

# REMOVAL OF H<sub>2</sub>S FROM BIOGAS USING SOYBEAN-BASED INK WASTE FROM PRINTING INDUSTRIES AS AN ADSORBENT

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## Abstract

In this study, the adsorption capacity of soybean-based ink waste adsorbent to remove H<sub>2</sub>S from biogas was studied. First, the physical and chemical properties of the soybean-based ink waste adsorbent were determined. The moisture contents and iodine numbers at different pellet sizes varied from 5%-9% and 956.00-1237.00 mg/g, respectively. The high adsorption efficiency could be provided by its high iodine number but it could be reduced by its middle moisture content. Secondly, the effect of the pellet size and initial H<sub>2</sub>S concentration on the adsorption capacity was investigated. Breakthrough curves for different pellet sizes showed that soybean-based ink waste adsorbent presented a high adsorption capacity for H<sub>2</sub>S but very low adsorption capacity for CH<sub>4</sub> and CO<sub>2</sub>. The smaller pellet sizes' adsorbent showed a higher removal efficiency than the largest pellet size owing to its larger surface area. Moreover, the breakthrough capacity for the initial H<sub>2</sub>S concentration of 1,040 ppm and 9,982 ppm was estimated to be 18.42 mg/g and 28.44 mg/g, respectively. A higher initial H<sub>2</sub>S concentration resulted in the higher breakthrough adsorption capacity. Finally, the SEM/EDX results showed significant changes in the morphological and chemical properties after the adsorption process. Therefore, soybean-based ink waste material could be used as a good alternative adsorbent for removing H<sub>2</sub>S from biogas.

**Keywords:** Soybean-based ink waste, adsorbent, biogas, hydrogen sulfide

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## Introduction

Biogas, a potential renewable source for heat and electricity for the foreseeable future, is a mixture of different gases produced by the biological decomposition of organic matter in the absence of oxygen. Biogas mainly consists of methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and trace amounts of other gases such as hydrogen sulfide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>), hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>), and carbon monoxide (CO). The presence of elevated concentrations of H<sub>2</sub>S is problematic because of its high corrosiveness and toxicity (Heubeck and Craggs, 2010) as well as its serious environmental concerns due to the oxidation to sulphur dioxide (SO<sub>2</sub>) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). Several physicochemical processes have been studied in order to remove H<sub>2</sub>S from biogas, such as the absorption process (Horikawa *et al.*, 2014), catalytic processes which employ a catalyst to convert H<sub>2</sub>S into elemental sulphur (Wang *et al.*, 2013), biological processes which use bacteria to consume H<sub>2</sub>S for growth (Omri *et al.*, 2011), and hydrate formations (Sun *et al.*, 2015). However, these technologies require a high cost operation as well as technical complications, preventing their application by small-scale users.

The adsorption process (Mitomo *et al.*, 2003) is a promising technology to remove H<sub>2</sub>S contained in biogas for small-scale users, especially in households, owing to its low cost operation and uncomplicated utilization and maintenance. Many investigations have focused on adsorbent types since it is an important factor affecting the efficiency of such a process. Activated carbon is one of the most suitable adsorbent materials, but the cost of using carbon-based commercial adsorbent acts as a barrier to the adoption of biogas technology at the small scale. Much research has focused on the efficiency of low-cost alternative adsorbents such as agricultural and industrial wastes or by-products (Ros *et al.*, 2006; Dias *et al.*, 2007; Mohamad Nor *et al.*, 2013; Gil-Lalaguna *et al.*, 2015; Xu *et al.*, 2015).

Although there is a high potential for these low-cost materials, geographical and economic suitability between the adsorbent types and the areas of biogas utilization is required for the possibility of real application.

Nowadays, industrial activities generate a huge amount of solid waste which causes major disposal and environmental problems. The possibility of the reuse of these materials as an adsorbent represents an interesting solution. Soybean-based ink waste, a solid waste discharged from printing industries, becomes an attractive material for biogas cleaning through the adsorption process. It mainly contains aluminum oxide (Al<sub>2</sub>O<sub>3</sub>). According to an open literature investigation (Glass and Ross, 1973), H<sub>2</sub>S can be adsorbed on Al<sub>2</sub>O<sub>3</sub> through 2 different channels; on a Lewis acid site and on a Lewis basic site. Rodriguez *et al.* (1998) used synchrotron-based high-resolution photoemission to assure interaction between the sulfur atom of H<sub>2</sub>S and Al atoms of Al<sub>2</sub>O<sub>3</sub>. Many theoretical investigations have reported the adsorption of H<sub>2</sub>S on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> using different methods (Lo *et al.*, 2011; Ren *et al.*, 2015), leading to the application of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a catalyst in various industries. However, no investigation in the literature focuses on the utilization of materials contained Al<sub>2</sub>O<sub>3</sub>, such as soybean-based ink waste to remove H<sub>2</sub>S from biogas.

In this work, the adsorption capacity of soybean-based ink waste adsorbent was studied in order to remove H<sub>2</sub>S from biogas. First, the physical and chemical properties of the adsorbent were investigated to evaluate its adsorption ability. Secondly, the effect of the pellet size and initial concentration of H<sub>2</sub>S on the adsorption efficiency was examined to study the optimal adsorption conditions. Finally, the morphological characteristics of soybean-based ink waste material before and after adsorption were compared to assure the H<sub>2</sub>S adsorption.

**Table 1. Composition of raw biogas for each adsorption experiment**

| Biogas component       | pellet size (cm) |      |      |      | H <sub>2</sub> S concentration (ppm) |       |
|------------------------|------------------|------|------|------|--------------------------------------|-------|
|                        | 0.25             | 0.50 | 1.00 | 1.50 | 1,040                                | 9,982 |
| CH <sub>4</sub> (%)    | 60.8             | 58.6 | 58.9 | 60.5 | 54.2                                 | 47.6  |
| CO <sub>2</sub> (%)    | 36.4             | 38   | 37.9 | 38.1 | 42.9                                 | 46.8  |
| H <sub>2</sub> S (ppm) | 412              | 398  | 421  | 405  | 1,040                                | 9,982 |

## Materials and Methods

### Materials

The soybean-based ink waste used as a novel adsorbent in this study was collected from Samui Aksorn Ltd., Koh Samui, Surat Thani province, Thailand. This material was sieved to a powder and dried at 80°C for 24 h in an oven in order to eliminate all volatile impurities and the water. The temperature of 80°C was selected to prevent the material's destruction. The pretreated material was then extruded in a spherical form using starch as a binder. The ratio between the pretreated soybean-based ink waste, starch, and distilled water was 7:1:2. Different pellet sizes of adsorbent (0.25 cm, 0.50 cm, 1.00 cm, and 1.50 cm in diameter) were prepared, dried at 40°C for 48 h in an oven, and finally stocked in zip lock bags.

The adsorption tests in this work were performed with raw biogas to evaluate the impact of this complex matrix on the purification performance of the adsorbent. The raw biogas used in this work was produced from organic domestic waste and natural rubber sheet production wastewater using an anaerobic digestion system. Such a system consists of a 200 L digester tank and a 150 L storage tank. Biogas was collected using the water displacement method. It must be mentioned that the experimental conditions, especially the biogas composition, could not be accurately controlled. The composition of the raw biogas for each adsorption experiment was strictly controlled by inoculum and feedstocks, as listed in Table 1.

### Physicochemical Properties of Soybean-based Ink Waste Adsorbents

The determination of the physicochemical properties of the adsorbent (moisture content

and iodine number) was performed using standard procedures. The percentage of the moisture content was determined according to ASTM D2867-95 standard procedure (ASTM International, 1998b) using a laboratory chamber furnace (CWF 13/23, Carbolite Gero Ltd., Hope Valley, UK). One g of the sample was transferred into a chamber furnace. The temperature of the chamber furnace was raised and the sample was degassed for 5 min. Nitrogen gas was passed through the chamber furnace to ensure an inert atmosphere. The sample was heated from ambient temperature to 105°C until it obtained a constant weight. The percentage of the moisture content was calculated using the following Equation (1), where  $W_1$  and  $W_2$  were the weight of the sample (g) before and after the heating process, respectively.

$$\text{Moisture percentage} = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

The iodine number is the mass of the iodine (g) that is consumed by 100 g of a substance. The iodine number was determined according to ASTM D4607-94 standard procedure (ASTM International, 1998a). An iodine solution was prepared containing 2.7 g of iodine and 4.1 g of potassium iodide per liter, standardized using a standard solution of sodium thiosulphate. Then, 0.5 g of soybean-based ink waste adsorbent and 10 ml of 5% (v/v) hydrochloric acid were introduced in a 250 ml volumetric flask and boiled to eliminate the sulfur content. One hundred ml of the stock iodine solution was added to the volumetric flask and agitated using an electric agitator for 60 min. The mixture was filtered through a sintered glass crucible and a number 1 filter paper. Twenty ml of an aliquot portion was pipetted, introduced into an erlenmeyer flask, and titrated with 0.1 M sodium

thiosulphate using a starch solution as an indicator. The concentration of the iodine adsorbed by the adsorbent sample at room temperature was calculated as the amount of the iodine adsorbed using the following Equation (2):

$$\frac{X}{M} = \frac{(B - S)}{B} \times \frac{VM}{W} \times 253.81 \quad (2)$$

where  $X/M$  is the iodine absorbed per gram of the sample (mg/g),  $B$  and  $S$  are the volumes of thiosulphate solution required for blank and sample titrations (ml), respectively,  $V$  is the aliquot portion used for titration (ml),  $W$  is the mass of the sample (g),  $M$  is the concentration (mol) of the iodine solution, and 253.81 is the atomic mass of iodine.

### Adsorption Experiments

The adsorption experiments were divided into 2 steps. In the first step, the removal efficiency of the soybean-based ink waste adsorbent was studied for different pellet sizes: 0.25 cm, 0.50 cm, 1.00 cm, and 1.50 cm in diameter to evaluate the effect of the pellet size of the adsorbent on the adsorption capacity. The experiment was performed to remove H<sub>2</sub>S from the raw biogas produced from organic domestic waste which contained 400–420 ppm of H<sub>2</sub>S. The adsorbent material was packed in a column, as shown in Figure 1. The column was made from acrylic with an internal diameter of 8.00 cm and a total effective length of 50.00 cm. The configuration consists of a gas inlet, gas inlet sampling, gas outlet, and gas outlet sampling. The gas inlet of the packed column was connected to the biogas production system. In the real application, an adsorption packed column is connected between a biogas system and a gas burner tip. This is the reason why the gas is designed to flow downward. The biogas flowrate was kept at 500 mL/min at 30°C and 2 atm. The biogas composition was analyzed before and after the adsorption process using a biogas analyzer (GFM 406, Gas Data Ltd., Coventry, UK). The biogas composition measurement was carried out at room temperature every 10 min for 1 h. The

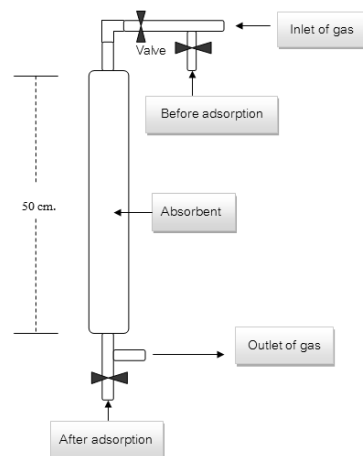
adsorption percentage was calculated using the following Equation (3):

$$\text{adsorption percentage (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3)$$

where  $C$  is the concentration of adsorbate at time  $t$  and  $C_0$  is the initial concentration of the adsorbate. A breakthrough curve was established from  $C/C_0$  and the time. The adsorption capacity of the adsorbents was expressed from the adsorption breakthrough capacity at 5% from the initial gas concentration and it was calculated using the following Equation (4).

$$q_t = \left(1 - \frac{C_t}{C_0}\right) \frac{Q_f t_f y_f}{m_c} \quad (4)$$

where  $q_t$  is the breakthrough adsorption capacity at 5% from the initial gas concentration,  $C_t$  is the concentration of gas  $i$  at the time  $t$ ,  $C_0$  is the initial feed concentration of gas  $i$ ,  $Q_f$  is the volumetric feed flowrate at the standard temperature and pressure,  $y_f$  is the mole fraction of the adsorbate in the feed,  $m_c$  is the mass of adsorbent used inside the packed



**Figure 1.** Schematic diagram of the experimental packed column setup used in this work, consisting of inlet gas, gas sampling before adsorption, column, outlet gas, and gas sampling after adsorption

column, and  $t$  is time. A comparison of the  $H_2S$  breakthrough curve ( $C/C_0$  versus time) at different conditions of the adsorption provides information about the optimal adsorption condition.

In the second step, the removal efficiency of the soybean-based ink waste material was investigated at different  $H_2S$  concentrations: 1,040 ppm and 9,982 ppm to evaluate the effect of the  $H_2S$  concentration on the adsorption capacity of the adsorbent. The biogas contained 1,040 ppm and 9,982 ppm of  $H_2S$  which was produced by anaerobically digesting organic domestic waste and natural rubber sheet production wastewater, respectively. The optimal pellet size of the adsorbent obtained from the first experiment was used. The adsorption process was carried out in the same column geometry (8.00 cm of diameter and 50.00 cm of length). The biogas composition was analyzed before and after the adsorption process using the GFM 406 biogas analyzer. Then, the experimental data were used to establish the breakthrough curve at different initial concentrations of the  $H_2S$ .

### Morphological and Chemical Properties

The morphological and elemental analyses of the soybean-based ink waste material were determined using scanning electron microscopy/energy dispersive x-ray (SEM/EDX) in order to obtain the sorbent surface morphologies as well as to determine the localized chemical composition. The SEM/EDX was performed with a scanning electron microscope (Qanta 400, FEI Co., Hillsboro, OR, USA) at an accelerating voltage of 3 kV. The adsorbent material was ground into powder, dispersed on double-faced conducting tape fixed on a graphite support, and covered with a conductive film of gold. Its

characterization capabilities are due to the principle that each element has a unique atomic structure, allowing a unique set of peaks on its X-ray spectra. The SEM/EDX analysis of soybean-based ink waste material was performed before and after the adsorption process to confirm a change in the elemental and morphological properties of the adsorbent materials.

## Results and Discussion

### Physiochemical Properties of Adsorbent

The physical and chemical properties of soybean-based ink waste adsorbent were determined according to standard procedures. The percentage of the moisture content and iodine number at different pellet sizes of the adsorbent are listed in Table 2. The moisture content varied from 5.00% to 9.00%. This indicates an affinity between the adsorbent surface and water. Generally, a high moisture content can reduce the adsorption capacity of the material. The moisture content in the adsorbent not only occupied some pore volumes, but also changed the surface chemical character of the adsorbent. Therefore, pretreatment processes are necessary to eliminate the moisture content in the soybean-based ink waste material prior to its application. The iodine number is a fundamental parameter used to characterize the adsorbent's performance. The pore contents of the adsorbent, determined by the adsorption of iodine from a standard solution, are responsible for the large surface area of the adsorbent material where adsorption largely takes place (Bello *et al.*, 2017). Soybean-based ink waste adsorbent with different pellet sizes processed the iodine number varying from 956.00-1,237.00 mg/g.

**Table 2. Percentage of moisture content and iodine number of soybean-based ink waste material at different pellet sizes**

| Pellet sizes of adsorbent (cm) | Moisture content (%) | Iodine number (mg/g) |
|--------------------------------|----------------------|----------------------|
| 0.25                           | 5.02 ± 0.06          | 1,237.51 ± 0.99      |
| 0.50                           | 8.24 ± 0.20          | 1,145.38 ± 1.26      |
| 1.00                           | 9.16 ± 0.56          | 957.89 ± 1.58        |
| 1.50                           | 9.22 ± 0.68          | 956.41 ± 0.87        |

As can be seen in Table 1, the iodine number decreases with increasing the diameter size of the spherical adsorbent. For activated carbons, the iodine number value varies in the range of 500.00 – 1200.00 mg/g (Gisi *et al.*, 2016). The iodine number of soybean-based ink waste material was slightly higher than that of activated carbon. According to the investigation of Ekpete *et al.* (2011), the higher the iodine number, the greater is the adsorption capacity. However, the information about the Brunauer-Emmett-Teller surface area, and the micropore and mesopore volumes of soybean-based ink waste material are necessary. The difference between the moisture content and iodine number of the different pellet sizes could be explained by the use of the same procedure for preparing different pellet sizes of adsorbent.

### Adsorption Capacity

The adsorption capacity of soybean-based ink waste adsorbent was studied in order to evaluate its potential to remove H<sub>2</sub>S from biogas. In the first step, the effect of the pellet size on the adsorption efficiency was studied at 4 different sizes (0.25 cm, 0.50 cm, 1.00 cm, and 1.50 cm in diameter). The biogas composition analysis was carried out using the GM 406 biogas analyzer every 10 min for 1 h. The adsorption percentages of the H<sub>2</sub>S, CH<sub>4</sub>, and CO<sub>2</sub> at different pellet sizes are listed in Tables 3-5, respectively. Breakthrough curves represent the time profile for saturation of a given amount of adsorbent. A breakthrough

time is the point on the breakthrough curve where the adsorbate reaches its maximum allowable concentration and the breakthrough capacity is defined as the mass of the adsorbate removed by the adsorbent at the breakthrough time. Figure 2 show the H<sub>2</sub>S breakthrough curves of soybean-based ink waste adsorbent at different pellet sizes. The experimental results demonstrate that soybean-based ink

**Table 3.** Adsorption percentages of H<sub>2</sub>S at different pellet sizes of soybean-based ink waste adsorbent

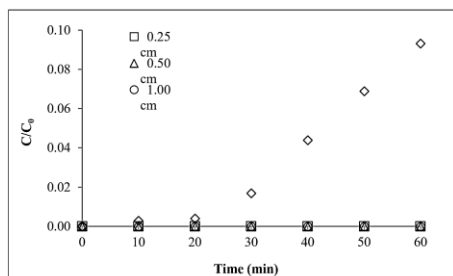
| Time (min) | Adsorption percentage of H <sub>2</sub> S (%) |         |         |         |
|------------|-----------------------------------------------|---------|---------|---------|
|            | 0.25 cm                                       | 0.50 cm | 1.00 cm | 1.50 cm |
| 10         | 100.00                                        | 100.00  | 100.00  | 99.71   |
| 20         | 100.00                                        | 100.00  | 100.00  | 99.61   |
| 30         | 100.00                                        | 100.00  | 100.00  | 98.30   |
| 40         | 100.00                                        | 100.00  | 100.00  | 95.60   |
| 50         | 100.00                                        | 100.00  | 100.00  | 93.11   |
| 60         | 100.00                                        | 100.00  | 100.00  | 90.68   |

**Table 4.** Adsorption percentages of CH<sub>4</sub> at different pellet sizes of soybean-based ink waste adsorbent

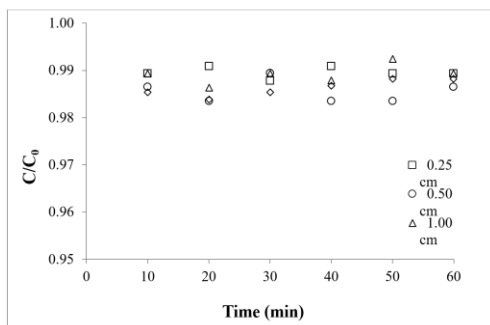
| Time (min) | Adsorption percentage of CH <sub>4</sub> (%) |         |         |         |
|------------|----------------------------------------------|---------|---------|---------|
|            | 0.25 cm                                      | 0.50 cm | 1.00 cm | 1.50 cm |
| 10         | 1.06                                         | 1.35    | 1.06    | 1.47    |
| 20         | 0.91                                         | 1.65    | 1.37    | 1.62    |
| 30         | 1.22                                         | 1.05    | 1.06    | 1.47    |
| 40         | 0.91                                         | 1.65    | 1.21    | 1.32    |
| 50         | 1.06                                         | 1.65    | 0.76    | 1.18    |
| 60         | 1.06                                         | 1.35    | 1.06    | 1.18    |

**Table 5.** Adsorption percentages of CO<sub>2</sub> at different pellet sizes of soybean-based ink waste adsorbent

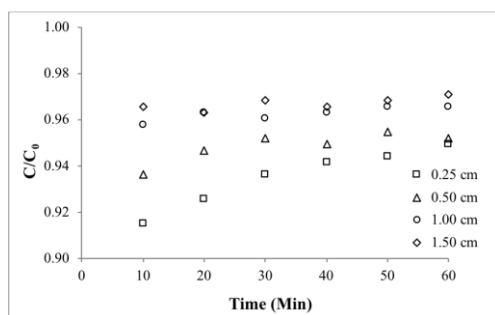
| Time (min) | Adsorption percentage of CO <sub>2</sub> (%) |         |         |         |
|------------|----------------------------------------------|---------|---------|---------|
|            | 0.25 cm                                      | 0.50 cm | 1.00 cm | 1.50 cm |
| 10         | 8.51                                         | 6.38    | 4.26    | 3.86    |
| 20         | 7.45                                         | 5.62    | 3.82    | 3.78    |
| 30         | 6.38                                         | 4.79    | 4.09    | 3.49    |
| 40         | 5.85                                         | 5.25    | 3.72    | 3.46    |
| 50         | 5.59                                         | 4.52    | 3.46    | 3.19    |
| 60         | 5.05                                         | 4.79    | 3.59    | 2.97    |



**Figure 2.** H<sub>2</sub>S breakthrough curves at different pellet sizes of adsorbent: (□) : 0.25 cm, (Δ) : 0.50 cm, (○) : 1.00 cm, and (◇): 1.50 cm



**Figure 3.** CH<sub>4</sub> breakthrough curves at different pellet sizes of adsorbent: (□) : 0.25 cm, (Δ) : 0.50 cm, (○) : 1.00 cm, and (◇): 1.50 cm



**Figure 4.** CO<sub>2</sub> breakthrough curves at different pellet sizes of adsorbent: (□) : 0.25 cm, (Δ) : 0.50 cm, (○) : 1.00 cm, and (◇): 1.50 cm

waste material was effective for H<sub>2</sub>S adsorption. The small pellet size adsorbent showed higher removal efficiency than the large pellet size adsorbent. Soybean-based ink waste adsorbents with 0.25 cm, 0.50 cm, and 1.00 cm pellet size possessed a maximum adsorption capacity during the entire experiment whereas the breakthrough time of the adsorbent having the diameter of 1.50 cm can be observed after 20 min of adsorption. A decrease in the pellet size leads to an increase in the surface area of the adsorbent, providing a greater number of adsorption sites for H<sub>2</sub>S, and thus increasing the breakthrough time. Our experimental results agree well with the investigation of Shang *et al.* (2012) who studied hydrogen sulfide adsorption by camphor-derived biochar

and confirmed the effect of the pellet size on the breakthrough time. Figure 3 presents the CH<sub>4</sub> breakthrough curves of soybean-based ink waste adsorbent at different pellet sizes. The CH<sub>4</sub> breakthrough capacity clearly showed that soybean-based ink waste adsorbent had no capacity to adsorb CH<sub>4</sub> for all the different pellet sizes. This could be due to the competition between the H<sub>2</sub>S and CO<sub>2</sub>, which have smaller molecular sizes than CH<sub>4</sub>. This is advantageous for biogas upgrading as CH<sub>4</sub> must be retrained to assure the biogas potential. The CO<sub>2</sub> breakthrough curves of soybean-based ink waste adsorbent at different pellet sizes are presented in Figure 4. The soybean-based ink waste adsorbent adsorbs CO<sub>2</sub> with low adsorption capacity. According to Shang *et al.* (2012), the H<sub>2</sub>S breakthrough time was longer than the CO<sub>2</sub> breakthrough time. This is because the adsorption of CO<sub>2</sub> was mainly through physisorption whereas the adsorption of H<sub>2</sub>S may be governed by both physisorption and the local pH within the pores. However, Sitthikhankaew *et al.* (2014) studied the effects of CO<sub>2</sub> on H<sub>2</sub>S adsorption onto potassium hydroxide (KOH) impregnated activated carbons and stated that the presence of CO<sub>2</sub> inhibited H<sub>2</sub>S adsorption due to the competitive adsorption and reaction between CO<sub>2</sub> and H<sub>2</sub>S on the surface of the activated carbon. The breakthrough curve serves to validate the adsorbent efficiency as well as to establish the breakthrough time, especially based on technical and economic criteria. For this reason, the 1.00 cm pellet size adsorbent was selected for testing in the next experiment.

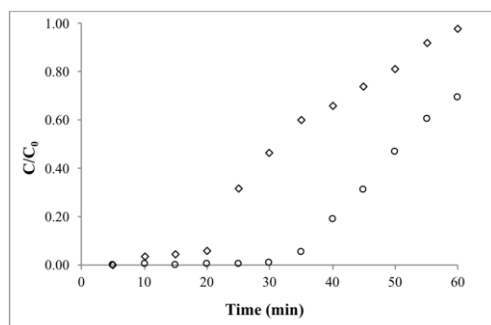
In the second part, the effect of the initial concentration of H<sub>2</sub>S on the adsorption capacity of soybean-based ink waste material was studied using the packed column with adsorbents having a diameter of 1.00 cm. The removal efficiency was investigated at 2 different initial concentrations of H<sub>2</sub>S: 1,040 ppm and 9,982 ppm. The biogas composition analysis was carried out every 5 min for 1 h. The adsorption percentages of H<sub>2</sub>S, CH<sub>4</sub>, and CO<sub>2</sub> at different initial H<sub>2</sub>S concentrations are listed in Table 6. The H<sub>2</sub>S breakthrough curves for different initial concentrations of H<sub>2</sub>S are presented in Figure 5. The breakthrough

**Table 6. Adsorption percentages of H<sub>2</sub>S, CH<sub>4</sub>, and CO<sub>2</sub> at different initial concentrations of H<sub>2</sub>S**

| Time (min) | Adsorption percentage (%) |                 |                 |                  |                 |                 |
|------------|---------------------------|-----------------|-----------------|------------------|-----------------|-----------------|
|            | 1,040 ppm                 |                 |                 | 9,982 ppm        |                 |                 |
|            | H <sub>2</sub> S          | CH <sub>4</sub> | CO <sub>2</sub> | H <sub>2</sub> S | CH <sub>4</sub> | CO <sub>2</sub> |
| 5          | 100.00                    | 0.29            | 4.09            | 100.00           | 1.42            | 4.45            |
| 10         | 99.51                     | 0.73            | 3.97            | 96.67            | 1.17            | 4.27            |
| 15         | 99.70                     | 0.89            | 4.16            | 95.31            | 1.43            | 4.15            |
| 20         | 99.60                     | 1.18            | 4.27            | 93.93            | 1.04            | 4.27            |
| 25         | 99.43                     | 1.47            | 3.87            | 68.19            | 0.92            | 4.11            |
| 30         | 98.68                     | 1.63            | 3.94            | 53.33            | 1.05            | 3.97            |
| 35         | 94.55                     | 1.80            | 3.87            | 40.00            | 1.44            | 3.71            |
| 40         | 80.99                     | 1.52            | 3.84            | 33.84            | 1.57            | 3.84            |
| 45         | 68.83                     | 1.23            | 3.91            | 26.23            | 1.70            | 3.67            |
| 50         | 53.21                     | 1.96            | 3.79            | 19.01            | 1.32            | 3.57            |
| 55         | 39.35                     | 2.05            | 3.55            | 7.88             | 2.06            | 3.66            |
| 60         | 30.35                     | 2.06            | 3.49            | 2.46             | 2.59            | 3.60            |

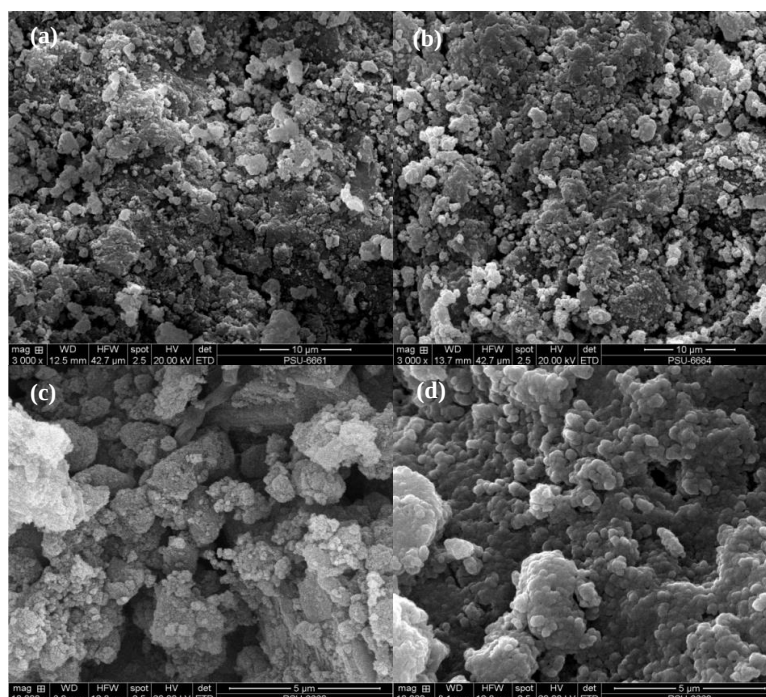
**Table 7. Elemental composition of soybean-based ink waste material before and after the adsorption process**

| Elements (w%)             | O    | Si  | Fe  | C    | Al   | Ca  | S   | Na  | P   | Cu  | K   |
|---------------------------|------|-----|-----|------|------|-----|-----|-----|-----|-----|-----|
| Before adsorption process | 42.6 | 1.5 | 0.2 | 33.2 | 12.5 | 1.8 | 2.6 | 2.2 | 2.6 | 0.3 | 0.1 |
| After adsorption process  | 42.7 | 1.6 | 0.2 | 31.2 | 13.0 | 1.5 | 3.7 | 2.6 | 2.7 | 0.3 | 0.2 |

**Figure 5. H<sub>2</sub>S breakthrough curves at different initial concentration of H<sub>2</sub>S: (○): 1,040 ppm and (◇): 9,982 ppm**

curves indicate that, once again, soybean-based ink material showed a high capacity to adsorb H<sub>2</sub>S but a very low capacity to adsorb CH<sub>4</sub> and CO<sub>2</sub>. The breakthrough times of 1,040 ppm H<sub>2</sub>S and 9,982 ppm H<sub>2</sub>S were observed after 35 min and 5 min, respectively. The H<sub>2</sub>S breakthrough capacity of the initial concentrations of 1,040 ppm and 9,982 ppm was found to be 18.42 mg/g and 28.44 mg/g,

respectively. Shang *et al.* (2012) found that the H<sub>2</sub>S breakthrough capacity of camphor-derived biochar prepared through pyrolysis at various temperatures (100°C to 500°C) ranged from 1.2 mg/g to 121.4 mg/g. Sarperi *et al.* (2014) studied the use of industrial by-products as a sorbent to remove CO<sub>2</sub> and H<sub>2</sub>S from biogas. The H<sub>2</sub>S removal capacity of basic oxygen furnace slugs was estimated to be 140 mg/g. Sethupathi *et al.* (2017) studied the adsorption of CH<sub>4</sub>, H<sub>2</sub>S, and CO<sub>2</sub> onto 4 different types of biochar (Perilla, Korean oak, Japanese oak, and Soybean stover). The H<sub>2</sub>S breakthrough capacity of soybean-based ink waste adsorbent was similar to that of Perilla biochar but higher than that of Korean oak biochar, Japanese oak biochar, and Soybean stover biochar. Moreover, the higher initial H<sub>2</sub>S concentration resulted in a higher breakthrough adsorption capacity. The results obtained in this work agree well with the investigation of Xue and Liu (2012) who found that the breakthrough capacity increased with a higher H<sub>2</sub>S concentration. They studied the H<sub>2</sub>S adsorption on impregnated activated



**Figure 6. SEM of soybean-based ink waste material before and after adsorption at various magnifications: (a): 3,000X before adsorption, (b): 3,000X after adsorption, (c): 10,000X before adsorption, and (d): 10,000X after adsorption**

carbon under anaerobic conditions at the initial  $\text{H}_2\text{S}$  concentration ranging from 210 ppm to 630 ppm. But the results obtained in this work contradict those reported by Lau *et al.* (2013) who studied the adsorption of  $\text{H}_2\text{S}$  using palm shell activated carbon at different initial  $\text{H}_2\text{S}$  concentrations ranging from 1,000 ppm to 5,000 ppm. In addition, the saturation time for 9,982 ppm  $\text{H}_2\text{S}$  starts at 60 min of adsorption whereas the saturation time for 1,040 ppm  $\text{H}_2\text{S}$  do not reach during the entire experiment. The 9,982 ppm  $\text{H}_2\text{S}$  breakthrough curve showed a tendency to exhibit an S-sharp curve, a quick increase in the  $\text{C}/\text{C}_0$  ratio followed by the tendency of a quasi-plateau after 60 min. This is the combination of 2 mechanisms of adsorption: a physisorption-controlled phase followed by a chemisorption-controlled phase. Such a phenomenon was also observed in the adsorption of  $\text{H}_2\text{S}$  on 13X zeolite and activated carbon (Sigot *et al.*, 2016). Moreover, the S-sharp breakthrough curve indicates that the system (adsorbate/adsorbent) is a favorable

sorption type (Lau *et al.*, 2016). Breakthrough curves determined in this work carry the information about the dynamic behavior of the effluent concentration in time, allowing the adsorption column design.

### Morphological and Chemical Properties

Figure 4 shows the comparison of SEM micrographs of soybean-based ink waste adsorbent before and after the adsorption process, at various magnifications. Before the adsorption process, the surface of the soybean-based ink waste material was observed to be cratered and rough at the magnification of 3,000x and it was found to possess rough cavities distributed over the surface at the magnification of 10,000x. This porous surface corresponds to the high iodine number value of soybean-based ink waste adsorbent. After the adsorption process, the surface of the soybean-based ink waste material was covered by small spherical drops over the entire surface and the cavities disappeared. Table 6 presents the EDX

results. Before the adsorption process, the soybean-based ink waste material contained 42.6% oxygen (O), 33.2% carbon (C), 12.5% alumina (Al), 2.6% sulfur (S), 2.6% phosphate (P), 2.2% sodium (Na), 1.8% calcium (Ca), 1.5% silicon (Si), and small traces of other elements. High concentration of oxygen and alumina presented in the soybean-based ink waste material may come from the aluminum oxide compound, and make it possible that H<sub>2</sub>S dissociates on the oxide active center where it is oxidized to elemental sulfur (Aguilera and Gutiérrez Ortiz, 2016). This is the reason why the concentration of sulfur increased from 2.6% before the adsorption process to 3.7% after the adsorption process.

### Conclusions

In this study, the adsorption capacity of soybean-based ink waste adsorbent was studied in order to remove H<sub>2</sub>S from biogas. First, the moisture content and iodine number at different pellet sizes of adsorbent varied from 5% - 9% and 956.00 – 1,237.00 mg/g, respectively. Secondly, for the effect of pellet size of the adsorbent, the soybean-based ink waste adsorbent presented high adsorption capacity for H<sub>2</sub>S but very low adsorption capacity for CH<sub>4</sub> and CO<sub>2</sub>. The pellet sizes of 0.25 cm, 0.50 cm, and 1.00 cm possessed the adsorption percentage of 100% during the entire experiment (1 h) whereas the pellet size of 1.50 cm possessed the breakthrough time after 20 min of adsorption. A decrease in pellet size provides a higher surface area and a greater number of adsorption sites for H<sub>2</sub>S. For the effect of the initial H<sub>2</sub>S concentration, the breakthrough capacity for the initial H<sub>2</sub>S concentration of 1,040 ppm and 9,982 ppm was estimated to be 18.42 mg/g and 28.44 mg/g, respectively. A higher initial H<sub>2</sub>S concentration resulted in the higher breakthrough adsorption capacity. Finally, the SEM/EDX results showed significant changes in the morphological and chemical properties after the adsorption process, assuring the H<sub>2</sub>S adsorption. Therefore, soybean-based ink waste material could be used as a good alternative adsorbent for removing H<sub>2</sub>S from biogas.

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