Surface Modification of Biochar Derived from Gaharu Waste Via Pyrolysis

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Abstract—**Biochar is a solid material obtained from the carbonization of biomass. This research objective is to produce biochar derived from gaharu waste. The gaharu waste was taken from Bukit Larut, Perak. The production biochar was at 3 different temperature, 400°C, 500°C and 600°C. This research also analyzes the adsorption ability of the biochar using methylene blue. The biochar undergoes modifications using H_3PO_4, NaOH and hot water before the analysis was being performed. The yield of the biochar produced was 42%, 38% and 24% for 400 °C, 500 °C and 600°C respectively. The adsorption of methylene blue for H_3PO_4 modification was 0.3547mg/g , 0.2678mg/g and 0.2590mg/g for 400 °C, 500 °C and 600°C respectively. For NaOH modification, the adsorption value was 0.8706mg/g for 400 °C, 0.7305mg/g for 500 °C and 0.8076mg/g for 600 °C. The adsorption of methylene blue for hot water modification was 0.8830mg/g, 0.7083mg/g and 0.7681mg/g for 400 °C, 500 °C and 600°C respectively. The optimum temperature to produce biochar was 400°C and the chemical modifications using NaOH and hot water can increase the ability of methylene blue adsorption.**

Keywords*— *Biochar, pyrolysis, adsorption, Methylene blue.

I. INTRODUCTION

Agarwood or gaharu is the resin impregnated, fragrant and exceedingly profitable heartwood found in family of Aquilaria [16] Aquilaria malaccensis Lam or gaharu after disease by specific organisms builds up a fragrant substance called agar in its wood [23]. The agarwood has been categorized as endangered species.

Gaharu been traded since centuries for its utilization in religious, therapeutic, and fragrance preparations [23]. The gaharu oil is additionally utilized as a part of the creation of conventional drug as against asthma immunizing, cancer prevention agent, hypertension (hostile to stretch), hepatitis, sirosis, diuretic, painkiller, and numerous different illnesses. In traditional Malay medicine, the high quality gaharu or kalambak is utilized to regard different conditions, for example, weakness, pain in the stomach or chest, oedema and as tonic for men and ladies and in addition baby blues solution [16].

The agarwood or gaharu produce an essential agar oil which is used as a base component in perfumes. The value of the agar oil is sells at a very high price. Usually to extract 30ml of Agar oil, it needs 100kg of precious Agarwood, thus, producing biochar from the gaharu waste can benefits the waste instead of throwing away the waste. Therefore, the waste of the gaharu is fully utilize and can be commercialize.

Biochar is a known as charcoal which come from biomass through pyrolysis. Biochar acts by improving dampness and nutrient holding capacity of the soil. Likewise, because of its chemical inertness, biochar is viewed as a strategy for longterm storage of carbon in soils. These can imply that transformation of biomass to biofuels and biochar can turn into an imperative carbon negative technology [15]. Biochar is the product from pyrolysis of biomass. Biochar has a few applications, enhancement of soil quality, storing of carbon to moderate worldwide climate change, improvement of soil water and nutrient retention, and diminishment of water defilement and soil erosion [9]. Since gaharu or agarwood price is expensive, converting the gaharu waste into biochar is one way to make full use of the agarwood. Besides that, during the process of converting gaharu waste to biochar, it also produced other product such as bio-oil and syn gas.

Pyrolysis is the process of breaking down of larger molecules to smaller molecules in presence of heat as the word pyro means heat while lysis means break down. The most outstanding thermochemical processes is pyrolysis. The product from pyrolysis process are char, liquid product and volatile gas which is due to decomposition of raw material. There are many parameters affect the pyrolysis rate and the yields, composition and properties of the products.

There are three types of pyrolysis which are slow pyrolysis, fast pyrolysis and flash pyrolysis. The types of pyrolysis are differing by their temperature, residence time, heating rate and the product produced. Usually the slow pyrolysis or also known as conventional pyrolysis is used to modify the solid material. It also minimizing the oil that is produced. For fast pyrolysis, the desired product is bio-oil and it is a common method used. Flash or ultra-fast pyrolysis is an extremely rapid thermal decomposition. Gases and bio-oil are the main products. Normally, the pyrolysis temperature in producing bio oil and biochar is above 400°C. At these high temperature, it will produce biochar with the best composition and properties [14].

Chemical activation of biochar is purposely to activate and improve the physicochemical properties. There are acid, alkali and oxidation treatment. Biochar surface modifications using acid could improve the pore properties such as surface area and porosity which it increasing the amounts of micropores and mesopores on biochar. For alkali treatment, the effects are it improves of pore properties and functional groups of biochar.

The methylene blue is use to analyse the adsorption ability of the biochar. Biochar is use to remove methylene blue from an aqueous solution. Besides that, the adsorption capacity of biochar can be observed using methylene blue adsorption test. Based on past study by Linson Lonappan and associates on adsorption of methylene blue on biochar microparticles derived from different waste materials, the adsorption were performed to determine and compare the adsorption potential of different biochar samples.

The aim of this research is to produce biochar from gaharu waste by pyrolysis and to analyze absorption ability of the produced biochar. The biochar is produced with 3 different temperatures. Pyrolysis temperature of biochar is at 400°C, 500°C and 600°C. The absorption ability of the biochar is analyzed with different sets of biochar pyrolysis temperature and 3 different types of modification of the biochar which are H3PO4, NaOH and hot water.

II. METHODOLOGY

A. Materials

The gaharu waste was taken from Bukit Larut, Perak. The gaharu waste was converted to biochar after undergo pyrolysis in the fixed bed reactor. The biochar produced was modified with H_3PO_4, NaOH and hot water before it was analyzed. Methylene blue solution was used to determine the adsorption ability of the biochar. UV/VIS spectrometer was used to obtained the absorbance value of the methylene blue solution after being soaked with biochar.

B. Pyrolysis

The pyrolysis was performed using a fixed bed reactor with the absent of oxygen. The gaharu waste was dried in the laboratory at room temperature for a day. After that, dried gaharu was grind. In order to reduce the moisture content below 10% the sample was dried overnight at 100˚C in oven. About 250g of gaharu waste was weighted and put in the fixed bed reactor. The temperature was set up to 400ºC. Nitrogen gas (N_2) was continuous supplied into the reactor to purge the pyrolysis vapor. The pyrolysis process was left to complete about 60 minutes at 400ºC. After the pyrolysis process completed, the reactor was left to cool down then the solid product, biochar was taken out from the reactor. The biochar was ready for modifications. The similar procedure was repeated using different temperature of pyrolysis 500ºC and 600ºC.

C. Modifications

The biochar was set to undergo 3 modifications before it was analyzed with methylene blue. The modifications used H_3PO_4, NaOH and hot water.

2.0g of biochar from each temperature was weighted using electronic balance. H_3PO_4 was measured to 200mL. The biochar was soaked completely into the H_3PO_4. The sample was let in the H_3PO_4 for 12 hours. 500mL distilled water was used to washed the samples. All the samples were dried at 80ºC in the oven for 8 hours.

Another 2.0g of biochar from 400ºC, 500ºC and 600ºC pyrolysis temperature was weighted. About 200mL of NaOH was measured using measuring cylinder. Then, the biochar was soaked completely into the NaOH. The sample was left for 12 hours. The samples were washed with 500mL of distilled water. All the samples were dried at 80ºC in the oven for 8 hours.

For hot water modifications, the same procedure was carried out. 2.0g of biochar was soaked into 200mL of hot water at 80ºC. The biochar was soaked completely into the hot water and left for 12 hours. After that, the samples were filtered and dried 8 hours in the oven at 80ºC.

D. Methylene Blue adsorption analysis

Stock solution of 1000ppm was prepared using 0.1g methylene blue powder diluted with 100mL of distilled water. Then, the concentration was diluted into 100ppm, 10ppm, 8ppm, 6ppm, 4ppm and 2ppm using distilled water. The solution was then analyze using Perkin-Elmer Lambda 750 UV/VIS Spectrometer at 645nm to obtained the calibration curve. 10ppm of methylene blue solution was used for the analysis. 0.2g of biochar was soaked in 20mL of 10ppm of methylene blue solution for 1 hour. The samples were filtered and the methylene blue solutions were analyzed again with UV/VIS Spectrometer. The adsorbance number was obtained from the analysis.

III. RESULTS AND DISCUSSION

A. The effects temperature on product yield.

The biochar yields were determined at pyrolysis temperature of 400ºC, 500ºC and 600ºC. The weight of biochar was measured before and after the pyrolysis process.

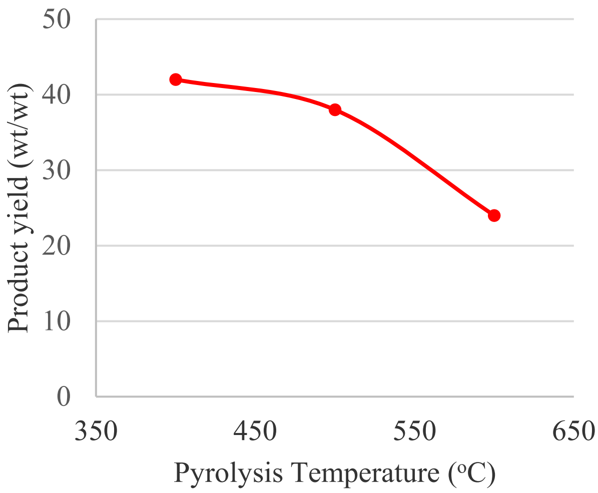

Fig. 1: Product yield of biochar at different pyrolysis temperature.

At temperature 400ºC, the product yield of biochar was 42%. As the temperature increases, the biochar yield decreases to 38% at 500ºC and 24% at 600ºC. As the pyrolysis temperature increases, the biochar yield decreases and the syngas yield increases [2]. This is because in slow pyrolysis process, the pyrolyzed vapors reside for a long time in the reactor at low temperatures, continuing vapor-phase reactions. Thus, it increased the char yield. Similar to this experiment, the yield of the biochar decreases when the temperature of pyrolysis increases.

B. The effects of temperature to adsorption ability

The pyrolysis temperature of biochar possessed the adsorption of biochar in methylene blue. The higher the pyrolysis temperature, the lower the adsorption of the biochar. All the 3 different modifications show the same trend of decreasing of the adsorption with increasing temperature.

Table 1 : UV-Visible spectrometer result.

Samples	Absorbance	Concentration (ppm)	Adsorption capacity, q_{eq} (mg g^{-1})
A1	0.8995	6.453	0.3547
A2	1.0187	7.3228	0.2677
A3	1.0307	7.4100	0.2590
B1	0.1922	1.2941	0.8706
B2	0.3842	2.6947	0.7305
B3	0.2786	1.9245	0.8076
C1	0.1752	1.1701	0.8830
C2	0.4146	2.9167	0.7083
C3	0.3327	2.3192	0.7681

Biochar modified with H_3PO_4 decreased from 0.3547mg/g at 400ºC to 0.2590mg/g at 600ºC. At 500ºC, the adsorption was

0.2678mg/g. The adsorption value of biochar modified with NaOH also decreased by temperature but increases at 600°C. The adsorption value at 400°C was 0.8706mg/g, 0.7305mg/g at 500°C and 0.8076mg/g at 600°C.

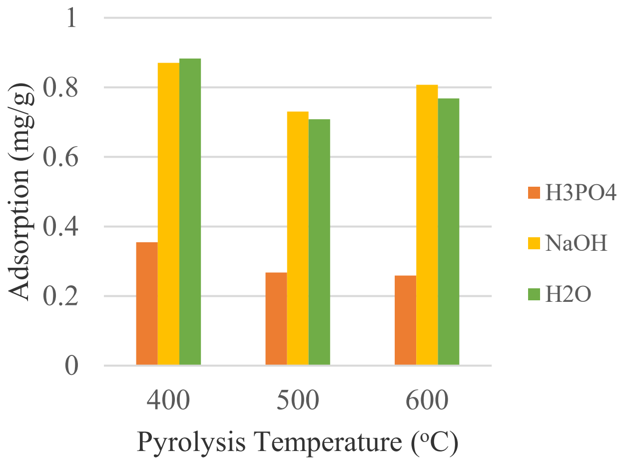

Fig. 2: Adsorption of methylene blue at different pyrolysis temperature.

For biochar modified with hot water, the adsorption value was 0.8830mg/g, 0.7083mg/g and 0.7681 mg/g at 400°C, 500°C and 600°C respectively. Thus, at higher temperature, the biochars had low adsorption ability. The higher the pyrolysis temperature used to produce biochar, the lower the Methylene Blue adsorption capacities.

C. *The effects of biochar modifications*

Biochar modifications usually used to activate it. Most activation methods mainly focus on improving one target property of biochar. For a specific treatment process, it can significantly modify one kind of biochar properties. The activation methods are divided into physical activation and chemical activation. This experiment focus on chemical activation using H_3PO_4 , NaOH and hot water.

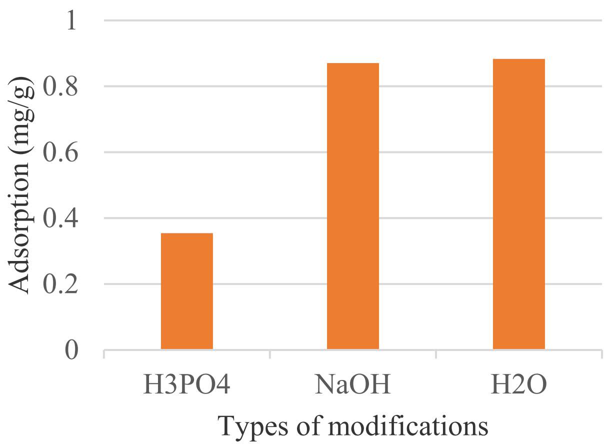

Fig. 3: The adsorption of methylene blue with different types of modifications at 400°C.

At pyrolysis temperature of 400°C, different types of modifications show different value of adsorption of methylene blue. Biochar undergo H_3PO_4 modification had a methylene blue adsorption value of 0.3547mg/g. NaOH modified biochar had the methylene blue adsorption value of 0.8706 mg/g while 0.8830 mg/g for biochar modified with hot water. Biochar modified with hot water had a highest methylene blue adsorption value compared to H_3PO_4 and NaOH at 400°C.

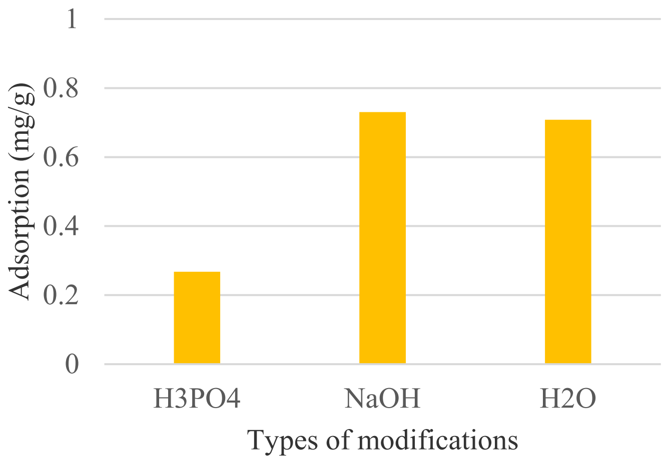

Fig. 4: The adsorption of methylene blue with different types of modifications at 500°C.

From fig.4, the biochar that undergo modification using NaOH had the highest value or methylene blue adsorption which was 0.7305mg/g followed by the hot water with the value of 0.7083mg/g. The biochar modified with H_3PO_4 still had the lowest value of methylene blue adsorption of 0.2678mg/g.

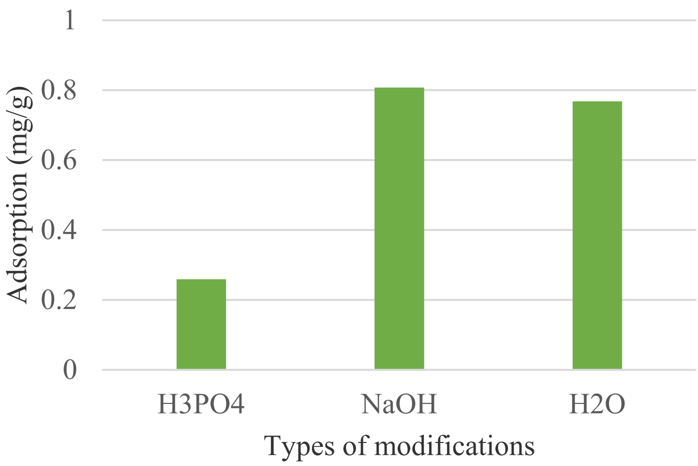

Fig. 5: The adsorption of methylene blue with different types of modifications at 600°C.

Fig. 5 above shows the adsorption of biochar in methylene blue at pyrolysis temperature of 600°C. H_3PO_4 modification biochar had the adsorption value of 0.2590mg/g, NaOH modification biochar had adsorption value of 0.8076mg/g and biochar modified with hot water had the adsorption value of 0.7681mg/g.

The chemical modifications for biochar was significant for the adsorption of methylene blue. The purpose of these chemical modifications was to act as an activating agent. From the results obtained, NaOH was the best activating agent as it had a highest methylene blue adsorption value for all three temperatures. These was proof by past studies which stated that the specific surface area and pore volume of biochar increased by activating agent, NaOH. Rank number 2 as a good activating agent was hot water. For all of the three temperatures, biochar modified with hot water had a high value of adsorption but slightly lower than the NaOH. H_3PO_4 modification had the lowest value of methylene blue adsorption for all temperatures. Cha et al. [2] stated that the sludge char pore volume and specific surface area did not increase by modifying with H_3PO_4.

IV. Conclusion

Biochar was successfully produced by gaharu waste using pyrolysis. The yield of the biochar produced was 42%, 38% and 24% for 400 ^{o}C, 500^{o}C and 600^{o}C respectively. The yield of the biochar produced was decreased as the temperature increases. Thus, 400^{0}C is the optimum temperature for biochar production. The adsorption values from all the samples was analyzed. The adsorption of methylene blue for H_3PO_4 modification was 0.3547mg/g , 0.2678mg/g and 0.2590mg/g for 400^{o}C, 500^{o}C and 600^{o}C respectively. For NaOH modification, the adsorption value was 0.8706mg/g for 400^{o}C, 0.7305mg/g for 500^{o}C and 0.8076mg/g for 600^{o}C. The adsorption of methylene blue for hot water modification was 0.8830mg/g, 0.7083mg/g and 0.7681mg/g for 400^{o}C, 500^{o}C and 600oC respectively. Higher pyrolysis temperature to produce biochar will cause the lower capacities of biochar to adsorb methylene blue. Therefore, producing biochar from gaharu waste was economic as the waste from the extraction of oil in agarwood or gaharu is converted into a new product. This study shows that modifications of biochar using NaOH and hot water had the highest value of methylene blue adsorption. Thus, it was good chemical for activation.

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