Adsorption of Hydrogen Sulphide by Commercialized Rice Husk Biochar (RHB) & Hydrogel Biochar Composite (RH-HBC)

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Abstract: Hydrogen sulfide (H₂S) is a naturally occurring component found during microbial disintegration and processing of natural gas & oil which can cause wellbeing and condition issue if being discharged into a climate at high fixation. Activated carbon which cost a lot in manufacturing is used as an adsorbent for removing these hazardous gases. As an alternative, the abundance waste of biomass available can be converted into good use. Biochar is one of the most practical and promising adsorbents that shows incredible potential as an adsorbent for the expulsion of contaminants in wastewater and gas treatment. This study covered on the characteristics and adsorption performance of two adsorbents Activated Rice Husk Biochar (RHB) and Rice Husk Hydrogel Composite (RH-HBC) on hydrogen sulfide. RHB is prepared by treating grinded rice husk biochar using aqueous Zinc Chloride (ZnCl₂) and hydrochloric acid (HCl) solution to increase the size of pores of active sites and remove the impurities present in on the adsorbents. Polymerization is conducted by using initiator (ammonium persulfate, APS), monomer (acrylamide, AAm) and crosslinker (N,N’-methylenebisacrylamide, MBA) to create treated hydrogel biochar (RH-HBC). The adsorption performance is done to evaluate the effect of sorbent weight (20 g, 25 g, 30 g), H₂S gas flow rate (200 L/hr, 150 L/hr, 100 L/hr) and temperature (30 °C, 50 °C, 70 °C). RHB shows better porosity compared to RH-HBC where it has a higher surface area (222.85m²/g) compared to RH-HBC (6.68m²/g). While the presence of alkene group C=C in RH-HBC gives more stability to withstand high temperature compared to RHB. From the result, it can be concluded that the increased the sorbent weight, give an increased in adsorption capacity. When increased the gas flow rate, it gives a shorter contact time between gas and adsorbent which result in less adsorption capacity. RH-HBC give longest breakthrough time and highest adsorption capacity compared with RHB in all experiment.

Index Terms: Biochar, Brunauer-Emmett-Teller (BET), Elemental Analysis (EA), Fourier Transform infrared spectroscopy (FTIR), Hydrogel Biochar Composite, Thermogravimetry Analysis (TGA),

I. INTRODUCTION

Hydrogen sulfide is recognized as one of the vital contaminates that is corrosive to internal combustion engines and should be removed from the biogas. The common industries encountered with hydrogen sulfide are swine containment services and enterprise that involve in manure and sewage handling [1]

Due to its toxicity toward a surroundings and human health, a gas conditioning process should be performed before releasing effluent into environment. Activated carbon is most commonly used to treat hydrogen sulfide as its porous structure and area which provide a greater charge of adsorption [2]. Despite this gain, producing activated carbon requires an excessive amount of cost for manufacturing and regeneration process.

In Malaysia, biomass waste on hand abundantly available from harvesting and producing rice. Hence, Rice Husk is chosen as a raw material. A huge quantity of hydrocarbon existing in rice which derived from constituent polymers includes cellulose, hemicellulose, and lignin gives a complicated porous shape for greater adsorption capability of H₂S [3].

The solid product of biomass pyrolysis is called biochar, which undergoes an oxygen-limiting or absent at high-temperature heating technique for biofuel production [4]. Considering its full-size adsorptive potential due to its high and unique surface area and numerous surface purposeful groups, biochar has been often used as an adsorbent for soil and water remediation [5].

Chemical activation is used as it leads to increment in surface area and reduce the crystallinity by impregnating rice husk biochar with ZnCl₂ aqueous solution. The porosity is developed by dehydration reaction of activating reagent [6, 7,8,9].

RHB will undergo polymerization process. The use of Acrylamide (AAm) monomer and N,N’-methylenebisacrylamide (MBA) as a crosslinker to produce rice husk hydrogel biochar composite (RH-HBC). The presence of the hydrogel coating the biochar helps improve the adsorption effectiveness by adding a chain that will attract and form bonding with hydrogen sulfide component. Due to the affinity towards water and porous structure networks, the hydrogel will assist more solute [10].
Adsorption of Hydrogen Sulphide by Commercialized Rice Husk Biochar (RHB) & Hydrogel Biochar Composite (RH-HBC)

This study aims to enhance rice husk biochar adsorption capability as adsorbent using multi-step chemical substances conditioning to produce RHB and RH-HBC and comparing both adsorption performances on hydrogen sulfide.

II. MATERIALS AND METHODS

A. Raw Material & Chemical

Commercialized biochar mainly derived from rice husk was acquired from Sendi Enterprise located at Tanjung Karang, Selangor. The biochar was dried first in an oven at a temperature of 110°C for an hour. The rice husk biochar was granulating into powder structure and sifter for the size of <500µm then moved into a plastic seal for capacity. The activation agent for this study was Zinc Chloride (ZnCl₂) aqueous solution. As dilution agent, 0.1M of Hydrochloric acid (HCl) and distilled water was used. Acrylamide (AAm), N,N’-methylenebisacrylamide (MBA) and ammonium persulfate (APS) were used as monomer, crosslinker and initiator, respectively.

B. Chemical Treatment

Chemical activation of the raw grinded rice husk biochar was carried out using ZnCl₂. The mass ratio of ZnCl₂ to biochar was 1:10. Biochar and ZnCl₂ solution was mixed in a ratio of 10g:100mL. The mixing was performed at 25°C for 24 hours [7, 11]. After mixing, the slurry was dried in an oven at 105°C for overnight. The activated biochar was then washed with 0.1M HCl solution by stirring it for 4 hours at 25°C. The solid activated biochar was then washed with distilled water until the final pH reached 6.5 to 7. The final step was drying the treated biochar (RHB) at 110°C for 24 hours.

C. Polymerization Process to Hydrogel Composite

0.01g of MBA crosslinker was mixed with 0.6g RHB and combined with acrylamide (AAm) solution consists of 1.0g of AAm monomer dissolved in 1mL of distilled water. Polymerization was created by mixing 0.2mL of 0.1g solution of APS initiator. The precursor solution is placed into plastic mold in an oven for 40°C for 30 minutes. Then, the precursor solution is left for 24 hours before the RH-HBC was taken out from the plastic mold and cut to the desired size. Then, the unreacted monomer and low molecular weight matter are removed from RH-HBC by washing it with distilled water before been dried in a vacuum oven at 40°C for 24 hours. The RH-HBC was then grinded to smaller size (<500 µm) and stored in a plastic seal for further used. The method of hydrogel composite production is followed by Karakoyun et al. (2011) with amendment from previous research [12].

D. Characterization Analysis

The characterization of the elemental composition present in samples was done on raw grinded rice husk, RHB, RH-HBC using Elemental Analyzer (EA). The changes of functional groups present in samples adsorbent are analyzed using Fourier Transform Infrared (FTIR). Further, the sample was analysed using Brunauer-Emmett-Teller (BET) method to know the value of pore volume, average pore size and surface area. Nitrogen gas is used in the BET method for adsorption and desorption study at room temperature.

E. Adsorption Performance

Adsorption equipment consists of three layers stainless steel column with 3 inch height of each layer with 1.785 inch diameter. The middle bed column is filled with the adsorbent. The experiment was carried out with 2 of the 3 parameters maintain as constant (eg. effect of sorbent weight, gas flow rate and temperature on adsorption of hydrogen sulfide gas using 20g, 25g and 30g at constant temperature and gas flow rate of 30°C and 100L/hr respectively).

Each layer was bolstered with wire work and cotton fleece to forestall the fine particles pass through. Then, the outlet stream was connected with Crowcon Gasman H₂S gas detector. The system was illustrated in Fig. 3 Analyses were led to ponder the impact of sorbent weight, gas flow rate and temperature on adsorption of hydrogen sulfide gas using activated Rice Husk Biochar (RHB) and Rice Husk Hydrogel Biochar Composite (RH-HBC) as adsorbents.
The details of the experimental data were shown in Table I. For the first experiment, to evaluate the effect of bed heights in adsorption of H2S, middle bed column was filled with 20g of adsorbent and 25 ppm of the initial concentration of H2S gas was supplied. It then followed by means of subsequent run of 25g and 30g of RHB. Next, the experiment was repeated by using RH-HBC to study the comparison in adsorption of H2S between these two adsorbents. Then, the experiment conducted for RHB and RH-HBC repeated for gas flow rate and temperature variation. Each experiment repeated thrice for average data. The adsorption capacities of the adsorbent samples were calculated in terms of mg/g (mg of H2S/g of RHB/RH-HBC) by integrating the area above the breakthrough curve between the curve and the inlet gas concentration until the breakthrough point was reached as shown in Fig. 4 [16].

**Table I: Experiment's details for adsorption experiment of RHB and RH-HBC.**

| Parameter | Value |
|-----------|-------|
| Sorbent Weight (values in g) | 20 | 25 | 30 |
| Flowrate of H2S (values in L/hr) | 100 | 150 | 200 |
| Temperature (values in °C) | 30 | 50 | 70 |

**III. RESULTS AND DISCUSSIONS**

A. Characterization of Adsorbents

**Elemental Analysis**

Table II shows the percent elemental content of grinded rice husk biochar, activated rice husk biochar (RHB) and rice husk hydrogel biochar composite (RH-HBC).

**Table II: Elemental Composition Analysis Result.**

| Samples | Elemental Composition (%) |
|---------|---------------------------|
| Grinded Rice Husk Biochar | 48.27 | 3.31 | 2.50 | 45.93 |
| Activated Rice Husk Biochar (RHB) | 37.17 | 3.78 | 2.61 | 56.44 |
| Rice Husk Hydrogel Biochar Composite (RH-HBC) | 40.46 | 8.13 | 9.41 | 42.00 |

The carbon substance of activated rice husk biochar (RHB) had been reduced as compares to granulated rice husk biochar which was found to contain 37.17% and 48.27% respectively. The reduction may be due to treating the grinded rice husk biochar by the aqueous solution of zinc chloride and 0.1 M hydrochloric acid which fundamentally break up carbon component inside RHB. However, the carbon content increase in rice husk hydrogel (RH-HBC) with 40.46% from the formation of the carbon polymer chain. On the other hand, hydrogen and nitrogen composition is increased and was highest in RH-HBC. Then again, hydrogen and nitrogen creation are expanded and was most astounding in RH-HBC. In the past examination, there is no critical contrast in nitrogen content between the adsorbent which confirmed that substance actuation and treating do contribute an expansion in nitrogen content [13].

Oxygen substance was determined as a fair part on the aggregate sum of essential segment. The increase in oxygen content in RHB with 56.44% compared to grinded rice husk biochar 45.93% may be due to constant mixing during actuation and synthetic treatment. It was seen that after RHB being polymerized into RH-HBC, the oxygen substance decline because of polymerization response and development of carbon oxide happened during the procedure. There was no sulfur substance distinguished in all adsorbent.
Adsorption of Hydrogen Sulphide by Commercialized Rice Husk Biochar (RHB) & Hydrogel Biochar Composite (RH-HBC)

This additionally explained in concentrates done by Ahmad, 2017 which expressed there zero sulfur content in biochar [14].

**FTIR Analysis**

The functional group were observed in FTIR spectra for HBC, RHB and grinded Rice Husk Biochar shows in Fig. 5. The spectrum for FTIR of grinded rice husk biochar shows a broad characteristic peak at 3184.84 cm⁻¹ which indicate the presence of O-H stretching functional group of the hydrogen-bonded hydroxyl group (O-H), indicative presence of phenols and alcohols.

This is sure as the outcome is like examinations demonstrating the equivalent useful gathering in biochar [13]. In the wake of experiencing concoction treatment utilizing Zinc Chloride arrangement and hydrochloric corrosive (HCl), the O-H extending was lessened on the grounds that a portion of the unstable components is discharged during the treatment. Subsequently, there is no hydroxyl gathering identified in RHB.

Besides, both blended rice husk biochar and RHB show same bending vibration for N-O stretching (1542 cm⁻¹), C-N stretching (1066 cm⁻¹) and the strong bond of alkane C-H group (792 cm⁻¹). After the polymerization process, RH-HBC shows the presence of O-H stretching with bending vibration 3195 cm⁻¹. There are also some changes in the functional group with the addition of C=C stretching alkene with wavelength 1652 cm⁻¹ and amine group C-N stretching on 1077 cm⁻¹ due to polymerization reaction that forms carbon double bond chain.

**BET Analysis**

Table III shows the results of BET surface area (m²/g), total pore volume (cm³/g) and average pore size (Å) for the adsorbent samples.

![BET Spectrum](image)

**Table III: BET Surface Area and Porosity results.**

| Sample               | BET surface area (m²/g) | Total pore volume (cm³/g) | Average Pore Size (Å) |
|----------------------|-------------------------|---------------------------|-----------------------|
| Grinded Rice Husk Biochar | 197.0509                | 0.05412                   | 22.3548               |
| RHB                  | 223.8534                | 0.05989                   | 21.0461               |
| HBC                  | 8.6824                  | 0.0006271                 | 21.4428               |

In Table 3, RHB shows higher surface area with 223.8534 m²/g compared to granulated rice husk biochar 197.0509 m²/g coming about because of synthetically treated with ZnCl2 and HCl fluid arrangement which go about as an oxidizing specialist to evacuated fractional lignin and make the hemicellulose divider become more slender and enacts more pores on biochar surface [15]. Then, as the examination studies were finished by Hidayah Meri, 2017 likewise demonstrated that the biochar that accomplished compound pre-treatment biochar have higher surface territory contrasted with regular biochar [9]. HBC show a lower surface area and total pore volume with 8.6824 m³/g and 0.000627 cm³/g respectively. Meanwhile, the average pore size of HBC is 21.4428 nm which is higher compared to RHB 21.0461 nm.

**B. Adsorption Performance**

**Effect of Sorbent Weight**

Fig. 6 and 7 demonstrates the leap forward profile for impact of RHB and RH-HBC sorbent weight in the expulsion of H₂S. After H₂S was supplied, the concentration at outlet gas increase. Then a breakthrough curve was plotted by C_outlet/C_inlet (Outlet concentration/Inlet Concentration) against Time (s), and the breakthrough times were determined from the moment it reacts to saturation state. As shown in both Fig. 6 and 7, the higher the sorbent weight, the longer the time taken to reach a breakthrough. The highest sorbent weight 30g has a longer breakthrough time, which is 34 min for RHB and 48 min for RH-HBC, followed by 25g with 28 min (RHB) and 42 min (RH-HBC), and the shortest are 24 min (RHB) and 36 min (RH-HBC) for 20g sorbent weight. Then, as stated by Choo et al., 2013, the longer the breakthrough time is because of the portion of adsorbent in front of the mass transfer zone had not yet been exposed to H₂S hence the H₂S adsorption capacity increased [17]. 30g sorbent weight provides more breakthrough capacity for RHB and RH-BC..
Fig. 6: Effect of RHB’s weight on breakthrough profile for adsorption of H$_2$S.

**Effect of Gas Flowrate**

Impact of gas stream rate gives a colossal contrast in adsorption execution as demonstrated by the breakthrough conduct appeared in Fig. 8 and 9 for RHB and RH-HBC. Breakthrough time resulted at 200 L/hr of inlet gas flow rate is 15 min for RHB while 22 min for RH-HBC which is too quick arriving at its immersed state contrasted with the stream pace of 100 L/hr and 150 L/hr. When reducing the flow rate to 150 L/hr the breakthrough time is shows approximately to 22 min (RHB) and 32 min (RH-HBC) which still shows the shorter time to reach the saturated state. Meanwhile, further reduced the flow rate to 100 L/hr produced improvement to the longer breakthrough time which is 34 min (RHB) and 46 min (RH-HBC). This marvel was clarified by Choo et al., 2013, a lower gas stream rate gives a more extended contact time among gas and adsorbents' surface which add to breakthrough limit. The achievement is a lot higher for 100L/hr.

Fig. 8: Effect of gas flowrate on RH-HBC breakthrough profile for adsorption.

**Effect of Temperature**

Fig. 10 and 11 showed the breakthrough behavior of RHB and RH-HBC at 30°C, 50°C, and 70°C. However, at 70°C the adsorptions are significantly reduced. The breakthrough time and breakthrough capacity of the RH-HBC are much better compared to RHB. Based on the experiment the longer breakthrough is 30°C with longer breakthrough time as 48 minutes compared with RH-HBC is only in 36 min.
Adsorption of Hydrogen Sulphide by Commercialized Rice Husk Biochar (RHB) & Hydrogel Biochar Composite (RH-HBC)

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**IV. CONCLUSIONS**

Based on the results It can be concluded that the maximum adsorptions occurred at 30gram sorbent weight, 100 l/hr gas velocity and 30°C operating temperature for RHB and RH-HBC. Increasing volumetric flowrate, in other words, is also increasing the gas velocity which directly reduces the gas retention time.

Few factors also affected the adsorption of gas at elevated temperature. As heat is supplied to the gas by increasing the temperature, the molecule becomes very active and makes it difficult to stick on the adsorption surface. Higher operating temperature leads to less gas adsorption on the RHB and RH-HBC from 38minutes to 8 minutes and from 48minutes to 9 minutes respectively.
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