flow velocity with variations of 100 and 500 ml/min seen through a flow meter. The gas mixture was flowed into the adsorption column containing chitosan coating silica aerogel as an adsorbent of CO₂. After the gas was flowed, the chitosan coating silica aerogel was measured by weight until there was no change in the weight of chitosan coating silica aerogel and the equilibrium time was obtained. This showed that the adsorption had reached saturation so that the adsorption equilibrium time was obtained (Kusrini et al., 2017).

Analysis of CO₂ Adsorption Kinetics

Pseudo first and second order models can be utilized to evaluate the kinetics of gas adsorption on silica aerogel (Loganathan et al., 2014).

A. Pseudo first order

Based on equation (1), q_t (mmol/g) and q_e (mmol/g) indicate the amount of the adsorbed CO₂. q_e can be obtained when the equilibrium of the weight of silica aerogel after CO₂ gas flowed under conditions of constant temperature and pressure. Whereas q_t is obtained when silica aerogel absorbs CO₂ gas at a certain time by measuring its weight. Weight difference (ΔW) will get the value of q_e and q_t . k_f (s⁻¹) indicates first order constants (Loganathan, et al., 2014)

$$\frac{dq}{dt} = k_f(q_e - q_t) \quad (1)$$

To get the k_f value, boundary condition (namely $t=0$, $q_t=0$, and $t=t_{\infty}$, $q_t=q_e$) is integrated to equation (1), so k_f is obtained (Ghrab et al., 2017).

$$q_t = q_e(1 - e^{-k_f t}) \quad (2)$$

B. Pseudo second order

The pseudo-second order model is based on the hypothesis that the rate of adsorption is related to the square of the number of vacant adsorption sites linearly (Kamal et al., 2017), therefore the rate of kinetic can be showed as:

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \quad (3)$$

q_e can be obtained when the equilibrium of the weight of silica aerogel after CO₂ gas flowed under conditions of constant temperature and pressure. Whereas q_t is obtained when silica aerogel absorbs CO₂ gas at a certain time by measuring its weight. Weight difference (ΔW) will get the value of q_e and q_t . The value of k_s (g mmol⁻¹s⁻¹) is the constant of second order rate. To get k_s value by applying and integrating the boundary conditions $t=0$, $q_t=0$, and $t=t_{\infty}$, $q_t=q_e$ in equation (3) turns into:

$$q_t = \frac{q_e^2 k_s t}{1 + q_e k_s t} \quad (4)$$

The values of k_s for all analyzed temperature and pressure conditions are gained from equation (4).

An error function from the assigned standard deviation is determined by a method expressed in the literature to assume the exactness of the fit of the kinetic models (Loganathan et al., 2014),

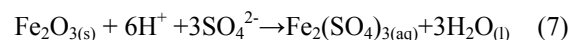
$$\Delta q(\%) = \sqrt{\frac{\sum[(q_{exp} - q_{model})/q_{model}]^2}{N-1}} \times 100\% \quad (5)$$

Δq (%) is the defined standard deviation, and q_{exp} & q_{model} are the calculated and experimental number of the adsorbed CO₂, and number of available data points in each isotherm is described as N (Loganathan et al., 2014).

3. Result and Discussion

3.1. Preparation of Silica Purification

Silica waste geothermal has high metal oxide content as can be seen in Fig. 1. This must be removed because it will decrease the quality of pure silica and reduce the metal impurity content. One of the standard specifications required in Na₂SiO₄ is to contain silica of approximately 97% (Ranawat, 2000). Purification of metal oxide particles contained in geothermal silica can be reduced using acid solution (Anas Boussaa, Kheloufi, Boutarek Zaourar, & Bouachma, 2017; Purnomo, Dalanta, Oktaviani, & Silviana, 2018). Research using silica purification with acid has been investigated (Boussaa et al., 2017). The purification of geothermal silica using H₂SO₄ solution can be seen in Fig. 1, and the results showed that the optimum silica product was produced from purification using 20% v/v H₂SO₄ with silica content of 98.2% in table 1. The reaction between H₂SO₄ and metal oxide caused damage to ionic bonds in metal compounds with oxygen. SiO₄²⁻ ions are highly reactive to metals, especially alkali metals and from transition groups such as Fe, Ni, Cu, Pb and others. These ions will bind the impurities found in the sample to form sulfate salts from metals. SO₄²⁻ ions bind to metal compounds to form sulfate metal compounds when the H⁺ ion bonds with oxygen to produce H₂O compounds. The characteristics of these two ions are interrelated so that they can reduce the metal content in silica. (Fraenkel, 2015). The reactions that occur in metal oxides can be seen in these following equations:



Silica produced with purification using H₂SO₄ 20% has silica content of 98.2%. Impurity compounds and metal oxides are very low with Mn, Fe, and Ca levels respectively 0.066, 0.531, 0.95%. This shows that silica from geothermal solid waste can be synthesized to be developed as a material for making silica adsorbent.

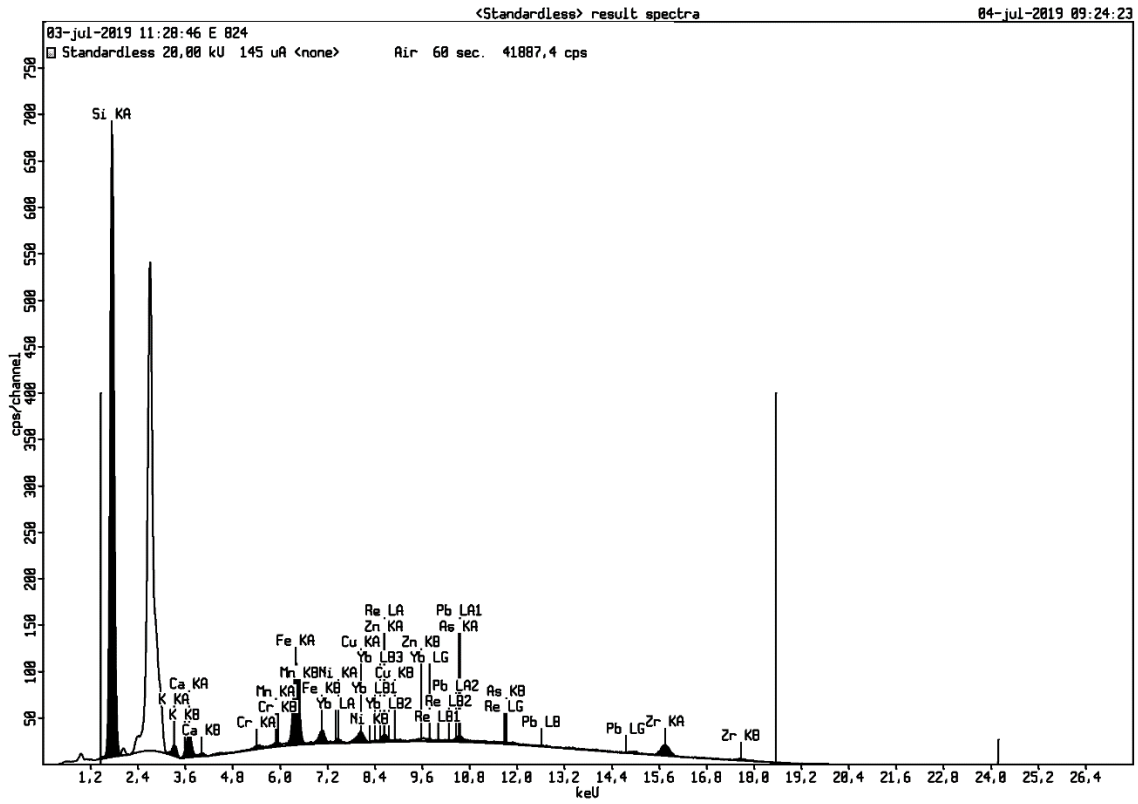


Figure 1. XRF spectra of geothermal silica prior to leaching process

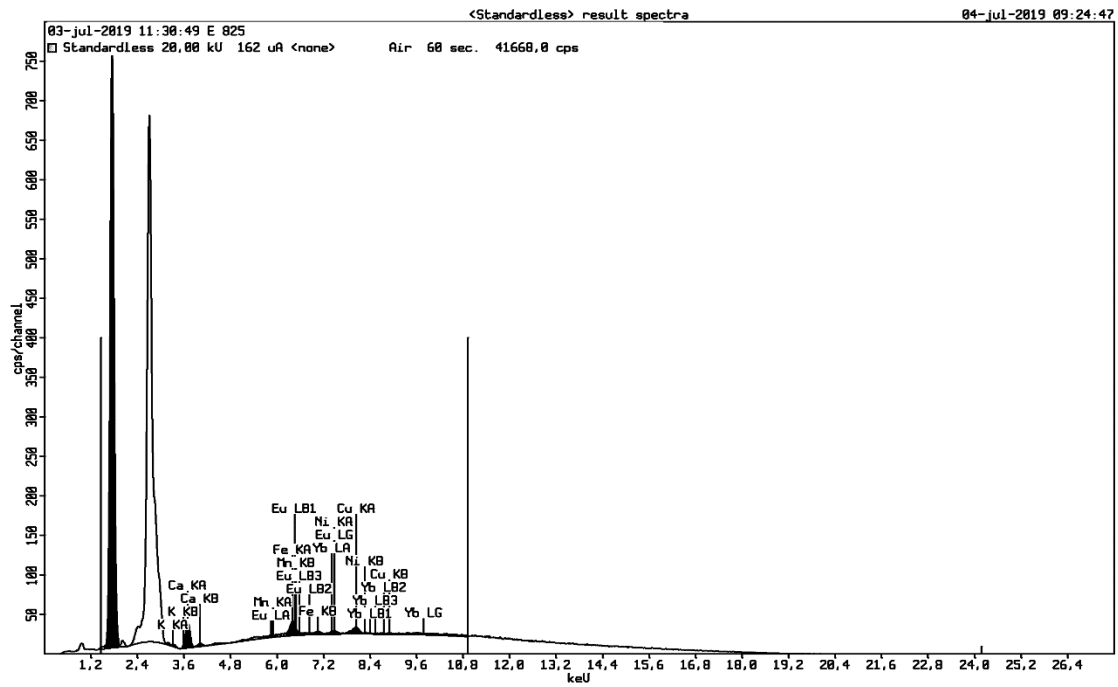


Figure 2. XRF spectra of geothermal silica post to leaching process

Table 1. XRF Analysis of Geothermal Silica

Element	Before Purification (%)	Element	After Purification (%)
Si	86.30	Si	93.20
Sc	0.11	Mn	4.40
Nd	12.00	Mg	0.59
Ca	1.10	Ca	0.92
Cr	0.95	Cr	0.88

3.2. Silica Aerogel Synthesis

The schematic diagram of silica aerogel preparation is shown in Fig. 3. Synthesis of silica aerogel ensued through the sol-gel stage where contact between silica and NaOH formed a solution of Na₂SiO₃ precursor replacing the Si-OH silanol group into Si-ONa ionic bonds. In this manner, Na₂SiO₃ dissolved in water and later subjected to

hydrolysis to transform into silicic acid Si(OH)₄ through the addition of HCl. The polycondensation of Si(OH)₄ caused the formation of colloidal spherical silica with hydroxyl groups. Then, silica hydrogel bonding siloxane (Si-O-Si) groups was formed by inducing polycondensation by adding IPA. After washing and drying at atmospheric pressure, silica aerogel was obtained as the final product. Several studies have succeeded in synthesizing aerogel under atmospheric conditions (Feng et al., 2018; Lee et al., 2017). Therefore ambient pressure drying conditions can be used to produce silica aerogel. The research that has been done obtained surface area and pore volume respectively 819 m²/g, 12.00 nm and 945,8 m²/g, 3.8 nm (Feng et al., 2018; Lee et al., 2017).

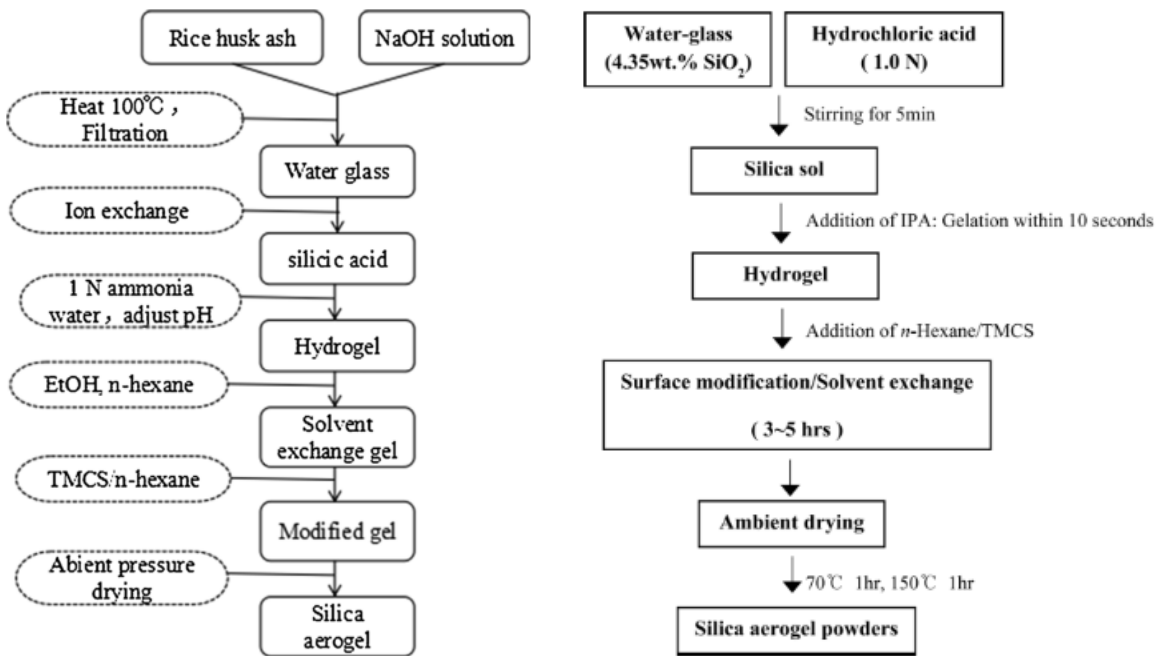
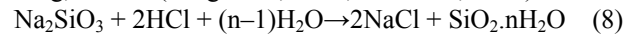


Figure 3. Flowchart for synthesis of water glass to silica aerogel (Feng et al., 2018; Lee et al., 2017)

3.3. Adsorbent Column Preparation for Biogas Purified

Figure 4. shows an experimental schematic for CO₂ purification with a fixed-bed two columns (Kusrini et al., 2017). The size of the fixed-bed column adsorption is 15 cm in length and 0.8 cm in diameter. Biogas is used from the Palm Oil Mill Effluent (POME). This research uses zeolite (2M) adsorbent coated with 2.5 g chitosan. The formula is shown in table 1. Surface areas are 39.06 and 8.25 m²/g. While the average adsorption capacity is 8.5 nm. The results obtained are zeolite (2M) coated with chitosan that can absorb ~ 83% CO₂ adsorption. This shows that the amine group contained in chitosan is capable in binding CO₂ from biogas from POME.

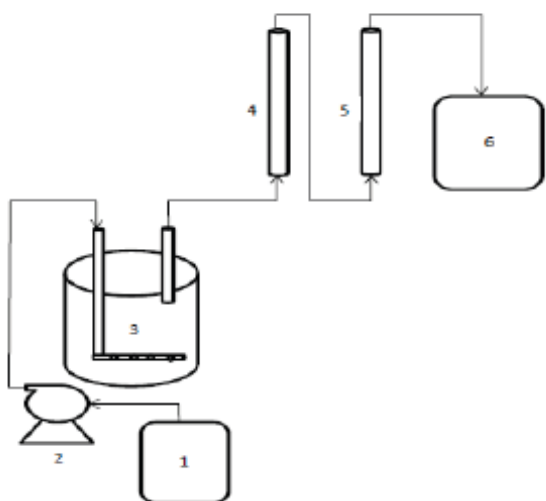


Figure 4. Schematic process for purification of biogas with zeolite/chitosan (Kusrini et al., 2017)

Table 2. Elemental analysis of zeolite coated chitosan (Kusrini et al., 2017)

Element	%weight composition
C	4.23
O	50.68
Na	2.41
Al	6.93
Si	30.94
K	1.85
Ca	1.24
Fe	1.71
Si/Al Ratio	4.31

According to (Kusrini et al., 2017; Lee et al., 2017), the required silica weigh is 30.94% wt and 4.35% wt. Whereas the geothermal solid waste silica shows a relatively high Si content of 98.2% as shown in Figure 5. This shows that geothermal solid waste has the potential to be developed as a source of silica as a material for making CO₂ adsorbent.

Therefore, the innovation is to use silica sources from

geothermal waste. Adsorbent used in this research denoted as chitosan coating to silica aerogel. The schematic process for further research is shown in Fig. 5. The height of the packed column adsorption with the length is 15 cm and the diameter is 5 cm. The biogas used is artificial biogas, i.e. mixture of methane (70%) and carbondioxide (30%).

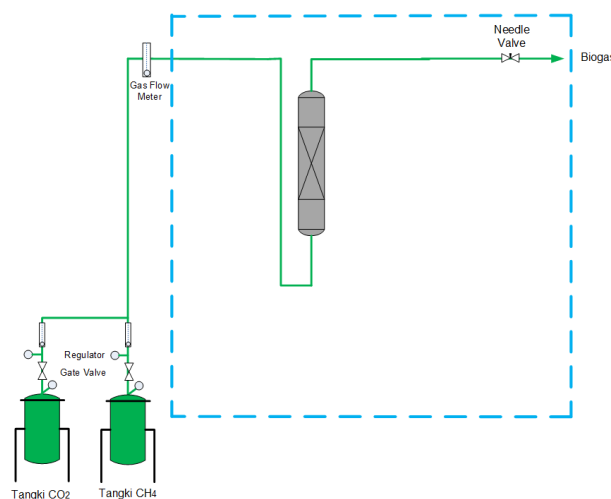


Figure 5. Proposed schematic process for purification biogas with silica aerogel coated chitosan

3.4. Response Data of Kinetics Study

The gas adsorption kinetics in silica aerogel can be calculated by the pseudo first and second order (Loganathan et al., 2014).

A. Pseudo First Order

The Calculation of adsorption kinetics with equations (9):

$$\frac{dq}{dt} = k_f(q_e - q_t) \quad (9)$$

q_e (mmol/g) and q_t (mmol/g) represent the number of the adsorbed CO₂. q_e can be obtained when the equilibrium of the weight of silica aerogel after CO₂ gas flowed under conditions of constant temperature and pressure after silica aerogel adsorbing CO₂ gas at a certain time. k_f (s⁻¹) indicates the constant of first order (Loganathan et al., 2014). After equation (9) is integrated with boundary conditions ($t=0, q_t=0, t=t, q_t=q_t$), equation (10) is gained.

$$q_t = q_e(1 - e^{-k_f t}) \quad (10)$$

The value of k_f for adsorption of CO₂ on silica aerogel under various temperature and pressure is obtained from equation (10) (Loganathan et al., 2014).

B. Pseudo second order

Adsorption kinetic rate can be showed as equation (11):

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \quad (11)$$

The value of q_e and q_t will be determined by weight difference (ΔW). k_s ($\text{g mmol}^{-1} \text{ s}^{-1}$) indicates the constant of second order rate. After equation (11) is integrated with boundary conditions ($t=0$, $q_t=0$, $t=t\infty$, and $q_t=q_e$), equation (12) is gained.

$$q_t = \frac{q_e^2 k_s t}{1 + q_e k_s t} \quad (12)$$

the values of k_s for entire evaluated temperature and pressure conditions are gained based on equation (12) (Loganathan et al., 2014).

4. Conclusions

The content of geothermal silica waste still contains a lot of impurities, so it needs to be purified and it can be synthesized into silica aerogel. The remaining geothermal can act as adsorbents to silica aerogel coated with chitosan by using packed column. The data obtained is the equation of kinetic data from the differences in the weight of silica that has adsorbed CO_2 . This shows that silica from geothermal waste has the potential as a CO_2 capture. Therefore, the improvement of innovation in the future of this research is to prepare chitosan coating silica aerogel to adsorbent.

Acknowledgment

Much appreciation goes to the Advanced Materials Laboratory (AMaL) and colleagues who have provided support throughout the course of this study.

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