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Research paper

Effect of Sorbent Weight on H_2S removal by Biochar and Hydrogel Biochar derived from Rice Husk

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Abstract

Biochar has received great attention recently as it has the potential to be alternative absorbent beside the long existence, activated carbon. In this study, biochar was produced from rice husk by slow pyrolysis at temperature of 450°C. To increase the performance of the biochar in absorbing H2S, hydrogel biochar was produced by performing polymerization. The characteristics analysis in elemental analysis, functional group, surface area, pore volume and pore size had been done on rice husk, biochar and hydrogel biochar. Then, the absorption of H2S with sorbent weight as parameter has been performed on biochar and hydrogel biochar. The result of H2S absorption by biochar showed that the mass of H2S per weight of sorbent increase as the sorbent weight increase. However, the hydrogel biochar unable to perform the result that has been predicted.

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

1. Introduction

Rice husk is available in abundance as biomass waste from agriculture industries, in which this waste is treated using traditional methods such as composting and incineration [1]. However, this organic solid waste is not suitable for composting and incineration, as small concentration of nitrogen present in the rice husk can lead to release of unwanted gases, particularly NOx gases into the environment during incineration process. Carbonaceous materials can be produced, using rice husk as raw material, as rice husks contains significant amounts of hydrocarbons such as cellulose and lignin, which form complex porous structures [2]. Hence, biochar, which is a carbonaceous material, can be easily derived from rice husk biomass.

Biochar is carbon-rich product when biomass, such as rice husk, is heated in a closed air-tight container with limited or no oxygen and air, better known as pyrolysis [3]. In technical term, biochar is produced by thermal decomposition of organic material at relatively low temperature with limited supply of oxygen [3]. In a chemical point of view, the organic portion of biochar has a high carbon content, which mainly comprises of aromatic compounds characterized by rings of six-carbon atoms linked together without oxygen or hydrogen, the otherwise more abundant atoms in living organic matter [4]. Applications for biochar currently, involve sectors such as energy production, agricultural industries, carbon sequestration, activated carbon adsorbent and biorefineries [5].

Activated carbon is widely used in flue gas control due its properties of large surface area, good pore structure, abundant functional group and high effectiveness related to in-situ deoxidizing ability [6]. In commercial processes, activated carbon is produced by degraded and coalified plant matter [7]. However, with high temperature requirement and additional activation process required to produce the activated carbon, researcher currently focusing on producing alternatives of activated carbon that requires lower energy and cheaper feedstock [8], hence reducing production costs. Biochar derived from rice husk can be viewed as potential replacement for activated carbon. This is because biochar is cheaper to produce, while, at the same time, possess high porosity and basic functional group; the traits that make it an efficient sorbent of gas pollutants such as hydrogen sulfide H_2S [9,10]. With charged surface and porous structure, biochar also occupies some surface functional groups such as carboxyl, hydroxyl, phenolic hydroxyl and carbonyl groups [3]

Industrial pollution and degradation of urban environment is the cost that Malaysia needs to pay for the associated rapid economic growth and to achieve the industrial status by the year of 2020 [11]. Among the industrial pollution, air pollution is the major issue that has been affecting human health, agricultural crops, forest species and ecosystems [11]. One of the contributor to the air pollution is the notorious hydrogen sulfide (H_2S).

Naturally, H_2S is produced from the breakdown plant and animal material and from geothermal fields. For example, in industrial field, the release of H_2S gas can be from rayon textile production, oil and gas refineries, and pulp and paper manufacturing [12]. The exposure dosage of H_2S affects greatly the human health, ranging from a rotten egg smell at 0.13 to 0.15 ppm, to respiratory, eye and throat irritation at 100 ppm, to olfactory nerve paralysis at 150 ppm and coma at 1000 ppm [13, 14, 15]. Immediate collapse and death can be the result of exposure to high concentrations as it is extremely hazardous and deaths of workers were recorded to occur in industrial sectors, due to H_2S exposure [16].

Biochar that is derived from readily abundant biomass like rice husk has a potential option to replace activated carbon as adsorbent to reduce the H_2S pollution, via adsorption process. Hydrogel biochar (HBC) is a chemically modified version of biochar that is newly revolutionized through polymerization process. Hydrogels, which are another widely used absorbent for the removal of heavy metals from aqueous media, are three-dimensional networks containing hydrophilic functional groups [17]. Meri et al. [18] studied on empty fruit bunch-HBC composite properties and found that with the synthesis of HBC, the lignocellulosic structure of biomass became stronger and protected by the presence of cross-linker. In addition, a study conducted by [19] stated that the composite HBC demonstrated a high swelling ability and possessed functional groups which contributed to the effectiveness in removal of zinc ion contaminants from aqueous environments. Moreover, in HBC, the concentrations of extractable toxic elements such as polycyclic aromatic hydrocarbon (PAH) were confined within the biochar. Thus, the topic of hydrogel biochar has become a research interest, for development and application of this material in wastewater and gas treatment as a potential novel adsorbent [18].

There are various parameters that affect the efficiency of the adsorption process. This study is conducted to determine the effect of sorbent weight on the adsorption of H_2S, using biochar and hydrogel biochar.

2. Methodology

2.1. Raw Material Preparation

Rice husk samples were collected at Sendi Enterprise factory at Tanjung Karang, Selangor. The rice husk then was dried under sunlight for a day in order to avoid the growth of orange fungus and grey mould that can fill up the pores in the rice husk thus making it less effective for adsorption process. Furthermore, the rice husk was kept in a sealed plastic to avoid limit the contact of the rice husk with surrounding air as at the atmospheric condition contain moisture.

2.2. Pyrolysis

The biochar preparation from the rice husk was done by pyrolysis process using furnace. The temperature of the furnace was one of the parameter that was controlled to obtain the desired product. The preparation of biochar by slow pyrolysis ranges from 350°C to 650°C, so in this study the defined temperature for the pyrolysis process was 450°C [20]. Approximately, 200g of rice husk was weighed and folded using aluminium foil before being placed in the furnace. The folded sample containing rice husk then was put inside the furnace, and the temperature of the furnace was set to 450°C and the pyrolysis time was set at 20 minutes [21]. After the pyrolysis process was completed, the sample was allowed to cool for approximately one day.

2.3. Pre-treatment

The biochar produced was pre-treated via grinding and washing process. For grinding, the biochar was grinded, to enable it to pass a 10m sieve. The grinded biochar was then kept at room temperature prior to analysis [20].

Washing of the biochar was carried out to remove all the impurities in the biochar, by using distilled water. The washing step was done several times to obtain more accurate results. The biochar was filtered by using filter pump each time the wash step was performed. The washed biochar was then dried in the oven for 24 hours at temperature of 100°C [21, 22]

2.4. Hydrogel Biochar Formation

Hydrogel biochar were synthesized by dissolving 1.0g of Acrylamide (AAm) in 1.0mL of distilled water. Then, the rice husk and 0.001g of N,N'-methylenebisacrylamide (MBA) were added to the AAm solution. To initiate the polymerization, 0.2mL 0f 0.1g aqueous solution of Ammonium persulfate (APS) was added after through mixing. Then, the hydrogel biochar precursor solution was immediately placed into a petri dish and placed on a heating dish at 100°C for 10 minutes. The source of this hydrogel formation method obtained from Karakoyun et,al. (2011). Scaled up had been performed to increase the production of hydrogel biochar.

2.5. Characterization Analysis

The elemental compositions of all samples were analyzed using Elemental Analyzer (CHNS-O) by Thermo Finnigan FlashEA1112 manufactured by Thermo Fischer Scientific. Approximately 10 to 15g samples were placed and weighed in a tin capsule and crimped. The sample was then folded using the aluminium foil. Then, the samples were placed in the autosampler. The samples in the autosampler were then inserted in the combustion reactor and kept at temperature between 900 to 1000°C. the exact amount of oxygen was introduced for optimum reaction in the combustion reactor and heated up to 1800°C. at high temperature, the samples were converted into elemental gases through reduction process using copper. Lastly, the elemental gases were detected by highly sensitive thermal conductivity detector (TCD).

Brunauer-Emmett-Teller (BET) was used to determine the surface area and pore volume of the samples. This instrument used gas sorption techniques to measure the surface area and pore size. The samples were degassed at 120°C under a continuous nitrogen flow of 10L/min for 24-hour prior analysis. In addition, the functional groups present in the samples were determined using a Fourier Transform Infrared (FT-IR) spectrometer by Perkin Elmer Spectrum One FT-IR. The spectra range chosen was from 4000 to 400cm^{-1}.

2.6. Adsorption Experimental Setup

The adsorption part of study was done by using the adsorption system. Fig. 1 shows the schematic diagram of the adsorption unit.

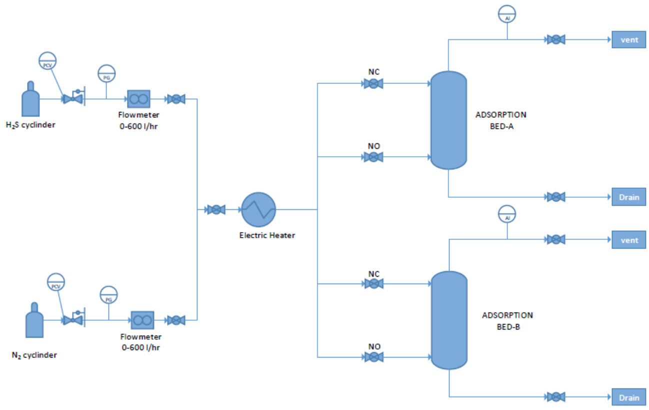

Fig. 1: Adsorption Unit Schematic Diagram

The adsorption feed has two feed streams, one for H_2S gas and the other one for Nitrogen gas. The function of nitrogen gas is to purge H_2S gas in the adsorption system. In this study, only Adsorption Bed-A was used. Adsorption Bed-A consists of three smaller bed and in only two beds were used in this study.

H_2S gas was flown in to the adsorption system and the flowrate was fixed at 2L/minutes by using the flowmeter. Two beds in the Adsorption Bed-A were filled with 20g, 30g and 40g of the samples, biochar and hydrogel biochar each. A gas detector was connected to the outlet to record the concentration of H_2S gas that flow out from the adsorption system. Each run was fixed at 10 minutes.

3. Results and Discussions

3.1. Elemental Analysis

The elemental analysis was carried out to determine percentage of carbon, hydrogen and nitrogen content in the samples. Table 1 shows the elemental analysis of rice husk, biochar and hydrogel biochar. The value of carbon, hydrogen and nitrogen percentage in rice husk and biochar is almost similar as shown in study of Claoston et,al. (2014) [20]. Based on Table 1, the percentage of carbon in the biochar is higher compare to in the rice husk. The reason of this increase of carbon is because of the rice husk has undergone pyrolysis to become biochar. During pyrolysis, the carbonization process changes the organic component, followed by a gradual degradation, decomposition and charring [20, 23, 24]. Depolymerization, hydrolysis, oxidation, dehydration and decarboxylation are included in the initial degradation. For the elemental content of hydrogel biochar, the value of carbon, hydrogen and nitrogen percentage shows almost similar value as in the past study [21]. As the monomer, acrylamide started linking together to form a polymer, the amount of hydrogen increased as acrylamide mostly formed hydrogen atoms.

Table 1: Elemental Analysis of Rice Husk, Biochar and Hydrogel Biochar

Samples	Elemental Content (%)		
	C	H	N
Rice husk	35.02	5.31	0.00
Biochar	73.45	3.45	4.84
Hydogel Biochar	24.55	12.06	12.04

3.2. FTIR Analysis

Fig. 2 to 4 show the peaks obtained from FTIR analysis of the rice husk, biochar, and hydrogel biochar, respectively.

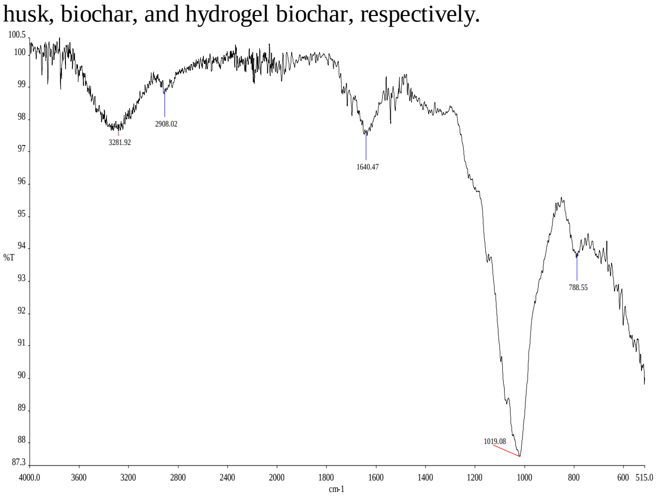

Fig. 2: Rice Husk FTIR Results

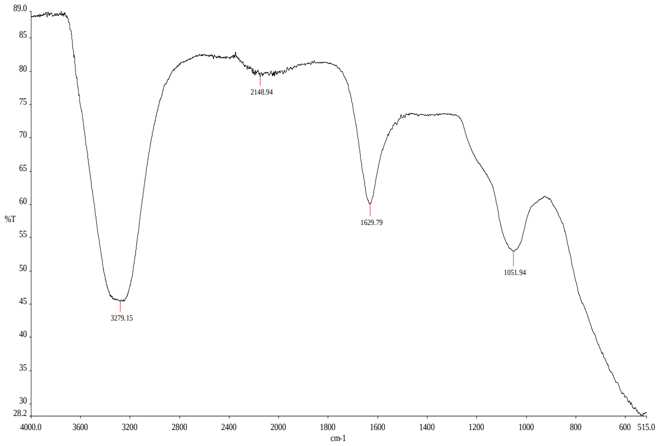

Fig. 3: Biochar FTIR Results

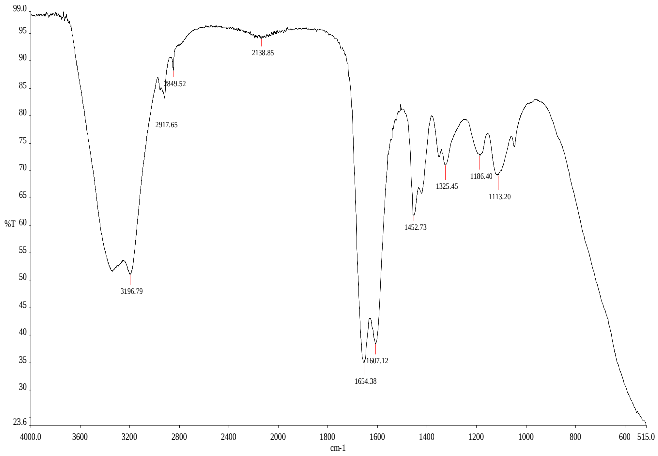

Fig. 4: Hydrogel Biochar FTIR Results

Based on Table 2, both rice husk and biochar have functional group of O-H. The missing O-H vibration in hydrogel biochar may suggest that phenolic compounds in lignin had been degraded [20]. The functional groups of =C-H and C=C that are only detected in hydrogel biochar may result from the polymerization process. FTIR spectra of biochar revealed a decrease in H-bonded hydroxyl groups that may be due to the acceleration of dehydration reaction in biomass, as temperature increased during pyrolysis [20].

Table 2: Functional Group of Rice Husk, Biochar and Hydrogel Biochar

Wave number (cm^{-1})	Rice Husk	Biochar	Hydrogel biochar	Vibration characteristics
3400-3200	3281.92	3279.15	-	O-H stretching
3100-3000	-	-	3196.79	=C-H stretch
2950-2840	2908.02	-	2917.65	-C-H stretch
1680-1600	-	-	1654.38	C=C alkene
1650-1550	1640.47	1629.79	1607.12	N-H bend

3.3. BET Analysis

As shown by Table 3, the surface area is decreased as rice husk undergoes pyrolysis to produce biochar. The explanation that can be given about the surface area decrease is the lignin break down by extensive cleavage of b-aryl ether linkages during steaming under 488K [23]. The decomposition of lignin begins at about 550K with maximum rate occurring between 635K and 725K and the completion of the reaction occurs at 725K and 775K [23]. As the lignin decomposed, pores were produced on the biochar and the pore size increased all together. As for hydrogel biochar, the polymerization increased the BET surface area as acrylamide polymer was added to the biochar. This polymer filled in the pore on biochar and explains the reason behind the pore volume of hydrogel biochar being lower than biochar. As the pore volume decreased, the pore size absorption area also decreased.

Table 3: Analysis of BET Surface Area, Pore Volume and Pore Size

Samples	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size Adsorption (Å)
Rice Husk	24.7105	0.027714	44.8624
Biochar	2.8296	0.11716	165.6189
Hydrogel Biochar	3.8661	0.00908	93.904

3.4. Effect of Sorbent Weight

From Fig. 5, the graph show that mass of H_2S absorb per absorbent mass increase exponentially at the first minute. After the first minute, the absorbent show trend of slowly increase in absorbing the H_2S. The percentage of H_2S removal increased with increasing the sorbent weight [21].

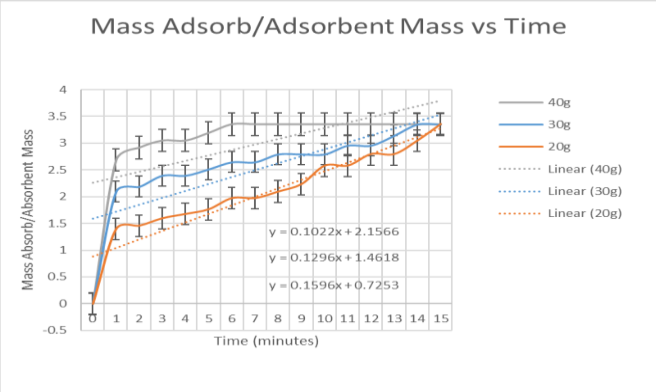

Fig. 5: Mass Adsorb/Adsorbent Mass vs Time of Biochar

For the removal of H_2S by using hydrogel biochar, low H_2S adsorption was recorded. The low presence of water inside the hydrogel biochar is the most likely the main reason of low performance in removal of H_2S. Ideally the hydrogel biochar in this experiment needs to be increased its moisture content to increase the adsorption performance.

4. Conclusion

All the result from the characterization show that biochar has the ability to become an alternative for activated carbon as a sorbent to remove H_2S. Sorbent weight parameter shows that it can affect the removal of H_2S with the increase in weight of the sorbent, then removal also increase. However, hydrogel biochar does not achieve the initial hypothesis that it will increase the performance of the biochar in adsorb the H_2S. With the lack in amount of research about the hydrogel biochar derived from rice husk and the role of hydrogel in removing H_2S, more studies hopefully can be performed

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