Effect of Loading and H_2O Wetness of Hydrogel Biochar Derived from EFB for H_2S gas Sorption

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Abstract—**Hydrogel biochar is the non-toxic, biocompatibility and water absorbent polymeric materials, evaluated for their characterization and ability to absorb hydrogen sulfide (H_2S) in gas phase. The H_2S gas is very hazardous gas as it is produced from natural and human-made process and due to its higher density than air, it become more dangerous to the atmosphere. The purpose of conducting this research were to determine the characterization of empty fruit bunch hydrogel biochar, HBC-EFB in removal of H_2S gas and to determine the ability of HBC-EFB in absorption of H_2S gas. In order to achieved the objective of this research, the empty fruit bunch hydrogel biochar (HBC-EFB) was prepared by using acrylamide (AAm) as monomer, with N-N'-methylenebisacrylamide (MBA) as crosslinker and ammonium persulfate as initiator. The HBC-EFB was characterized by using Thermal Gravimetric Analyzer (TGA), Elemental Analyzer (EA), Brunaeur Emmet Teller (BET) and Scanning Electron Microscopy (SEM). The absorption rate of HBC-EFB was determine by using Multi Sorption Bed. The experimental data showed that the absorption rate of HBC-EFB was efficient when the bed was full up to three bed with 91% absorption in wet condition.**

***Keywords*— Biochar, hydrogel biochar, absorption, hydrogen sulfide**

I. INTRODUCTION

The H_2S is defined as an odorous and hazardous gas that produced from the natural process such as microbial decomposition and human-made process such as from wastewater treatment plant. According to (Guofeng Shang, 2012), this gas is extremely toxic to be exposed to living organism and even corrosive to the concrete and steel. From the previous study, the activated carbon was chosen as the material used in removing H_2S gas due to its advantages in the aspects of high surface area and porosity for adsorption process (Xiaoyun Xu, 2014), (Mohammed Danish, 2013) and (S. Sircar, 1996). However, since there are a few flaws in activated carbon application for this purpose such as it demanded high temperature, high pressure and an activation process in its manufacturing (Guofeng Shang, 2013), the researchers had turned their focus on more environmental friendly and less costly materials such as biochars.

Biochar is the carbon-based materials of organic material thermal decomposition that produced at low temperature and under limited amount of oxygen. Not only it is applied in the investigation on heavy metals, it also suitable in the gas analysis. In the same time, it is able to balance the nutrient deficiency, neutralized the acidity of the soil, improved the soil physical properties and increase the soil retention at surface functional group as mentioned by (R. Calvelo Pereira, 2015) and (Talberg, 2009). The empty fruit bunch biochar is chosen to be main material because of its availability in Malaysia as this country is the largest producer of palm oil and the palm oil mills produced large amount of biowastes (K.H. Khor, 2008), (Muhammad Afif Ariffin, 2014).

The empty fruit bunch biochar then was modified to hydrogel because of its excellent properties like hydrophilicity, high swelling capacity and non-toxic. Also, its ability in absorbing water due to hydrophilic characteristic of functional groups on the polymeric chain is very favourable in H_2S sorption (Lamin Samyang, 2013),(Ahmed, 2015).

As claimed by (Necdet Karakoyun, 2011), hydrogel biochar is a three-dimensional network polymer that very sensitive to the change of their environment for instance ionic strength, pH, temperature, chemical reaction and interaction with absorbent. This statement also being supported by the (Lamin Samyang, 2013) and (Guiyin Zhou, 2015).

The objectives of this study were to investigate the characterization of empty fruit bunch hydrogel biochar as an absorbent for the H_2S removal and its efficiency in absorbing the H_2S from being released to the atmosphere. The result show that HBC-EFB is the appropriate materials in H_2S sorption.

II. METHODOLOGY

A. Materials

On the report made by (Necdet Karakoyun, 2011), (Lamin Samyang, 2013), (Guiyin Zhou, 2015) and (Wan Azlina Wan Ab Karim, 2014), acrylamide (AAm), N-N'-methylenebisacrylamide (MBA) and ammonia persulfate (APS) were used as a monomer,cross-linker and initiator respectively were purchased from Chemistry Lab, Universiti Teknologi Mara. Distilled water (DI) had been used throughout the experiments. Thermal Gravimetric Analyzer (TGA), Elemental Analyzer (EA), Brunaeur Emmet Teller (BET) and Scanning Electron Microscopy (SEM) were performed for samples characterization. Multi Sorption Bed was used to determine the H_2S absorption rate of the hydrogel biochar.

B. Preparation of Hydrogels

Based from the previous study by (Lamin Samyang, 2013), (Necdet Karakoyun, 2011), (Nurettin Sahiner, 2013) and (Wan Azlina Wan Ab Karim, 2014), the hydrogel biochar of empty fruit bunch (HBC-EFB) production process is as follows: 30 g of AAm was dissolved in 30 ml of distilled water. Then, 18 g of empty fruit bunch biochar was mixed with 0.033 g of MBA. The mixture of the biochar and the cross linker were added to the AAm solution to initiate the polymerization process. The hydrogel precursor solution was placed in the small ice cube tray and placed in the oven at 40°C for 30 minutes. Next, the precursor solution was left for 24 hours at room temperature for polymerization and cross-linking process complete. Finally, the HBC-EFB was cut into desired size and washed with distilled water. The hydrogel biochar were dried in the oven at 40°C until the weight constant. The HBC-EFB and raw EFB then later characterized and utilized for the absorption test.

C. Characterization methods

The moisture content, volatility, fixed carbon and ash content were determined by placing 10 mg each of the samples in the crucible of Thermal Gravimetric Analyzer (TGA) as shown in Figure 1 and were heated to 1200°C with the heating rate of 20°C/min. The samples was heated up under nitrogen and air atmosphere at 25 ml/min flow velocity (ASTM D1762-84).

Figure 1 : Thermal Gravimetric Analyzer Mettler Toledo TGA/DSC TGA)

The elements that presence in the HBC-EFB and raw EFB were determined by placing 10g to 15 g of the samples in the aluminum foil and were folded. The samples were placed in the Autosampler of Elemental Analyzer (EA) CHNS-O, FlashEA 1112 series as shown in Figure 2. The samples then dropped to the combustion reactor, and the temperature was controlled at temperature 900°C to 1000°C. For optimum reaction, the exact amount of oxygen was introduced and heated up to 1800°C. The samples was converted to elemental gases at high temperature by reduction using copper. The elemental gases was detected by the highly sensitive thermal conductivity detector (TCD) (ASTM D3176-84).

Figure 2 : Flash EA 1112 Elemental Analyzer

The surface area, pore volume and size were determined by using Brunaeur Emmet Teller (BET) V-Sorb 4800S (Chamberland, 2008) as shown in Figure 3. The HBC-EFB and raw EFB were degassed at 120°C under a continuous nitrogen flow of 10L/min for 24 hours (ASTM D6556-16).

Figure 3: Brunaeur Emmet Teller V-Sorb 4800S

Scanning Electron Microscopy (SEM) SU5000 (Takagi, 2001) was used to determined the surface morphology for both types of samples. The image was ranging from 1cm to 5 microns in width with spatial resolution of 50 to 100 nm at 10 kV of scanning voltages (ASTM F1372-93).

Figure 4 : Scanning Electron Microscopy (SEM) SU5000

D. Equipment setup

Based on the schematic diagram of Multi Sorption Bed in Figure 6, the nitrogen gas was allowed to flow throughout the Multi Sorption bed at 10 L/min for zeroing and to removed the H_2S gas that still trapped in the bed. The concentration of the outlet gas was measured by using H_2S detector. The concentration of outlet gas will be recorded until 25 ppm.

E. Effect of loading

The HBC-EFB was filled up to 0.5 inch of the bed height. Then 1L/s of H_2S gas flow was allowed to flow pass through the HBC-EFB. The outflow of the gas was detected by using H_2S gas detector in ppm and recorded. The process were repeated by filling the HBC-EFB to 1 inch and 2 inch of the bed height.

F. Effect of H_2O wetness

The HBC-EFB that was filled to 0.5 inch of the bed height was mixed with 5 ml of distilled water and let it to absorbed all the water. The H_2S gas was allows to flow through the samples and the final concentration in ppm was detected using H_2S gas detector and recorded. The process were repeated for 1 inch and 2 inch of the bed height with 10 ml and 15 ml of distilled water.

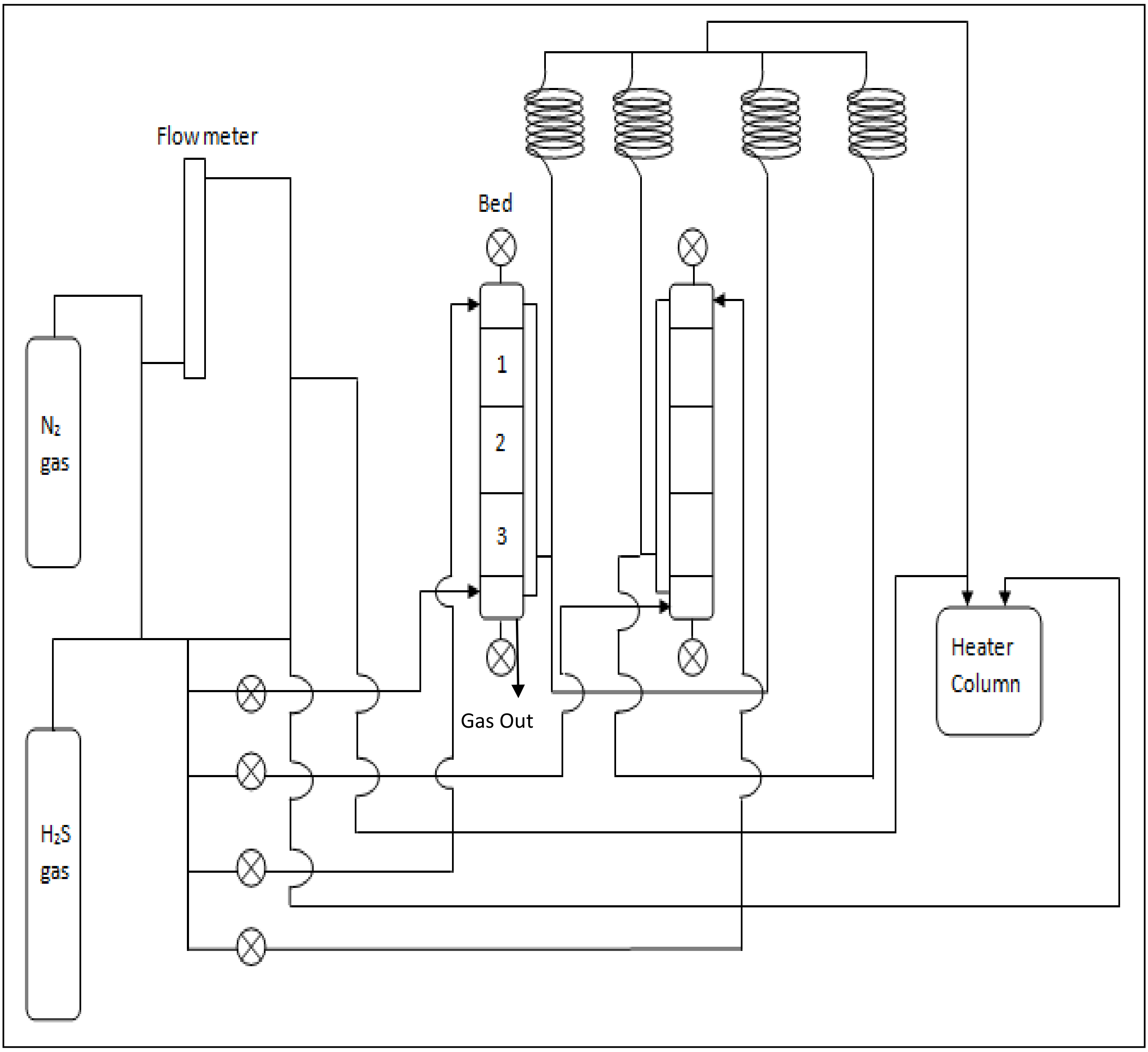


Figure 5 : Schematic diagram of Multi Sorption Bed

III. RESULTS AND DISCUSSION

A. *Characterization of the samples*

The weight loss of the samples for TGA indicates the moisture, volatility, fixed carbon and ash contents in the both HBC-EFB and raw EFB. In line with (ASTM D1762-84), Table 1 was prepared.

Table 1: Proximate analysis of raw EFB and HBC-EFB

Sample	Moisture (%)	Volatile (%)	Ash (%)	Fixed Carbon (%)
Raw EFB	3.73	75.90	3.92	16.45
HBC-EFB	5.20	66.88	4.44	23.45

By comparing the data from both samples, the HBC-EFB had higher moisture, ash and fixed carbon contents than raw EFB except for volatile content. HBC-EFB had 5.20% of moisture content, 66.88% of volatile content, 4.44% of ash content and 23.45% of fixed carbon content. In the interim, raw EFB had 3.73% of moisture content, 75.90% of volatile content, 3.92% of ash content and 16.45% of fixed carbon. The HBC-EFB had higher moisture content because of its hydrophilic nature that make it able to retain the moisture in the sample (Lamin Samyang, 2013). Unlike ash, the volatile matter depended more on temperature than the raw materials. The HBC-EFB is more exposed to higher temperature since it undergo pyrolysis process that required the temperature to be 700°C without the presence of oxygen to be converted to biochar. Then, the biochar was modified to hydrogel which it required to be heated in the oven at 40°C. Thus, the volatile matter would reduce at high temperature. However, raw EFB only exposed to hot sun for it to be dried (S. Ghazali, 2016). The ash content of the samples can be categorized from type of feedstock material and temperature. Since the materials used were from the same source, the ash content in this study will be analyzed from the temperature aspect. From the previous study by (Akio Enders, 2012), when the raw EFB was pyrolyzed, the ash content increased due to dewatering of anaerobic digestion and passive aggregation of mineral elements throughout the decomposition of organic C,O and H elements. Fixed carbon content in the samples was influenced by increasing of temperature. As stated by (Kwang Ho Kim, 2012), HBC-EFB would became more stable carbon form where it had higher resistance to heat as the temperature increase.

Table 2 : Ultimate analysis of raw EFB and HBC-EFB

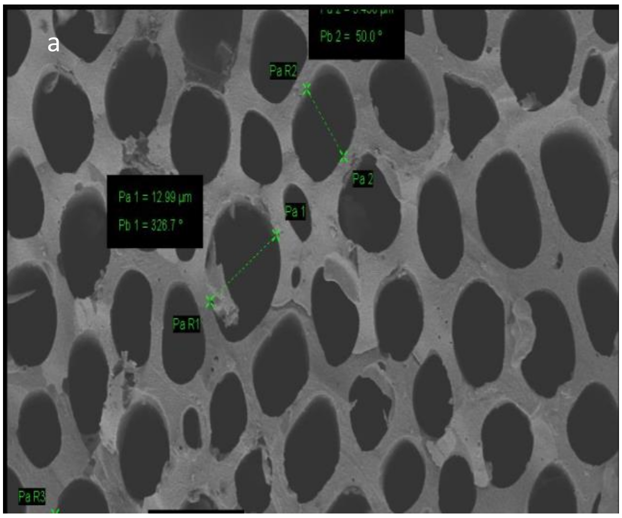
Sample	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Sulfur (%)	Oxygen (%)
Raw EFB	0.86	43.21	7.42	0.00	43.84
HBC-EFB	14.95	46.58	5.72	0.00	32.75

There were some difference in the amount of the element between raw EFB and HBC-EFB. The raw EFB was contain majorly 43.84% oxygen which was higher than HBC-EFB which was made up from 32.75% oxygen and 7.42% hydrogen higher than HBC-EFB. Other than these element, the HBC-EFB had the higher elements content compared to raw EFB. The HBC-EFB was rich with carbon content where it contain 3.37% more carbon than raw EFB. Then, it followed by 14.09% of more nitrogen element in the HBC-EFB. However, there was no sulfur content had been detected by the analyzer for both type of samples. It is because the biochar does not have any sulfur presence in it from the beginning. The carbon content and fixed carbon content are correlate to each other. From the above data, it shows that the higher the carbon content will produce higher amount of ash. According (Charles A. Mullen, 2010), the carbon content in biochar is very stable in the soil ambiance and can be removed for much longer time. The C, H,O, N and S content in the biochar is affected by the temperature of pyrolysis process and its residence time. Referring to the journal written by (Kwang Ho Kim, 2012) , the carbon content is higher in the hydrogel biochar is due to the increasing of degree of carbonization with increasing of pyrolysis temperature. The other elements are detected to be lower than carbon is cause by the cleavage and cracking of weak bonds within the structure of the biochar. As stated by (Muhammad Afif Ariffin, 2014), the difference of carbon content in the samples showed that only small amount of carbon content that involved in the vaporization process. The oxygen reduction indicates that more oxygen is used during gasification process. By referring to the carbon and nitrogen contents, it show that HBC-EFB is an ideal materials for soil application in sequestration strategy and nutrient supplier in the agricultural sector.

Table 3: Analysis of surface area, pore volume and pore size

Samples	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
Raw EFB	1.57	0.002	54.31
HBC-EFB	1.26	0.001	30.02

The raw EFB had higher surface area, pore volume and pore size which are 1.57 m^2/g, 0.002 cm^3/g and 54.3138 Å. While for HBC-EFB, it does not have much difference with raw EFB in its surface area but it have almost 50% and 47% difference in their pore volume and pore size respectively. The surface area of the samples were depends on the feedstock characteristics and process conditions. According to (Jayne H. Windeatt, 2014), the HBC-EFB had lower surface area because of low H/C ratio compared to raw EFB as the result from low graphitization of the structure during pyrolysis process. As mention by (Tahmina Imam, 2012) , the higher pyrolysis temperature will lead to higher devolatilization which also affecting the surface area, pore volume and adsorption behavior to increased. On the report of (Kwang Ho Kim, 2012), the pyrolysis reaction undergo by HB-EFB could weaken the biomass molecular structure and decreased the HBC-EFB particles as well as their size.



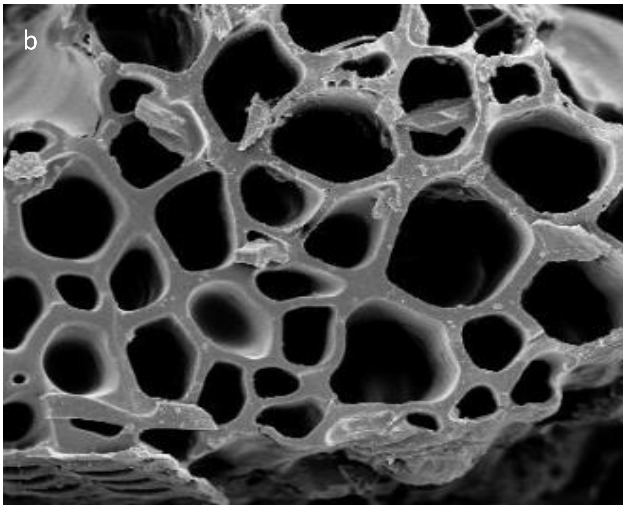


Fig. 6: SEM images of a) raw EFB and b) HBC-EFB

SEM images of raw EFB and HBC-EFB (1000X) indicated the pore size distribution of the samples. Based on the study by (S. Ghazali, 2016), the presence of holes and pores with different size would allowed water diffusion into the structure quickly in large amount. Based on the comparison of the images for both samples leads to the resultant that the morphological changes happened during the formation of the hydrogel. The raw EFB had a regular pattern of pore size than EFB. From the observation of these images, it proved that the pore size of HBC-EFB was shrunk compatible with the data analyzed in the analysis made by BET. The mechanical strength during pyrolysis affect the biochar structure continuously as the temperature increased. The structures become more fragile and the number of micropores decrease as the number of macropores increased (N. Claoston. AW Samsuri, 2014). According to (Kwang Ho Kim, 2012), the chemical bonds and the original material structure can broke from the thermal degradation of chemical bonds and melting of some compounds. Even though the BET surface area, pore volume and pore size of HBC-EFB is lower than raw EFB, the effectiveness of HBC-EFB may related to the pore structure, functional group and surface chemistry as mention by (Nur Zalikha Rebitanim, 2012)

B. *Effect of loading*

As illustrated in Figure 7(a), the absorption rate of H_2S gas increase as the height of the sample in the bed increase. The time taken for the gas to diffused out from the absorbent is longer as more HBC-EFB were filled into the bed. From the plotted graph, it show that the bed that filled with HBC-EFB until 2 inch of bed height absorbed the highest amount of H_2S gas than the HBC-EFB filled for 0.5 inch and 1 inch of bed height. This indicates its efficiency in absorbing H_2S gas. The HBC-EFB that filled until 2 inch of bed height had 92% of absorption rate, followed by 90% of absorption rate from HBC-EFB in 1 inch of bed height and 89% of absorption rate from HBC-EFB in 0.5 inch of bed height. The higher the loading of HBC-EFB also indicates that more surface area will presence in the bed. (Guofeng Shang G. S., 2012) reported that the increase in surface area gives a higher number of adsorption site and space in HBC-EFB for H_2S gas.

C. *Effect of H_2O wetness*

Figure 7(b) show the result on the effect of H_2O wetness on HBC-EFB for H_2S sorption by comparing it with dry HBC-EFB. Since from the above study, the most efficient in absorbing H_2S gas was HBC-EFB that filled until 2 inch of bed height, the same parameter was used for this investigation.

The absorption curve indicates that the H_2S gas was trapped in the absorbent more efficiently when HBC-EFB was in wet condition than in dry condition. The absorbent was tested in the wet condition was based on the hypothesis. When the HBC-EFB was washed with the distilled water, the HBC-EFB tends to expand as it absorbing the water. From the previous study, water absorbency characteristic was affected by the carbon content and porous structure of the HBC-EFB. (S. Ghazali, 2016) stated that the presence of carbonaceous particles enhanced the water absorbency of the absorbent. Also, the pores presence in HBC-EFB allowed the water to diffuse and filled the space. Since the nature of H_2S gas that able to dissoved slightly in water lead to more absorption of this gas in the absorbent. Besides, the absorbent become more stickier where it stick to each other. This will give an advantages when the absorbent was filled in the bed. The wet HBC-EFB will reduced the possiblities of blank space existence in the bed and increase the contact area of H_2S gas with the HBC-EFB. By comparing both data, it shows that the wet HBC-EFB has 91% absorption rate which is higher than dry HBC-EFB where it had 90% absorption rate.

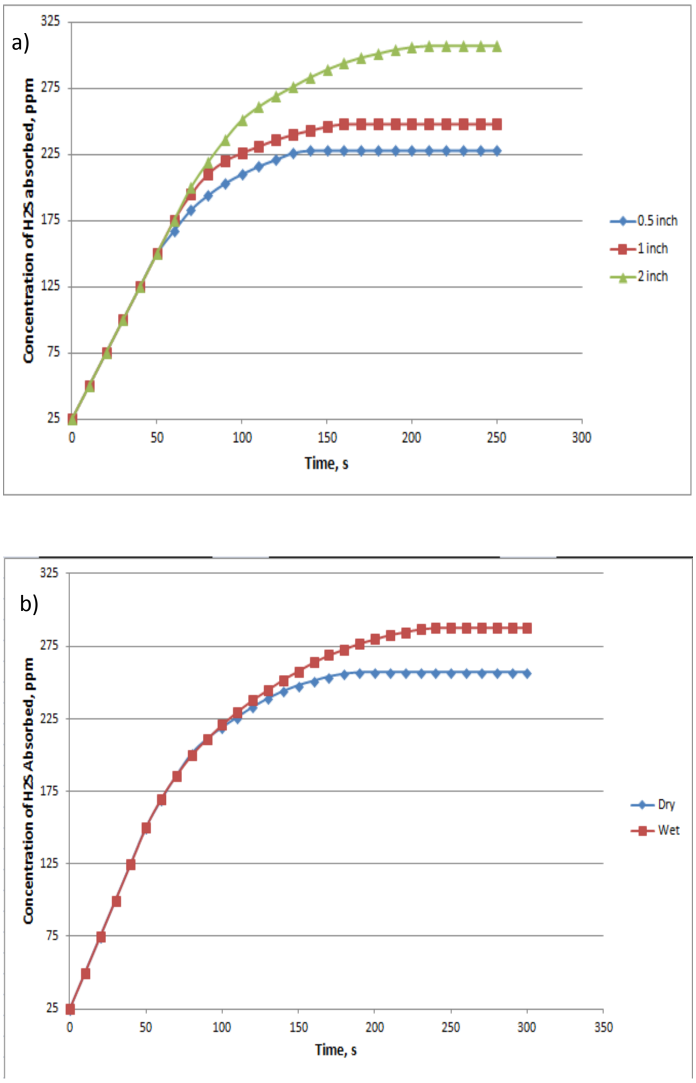


Figure 7: (a) Effect of loading of the HBC-EFB and (b) Effect H_2O wetness on HBC-EFB

IV. CONCLUSION

In conclusion, the empty fruit bunch hydrogel biochar, HBC-EFB were affective in H_2S sorption. The sorption capacity of the hydrogel biochar for H_2S removal is affected by the loading and wetness of the absorbent. The most effective HBC-EFB in absorbing H_2S gas is when the absorbent filled to 2 inch bed height in wet condition. The raw RFB and HBC-EFB were characterized.

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