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Effect of Washing Pre-treatment of Empty Fruit Bunch Hydrogel Biochar Composite Properties as Potential Adsorbent

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Hydrogel biochar composite (HBC) showed a great potential as effective organic contaminant removal in various wastewater and gas treatment. The effectiveness is depending upon quality of biochar used during the preparation of the HBC. In this work, pre-treatment of the biochar samples (EFB in this case) through washing was investigated. The raw EFB biochar was prepared using microwave assisted pyrolysis under 1,000 W for 30 min under N_2 flow with 150 mL/min. The prepared biochar is chemically treated using either acid solution (HCl) or oxidising agent (H_2O_2) to enlarge the pores and remove impurities. The biochar is then polymerised by using acrylamide (AAm) as monomer, N,N'-methylenebisacrylamide (MBA) as crosslinker and ammonium persulfate (APS) as initiator to form the treated hydrogel biochar composite (EFB-HBC). The H_2O_2 treated biochar [EFB-HBC (P100)] shows better porosity compared to HCl treated biochar [EFB-HBC (H100)] where EFB-HBC (P100) has higher surface area (1.5997 m^2/g) compared to EFB-HBC (H100) (1.2562 m^2/g). The HBC is porous and carbonaceous material with 21 % and 31 % of carbon content in EFB-HBC (P100) and EFB-HBC (H100) which have potential as an adsorbent in wastewater and gas treatment.

1. Introduction

Biochar is highly porous material and has been studied as activated carbon for various adsorption of inorganic pollutants, heavy metals, dyes and hazardous gas (Kołodyńska et al., 2012). Hunt (2010) stated that biochar contain stable carbon and have good potential in adsorption which can attract the molecule, in the same time, remove the hazardous molecule but limited to low adsorption rate due to the low active site and post separation in handling saturated biochar adsorbents. HBC is a unique material in terms of physical and chemical properties because it is hydrophilic, swell able and modifiable composite (Okay, 2010). In recent years, HBC was become research interest in the development and application of this material in wastewater and gas treatment as potential novel adsorbent. As presented by Sanyang et al. (2014), the experiment 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). As stated in a review by Tan et al. (2015), the concentrations of extractable toxic elements such as polycyclic aromatic hydrocarbon (PAH) is contained within the biochar which affected by the preparation of biochar itself especially in pyrolysis process. The aim of this study is to enhance the performance of biochar as adsorbent in washing pre-treatment with 0.1 M HCl and 0.1 M H_2O_2 in order to remove the impurities, toxic element and enlarge the porosity. The dilute acid such as 0.1 M HCl is suitable to use because it could prevent the damage of lignocellulose and can protect the structure of biochar (Sadaka, 2008). H_2O_2 (Peroxide) is chosen because it is an oxidising agent which have potential to bleach and in the same time will remove the impurities (Diaz et al., 2013). This study will compare and investigate the effect of washing pre-treatment biochar by using HCl and H_2O_2 in the formation of hydrogel Biochar Composite (HBC). Biochar that washed by H_2O_2 should get a good result in term of porosity and pore structure and

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minimise the amount of toxic element because H_2O_2 will oxidising some lignins, cyanides, sulphides and phenols (Rust, 1959).

2. Material and Method

2.1 Raw Material & Chemical

Empty Fruit Bunch (EFB) used in this study was obtained from one of the palm oil industry located in Banting, Selangor. The washing agent for this study are 0.1 M of dilute Hydrochloric acid (HCl) and 0.1 M Hydrogen Peroxide (H_2O_2) for biochar pre-treatment and distilled water is used as diluting agent. Other chemicals for HBC synthesise, 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

Biochar were prepared using microwave assisted pyrolysis technique. 200 g of raw Empty Fruit Bunch (EFB) were placed in quartz reactor in the microwave pyrolyser at 1,000 W of microwave power level 30 min under nitrogen flow at 150 mL/min. The method is modified from Januri et al. (2014).

2.3 Acid Washing Pre-treatment

The acid washing experiments were carried out using Hydrochloric Acid (HCl) and Hydrogen Peroxide H_2O_2 (Yakout et al., 2015). 2 L of diluted 0.1 M HCl and 2 L of 0.1 M H_2O_2 solutions were prepared in 2 L volumetric flask separately for stock chemical solution. 10 g of EFB biochar were pre-treated with 200 mL of prepared acid solutions in a closed beaker for 6 hrs. The biochar were washed with distilled water until a neutral pH is obtained and oven dried at 80 ˚C overnights. The HCl and H_2O_2 treated biochar are named as biochar H100 and biochar P100.

2.4 Hydrogel Biochar Production

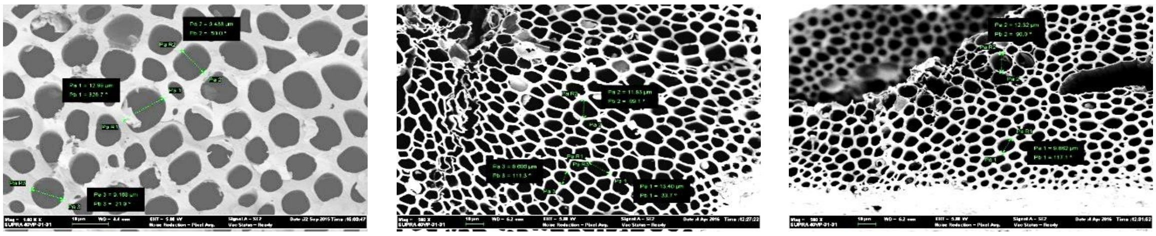
EFB-HBC were synthesised by dissolving 1.0 g of AAm in 1.0 mL of distilled water. Then, 0.6 g of Empty Fruit Bunch (EFB) biochar and 0.001 g of MBA were added to the AAm solution. After thorough mixing, 0.2 mL of 0.1 g aqueous solution of APS was added to initiate the polymerisation. The hydrogel biochar precursor solution was immediately placed into a plastic mould and placed in an oven at 40 ºC for 30 min. The hydrogel biochar composites were removed from the oven and left for 24 h at room temperature to ensure the complete polymerisation and crosslinking. EFB-HBC was taken out from the plastic mould, cut into desired sizes and washed several times with the distilled water to remove all unreacted monomers and low molecular weight polymeric matters from the hydrogel. The washed EFB-HBC was air dried before drying in a vacuum oven at 40 ºC for 24 h. The HCl and H_2O_2 treated hydrogel biochar are named as EFB-HBC H100 and EFB-HBC P100. This hydrogel formation method is adapted from Karakoyun et al. (2011).

2.5 Characterisation

The characterisation of the morphology trend of pores on the surface of samples was done on raw EFB, EFB biochar, EFB biochar pre-treated with HCl (biochar H100), EFB biochar pre-treated with H_2O_2 (biochar P100), EFB-HBC H100 and EFB-HBC P100 by using the Field Emission Scanning Electronic Microscopic (FESEM) (model SUPRA 40VP). FESEM was operated in accelerating voltage and the working distances used were 5 kV and 5 mm. Before proceed the FESEM analysis, all the samples were coated with gold in order to remove any residual ions on the samples. The image was captured under magnification of 500X in 10 µm size. The characterisation on surface area (m^2/g), pore volume (m^3/g) and average pore size (Å) was analysed by Brunauer-Emmett-Teller (BET) method (model Micromeritic 3 flex). The BET method is operated with Nitrogen (N_2) adsorption and desorption at room temperature. The maximum temperature of samples and element content such as, moisture content, volatile matter content, carbon content and ash content were determined and analysed by Thermogravimetry Analysis (TGA) under 10 ºC/min of proximate gas with initial sample mass of 20 mg.

3. Results and Discussions

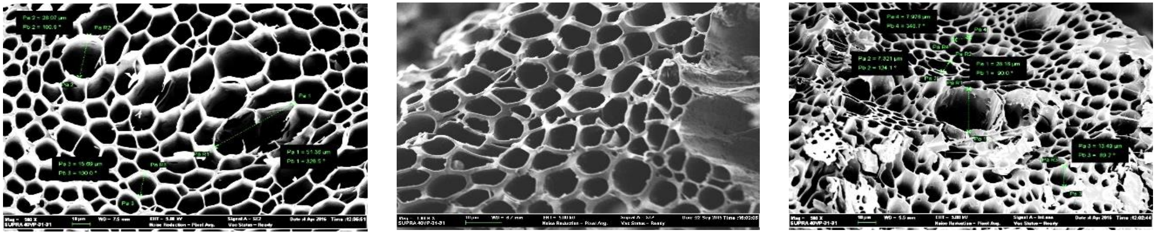
Figure 1 shows SEM image for all samples. The enlargement of pore was observed after the pyrolysis of raw EFB to biochar (Figure 1(a) and 1(b)). According to Sadaka (2008), the enlargement is caused by the breakdown of cellulose, hemicellulose and lignin during the pyrolysis process to form the volatile products with low molecular weight. Figure 1(c) shows the pore structure after HCl washing pre-treatment (biochar H100), no much different were observed between biochar H100 and biochar. The pores formed after H_2O_2 washing pre-treatment (biochar P100) (Figure 1(d)) were bigger compared to biochar and biochar H100. H_2O_2 is an oxidising agent and alkaline peroxide which can remove partial lignin and make the hemicellulose wall became thinner (Diaz et al. 2013). Figure 1(e) and 1(f) show the SEM image of EFB-HBC H100 and EFB-HBC P100. EFB-HBC H100 have thicker lignocellulose wall compared to EFB-HBC P100 and Gunawan et al. (2009) have stated that, these lignocellulosic fibre has characteristics such as good tensile strength and strong cellulose backbone (Gunawan et al., 2009). With the synthesis of HBC, the lignocellulose wall becomes stronger and protected by the presence of cross-linker. The SEM image results shows that, EFB-HBC P100 have a potential as an adsorbent since the ability of adsorption will depends on the surface area and pore structure (Rafatullah et al., 2010).



(a) Raw Empty Fruit Bunch (EFB)

(b) Empty Fruit Bunch Biochar

(c) Pre-reated Biochar with HCl (Biochar H100)



(d) Pre-treated Biochar with Peroxide (H_2O_2) (Biochar P100)

(e) EFB-HBC H100 (HCl)

(f) EFB-HBC P100 (Peroxide)

Figure 1: SEM Image

Table 1: BET Surface Area and Porosity results

Material	BET surface area, m^2/g	Total pore volume, cm^3/g	Average Pore Size, nm
Raw EFB	1.6061	0.001729	6.6628
Biochar	1.9431	0.005851	10.4459
Biochar H100	13.6074	0.009366	3.3589
Biochar P100	111.6225	0.045540	1.7544
EFB-HBC H100	1.2562	0.000951	3.0272
EFB-HBC P100	1.5997	0.000965	3.8381

Table 1 shows the results of BET surface area, total pore volume and average pore size for all samples. EFB-HBC P100 shows a higher BET surface area (1.5997 m^2/g) and total pore volume (0.000965 cm^3/g) than EFB-HBC H100 (1.2562 m^2/g and 0.000951 cm^3/g). The EFB-HBC P100 has an average pore size of 3.83805 nm which is higher compared to EFB-HB H100 average pore size of 3.0272 nm. The two HBCs are considered as a mesopore since the average pore sizes observed are in range between 2 to 50 nm. Figure 2 shows the type II BET isotherm for HBCs. This type of isotherm represent that, it is a uniform macropores and have strong interaction with surface (Al Othman, 2012). This can be concluded that, the BET surface area are low compared to biochar and treated biochar because of the presence of macropores on the surface structure with the size greater than 50 nm.

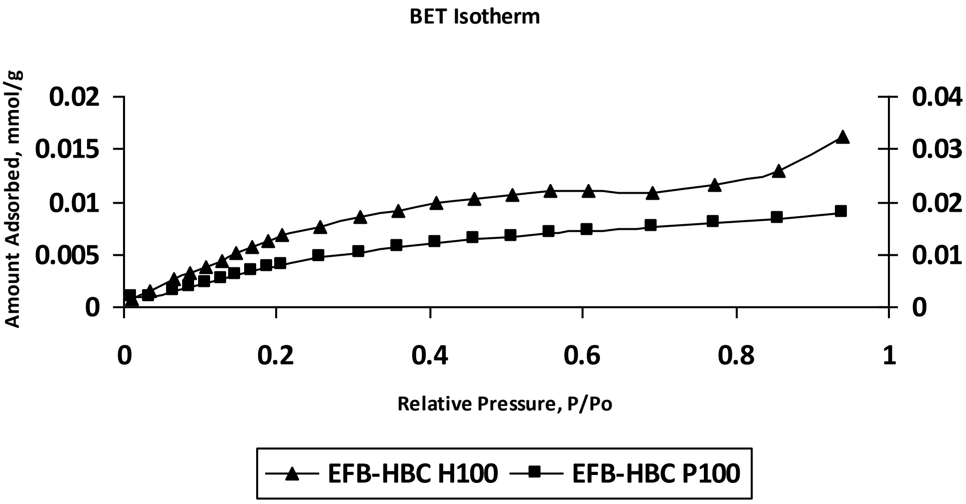


Figure 2: BET Isotherm for HBCs

The thermogravimetric (TG) and derivative of thermogravimetric (DTG) curves for EFB-HBC H100 and EFB-HBC P100 are shown in Figure 3 and 4. TGA results show that the peak temperatures of EFB-HBCs samples are almost the same and having the same thermal behaviour but different weight loss (%). The TG curve showed that, the thermal decomposition of EFB-HBCs is almost completed when the temperature is over 1,000 °C. This means that the HBCs can be exposed to high temperature. The first peak (25 °C < T < 135 °C) in DTG curve represent that, the mass loss is mainly due to the moisture evaporation (Rafatullah et al., 2010). DTG profile of EFB-HB H100 and EFB-HB P100 exhibited two peak temperatures around $Tp_{,1}$ = 300 °C and $Tp_{,2}$ = 400 °C. Around the temperature of 200 °C to 400 °C, volatile matter such as cellulose, hemicelluloses and some of polymer from hydrogel polymerisation are decomposed (Idris et al., 2010). The samples are then combusted in Oxygen at 750 °C to identify the carbon content in HBCs. Final peak at 950 °C is represented as the thermal degradation of carbon. At last, the residue left represented the ash content and some other inorganic materials in HBCs.

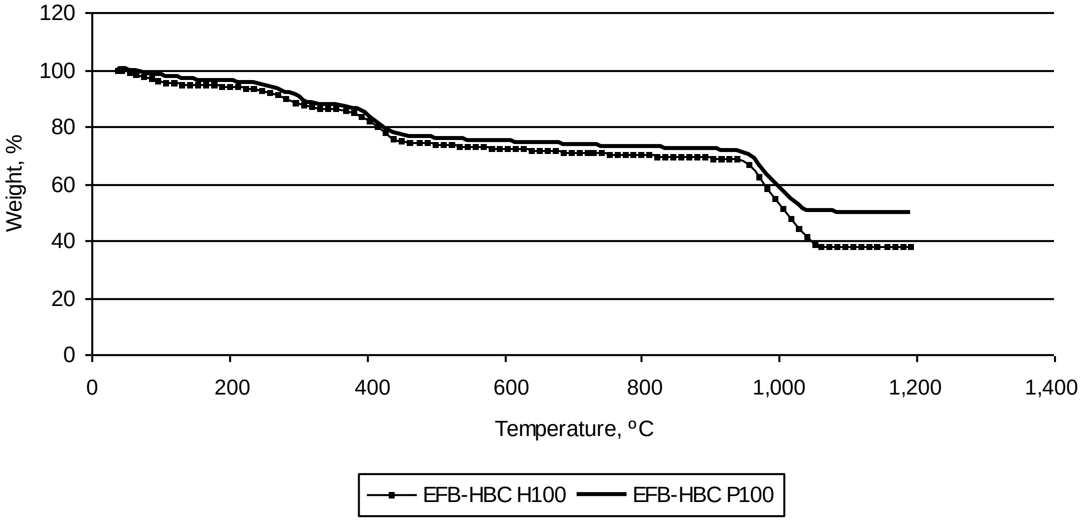


Figure 3: Thermogravimetric (TG) curve for EFB-HBC H100 and EFB-HBC P100

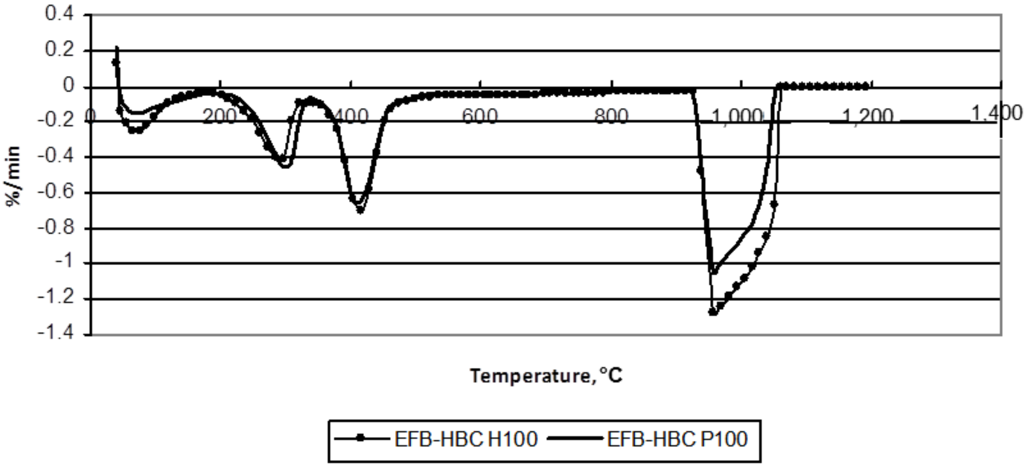


Figure 4: Derivative Thermogravimetric (DTG) curve for EFB-HBC H100 and EFB-HBC P100

Table 2: Proximate Analysis Result for HBCs.

Material	Moisture Content (%)	Volatile Content (%)	Carbon Content (%)	Ash Content (%)
Raw EFB	7.82	26.82	6.44	36.08
Biochar	7.28	11.61	41.81	39.26
Biochar H100	8.81	10.99	65.05	15.14
Biochar P100	7.52	8.08	47.76	36.93
EFB-HBC H100	5.19	25.85	30.97	37.88
EFB-HBC P100	3.39	24.53	21.00	50.00

The proximate analysis results are provided in Table 2. It can be observed that, the decreasing moisture content are observed when treated biochar (Biochar H100: 8.81 % and Biochar P100: 7.52 %) became Hydrogel Biochar Composite (HBC) (EFB-HBC H100: 5.19 % and EFB-HBC P100: 3.39 %). After polymerisation process, the increased of volatile matter were when treated biochar (Biochar H100: 10.99 % and Biochar P100: 8.08 %) became HBC (EFB-HBC H100: 25.85 % and EFB-HBC P100: 24.53 %). EFB-HBC H100 has higher carbon content whish is 30.97 % compared to EFB-HBC P100 (21 %). The reason is that the H_2O_2 treated biochar had oxidised some amount of carbon in the EFB biochar. EFB-HBC P100 has a higher ash content which is 50 % compared to EFB-HBC H100 which is only 37.88 %.

4. Conclusion

The combination of hydrogel and biochar give a new modified adsorbent in order to improve the adsorption capacity. Washing pre-treatment of EFB biochar before synthesised the HBCs give some improvement on pore structure and BET surface area especially the H_2O_2 treated EFB biochar (Biochar P100). EFB-HBC P100 has higher BET surface area (1.5997 m^2/g) compared to EFB-HBC H100 (1.2562 m^2/g). SEM image showed that the pore structure of biochar P100 and EFB-HBC P100 was increased with thin lignocellulose wall. The pore structure become stronger and protected by presence of cross-linker after synthesised to EFB-HBC P100. Although HBCs were categorised under lower BET surface area, HBCs can be a potential adsorbent with the presence of uniform macropores and strong interaction with surface. The TGA showed that, HBCs is a carbonaceous material which can exposed to temperate greater than 1,000 °C.

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