

Effect of Chemical Washing Pre-treatment of Empty Fruit Bunch (EFB) biochar on Characterization of Hydrogel Biochar composite as Bioadsorbent

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Abstract. Hydrogel biochar composite (HBC) is a recent interest among researchers because of the hydrophilic characteristic which can adsorb chemical fluid and showed a versatile potential as adsorbent in removing hazardous material in wastewater and gas stream. In this study, the effect of chemical washing pre-treatment by using two different type of chemical agent Hydrochloric Acid (HCL) and Hydrogen Peroxide (H_2O_2) was analysed and investigated. The raw EFB biochar was prepared using microwave assisted pyrolysis under 1000W for 30 min under N_2 flow with 150 mL/min. To improve the adsorption ability, the EFB biochar has been chemical washed pre-treatment with Hydrochloric Acid (HCL) and Hydrogen Peroxide (H_2O_2) before polymerization process with acrylamide (AAm) as monomer, N,N' -methylenebisacrylamide (MBA) as crosslinker and ammonium persulfate (APS) as initiator. The characterization has studied by using Fourier transform infrared spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC). FTIR result shows that, the formation of Raw EFB to Hydrogel Biochar Composite (Raw EFB > EFB Biochar > Treated Biochars (HCL & H_2O_2) > Hydrogel Biochar Composite) have changed in functional group. For DSC result it shows that the thermal behaviour of all samples is endothermic process and have high thermal resistance.

1. Introduction

Palm oil industry is the largest agricultural industry in Malaysia aligned with wastes and residues produced and became the major disposal problems [1]. Palm fibre (PF), palm kernel (PK), Empty Fruit Bunch (EFB), and palm oil mill effluent (POME) are the biomass produced from oil palm industry [2]. It is a good opportunity to produce more beneficial product from the agriculture waste such as biochar which is high potential in adsorption sector. Some methods were used to produced biochar they are included the fixed bed pyrolyser, carbonizer and furnace [3]. But in recent years, researchers found a new alternative technique applied for pyrolysis in producing biochar with high efficiency, energy saving, selective, no pollution and also friendly used which is by using microwave assisted pyrolysis [4]. Microwave is very effective equipment in producing chars product from biomass such as Empty Fruit Bunch or materials have high moisture content because microwave mechanism in particle heating where the electromagnetic field will penetrates the solid and interacts directly with dipoles in the chemical structure to vaporize the moisture [5]. On the other hands, Hydrogel Biochar Composite (HBC) is recent findings combination of biochar and hydrogel polymer. Hydrogel is a unique material in terms of physical and chemical properties because it is hydrophilic, swellable and modifiable composite which is good in adsorption process [6]. Then the aim of this study is to enhance the performance of biochar as bioadsorbent by chemical washing pre-treatment with Hydrochloride Acid (HCL) and Hydrogen Peroxide (H_2O_2) in order to remove the impurities and enlarge the porosity. Uses



of dilute acid such as 0.1M HCl as chemical agent because the dilute HCl will not damage the lignocellulose [7].

Meanwhile, H_2O_2 is an oxidizing agent which have potential to bleach and in the same time will remove impurities and toxical element [8]. Then two types of Hydrogel Biochar Composite (HBC) were produced, which are the biochar were pre-treated with HCl (EFB-HBC H100) and the other one is biochar were pre-treated with H_2O_2 (EFB-HBC P100). This paper are going to compare the characteristic of EFB-HBC H100 and EFB_HBC P100. As previous sturdy, experiment by Sanyang et al. [9] was successful with 99% and 35.75 mg/g sorption capacity of zinc removal in wastewater by modified RH-HBC (hydrogel biochar composite form rice husk). Earlier researcher, Karakoryun et al. [10] has conclude that, hydrogel biochar composites has great application in removing of toxic organic species such as phenols from wastewater. As expected, the HBC will apply in industrial waste treatment for example in removing hazardous gas with high temperature. This study will compare and investigate in terms of their functional group and thermal behaviour in production of HBC.

2. Material and Method

2.1. Raw Material & Chemical

Empty Fruit Bunch (EFB) has chosen as raw material and obtained from one of the palm oil industry located in Banting, Selangor. The chemical washing agent for this study are 0.1M of dilute Hydrochloric acid (HCl) and 0.1M Hydrogen Peroxide (H_2O_2) for biochar washing pre-treatment and distilled water is used as diluting agent. Other chemical for HBC synthesize such as Acrylamide (AAM) as monomer, N,N'-methylenebisacrylamide (MBA) as cross-linker and ammonium persulfate (APS) as initiator are supplied from R&M chemical.

2.2. Biochar Production

Microwave assisted pyrolysis technique has applied in producing EFB biochar in this study. 200g of raw Empty Fruit Bunch (EFB) were placed in quartz reactor in the microwave pyrolyzer at 1000 W of microwave power level 30 minutes under nitrogen flow at 150 mL/min. The method to prepared EFB char by using microwave assisted pyrolysis is referring to Zakiuddin Januri et al. [5] with some modification.

2.3. Acid Washing Pre-treatment

The acid washing experiments were carried out using Hydrochloric Acid (HCl) and Hydrogen Peroxide H_2O_2 [10][11]. 2 L of diluted 0.1 M HCl and 0.1 M H_2O_2 solutions were prepared in 2 L volumetric flask for stock chemical solution. Then 10g of EFB biochar were pre-treated with 200 mL of prepared acid solutions in a closed beaker for 6 hrs. Finally, the biochar were washed with distilled water until a neutral pH is obtained and oven dried at 80 °C overnights. Then pre-treated biochar named as biochar H100 and biochar P100 for HCl and H_2O_2 solutions respectively.

2.4. Hydrogel Biochar Production

EFB-HBC were synthesized using 1.0 g of AAM was desolved in 1.0 mL of distilled water. Then, 0.6 g of Empty Fruit Bunch (EFB) biochar and 0.001 g of MBA were added to the AAM solution. After thorough mixing, 0.2 mL of 0.1 g aqueous solution of APS was added to initiate the polymerization. The hydrogel biochar precursor solution was immediately placed into plastic mould and placed in an oven at 40 °C for 30 min. The plastic mould containing hydrogel biochar composites were removed from the oven after 30 min and left for 24 hrs at room temperature to ensure complete polymerization and crosslinking. EFB-HB was taken from the plastic mould, cut to desired sizes and washed several times with distilled water to remove all unreacted monomers and low molecular weight polymeric matter from the hydrogel. The washed EFB-HB was first dried in air before drying in a vacuum oven at 40 °C for 24 hrs. Then, hydrogel biochar named as EFB-HB H100 and EFB-HB P100. This hydrogel formation method are following to procedure used by [10].

2.5. Characterization

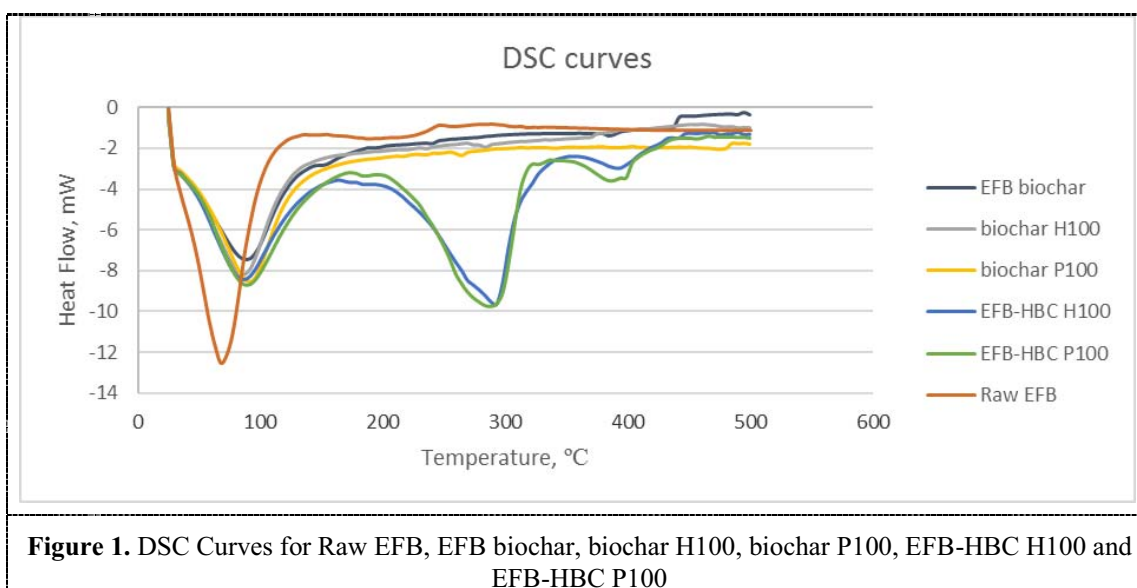
Fourier transform infrared spectroscopy (FTIR) will be measuring and analysing the functional group of samples. This instrument also can be applied to investigate the structural changes of biochars as a

function of different sample preparation (pre-treatment process). In this research, FTIR will be performed by using Perkin – Elmer Spectrum 2000 FTIR with the wavelength $4000 - 600\text{ cm}^{-1}$ [12]. DSC is a thermal analysis technique that shows the relation between material's heat capacity changes by temperature or in other word is to determine the heat required to increase temperature of sample. This instrument operated with sample weight ranging 5 to 10 mg in powder form heating from 30°C to 300°C at a heating rate of $10^\circ\text{C}/\text{min}$ [13].

3. Result and Discussion

3.1. Differential Scanning Calorimetry Analysis (DSC)

Figure 1 shows the DSC curves for all samples (Raw EFB, EFB biochar, Biochar H100, Biochar P100, EFB-HBC H100 and EFB-HBC P100).



As shown in Figure 1, DSC curve for raw EFB showed a high endothermic peak that represented as the glass transition which exhibits enthalpy relaxation [14]. Because of the raw EFB only undergo a glass transition, the raw EFB were classified as amorphous substances [15]. The same result has shown for biochars (Biochar, Biochar H100 and Biochar P100) which also undergo the glass transition. Besides, comparing in glass transition temperature, from raw EFB pyrolysed became biochars, it shows that the peaks are shifted to the right from $T_g = 68^\circ\text{C}$ to $T_g = 89^\circ\text{C}$ which mean it experienced some changes after pyrolysis (EFB biochar) and increasing the thermal transition. As seen from DSC curves for treated biochars (biochar H100 and biochar P100) are maintained at the same peak as biochar. This can be concluded that, in thermal reaction, the pretreated biochars (biochar H100 and biochar P100) has nothing much different from its biochar. This is because of, high amount of volatile matter was released during pyrolysis which make the material less reactive. Then the washing pre-treatment step is just to eliminate the remaining of volatile matter inside the biochar.

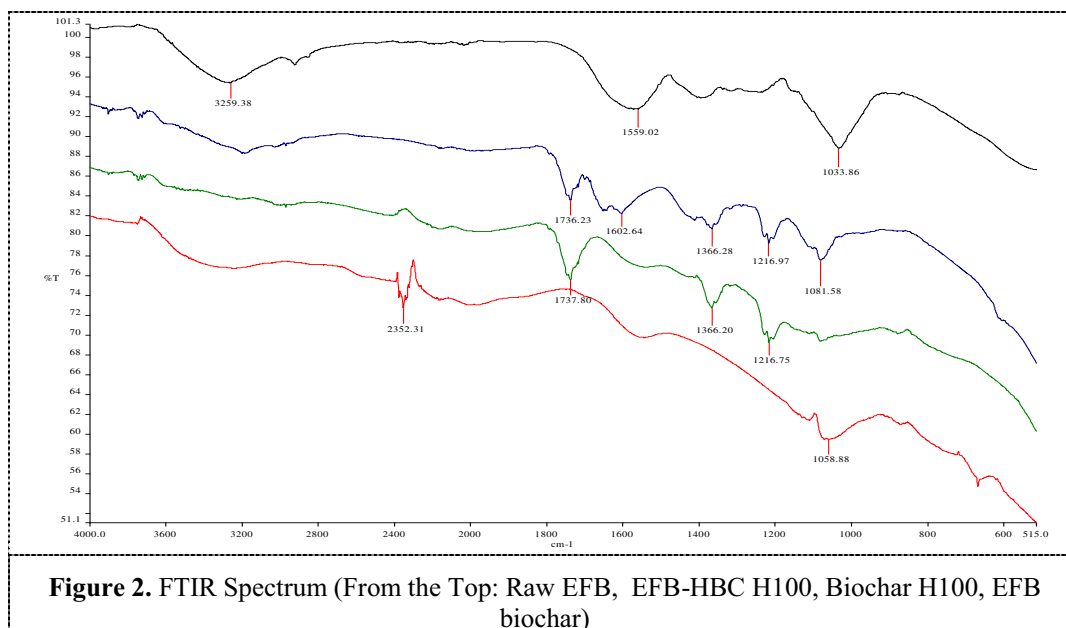
Moreover, three consecutive endothermic curves which means substances absorbed heat are observed for hydrogel biochars. Both of the hydrogel biochar composites (EFB-HBC H100 and EFB-HBC P100) have a quite similar thermal behaviour, which means both of HBCs have approximately same glass transition temperature, T_g around 86°C to 89°C and they start to degrade around 200°C . Another two curves are represented as the decomposition of substances. Michalak et al. [16] stated on their study if there is two peak existing in DSC curves after transition phase means, they found that it lose crystallization water in two steps. Then, in this study, DSC curves shows that both of HBCs lose crystallization water in two steps at T_{m1} , 298°C and T_{m2} , 400°C . In addition, the present of double endothermic peak conclude that HBCs is enantiotropic and polymorphic compound [17].

Polymorphism is a single substances that exhibits multiple different crystal structures or in other words they have various melting phase transitions [18].

3.2. Fourier transform infrared spectroscopy (FTIR)

3.2.1. FTIR Spectrum (From the Top: Raw EFB, EFB-HBC H100, Biochar H100, EFB biochar)

FTIR were used to identify the changes of functional groups before and after chemical treatment and also in Hydrogel Biochar Composites (HBCs) form [19]. Figure 2 shows FTIR spectrum for the first part of the research.

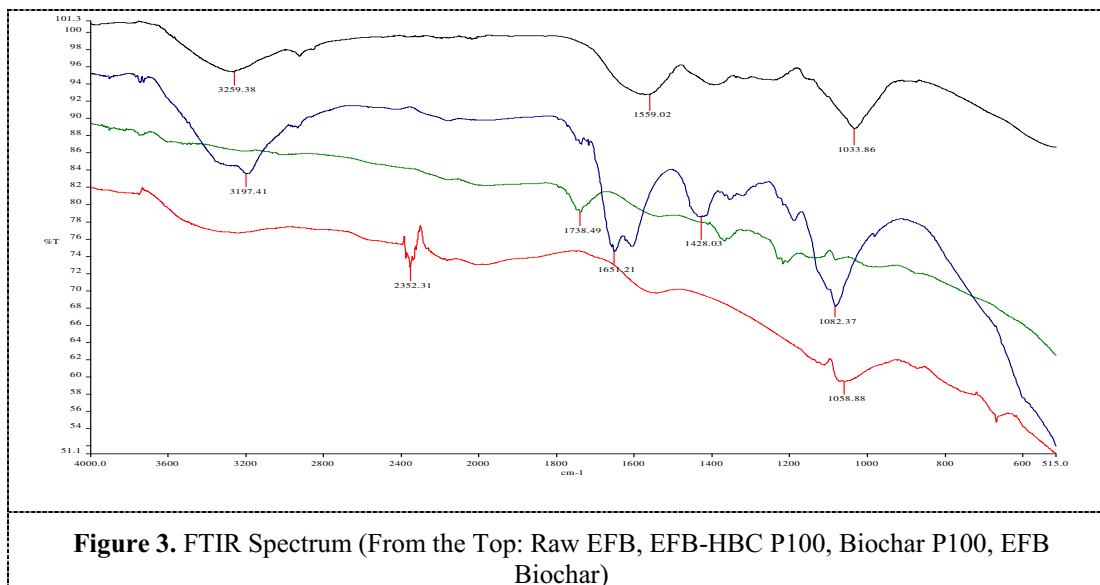


For the first part of this research are producing EFB-HBC H100 which is from Raw EFB > EFB Biochar > Biochar H100 > EFB-HBC H100. The spectrum of raw EFB shows a broad characteristic peak at 3259.38 cm^{-1} , which indicates the presence of O–H stretching. Same result shows in Claoston et al., [20] which recognized the stretching functional group of hydrogen-bonded hydroxyl group (O–H), indicative presence as phenols and alcohols. After pyrolysis process in producing EFB biochar, the O–H groups were diminished because of the mass loss during thermal decomposition. The same result are shown for biochar that was treated by HCl (Biochar H100) which is the O–H stretching were more diminished because some of volatile matter are released during washing pre-treatment. Stretching vibration of $\text{O}=\text{C}=\text{O}$ (CO_2) with wavelength 2352.1 cm^{-1} was observed. The presence of CO_2 in EFB biochar is from the pyrolysis process which is generally produced gaseous product rich in CO_2 . In addition, CO_2 was removed and diminished after treated with HCl (Biochar H100) and shown on the FTIR spectrum for Biochar H100. The diminished of CO_2 can be conclude that, the pre-treatment is able to remove the toxical material such as CO_2 as mention by Samy Sadaka [7].

According to Asim et al., [19], peaks are around 1700 cm^{-1} indicated the presence of holocellulose and lignin which has shown for Biochar H100 and EFB-HBC H100 with wavelength 1737.80 cm^{-1} and 1736.23 cm^{-1} the respectively. This means is, by formation of hydrogel biochar composite, does not destroy the lignin which is important to structure the HBC. For EFB biochar and EFB-HBC H100 have a same bending vibration on 1366 cm^{-1} represent as existing the C–H (alkane) group and a same stretching vibration on 1216 cm^{-1} shows the existing of C–O group. After the polymerization process become hydrogel biochar, have some of changes in functional group with addition of C=C stretching and amine C–N stretching on 1602 cm^{-1} and 1081 cm^{-1} respectively. This is because of the addition Acrylamide (AAM) as monomer, N,N'-methylenebisacrylamide (MBA) as cross-linker in polymerization process.

3.2.2 FTIR Spectrum (From the Top: Raw EFB, EFB-HBC P100, Biochar P100, EFB Biochar)

Then, Figure 3 shows the FTIR spectrum for Raw EFB, EFB-HBC P100, Biochar P100 and EFB biochar. Based on FTIR spectrum in Figure 3, it shows that, the peaks of EFB-HBC P100 show that there is low transmittance, and hence large absorption ability compared to EFB-HBC H100.



As we can see the biochar H100 have a same pattern or spectrum which have peaks are around 1700 cm^{-1} indicated the presence of holocellulose and lignin, 1366 cm^{-1} existing the C-H (alkane) group and a peak are around 1216 cm^{-1} shows existing of C-O group. In addition, CO_2 also was diminished after treated with H_2O_2 (Biochar P100). After polymerization become EFB-HBC P100, peak around 3197.41 represented as existing phenols and alcohols in the structure. Same as EFB-HBC H100, after the polymerization process, have some of changes in functional group with addition of C=C stretching and primary amine C-N stretching on 1651 cm^{-1} and 1082 cm^{-1} respectively. The FTIR spectrum of all sample from raw EFB to HBCs are summarized in Table 1.

Table 1. Functional Group Observed in FTIR spectra for Raw EFB, EFB biochar, Biochar H100, Biochar P100, EFB-HBC H100 and EFB-HBC P100

Wave number range (cm^{-1})	Raw EFB (cm^{-1})	EFB Biochar (cm^{-1})	Biochar H100 (cm^{-1})	Biochar P100 (cm^{-1})	EFB-HBC H100 (cm^{-1})	EFB-HBC P100 (cm^{-1})	Vibration Characteristic
3550-3200	3259.38	3236	-	-	3199	3197.41	O-H stretching (alcohol& phenols)
2349	-	2352.10	-	-	-	-	O=C=O stretching (Carbon dioxide)
1750-1735	-	-	1737.80	1738.49	1736.23	1739	C=O stretching (ester)
1650-1600	1559.02	-	-	-	1602.64	1651.21	C=C stretching (conjugate)

							alkene)
1440-1395	-	-	-	-	-	1428.03	O-H bending (carboxylic acid)
1370-1365	-	-	1366.28	1366	1366.20	-	C-H bending (alkane)
1275-1200	-	-	1216.75	1216.75	1216.97	1210	C-O stretching (alkyl aryl ether)
1250-1020	-	1058.88	-	-	1081.58	1082.37	C-N stretching (amine)

4. Conclusion

Hydrogel Biochar Composites (HBCs) is a new finding in adsorption technology. By treating the EFB biochar using HCl and H₂O₂ shows the changes in functional group. However, nothing to compare between biochar H100 and biochar P100 because the role of chemical agents is same which is to removed toxic material. The functional group was changed because of the diminished of CO₂ from its biochar in both washing pre-treatment step HCl. The Differential Scanning Calorimetry (DSC) shows that Hydrogel biochar are enantiotropic and polymorphic compound with various melting transitions. In addition, the HBCs can be exposed to high temperature to the high degradation temperature. However, the DSC results for treated biochar (biochar H100 and biochar P100) has not much different compared to biochar. This is because the biochar itself has loss reactivity from pyrolysis process. Finally, from the FTIR spectra, the peaks of EFB-HBC P100 shows there is low transmittance, and hence large absorption ability compared to EFB-HBC H100.

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