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***Research paper***

# Hydrogen Sulfide ($H_2S$) Removal by Commercialized Biochar Derived from Rice Husk: Effect of Flowrate, Temperature and Sorbent Weight

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**Abstract**

The presence of Hydrogen Sulphide ($H_2S$) is one of the major sources contributing to air pollution nowadays. Hence, proper action should be taken to reduce the emission of $H_2S$ to open air. This can be achieved by adsorbing the toxic gas onto adsorbent. The evolution of biochar as an effective adsorbent acted as a precursor to the active carbon, as it uses less energy during its production and has porosity similar to activated carbon. This study has focused on commercialized biochar derived from rice husk produced by local industry, Sendi Enterprise located in Tanjung Karang, Selangor. Characterizations of rice husk and rice husk biochar were determined using Elemental analysis, FTIR analysis, BET analysis and SEM. The effectiveness of commercialized on adsorbing $H_2S$ gas was investigated by using as adsorption system at different flowrates, sorbent weights, and process temperature. In the removal of $H_2S$ by using different sorbent weight, it was found that higher sorbent weight increased the adsorption rate of $H_2S$. As for flowrate, less flowrate contributed to higher adsorption capacity. Meanwhile, on temperature parameter, it can be verified when system used low temperature, high adsorption capacity was recorded.

***Keywords***: *Adsorption; Biochar; Hydrogen Sulfide; Rice Husk*

## 1. Introduction

Hydrogen sulfide ($H_2S$) is known as one of the critical toxic gases that is hazardous, can cause death by excess inhalation, and corrosive to metals, internal combustion engines and other mechanical parts [1]. Apart from that, uncontrolled $H_2S$ release can lead to environmental issues, and hazard to human, due to its foul odour and toxicity, and needs to be curbed. Acid gases, such as $H_2S$ and $CO_2$, commonly come from natural gas from anaerobic digestion process, and also originate from the petroleum production, refining, sewer and wastewater treatment [2]. These harmful gases can be removed by a number of processes including absorption and adsorption. In adsorption, the contaminants are removed from the gas mixture by using porous solid adsorbents ranging from carbon based, silica based, and metal organic frameworks (MOFs) adsorbents [3].

Rice husk is a type of lignocellulosic biomass and has the potential to be used as source of renewable energy. As a principal rice growing region, Asia, including Malaysia itself, has abundant rice residues, which estimated at about 560 million tons of rice straw and 112 million tons of rice husks, respectively [4]. Focusing on Malaysia, statistics compiled by the Malaysian Ministry of Agriculture stated that 408,000 metric tonnes of rice husk is produced in Malaysia each year [5]. Rice husk is traditionally used in manufacturing block, employed in civil construction as panels, or used by the rice industry itself as a source of energy for boilers [6]. Therefore, due to the presence of large amount of hydrocarbon such as cellulose and lignin content, rice husk can be used as a raw material to prepare carbonaceous materials which have complex porous structures [7]. Hence, rice husk could be a valuable resource for the production of biochar.

Biochar is a product formed from the pyrolysis process of biomass from various sources including agricultural wastes and forest residues. The production of biochar is achieved via thermal decomposition of organic material with limited supply of oxygen ($O_2$) conducted at a relatively low temperature below 700˚C, [8]. The application of biochar seems to be expanding and being revolutionized from time to time. Biochar, which can be obtained from pyrolysis of biomass wastes, is a cheaper alternative to activated carbon (AC) [9], while, at the same time, possesses good porosity, similar to AC, and basic functional groups. Furthermore, biochar can work well as a sorbent of gas pollutant in flue gas [10]. Although currently AC is widely used for this, but biochar is formerly known to form a lower cost alternative. In addition, the pore structure of biochar also matches the size of molecular dynamics of adsorbates [10]. The characteristics of the biochar is highly dependable on its biomass feedstock, as well as the method of manufacturing, such as via pyrolysis, or other methods.

Hence, in this research, the main objective is to determine the effectiveness of commerciallized biochar derived from rice husk on the removal of $H_2S$, at different process parameters, which are sorbent weight, flowrate of adsorbate $H_2S$, and operating temperature. This study focuses on local commercialized biochar derived from rice husk, as the rice husk possesses high percentage of hydrocarbons such as cellulose and lignin content, making it suitable to be used as a raw material to prepare activated carbons and char activation [11].

## 2. Methodology

### 2.1. Raw Material Preparation

Commercialized biochar specifically derived from rice husk was obtained from the supplier of Sendi Enterprise located at Tanjung Karang, Selangor. The biochar was dried first in an oven at temperature of 110˚C for an hour. The rice husk biochar was grind into powder form and transferred into plastic seal for storage. The sample was labelled as RHB as shown in Fig. 1.

RHB

**Fig. 1:** Commercialized Rice husk biochar after drying and grinding.

### 2.2. Characterization Analysis

The sample of rice husk biochar, RHB and HBC were sent to the Instrumentation Laboratory for characterization of Elemental Analysis, Fourier Transform Infrared (FTIR), Brunauer Emmett Teller (BET) and SEM for analysis.

#### 2.2.1. Elemental Analysis

In order to analyze the chemical composition for biochar, elemental analyzer model The Flash EA 1112, Organic Elemental Analyzer was used. It is important to know the chemical composition of that material as because it will prove the standard specification and the capability of this material in sorption efficiency. The sample standard size for the analysis is 3mg - 11mg based on user guidelines [4]. The results from this equipment showed the composition of Carbon (C), Hydrogen (H), and Nitrogen (N).

#### 2.2.2. Fourier transform infrared spectroscopy (FTIR)

FTIR is a measurement technique that allows one to record infrared spectra. This technique is very sensitive and it is useful for identifying organic chemicals in a whole range of applications. For this experiment, PerkinElmer Spectrum 100 FTIR with the wavelength 4000 - 600 $cm^{-1}$ is used to figure out functional groups in molecule of rice husk biochar [12].

#### 2.2.3. Brunauer-Emmett-Teller (BET)

Characterization on surface area ($m^2/g$), pore volume ($m^3/g$) and average pore size (Å) was analyzed with Brunauer-Emmett-Teller (BET) method by model Micromeritic 3 flex. The BET method is operated with Nitrogen ($N_2$) adsorption and desorption at room temperature [13].

#### 2.2.4. Scanning electron microscopy (SEM)

Microstructure observation was carried out to observe the propagation and tendency of surface area and pore size of biochar. This characterization is synchronized with the BET which mean when the pore size and large surface area are calculated, probably the microstructure of adsorbent much bigger. The equipment used is SEM with the model Hitachi TM3030Plus. The image was captured under magnification of 500X and 2000X [14].

### 2.3. Adsorption System

The simulation for adsorption of $H_2S$ by RHB was carried out by using a laboratory scale adsorption column unit. The system was well equipped with control panel, gas tanks, pressure gauges, flow meter, control valves and two columns of adsorption bed. However, in this research, only one unit of adsorption column was used during the simulation, as shown in Fig 2.

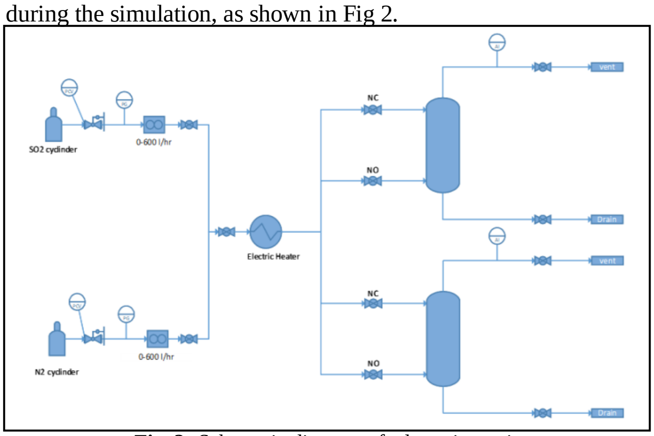


**Fig. 2:** Schematic diagram of adsorption unit

Two gas tanks were needed; $H_2S$ gas as the adsorbate while $N_2$ gas was used for purging purpose. Purging the system by using $N_2$ was one of the safety measures while dealing with the adsorption column. The adsorption column which holds adsorption bed can be detached and separated into two individual beds. For each of the parameter the fix parameter can be simplified as below:

a. $H_2S$ Adsorption at various flowrates

$H_2S$ gas at fix parameter of 343K, 10 ppmv inlet and 30g RHB were test at flowrate of 100 l/hr. A Crowcon single gas detector was used to determine the outlet concentration of the $H_2S$ gas. The time taken for $H_2S$ to reach 10 ppm at outlet was recorded. The experiment was repeated at different gas flowrate 150 l/hr and 200 l/hr.

b. $H_2S$ Adsorption at various Temperature

Similar as item a. above however the fix parameter were change to flowrate of 100 l/hr,10ppmv inlet and 30g RHB were test at flowing temperature of 343K. The experiment was repeated at 373K and 403K.

c. $H_2S$ Adsorption at various Sorbent weight

Similar as item a. above however the fix parameter were change to operating temperature of 343K,10ppmv inlet and 100 l/hr. RHB were test at sorbent weight of 20g, 25g and 30g.

The amount of $H_2S$ adsorbed per unit of mass biochar was calculated using the following equation:

$$Q_e = \frac{(C_o - C_f)\, V_{bed}}{W_b} \qquad (1)$$

Where $Q_e$is the amount of $H_2S$ adsorbed ($mg.g^{-1}$), $C_o$ and $C_f$ are the initial concentration and final concentration of $H_2S$ (ppmv), $V_{bed}$ is the gas density multiply by gas flowrate ($m^3/hr$) and $W_b$ is mass of biochar (g).

Summary of the variables investigated in this study are shown in Table 1.

**Table 1:** Summary of $H_2S$ Adsorption System Parameters

| Parameter | Value |
|---|---|
| | Rice husk Biochar (RHB) |
| Sorbent Weight (values in g) | 20 |
| | 25 |
| | 30 |

| Parameter | Value |
|---|---|
| | Rice husk Biochar (RHB) |
| Flowrate of $H_2S$ (values in L/hr) | 100 |
| | 150 |
| | 200 |
| Temperature (values in K) | 343 |
| | 373 |
| | 403 |

## 3. Results and Discussions

### 3.1. Elemental Analysis

Table 2 shows the percent elemental content of rice husk (RH) and rice husk biochar (RHB).

**Table 2:** Elemental Analysis of RH and RHB.

| Material | Elemental Content (%) | | | |
|---|---|---|---|---|
| | C | H | N | S |
| RH | 33.47 | 5.21 | 3.95 | 53.37 |
| RHB | 26.22 | 6.13 | 4.05 | 63.60 |

The carbon content of rice husk had been reduced as it was produced as RHB and HBC. The carbon content for RH and RHB were 33.47 and 26.22 respectively. The reduction amount of carbon content in HBC may be due to the polymerization reaction and formation of carbon oxide occurred during the production of RHB. On the other hand, the hydrogen content was highest in the RHB compared to RH. For nitrogen content, there was no significant difference among those three samples but it can be seen that nitrogen in RHB was higher than RH. Sulphur content were calculated as a balanced component based on total amount of elemental component. At the same time, the major content in the samples which was sulphur had shown a slight difference in each sample. In previous study, there was no sulphur content detected for RHB It has to be noted that the origin of rice husk also affected the content of element present in the respective rice husk. In earlier study stated that the chemical composition of rice husk is varied due to the differences in the type of paddy, crop year, climate and geographical conditions [16]. It was strongly supported by [17], saying that the soil chemistry, climatic conditions as well as the geographic of the culture were the factors affecting the rice husk content.

### 3.2. FTIR Analysis

In this study, RH had some functional groups which were alkane, alkene, carboxylic acids, ester, amines and amides. In previous research by [18], the same trend of functional groups had been discovered. Since rice husk is originally a lignocellulosic material, it consists of the structure of alkenes, esters, aromatics, ketones and alcohols with oxygen containing different functional groups. On the other hand, RHB composed of functional groups such as carboxylic acids, alcohol and/or ester, amines, anhydrides as well as diimides. RHB

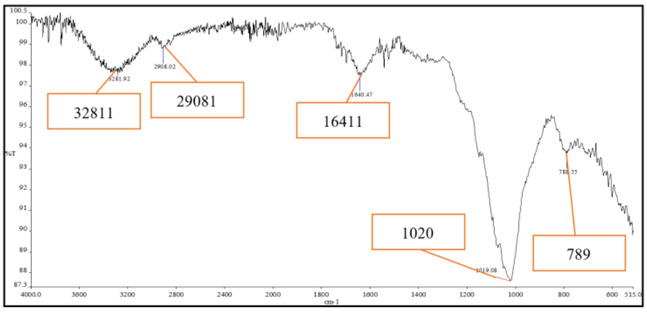


**Fig. 3**: FTIR results of RH

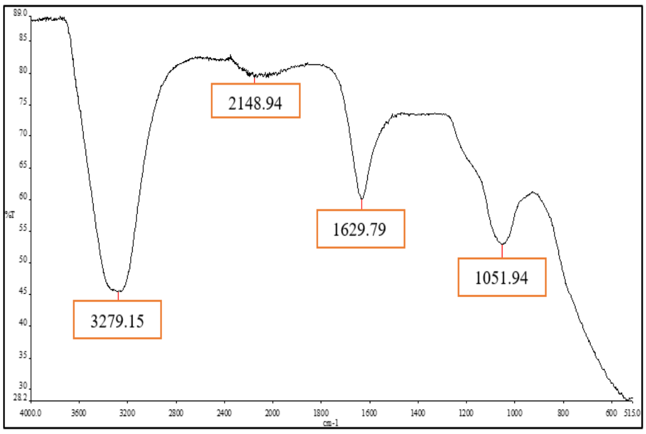


**Fig. 4**: FTIR results of RHB

Fig. 3 and Fig. 4 above shows the effect of heat towards RH after conversion to RHB. RHB were produced to increase surface area and pore volumes which are required for adsorptions however certain functional group has been remove during the process. It was observed that the functional group 2908cm$^{-1}$ and 789cm$^{-1}$ were removed which fall into group of alkane (2840cm$^{-1}$ to 3100cm$^{-1}$) and Cholro-alkane.

### 3.3. BET Analysis

Table 3 shows the BET analysis of RH, RHB and HBC carried out in this research.

**Table 3:** BET analysis of RH, RHB and HBC

| Material | BET Surface Area($m^2$/g) | Pore Volume ($cm^3$/g) | Average Pore Size(Å) |
|---|---|---|---|
| RH | 24.7105 | 0.027714 | 44.8624 |
| RHB | 93.6341 | 0.059343 | 25.3512 |

From Table 3, the surface area of RH, RHB and HBC are 24.7105 $m^2$/g, 93.6341 $m^2$/g and 72.1413 $m^2$/g respectively. The surface area of RHB is smaller compared to RH due to the undergoing process of producing biochar has altered the property. The surface area for HBC is much smaller than RHB. However, for the pore volume, HBC employs the highest pore volume compared to RH and RHB. The average pore size of RH is the highest compared to RHB and HBC which is 44.8624 Å.

### 3.4. Effect of Sorbent Weight

The outlet concentration of $H_2S$ were recorded and calculated by using Equation (1). Hence, a graph of mass of $H_2S$ adsorbed per 1 g biochar versus time was plotted as the adsorption capacity. The adsorption capacity of RHB for $H_2S$ are shown in Fig. 5.

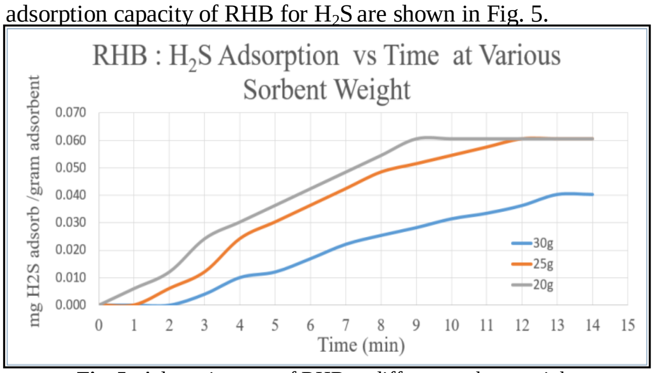


**Fig. 5:** Adsorption rate of RHB at different sorbent weight

Based on Fig. 5 above it was observed that at higher sorbent weight the gas adsorption is lower at 30g sorbent weight compared to 20g sorbent weight. It is expected due to the equation 1 above shows that per mg $H_2S$ adsorb is divided by mass of adsorbent. However, take note that the values show the values of amount being adsorb per gram of adsorbent not the adsorption capacity.

At lower adsorbent weight the adsorbent shows that it become saturated faster than higher sorbent weight. This is because the surface area available for molecule to adsorb is much lower for similar sorbent at higher sorbent weight. Higher sorbent weight provides more room for adsorptions and takes longer time for adsorbent to become saturate.

### 3.5. Effect of $H_2S$ Flowrate

For flowrate parameter, the results are displayed in Fig 6 where the adsorption capacity increased when low flowrate is used. On the result, when used 100L/h, the period takes to achieve 10ppm is extensively longer compared to 150L/h and 200L/h. From these results, the flowrate of the adsorbate ($H_2S$) can affect the quantity of biochar adsorption. The reason is the mass transfer occurring between solid biochar and gas flow is much lower. When the high flowrate was used, at higher gas velocity the contact time between the adsorbate is less which lead to the earlier adsorbent saturation as shown in Fig.6 below for 200L/hr flowrate.

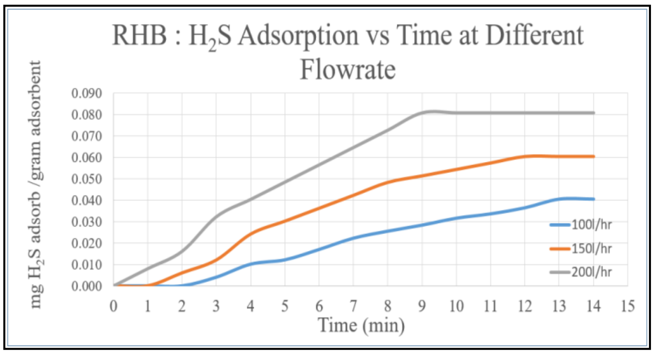


**Fig. 6:** $H_2S$ Adsorption on Biochar: Effect of Flowrate

### 3.6. Effect of Temperature

Based on Fig. 7, it shows the adsorption capacity occur highly in temperature 343 K, and then followed by 373 K, and 403 K. Gas adsorption was carried out at various temperatures of 343K, 373K and 403K. As the temperature increase and receiving energy from external and actively vibrate, the tendency for the molecule to adsorb on the adsorbent surface to its location is lower. This can be shown as Fig.7 above where at higher temperature the rate of adsorption is much lower compared to lower temperature. The molecular interaction between adsorption surface and “active” molecule is not sufficient to prevent from the molecule to desorb from the adsorbent surface. Hence at higher temperature the adsorbent unable to adsorb more $H_2S$ gas.

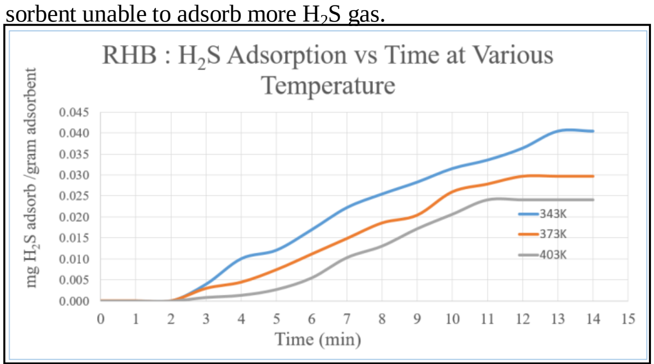


**Fig. 7:** $H_2S$ Adsorption on Biochar: Effect of Temperature

## 4. Conclusion

Based on the obtained results, the research has been done successfully and covered all of the objectives. In conclusion, commercialized biochar from Sendi Enterprise has employed the characteristics as close as activated carbon; hence it is suitable to be use as an adsorbent to remove toxic gas of $H_2S$.

Few perspectives have been investigated such as sorbent weight, variation of flowrates and temperatures. For removal of $H_2S$ by using different sorbent weight, it can be seen that higher sorbent weight will provide more room for adsorptions.

Variation in flowrates it can be conclude that, at higher flowrate the contact time is reduce due to higher gas velocity and higher operating temperature gives molecule extra energy to become more active. Hence it will reduce the tendency to stick onto the adsorption surface.

The operating envelops of the RHB need to be determine in order to optimize adsorptions $H_2S$ gas onto RHB abundant resource and challenge need to overcome in order to ensure RHB can be commercialized and accepted in the industry.

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