Effect of Sorbent Weight on H₂S 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 biocahr 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 being predicted.

Keywords— Rice Husk, Biochar, Hydrogel Biochar, Hydrogen Sulphide

I. INTRODUCTION

Rice husk is available in abundantly from agriculture industries that typically been treated using traditional methods such as composting and incineration [1]. The same source also indicated that this organic solid waste is not suitable for those process as small concentration of nitrogen contains inside them for composting and during incineration, smoke being generate by considerable amount of solid grain into the environment. Carbonaceous material can produce with rice husk as raw material as it presence with large amount of hydrocarbon such as cellulose and lignin content, which form complex porous structures [2]. Hence, biochar is proven can be derive from abundant source of biomass, namely rice husk.

Biochar is carbon-rich product when biomass, such as rice husk heated in closed container with little or no available air [3]. In technical term, biochar is produced by thermal decomposition of organic material at relatively low temperature with limited supply of oxygen [3]. In chemical point of view, the organic portion of biochar has a high carbon content, which mainly compromise socalled 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]. A list of applications for biochar involving energy production, agricultural industries, carbon sequestration, activated carbon adsorbent and bio-refinery [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 deoxiding ability [6]. In commercial process, activated carbon is produce by degraded and coalified plant matter [7]. However, with high temperature and additional activation process to produce, researcher currently focusing on producing alternatives of activated carbon that required lower energy and cheaper feedstock [8]. Biochar that can be produced from rice husk can be view as potential replacement for activated carbon. This is because biochar is cheaper to produce, while having good porosity and basic functional group, the trait that contribute to become sorbent of gas pollutant [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 has to pay for the associated rapid economic growth and to achieve the goal of 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 (H₂S).

Naturally, H_2S is produced from the breakdown plant and animal material and from geothermal fields. For the example of industrial sources of H_2S are rayon textile production, oil and gas refineries, and pulp and paper manufacturing [12]. The dose exposure to H_2S affect greatly the health effect, 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 most deaths have occurred in industrial settings [16].

Biochar that derive from readily abundant biomass like rice husk has a potential option to replace activated carbon as adsorbent to reduce the H₂S pollution.

II. METHODOLOGY

A. Sample 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.

B. Pyrolysis

The biochar preparation from the rice husk was done by pyrolysis process using furnace. The temperature of the experiment was one of the parameter that being controlled to obtained the desired product. The preparation of biochar by slow pyrolysis is 350°C to 650°C, so in this study the defined temperature for the pyrolysis process is 450°C [17]. Approximately, 200g of rice husk was weight and folded using aluminum 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 is 20 min [18]. After the pyrolysis process was completed, the sample was allowed to cool for approximately one day.

C. Grinding

The biochar then ground to pass a 10m sieve and kept at room temperature prior to analysis [17].

D. Washing Treatment

To remove all the impurities in the biochar, the biochar was then washed by using distilled water. The wash step was done severel times to maximize the result. The biochar being filtered by using filter pump each time the wash step was perform. Biochar needed to be dried at 80°C in the oven for 2 days, however with a few adjustments, the biochar was dried in the oven for 24 hours at temperature of 100°C [18, 19]

E. Hydrogel 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.

F. Characterization Analysis

The elemental composition 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.

G. Adsorption

The adsorption part of study was done by using the adsorption system. Figure 2.1 show the schematic diagram of the adsorption unit.



Figure 2.1: Adsorption Unit Schematic Diagram

The adsorption feed has two feed, 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 after of H_2S gas runned. In this study, only Adsorption Bed-A was used. Adsorption Bed-A consist of three smaller bed and in only two beds were used in this study.

 H_2S gas was been flown in to the adsorption system and the flowrate been 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 drain to read the concentration of H_2S gas that flow out from the adsorption system. Each run was fixed for 10 minutes.

III. RESULTS AND DISCUSSION

A. Elemental Analysis

Table 4.1: Elemental Analysis of Rice Husk, Biochar and Hydrogel Biochar

Samples	Elemental Content (%)			
_	С	Н	Ν	
Rice husk	35.02	5.31	0.00	
Biochar	73.45	3.45	4.84	
Hydogel	24.55	12.06	12.04	
Biochar				

The elemental analysis is to determine percentage of carbon, hydrogen and nitrogen content in the samples. Table 4.1 show 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) [17]. Based on Table 4..1, the percentage of carbon in the biochar is higher compare to in the rice husk. The reason of this increase of carbon show in Table 4 is because of the rice husk need to undergo pyrolysis to become biochar. During pyrolysis, the carbonization process changes the organic component, proceeds a gradual degradation, decomposition and charring [17, 20, 21]. Depolymerization, hydrolysis, oxidation, dehydration and decarboxylation are included in the initial degradation. For the elemental content of hydrogel biochar in Table 4.1, the value of carbon, hydrogen and nitrogen percentage shows almost similar value as in the past study [18]. As the monomer, acrylamide start linking together to form a polymer, the amount of hydrogen increase as acrylamide mostly form of hydrogen atom.



Figure 4.3: Hydrogel Biochar Functional Group

number			biochar	characteris
(cm ⁻¹)				tics
3400-	3281.92	3279.15	-	O-H
3200				stretching
3100-	-	-	3196.79	=С-Н
3000				stretch
2950-	2908.02	-	2917.65	-C-H
2840				stretch
1680-	-	-	1654.38	C=C
1600				alkene
1650-	1640.47	1629.79	1607.12	N-H bend
1550				

Based on Table 4.2, 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 [17]. The functional group of =C-H and C=C that only detected in hydrogel biochar may result from the polymerization. FTIR spectra of biochar revealed a decreased in H-Bonded hydroxyl groups that may attributed to the acceleration of dehydration reaction in biomass as increasing temperature during pyrolysis [17].

C. Brunauer, Emmett and Teller Surface Area Analysis (BET)

Table 4.3: Analysis of BET Surface Area, Pore Volume and Pore

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

As shown by Table 4.3, the surface area is decrease as rice husk undergo pyrolysis to produce biochar. The explanation that can be given about the surface area decrease is the lignin broken down by extensive cleavage of b-aryl ether linkages during steaming under 488K [20]. 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 [20]. As the lignin decomposed, pores are produced on the biochar and the pore size increase all together. As for hydrogel biochar, the polymerization increases the BET surface area as acrylamide polymer were added to the biochar. This polymer fills in the pore on biochar and explain the reason behind the pore volume of hydrogel biochar lower than biochar. As the pore volume decrease, the pore size absorption area also decreases.

D. Adsorption Rate

Table 4.2: Functional Group of Rice Husk, Biochar and Hydrogel Biochar

Bioenai					
Wave	Rice Husk	Biochar	Hydrogel	Vibration	



From Figure 4.4, the graph show that mass of H₂S absorb per absorbent mass increase exponentially at the first minute. After the first minute, the absorbent show trend of slowly increase in absorbing the H₂S. The percentage of H₂S removal increased with increasing the sorbent weight [18]. From the slope of the graph, rate of H₂S absorb can be conclude as increase as the sorbent weigh increase.

For the removal of H₂S by using hydrogel biochar, almost none H₂S adsorption recorded. After analyze the past study, conclusion that can be made is low presence of water inside the hydrogel biocahr is the reason of low performance in removal of H₂S. Ideally the hydrogel biochar in this experiment need to be wet to increase the adsorption performance.

IV. CONCLUSION

All the result from the characterization show that biochar has the perk to become the alternative of activated carbon as the sorbent to remove H₂S. Sorbent weight parameter shows that it can affect the removal of H₂S 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 H2S. With the lack in amount of research about the hydrogel biochar derived from rice husk and the role of hydrogel in removing H₂S, more studies hopefully can be performed.

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