Comparison of H$_2$S adsorption by two hydrogel composite (HBC) derived by Empty Fruit Bunch (EFB) biochar and Coal Fly Ash (CFA)

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Abstract. This study are covered the adsorption performance of two adsorbent Empty Fruit Bunch Hydrogel Biochar Composite (EFB-HBC) and Coal Fly Ash Hydrogel Composite (CFA-HC) on hydrogen sulphide. The EFB biochar were produce by pyrolysed and heated from room temperature to 550˚C at 10˚C/min under the Nitrogen flow. Meanwhile, coal fly ash collected from a power plant located in Selangor, Malaysia. Both of the materials is a waste from different industries and became the precursor to our adsorbents. EFB biochar and coal fly ash has been synthesized to become hydrogel by polymerization process with acrylamide (AAm) as monomer, N,N'-methylene bisacrylamide (MBA) as cross linker and ammonium persulfate (APS) as initiator. In addition, because of the speciality of hydrogel itself, which is has high ability in storing water, the effect of H$_2$O wetness on EFB-HBC and CFA-HC were investigate in adsorption of H$_2$S. EFB-HBC gave a longest breakthrough time and highest adsorption capacity compared with CFA-HC in both condition (dry/wet). The result also indicated that, the increased the bed height, increased the adsorption capacity.

1. Introduction

Hydrogen Sulfide (H$_2$S) is defined as hazardous gas produced from the natural process such as microbial decomposition and human-made process especially from wastewater treatment plant [1]. H$_2$S gas is extremely toxic to living organism and even corrosive to the concrete and steel [2]. In the H$_2$S treatment sector, activated carbon was chosen as the medium in removing H2S gas due to its advantages in the aspects of high surface area and porosity for sorption process [3]. 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, the researchers had turned their focus on more environmental friendly and less costly materials [4].

Empty fruit bunch is chosen as raw material because of its availability in Malaysia as abundance biomass waste as this country is the largest producer of palm oil [5]. Thermal conversion of raw EFB will produced carbonaceous material called biochars. Besides, Pyrolysis is suitable process to produce chars that used as precursor to activated carbon especially by slow pyrolysis around less than 700 °C [6]. Meanwhile, CFA produced as a waste product during the combustion process of coal in generation of electricity. They are cluster of spherical particles with a diameter ranging from 1 to 100 μm and typically grey in colour, quite abrasive and mostly alkaline in nature [7]. CFA are amorphous and its
high silica content with some alumina present makes it a suitable precursor as zeolites with application as adsorbent in wastewater treatment [8]. 

In this study, the empty fruit bunch biochar and coal fly ash will go through polymerization process by using Acrylamide (AAm) monomer to produce hydrogel biochar. The presence of the hydrogel coating of the biochar is known to help improves the adsorption efficiency by increasing the intake and holding up of water. Due to the high water content of the hydrogel plus porous structure networks, more solute will be trap by the hydrogel component [9].

2. Experimental procedure and methodology

2.1. Raw Material and Chemical
Raw Empty fruit bunch collected from palm oil mill in Negeri Sembilan, Malaysia. Meanwhile coal fly ash collected from a power plant located in Selangor, Malaysia. For the preparation of the hydrogel composite, acrylamide (AAm) used as monomer, N,N’-methylen ebsacry lamide (MBA) as cross linker and ammonium persulfate (APS) as initiator are supplied from R&M company. Distilled water used to remove unreacted monomer and to adjust the pH value of the biochar and coal fly ash.

2.2. Pyrolysis
Raw EFB dried at temperature of 100°C for 24 hours in an oven to reduce moisture content. The dried EFB pyrolysis in a fixed bed reactor and heated from room temperature to 550°C at 10°C/min under Nitrogen flow. Then the biochar has washed with distilled water to remove unwanted material. Then, the biochar dried in an oven with set temperature of 40°C for 24 hours.

2.3. Polymerization process to hydrogel composite
1.0g of acrylamide (AAm) monomer dissolved in 1mL of distilled water. 0.6g of the EFB biochar was mixed with 0.001g of MBA cross linker. The mixture of the EFB biochar and the cross linker then added to the AAm solution. 0.2mL of 0.1g aqueous solution of APS initiator added to the solution to initiate the polymerization. The precursor solution immediately place into plastic mould and place in an oven at 40°C for 30 minutes to speed up the polymerization and cross-linking process. Then the precursor solution left for 24 hours to let the polymerization and cross-inking process completed. After 24 hours, the EFB-HBC was taken out from the plastic mould and cut to desired size and washed with distilled water to remove unreacted monomer and low molecular weight matter from the EFB-HBC. Then the EFB-HBC dried in vacuum oven at 40°C for 24 hours. After 24 hours, the EFB-HBC was stored in desiccator until further used. The procedures repeated for coal fly ash to produced CFA-HC. This hydrogel formation method are following to procedure used by Karakoyun et al. (2011) with some modification [9].

2.4. Adsorption Performance

2.4.1. Effect of Bed Height. The adsorption studies were carried out in three layers stainless steel column with 3 inch height each of layer and 1.85-inch diameter. This experiment was carried out at constant temperature and flow rate at 27°C and 60 L/hr respectively. Every layers were supported with filter trays and 1 inch height of glass wool to prevent the fine particles pass through and damage the system. Then, the outlet stream were attached with Crowcon Gasman H₂S gas detector. The system was illustrated in Figure 1. Experiment were conducted to study the effect of bed height and H₂O wetness of EFB-HBC (Empty Fruit Bunch-Hydrogel Biochar Composite) and CFA-HC (Coal Fly Ash Hydrogel Composite). A comparison study of adsorption performance between EFB-HBC and CFA-HC were included in this study.

This study were conducted with different bed height of each trays. All the details of experiment were tabulated in Table 1, Table 2, Table 3 and Table 4. For the first experiment, in order to study the effect of bed heights in adsorption of H₂S, each trays were filled with 0.5 inch height of adsorbent
followed by next run were filled with 1 inch height of adsorbent for each tray. Finally, the maximum bed heights is 2 inch height of adsorbent were filled. Next, the experiment was repeated by using CFA-HC in order to study the comparison in adsorption of \( \text{H}_2\text{S} \).

In preparation of wet adsorbent, water has added to adsorbent until the adsorbent fully swelled and the mass of total wet adsorbent became double of its initial weight. Then, the wet adsorbent with 100% swelled has placed in column and compressed until achieved the required bed height, 0.5 inch, 1.0 inch or 2.0 inches.

The adsorption capacity \( q_e \) (mg/g), was calculated by using Eq. 1 [10]:

\[
q_e = \frac{(C_o - C_e)V}{W}
\]

Where \( C_e \) (mg/L) is the concentration of \( \text{H}_2\text{S} \) at equilibrium, \( C_o \) (mg/L) is the initial concentration of \( \text{H}_2\text{S} \) supplied. Meanwhile, \( V \) is the volume of the adsorbent (L) and \( W \) is the mass of adsorbent used (g).

To understand the adsorption behaviour, breakthrough curves \( \frac{C_f}{C_t} \) against time were analysed in this study.

\[\text{Figure 1. Multilayers adsorption column.}\]

\[\text{Table 1. Experiment's details for effect of bed height in adsorption of H2S by using dry EFB-HBC.}\]

| Bed height for each layers (Inch) | Total height used (Inch) | Total height used (cm) | Volume (L) | Total Mass (g) |
|----------------------------------|--------------------------|------------------------|------------|---------------|
| Dry 0.5 EFB-HBC                  | 0.5                      | 1.5                    | 3.81       | 0.066         | 12 g           |
| Dry 1.0 EFB-HBC                  | 1.0                      | 3                      | 7.62       | 0.132         | 18 g           |
Table 2. Experiment's details for effect of water wetness on EFB-HBC in adsorption of H₂S.

| Bed height for each layers (Inch) | Total height used (cm) | Total height used (cm) | Volume (L) | Total Mass (g) |
|----------------------------------|------------------------|------------------------|------------|---------------|
| Wet 0.5 EFB-HBC                 | 0.5                    | 1.5                    | 3.81       | 0.066         | 24 g         |
| Wet 1.0 EFB-HBC                 | 1.0                    | 3                      | 7.62       | 0.132         | 36 g         |
| Wet 2.0 EFB-HBC                 | 2.0                    | 6                      | 15.24      | 0.264         | 72 g         |

Table 3. Experiment's details for adsorption of H₂S by using dry CFA-HC.

| Bed height for each layers (Inch) | Total height used (Inch) | Total height used (cm) | Volume (L) | Total Mass (g) |
|-----------------------------------|--------------------------|------------------------|------------|---------------|
| Dry 0.5 EFB-HBC                  | 0.5                      | 1.5                    | 3.81       | 0.066         | 15 g         |
| Dry 1.0 EFB-HBC                  | 1.0                      | 3                      | 7.62       | 0.132         | 20 g         |
| Dry 2.0 EFB-HBC                  | 2.0                      | 6                      | 15.24      | 0.264         | 42 g         |

Table 4. Experiment's details for adsorption of H₂S by using Wet CFA-HC.

| Bed height for each layers (Inch) | Total height used (Inch) | Total height used (cm) | Volume (L) | Total Mass (g) |
|-----------------------------------|--------------------------|------------------------|------------|---------------|
| Dry 0.5 EFB-HBC                  | 0.5                      | 1.5                    | 3.81       | 0.066         | 30 g         |
| Dry 1.0 EFB-HBC                  | 1.0                      | 3                      | 7.62       | 0.132         | 40 g         |
| Dry 2.0 EFB-HBC                  | 2.0                      | 6                      | 15.24      | 0.264         | 84 g         |

3. Result and Discussion

3.1. Effect of bed height

Figure 2 shows the breakthrough profile for effect of bed height in removal of H₂S. In the beginning of experiment, no H₂S detected in the outlet gas just after the 25 ppm H₂S was supplied. Then after a few moment, the concentration started to increased gradually. After plotted a breakthrough curves by Cf/Ci (Final concentration/Initial Concentration) against Time (s), breakthrough times were calculated. As shown in Figure 2, the higher the bed heights, the longer the time taken to reach breakthrough. The highest bed height 6-inch has a longer breakthrough time, which is 80 s, followed by 3-inch bed height with 60 s, and the shortest is 50 s for 1.5-inch bed height. This is because increasing in bed heights will increasing the amount of adsorbent used. 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 H$_2$S hence the H$_2$S adsorption capacity increased [11]. By using Eq.1 the adsorption capacity were calculated. The adsorption capacity for 1.5-inch, 3.0-inch and 6.0-inch bed height of Dry EFB-HBC are 1.2485, 1.914 and 2.2513 respectively. Then, the adsorption capacities (mg/g) were increased with bed height increased.

![Breakthrough curves for Dry EFB-HBCs](image)

**Figure 2.** Effect of adsorbent's amount on breakthrough profile for adsorption of Hydrogen Sulphide.

### 3.2. Effect of water wetness in adsorbent

The specialty of hydrogel is able to absorbed water in the same time good in storing water without spilled. In addition, H$_2$S is soluble in water and it was predicted that the wet EFB-HBCs have significant adsorption performance. Then an experiment were proceed with wet adsorbent in removal of H$_2$S. As shown in Figure 3, wet EFB-HBCs have longer breakthrough time compared with dry EFB-HBCs which are 340 s, 360 s and 420 s for 1.5 inch, 3.0 inch and 6.0 inch bed height respectively. In the same time the adsorption capacity were increased by bed height and were compared with dry EFB-HBC shown in Figure 4. It shows that, the adsorption capacity (mg/g) for 1.5 inch, 3 inch and 6 inch bed heights of wet EFB-HBC are 2.7399, 2.7913 and 3.2551 respectively. Previous study were conducted by Wang, 2010 in investigation the effect of moisture content of adsrobert in removal of H$_2$S, stated that, the higher the moisture content the higher the capability of H$_2$S adsorption. This explained that the chemical reaction between H$_2$S and water were provide a good adsorption performance [12].
3.3. Adsorption Performance for Dry EFB-HC and Wet EFB-HC

The next experiment is to investigate another industrial waste Coal fly ash which were upgraded to hydrogel composite and used as adsorbent in removal of Hydrogen Sulphide. Figure 5 and Figure 6 shows the breakthrough curves for dry CFA-HC and wet CFA-HC respectively. Breakthrough time for dry CFA-HC at 1.5 inch, 3 inch and 6 inch of bed heights are 20 s, 40 s, and 60 s respectively. Meanwhile, wet CFA-HCs have a longer breakthrough time compared to dry CFA-HC, which are 100 s, 170 s and 230 s for 1.5 inch, 3.0 inch and 6.0 inch bed height respectively. The adsorption capacity also increased when the bed height were increased for both condition dry and wet CFA-HC. Adsorption capacity of dry CFA-HC and Wet CFA-HC has compared and plotted by a bar chat shown in Figure 7. It shows that, Coal Fly ash is a low surface area material compared to biochar [13]. Since
then, by upgraded the CFA became hydrogel composite can improved the adsorption performance especially in wet condition.

**Figure 5.** Breakthrough Curves of adsorption of H2S by Dry CFA-HC.

**Figure 6.** Breakthrough Curves for adsorption of H2S by Wet CFA-HC.
4. Conclusion
In conclusion, the idea for wet hydrogel composite in adsorption of Hydrogen Sulphide increased the adsorption performance. The results indicated that, hydrogel composite that derived from Empty Fruit Bunch biochar have a good adsorption performance especially in wet condition. This is because of the EFB biochar is a carbonaceous and porous material which good in adsorption, meanwhile the presence of water inside the hydrogel composite were helped in removal of Hydrogen Sulphide. The upgraded a non-porous material such as Coal Fly Ash became hydrogel composite gave a good result in adsorption performance. It proved that, the formation of hydrogel composite as binding agent between particle increased their capability in adsorption. Based on this study, increased the bed height, gave a longer breakthrough time and have a higher adsorption capacity. In this study, complete adsorption modelling for the adsorption process wa not shown in in this study because it will study and reported in subsequent publication.

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