Modelling on adsorption of hydrogen sulfide using hydrogel biochar

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***Abstract*— Hydrogen sulfide (H_2S) is a chemical hazardous gas which commonly found in oil and gas refinery industry, waste water treatment unit process, coal gasification unit prcoess, and other processes. These industries provide their own treatment unit process to treat H_2S gas by adsorbing the gas. Thus, this prevent the gas from emitted to the atmosphere. Some reaches had been done in order to optimize the adsorption of H_2S gas. Thus, biochar is introduced as an alternative source of adsorbent to adsorb H_2S and the biochar been upgrade its adsorption capability by merging with hydrogel. Hydrogel provides a moisture content that enhances the adsorption process. Isotherm model been proposed in order to describe the physical occurring on the adsorption process in real system. The main objective is to establish most suitable isotherm model for hydrogen sulfide adsorption on hydrogel biochar. Langmuir and Freundlich isotherm is been introduce and its equation been used to plot a linear graphs. There are some factors that affect the adsorption efficiency which include the effect of flow rates and bed height. By referring these factors with the proposed isotherm models, the adsorption capacity and intensity of each different flow rates and bed height can be found. The results shows that lower flow rate and high bed height is an alternative factors contribute to the enhancement of the adsorption process. From the plotted graph of Langmuir and Freundlich isotherm model, a correlation coefficient, R^2 can been determine in order to select the most suitable and fit isotherm model. The higher value of R^2 indicates the most suitable type of isotherm model that can be used for the adsorption. Therefore, the results shows that Langmuir isotherm is the most suitable isotherm model compared to Freundlich as at lowest flow rate of 60 L/h, value of R^2 for Langmuir is 0.9902 while Freundlich R^2 value is 0.9601. At highest bed height, R^2 of Langmuir is 0.990 while Freundlich is 0.96.**

***Keywords*—Adsorption, hydrogen sulfide, hydrogel biochar, modelling, Langmuir isotherm, Freundlich isotherm**

I. INTRODUCTION

H_2S is a chemical hazardous gas and a type of weak acid gas. H_2S gas is a toxic, corrosive, colourless and flammable gas that need a great concern on safety when handling with this gas. H_2S gas is one of the harmful gas that affect the environment ecosystem and human health. This gas can be produce either by industry or nature. At low concrentration, H_2S gas can be detected through smelling as the smell similar with a rotten egg smell. At high concentration, the gas can not be detected by the sense of smell instead by using a gas detector. Therefore, workers that work in the industry that has source of H_2S are strictly directed to equip gas detector to detect the present of this gas at high concentration. Industry such as petroleum refinery, paper industry, waste treatment industry and others produce this gas as a byproduct. Thus, these industry require a unit operation include adsorption unit process on treating H_2S gas to prevent the gas from been exposed to the workers and cause fatal at high concentration.

Biochar is one type of adsorbent that can be used to adsorb H_2S gas. As Malaysia is one of the country that had a major contribution towards plantation, biochar is easily obtained through the high availability of biomass source. It is a safe and economical adsorbent compared to activated carbon. Activated carbon require high heating, high pressure and activation process. Thus, activated carbon been replaced by biochar which is a more sustainable type of adsorbent. Hydrogel been merge with adsorbent to provide high capability on adsorption of H_2S gas. Hydrogel defines as water-swollen substances. It able to store a capable amount of water or biological fluid, bear a significant fraction of water content [2]. within its structure and allow distribution and attachment of molecules on the hydrogel [10]. The water-swelling of hydrogel tend to entrap H_2S thus improve the adsorption ability.

Adsorption model is used to determine the efficiency removal of adsorbent. The modelling used includes adsorption isotherm models to describe the experimental data gathered from analysis. The process of adsorption modelling is based on Langmuir and Freundlich isotherm model. The purpose of modeling an experimental adsorption is to predict the performance of an adsorption which is crucial to optimize for the adsorption mechanism pathway, effective adsorption design system and express on the adsorbent capacity [8]. The performance of the adsorption process needed to be predict by laboratory scale before been implied for industrial scale. Besides, the study on the mechanism of adsorption can lead to improvement in adsorption process [8]. Type of isotherm model need to be determine through the experiment conducted in order to select best type of isotherm model to determine the performance of adsorption process. Besides that, parameters include effect of H_2S gas flow rate and bed height been carried out in order to determine the adsorption efficiency. This parameter affect the performance of adsorbate to be adsorb to the adsorbent.

II. METHODOLOGY

A. *Preparation of biochar adsorbent*

First and foremost, sugarcane bagasse need to undergo drying process in furnace at 110℃ for about 24 hours to remove its moisture content. The dried bagasse is transferred into a pyrolyzer for pyrolysis process at 500℃ for 1 hour. Nitorgen is supplied with a flowrate of 3mL/min to the pyrolyzer. The gas act as purge gas to purge out the oxygen content in the bagasse. An hour later, the sugarcane bagasse biochar been left out for about 4 hours before been taken out from the pyrolyzer in order to cool down the biochar. Then, 0.1 M of hydrochloric acid, HCl solution is added into the biochar. HCl helps to enlarge the biochar pore and remove any unnecessary materials present. The biochar is then been neutralized with distillation water until achieve an optimum pH value of 6.0. Next, the biochar undergo drying process in an oven at temperature of 40℃ for 24 hours.

B. *Preparation of hydrogel*

An acrylamide (AAm) solution is been prepared by diluting 1.0 g AAm into 1 mL of distilled water and this solution is put aside.

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Next, an initiator of Ammonium persulfate (APS) is been prepared by diluting 0.1g APS with distilled water in obtaining of 0.2mL solution. First, a cross linker of N,N'-methylenebisacrylamide (MBA) and sugarcane bagasse biochar with its mass of 0.001g and 0.6 g been inserted into the dilute AAm solution. The mixture is been mix thoroughly for the cross-lingking process taken place. After that, ammonium persulfate (APS) solution is been added into the mixture to initiate the polymerization process. The mixture is immediately placed in the PVC straws and cooled in room temperature for about 24 hours in order for the completion of cross-lingking and polymerization of the hydrogel. After the hydrogel biochar cooled down, it is taken out from the straw and cut into a desired size. The hydrogel biochar is then been washed several times in order to remove its low molecular weight and the unwanted monomer that does not undergo polymerization and cross-lingking process. The washed hydrogel biochar is then been dried in air. Then it is been dried in an oven at temperature of 40°C for 24 hours. The hydrogel biochar is then been kept in a desiccator.

C. Isotherm models

Langmuir and Freundlich are the common type of model which being used as modelling adsorption isotherm. Linear and non-linear isotherm models used to determine the correlation coefficient (r^2) and standard error (S.E) for each parameter that need to be evaluate. For non-linear curve, it is more focus on the adsorption phenomena at constant temperature and pH, besides provide mathematical correlation to describe on the operational design and relevant practice for the adsorption [8]. Meanwhile, the linear analysis is an alternative mathematical method to determine the overall adsorption behavior [8]. Thus, the experimental data been plotted in linear graph in order to determine which type of isotherm that fit the most for the adsorption process of H_2S by using hydrogel biochar. Researchers found that linear analysis on the modelling isotherm may cause discrepancy between theoretical and experimental data [8].

1. Langmuir isotherm

Langmuir isotherm is the most useful and simplest type of isotherm for both chemical and physical adsorption. Langmuir isotherm been proposed by Irving Langmuir in 1969, with assumptions of [11]:
- fixed vacant number that available on surface of adsorbent.
- all vacant sites are equal in sizing and shape
- each of the vacant site hold maximum of only one gas molecule and constant heat energy released during adsorption process
- dynamic equilibrium between free gas molecules and adsorbed gas molecules.

Non-linear equation:

$$q_e = q_m K_L \left[\frac{C_e}{(1 + K_L C_e)} \right]$$

Linear equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Where,
q_e = number of adsorbate been adsorbed per unit mass of adsorbent (at equilibrium and constant temperature), (mg/g)
q_m and K_L= Langmuir constant related to adsorption capacity and energy
C_e = concentration of adsorbate at equilibrium (mg/L)

2. Freundlich isotherm

Freundlich proposed an empirical equation model that applied for multilayer adsorption process. Freundlich isotherm assumes heterogeneous surface energies [9]. It indicates the energy in Langmuir equation that differ as the function of surface coverage [9].
Non-linear equation:

$$q_e = K_f C_e^{\frac{1}{n}}$$

Linear equation:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) C_e$$

Where,
q_e = number of adsorbate been adsorbed per unit mass of adsorbent (mg/g)
K_f = Freundlich constant on adsorption capacity
1/n = Freundlich constant on adsorption intensity of adsorbate on adsorbent
C_e = concentration of adsorbate at equilibrium (mg/L)

The slope of graph represent 1/n. If the value of slope is in between 0 to 1, it indicates that this adsorption isotherm is favourable [12].

III. RESULTS AND DISCUSSION

A. Effects of flow rate

Gas flow rate is related to the contact time between H2S gas and hydrogel biochar adsorbent. It determine how much H2S adsorbate will be contact and adsorb to the biochar within a residence time. Lower H2S gas flow rate tend to have a longer contact time of adsorbate with adsorbent thus more H2S will be adsorb to the adsorbent. Therefore, longer time is needed for reaching the equilibrium amount of adsorbate been adsorb per unit mass of adsorbent. These relationship can be observe through adsorption isotherm model. The experiment conducted on different flow rate of 200, 100 and 60 L/h with respect to adsorbent bed height of 6 inches.
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The function of adsorption isotherm model is to describe the adsorption process such as interaction between solutes and adsorbents, and optimizing the adsorbent used. Basically, Langmuir isotherm tend to discuss on the homogeneous adsorption where a monolayer of adsorbate been adsorb on the surface of adsorbent. Langmuir isotherm model been used to plot graph on each flow rate. Figure 1 shows Langmuir model of linear equation on different H_2S gas flow rate of 200 L/h, 100 L/h and 60 L/h.

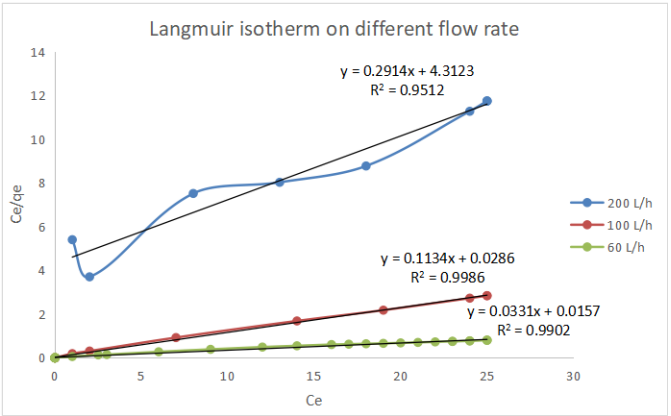

Fig. 1: Langmuir isotherm on different flow rate, L/h

Table 1 below is the data obtained from Figure 1a to Figure 1c. It represent on the data of slope, intercept, R2, K_L and q_m value where can be obtained from linear line.

Flow rate, L/h	Slope	Intercept	R^2	q_m	K_L	b
200	0.2914	4.3123	0.9512	3.432	0.068	14.799
100	0.1136	0.0258	0.9986	8.803	4.403	0.227
60	0.0331	0.0157	0.9902	30.211	2.108	0.474

Q_m indicates the maximum adsorbate adsorb which form a complete monolayer adsorbate on surface under given condition which from this experiment is in term of different flow rate. From Table 1, the value of q_m increase as the H_2S gas flow rate decrease. It shows that more amount of H_2S adsorbate been adsorb at lower flow rate as the contact time between adsorbate and adsorbent longer.

Parameters of b and K_L are Langmuir constants which relate to the capacity of monolayer adsorption and relation of adsorbent towards adsorbate [7]. By referring to Table 1, the value of b can be obtained by formula of $1/K_L$. Value of b increases as the H_2S gas flow rate decrease. Langmuir constant, b is relate to adsorption energy through the Arrhenius equation [1]. Increase in value of b indicates that the adsorbate and adsorbent has higher affinity.

Correlation coefficient, R^2 obtained are 0.9512, 0.9986 and 0.9902 of different flowrate. The obtained value of R^2 shows that Langmuir isotherm model is better graph fitting than Freundlich isotherm model. Thus, the adsorption of H_2S on hydrogel biochar is referring to Langmuir isotherm.

Meanwhile, Freundlich isotherm is relate to the multilayer or heterogenous surface adsorption. The adsorption will be more heterogeneous if the slope value approaches zero and the slop value range is within zero to one [3]. The slope tend to measure the adsorption intensity or heterogeneity surface. If the value of slope is exceed one, it indicate the cooperative adsorption. Adsorption isotherm deviation from Langmuir adsorption is because of cooperative adsorption, or interaction of adsorbate-adsorbate or adsorbate-adsorbent lead to deviation from ''uniform'' interactions [1]. Cooperative deviation can best be described by multilayer behavior of adsorption model include Freundlich isotherm model [1]. Freundlich isotherm model been used to plot graph on each flow rate. Linear graph of log q_e against log C_e been plotted. Figure 2 shows Freundlich model of linear equation on different H_2S gas flow rate of 200 L/h, 100 L/h and 60 L/h.

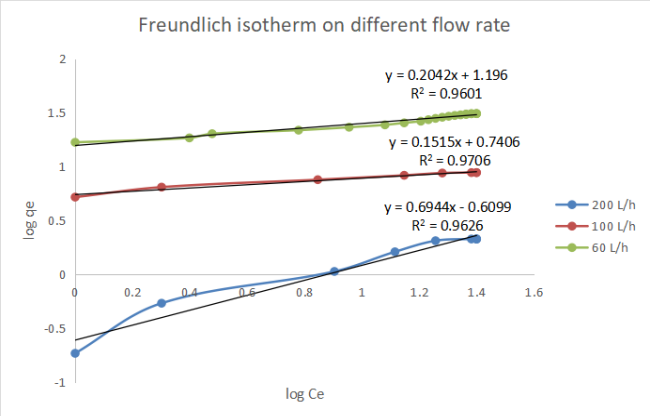

Fig. 2: Freundlich isotherm model for different flow rate L/h

Table 2 below is the data obtained from Figure 3a to Figure 3c. It represent on the data of slope, intercept, R2, K_L and n value where can be obtained from linear line.

Flow rate, L/h	Slope	Intercept	R^2	n	K_L
200	0.6944	-0.6099	0.9626	1.440	0.246
100	0.1515	0.7406	0.9706	6.601	5.503
60	0.2042	1.196	0.9601	4.897	15.704

From table 2, the values of slope is within the range of 0 to 1. The graph slope indicates as 1/n where n is the adsorption intensity. The slope determine type of adsorption process [3]. As the value of slope obtained within the range of 0 to 1, thus the adsorption is consider as favourable adsorption process.

Moreover, K_L is relate as adsorption capacity. As the flow rate decrease, K_L value increase. These shows that at lower H_2S gas flow rate, the adsorption capacity of H_2S adsorbate to be adsorb on adsorbent increase. Besides, the correlation coefficient, R^2 obtained for flow rate of 200 L/h, 100 L/h and 60 L/h are 0.963, 0.971 and 0.960. The obtained value of R^2 shows that Freundlich isotherm model indicate as poor graph fitting. This shows that Freundlich model is not suitable to be relate with the adsorption of H_2S on hydrogel biochar.

B. Effect of bed height

Bed height designate by the total amount of hydrogel biochar insert in the adsorption column. Increase of hydrogel biochar insert in column result in increase of adsorbent mass and increase the height of bed. Therefore, increase of the bed heigth lead to an increase of adsorption capacity as more hydrogel biochar present and longer residence time [5]. Langmuir isotherm model been used to plot graph on each bed height. Linear graph of C_e/q_e against C_e been plotted. Figure 3 shows Langmuir model of linear equation on different bed height of 1.5 inch, 3 inch and 6 inch.

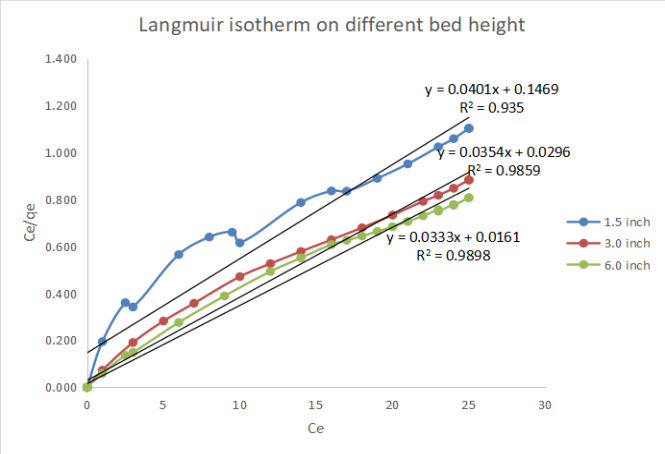

Fig. 3: Langmuir isotherm on different bed height

Table 3 below is the data obtained from Figure 5a to Figure 5c. It represent on the data of slope, intercept, R2, K_L and q_m value where can be obtained from linear line.

Bed height, inch	Slope	Intercept	R^2	q_m	K_L	b
1.5	0.040	0.147	0.935	24.938	0.273	3.663
3	0.035	0.030	0.986	28.249	1.196	0.836
6	0.033	0.017	0.990	30.211	2.006	0.498

The value of b is the Langmuir constant relate to the adsorption capacity of adsorbents. Large surface area and pore volume will increase the adsorbent capacity on adsorption [4]. From a previous studies by Alias. 2018, the value of b increases when the thickness of the adsorbent increases. The studies result is same goes to this experimental result obtained. The increase of bed height tend to increase the adsorption capacity of adsorbent. There will be more

amount of vacant site provided as amount of adsorbent increase therefore increase the adsorption adsorbent capacity.

According to the experiment conducted, the value of R^2 increase as bed height increase. Besides, the R^2 value obtained for each bed height of 1.5 inch, 3 inch and 6 inch are 0.935, 0.986 and 0.990. These shows that Langmuir isotherm is a better model to be fit in the graph plotted than Freundlich. As stated by Alisas. 2018, the drawback in increase thickness of adsorbent tend to decrease the correlation coefficient, R^2. The studies result is differ from this experiment result as the studies used multilayer adsorption while the experiment result relate to Langmuir isotherm model that used monolayer adsorption. This is the reason for the differ result value of R^2 with increase of adsorbent thickness.

Freundlich isotherm model used to plot graph on bed height of 1.5 inch, 3 inch and 6 inch. Linear graph of log q_e against log C_e been plotted in Figure 4.

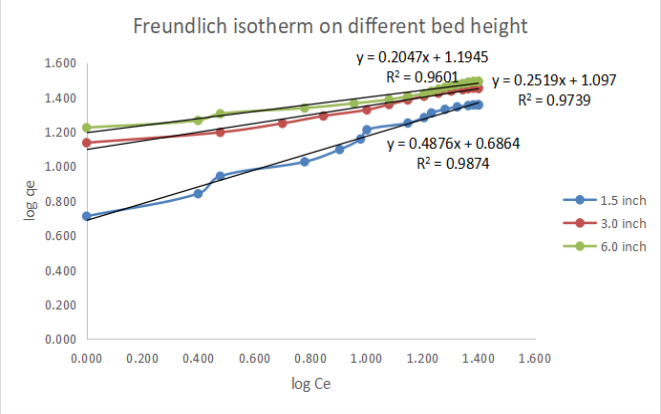

Fig. 4: Freundlich isotherm on different bed height

Table 4 below is the data obtained from Figure 3a to Figure 3c. It represent on the data of slope, intercept, R2, K_L and n value where can be obtained from linear line.

Bed height, inch	Slope	Intercept	R^2	n	K_L
1.500	0.488	0.686	0.987	2.051	4.857
3.000	0.252	1.097	0.974	3.970	12.503
6.000	0.205	1.195	0.960	4.885	15.649

Freundlich isotherm model basically describe on heterogeneous surface adsorption processes that occur on heterogonous surfaces [4]. K_L relate to the adsorption capacity meanwhile 1/n is the strength in process of adsorption [3]. Besides, value of 1/n also relate to the energy relative distribution and adsorbate site heterogeneity [4]. Graph slope interpret as 1/n. Based on Table 4 the values of 1/n are within the range of 0 to 1. As the value of slope obtained within the range, thus the adsorption is consider as favourable adsorption process.

Moreover, the value of K_L increase with the increase of bed height. By referring to study of Alisa.2018, the increase value of K_L with increase of bed height interpret that the adsorption process is normal with inconsistent of K_L value.

The correlation coefficient, R^2 obtained form this Freundlich isotherm graph is 0.987, 0.974 and 0.960 with their respective bed height. These R^2 value showed that Freundlich is poorly fitting in the graph compared to Langmuir isotherm. Besides, Freundlich model is most suitable to describe on the adsorption of different adsorbates from aqueous solution [12]. This can be the reason why Freundlich isotherm model is not fit on the adsorption of H_2S conducted by using hydrogel biochar.

IV. CONCLUSION

Hydrogen sulfide is a very harmful gas towards the environment and human health. It can lead to fatal at high concentration. Many industry such as paper manufacturing industry and petroleum refinery release these harmful gases. Therefore, these industry have their own operation on controlling the and adsorb this gas from release to the atmosphere. Therefore, this experiment promote another alternative and economical hydrogel biochar adsorbent that is efficient in adsorbing this harmful gases. Hydrogel biochar adsorbent is made from highly available biomass source. Isotherm model been introduce in order to optimze the adsorption system. Isotherm model used in this experiment are Langmuir and Freundlich isotherm. The experimental results show that Langmuir model is the most suitable model to be used in the adsorption process as it has the highest correlation coefficient, R^2 than Freundlich. Besides that, the flow rate of H_2S gas and adsorbent bed height tend to affect the adsorption system. The lower the flow rate, the higher the adsorption capacity. Increase of adsorbent bed height tends to increase in amount of adsorbent used. Thus, the adsorption capacity increase as there is more site provide for the adsorption of H_2S gas.

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