The Effects of Pyrolysis Temperature on Chemical Properties of Empty Fruit Bunch and Palm Kernel Shell Biochars

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Abstract. Biochar is a valuable by-product which has a potential as a new soil amendment in improving soil fertility. However, the properties of biochar highly depend on the types of feedstock used and the pyrolysis condition. Therefore, this study was conducted to evaluate the effects of pyrolysis temperature on chemical properties of biochar derived from oil palm. Two types of biochars were produced from empty fruit bunch (EFB) and palm kernel shell (PKS) by slow pyrolysis process applied at different levels of pyrolysis temperature (350, 500 and 750°C). The chemical properties of biochars such as pH, electricity conductivity (EC), total nutrients and cation exchange capacity (CEC) were determined. The adsorption capacities of cadmium on biochars also were investigated. The results showed that pH value, EC and total macronutrients for both EFB and PKS biochars increased with the increased of temperature. In contrast, CEC value decreased when pyrolysis temperature is increased. Biochar derived from EFB produced at 750°C showed the highest adsorption capacity of cadmium.

Keywords: empty fruit bunch, palm kernel shell, biochar, pyrolysis

1. Introduction
Biochar is a carbon rich product produced in a low oxygen environment called as pyrolysis process, has been gaining interest recently due to its potential to mitigate global climate change [18]. The high stability of biochar to sequester the carbon in soil is a key factor affecting the decrease of CO₂ emission into the atmosphere [4, 8]. This carbon (C)-rich char also can be used as additive for soil improvement of soil quality [22]. Several researchers have documented that the alkalinity property of biochar can increased the soil pH that leads to better yield of crops grown in acidic soil [2, 36]. Biochar can positively affect the nutrients availability in the soil as a result of its nutrient content and release characteristics [11]. Furthermore, the application of this amendment may increase the fertilizer efficiency due to its high surface area that may enhanced the sorption of nutrients and thereby reducing the nutrients leaching from soil. In addition, the sorption ability of biochar is suggested attribute from the oxidation of aromatic C and formation of carboxyl groups or other functional groups that increase its cation exchange capacity (CEC) [12]. As sorption is an effective remediation method, therefore, the application of biochar as an adsorbent to remove organic and inorganic pollutants have been widely investigated [13, 21, 31]. However, physicochemical properties and adsorption capacity of biochar is highly depending on the specific characteristic of the feedstock used and the pyrolysis condition [34].

The varying pyrolysis condition such as pyrolysis temperature, heating rate and holding time have influence on biochar physicochemical properties, hence effect its function as soil amendment [6, 35]. The pyrolysis temperature is reported strongly correlated with the final structural and physicochemical
properties of biochar due to the release of volatiles [14, 23]. There are three stages of pyrolysis process with different heating temperature applied namely as; pre-pyrolysis (less than 200°C), main-pyrolysis (200 to 500°C) and formation of carbonaceous soil products (above 500°C) [17]. Increasing the pyrolysis temperature attributed to the changes of the feedstock properties start from the volatilization until degradation of stronger chemical bonds and lignin [3]. Previous studies have reported that the biochar produces at higher temperature resulted in an increase of ash, surface area, fixed C content, pH and volatile matter [26, 27]. In contrast, the low pyrolysis temperature has high of CEC and less condensed C structure which beneficial for soil fertility [10]. Therefore, this study was conducted to investigate the effect of pyrolysis temperature on biochar chemical properties and adsorption isotherm.

The biomass used to produce biochar is another important factor that have influence on the final properties of this by-product. Different biomass varying from agricultural residues to municipal solid waste can be used as biochar feedstock [24, 32, 33, 37]. Although all biomass that containing carbon can be used in making of biochar through pyrolysis process, it is suggested that feedstock must be financially and environmentally viable. In Malaysia, there are abundance of waste materials from palm oil mills that can be converted into biochar such as empty fruit bunch (EFB) and palm kernel shell (PKS). It is reported that palm oil mill wastes produced approximately 90 million tonnes and 9% of that weight is represented by EFB [16]. However, EFB has low potential to be commercialized due to its high lignin and cellulose content, which contribute to the abundance of agricultural waste. The PKS on the other was produced approximately 4.46 million tonnes and increased to 4.72 million tonnes in 2014 and 2016, respectively [19, 30]. Thus, the conversion of EFB and PKS into biochar as carbon sequester and soil amendment is a sustainable approach in managing the waste. In addition, the potential of these by-product as adsorbents can be evaluated and added their commercial values in remediating contaminated soil. Therefore, this study was conducted to investigate the chemical properties and sorption ability of biochar derived from EFB and PKS produced at different temperature. Such understanding is crucial for the sustainable waste management of the oil palm industry in Malaysia.

2. Materials and methods

2.1. Biochar preparation

Empty fruit bunches (EFB) and palm kernel shell (PKS) were collected from Sime Darby Kempas Palm Oil Mill located at Jasin, Melaka, Peninsular Malaysia. The raw EFB and PKS were air-dried and shredded into smaller pieces prior to pyrolysis. The shredded samples were placed in ceramic crucibles and pyrolyzed at three different temperatures (350, 500, and 750°C) for 2 hours. The biochars produced under 350, 500 and 750°C are referred to as EFB350, EFB500, EFB750 (from EFB) and PKS350, PKS500, PKS750 (from PKS), respectively. The biochars were ground and sieved in the size less than 2 mm before transferred into glass vials and stored at room temperature for further characterization.

2.2. pH and electrical conductivity

The pH of biochar was measured by adding biochar to distilled water in a volume ratio of 1:20. The solution then was shaken for 90 minutes by using rotary shaker and allowed to stand for five minutes before measuring the pH with a Mettler Toledo pH meter. The biochar electrical conductivity (EC) was conducted similar as pH and the value was measured by using EC meter after shaking for 90 minutes.

2.3. Nutrients analysis

Total nutrients content in biochar was determined by using dry ashing method [1]. An amount of 0.1 g of biochar was weighed in ceramic crucible and placed in chamber muffle furnace and heated gradually at 300°C for 1 hour. Then, the temperature was raised up to 550°C for 5 hours until white or grayish ash was obtained. The crucible was taken out from furnace and left to cool down in the gel desiccator prior next step. A few drops of distilled water were added to moisten the ash and 2 mL of HCL was added before heated on hot plate. Then, 10 mL of 1.2% nitric acid was added on dried sample before placed in water bath for 1 hour at 100°C temperature. The mixture was transferred to a 100 mL of volumetric flask and made up to volume with distilled water. The sample was shaken and filtered with Whatman no. 2 filter paper. The phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg) in samples
were determined by using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) Optima 7300DV (PelkinElmer, Inc, Waltham, MA, USA).

2.4. Cation exchange capacity analysis

The cation exchange capacity (CEC) of biochar leachate was extracted by using leaching method with ammonium acetate (\(\text{NH}_4\text{OA}_c\)) buffered at pH 7.0 (Chapman, 1965). An amount of 10 grams of biochar was mixed with 100 ml of 1N \(\text{NH}_4\text{OA}_c\) and leached for 5 to 6 hours by using leaching tube. The biochar in leaching tube was washed with 100 mL of 95% ethanol to remove the remaining \(\text{NH}_4^+\) ions in biochar sample. The biochar then was leached with potassium sulphate 1 N \(\text{K}_2\text{SO}_4\) for 5 to 6 hours and CEC were determined by using the Lachat QuickChem FIA 800 series continuous flow Auto-Analyzer (Lachat Instruments, Milwaukee, WI, USA).

2.5. Adsorption isotherm experiment

Sorption isotherms of cadmium (Cd) by EFB and KS biochars were measured using a series of batch experiment. An amount of 2 g of biochar samples were placed in six centrifuge tubes and mixed with 0.01 M \(\text{CaCl}_2\) solution and a series of Cd concentrations of \(\text{CdCl}_2\) ranging from 20 to 100 mg L\(^{-1}\). The biochar mixture was shaken equilibrated on rotary shaker at 30 revolutions per minute (rpm) for overnight (16 hours). The samples were centrifuged at 3000 rpm for 15 minutes and then filtered by using Whatman No. 1 filter paper. The concentrations of Cd in clear extract solution were determined by using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) Optima 7300DV (PelkinElmer, Inc, Waltham, MA, USA). Difference between initial and final concentration of Cd was calculated in equilibrium solution to determine the amount of Cd absorbed by biochar. The data then was fitted to the Langmuir (Equation 1) and Freundlich (Equation 2) to quantify the adsorption capacities of the studied biochars.

\[
q = \frac{q_{\max} K_L C}{1 + K_L C} \quad (1)
\]

\[
q = K_f \frac{1}{C^{1/n}} \quad (2)
\]

where \(q\) is the amount of Cd sorbed by per unit of biochar (mg g\(^{-1}\)); \(C\) is the equilibrium concentration of Cd in aqueous solution (mg L\(^{-1}\)); \(q_{\max}\) (mg g\(^{-1}\)) is the maximum sorption capacity; \(1/n\) is the intensity of adsorption or affinity; \(K_f\) (mg g\(^{-1}\)) and \(K_L\) (L mg\(^{-1}\)) are Freundlich adsorption and Langmuir constant, respectively.

2.6. Statistical analysis of data

All data were reported as means ± standard deviation. The data were subjected to analysis of variance (ANOVA) using Minitab Version 16. The Tukey (p<0.05) test was applied to assess the differences among the means.
3. Results and discussion

3.1. pH, EC and CEC of different pyrolysis temperature

The higher pH values for EFB and PKS were observed produced under higher pyrolysis temperature (750°C) as shown in Figure 1. The pH increased with the increasing of pyrolysis temperature for both EFB and PKS biochars. This is attributed due to the separation of minerals from the organic matrix and formation alkaline metal salts (ash) [9, 28]. Therefore, the increase of pyrolysis temperature from 350 to 750°C contribute to the accumulated ash content which resulted the increase in pH. In general, all biochars pyrolyzed at 350 to 750°C in this study showed pH value more than 8.0, which are in alkaline range. This indicates the liming potential of EFB and PKS biochars in increasing the nutrients availability and reducing aluminium toxicity when applied to acidic soil [20].

Similar to the trend of pH value, EC increased with the increasing of pyrolysis temperature for both biochars. This is due to the loss of volatile matter and formation of ash content in biochar with the increasing of temperature [5]. Therefore, the higher mineral ash content in biochar probably resulted higher electrical conductivity. The presence of ion K⁺ has influence on the EC as well, due to the K⁺ ion mobility as reported by [15]. This result is in accordance with the higher EC on EFB biochar that might attributed by higher potassium (K) content in EFB biochar as compared to PKS biochar (Table 1).

The CEC of biochar derived from the PKS was lower than EFB biochar at all pyrolysis temperature. The difference was observed might be due to the higher of mineral content in the EFB than PKS biochar. These alkaline metals will promote the formation of O-containing surface functional groups that enhance its CEC [27]. The CEC of EFB biochar was observed decreased with an increase of temperature than 500°C. Meanwhile, the CEC of PKS biochars decreased with increasing temperature. Similar trend was observed by [25]. As temperature increased further, the negatively-charged groups on biochar surface such as carbonyl groups were reduced and resulting lower CEC [29].
3.2. Nutrients composition of biochars at different pyrolysis temperature

Table 1. Nutrients composition in EFB and PKS biochar produced at different pyrolysis temperature

| Biochar | Pyrolysis temperature (°C) | P          | K          | Ca          | Mg          |
|---------|-----------------------------|------------|------------|-------------|-------------|
| EFB     | 350                         | 0.449±0.081 ab | 8.287±1.853 b | 1.254±0.208 a | 0.512±0.078 bc |
|         | 500                         | 0.707±0.120 a | 12.417±1.322 a | 1.732±0.335 a | 0.784±0.096 a  |
|         | 750                         | 0.644±0.051 ab | 12.373±1.226 a | 1.793±0.090 a | 0.725±0.045 ab |
| PKS     | 350                         | 0.315±0.184 b | 0.980±0.367 c | 1.278±0.727 a | 0.226±0.110 d  |
|         | 500                         | 0.358±0.093 b | 1.148±0.399 c | 1.602±0.546 a | 0.263±0.073 d  |
|         | 750                         | 0.441±0.150 ab | 1.267±0.370 c | 2.078±0.596 a | 0.318±0.076 cd |

Note: Values in column followed by same letter are not significantly different at p<0.05 according to Tukey’s test. All data were reported as means±standard deviation (n = 3).

The results for nutrients composition in EFB and PKS biochars are shown in Table 1. The nutrients content in both biochars increased with the increasing of pyrolysis temperature that subjected to the mineral formation. Total P, K and Mg were found higher in biochar derived from EFB than PKS at all temperature range. Nutrients content in the biochar is attributed to the feedstock used [7]. Overall, both biochars exhibited essential nutrients which can be used as a supplement to soil and for plant uptake.

3.3. Sorption isotherms

Table 2. Sorption parameter of cadmium on the EFB and PKS biochars obtained from the Langmuir and Freundlich isotherm model

| Biochar | Pyrolysis temperature (°C) | Langmuir model | Freundlich model |
|---------|-----------------------------|-----------------|------------------|
|         |                             | q<sub>max</sub> | b                | R<sup>2</sup> | K<sub>f</sub> | n    | R<sup>2</sup> |
| EFB     | 350                         | 2.2894          | 0.1048           | 0.9131 | 0.2889 | 1.7185 | 0.8472 |
|         | 500                         | 3.9809          | 0.7290           | 0.9525 | 1.8642 | 1.2098 | 0.9293 |
|         | 750                         | 28.4900         | 0.1157           | 0.7633 | 1.4371 | 2.7510 | 0.5366 |
| PKS     | 350                         | 2.5471          | 0.0210           | 0.9119 | 0.3442 | 2.1739 | 0.9711 |
|         | 500                         | 1.4577          | 0.2656           | 0.9777 | 0.5784 | 1.1562 | 0.8962 |
|         | 750                         | 1.4813          | 0.2818           | 0.8951 | 0.3288 | 2.0730 | 0.8359 |

The high correlation coefficient (R<sup>2</sup>) of 0.7633-0.9777 in Table 2, suggested that adsorption data fits better to the Langmuir equation than to the Freundlich equation. The maximum sorption of Cd (q<sub>max</sub>) was found higher in the EFB biochar produced at 750°C than 350°C and 500°C. In contrast, the q<sub>max</sub> on PKS biochar was lower at higher pyrolysis temperature. The results show that the sorption capacity of Cd is influenced by the feedstock used in producing biochar. The K<sub>f</sub> for both biochars produced at 500°C showed higher value compare to 300°C and 750°C.

4. Conclusion

Pyrolysis temperature has great effect on chemical properties of biochars derived from EFB and PKS. The results show that, pH, EC value and total nutrients element were increased with increasing the pyrolysis temperature. However, CEC of biochars was decreased when produced at higher temperature. Based on the finding, EFB and PKS biochars that produced at lower pyrolysis temperature has potential to be used as soil amendment in helping to improve both physical and chemical properties of soil. In contrast, at high pyrolysis temperature, EFB biochar can be used as an adsorbent to remediate contaminated soil. However, further study in using these biochars with different level of pyrolysis temperatures on crops grown at actual field need to be conducted.
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