Date Palm (*Phoenix Dactylifera L.*) Seed Characterization for Biochar Preparation

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Abstract

Biochar has been increasingly used as a soil amendment, clean energy source and waste management tool. It is also promoted as a climate change mitigation tool through carbon sequestration in soil. Recently, there is an increasing interest in biochar utilization as a low cost adsorbent for organic and non-organic pollutant removal. Biochar can be prepared from a wide range of organic biomass. Date seed biomass (Phoenix dactylifera L.) is abundantly available but usually discarded as agricultural waste in many countries such as Iraq. The aim of this work was to evaluate date seed characteristics by using proximate and ultimate elementary analyses for biochar preparation. Results of this study showed that date seed biomass had high volatile content, high bulk density and low ash content suggesting that the biomass can be used as a suitable precursor for biochar preparation. The results revealed that the moisture content of biomass was 8.95% with a bulk density of 0.5 g/ml. The proximate analysis indicated that the biomass had 1.14% ash content, 65% volatile matter and 24.8% fixed carbon content on a dry–weight basis. The date seed biomass showed an acidity nature of pH of 4.8. The ultimate elementary analysis indicated that the biomass had a carbon content of 28.3% and nitrogen content of 0.7%. The effects of pyrolysis temperature on mass yield, porosity and pH of the biochar were also studied. The biochar was prepared by using a slow pyrolysis process under different temperatures (350, 450, 550 and 650 oC) for 2 h. The results of the analysis indicated that the biochar properties were strongly affected by the pyrolysis temperature. The biochar mass yield was inversely proportional to the pyrolysis temperature. The mass yields were 43.3%, 33%, 27% and 22% at temperatures (350, 450, 550 and 650 oC), respectively. The pH and porosity of the biochar increased with the pyrolysis temperature. Therefore, the biochar prepared from date seed had a highly porous structure and thus it is expected to a suitable adsorbent for heavy metal ion removal in wastewater systems.

Keywords: biochar, date seeds biomass, mass yield, proximate analysis, slow pyrolysis.

Introduction

The topic of utilizing agricultural or forestry waste as co-products such as biochar has received great interest from the scientific community. Around the world, there are growing initiatives on finding strategies to encourage collection of agricultural waste as new products in a logical and economical way to be used in other applications rather than disposal in landfill. Biochar is a pyrogenic carbonaceous material derived from thermal decomposition

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of biomass in partial or complete absence of oxygen (Lehmann et al., 2006; Hossain et al. 2010). Biochar has received much attention for many decades due to its environmental benefits such as soil amendment, energy production and waste management (Lehmann and Joseph, 2009). It is also promoted as a climate change mitigation mechanism through carbon sequestration in soil (Kloss et al., 2012; Inyang et al. 2010; Lehmann et.al 2011; El Hanandeh 2013), and therefore as a technology to minimize the global warming problem. It is also promoted as a material for treatment of organic waste streams (Lehmann et al., 2009). The International Biochar Initiative Organization has estimated that about 80% of agricultural residues can be converted to biochar and/or used as sources of energy by the year 2050 (Kołodyńska et al., 2012).

Over the last decade, biochar has been promoted as a low cost adsorbent with high adsorption capacity for organic and non-organic pollutant removal (Ates and Un, 2013). Various types of organic biomass are currently used for biochar production such as wood materials, rice husk, empty fruit bunch, peanut and wheat straw, orange wastes, and olive pomace (Hyder et al., 2014; Claoston et al., 2014; Pellera et al., 2012; Saleh et al., 2014; Chen and Chen 2009; El Hanandeh 2015). The physicochemical properties of biochar are influenced by the feedstock composition and pyrolysis conditions such as pyrolysis temperature and residence time (Downie et al., 2009; Kloss et al., 2012). Each type of biomass has a different composition including elemental composition, moisture content, inorganic and volatile content, and hence affect the respective biochar properties (Kloss et al., 2012). During the pyrolysis process, the biomass experiences physical and chemical changes. Volatilization during pyrolysis causes mass loss and therefore volume reduction without causing much change to the original structure of the feedstock (Kloss et al., 2012). The pyrolysis process involves alterations to the chemical composition such as carbon and hydrogen content and surface functional groups; as well as physical properties such as porosity and surface area (Chan and Xu, 2009).

Date seed is an abundantly available agricultural waste but is usually discarded as unwanted material in many date producing countries such as Iraq. Date is cultivated in arid and semi-arid regions and can thrive in long and hot summers, low rainfall and very low relative humidity (Ahmad et al., 2012). About 105 million trees are available around the world covering over a million hectares. Iraq is one of the largest producers of date fruits with more than 21 million date palm trees and an annual production rate of 650,000 tons (FAO, 2012). Date seed represents approximately 11-18% of the total weight of date fruit (Abdul Afiq et al., 2013; Besbes et al., 2004). As a result, large quantities of date waste is generated annually.

Several studies investigated the use of date seeds as base material of activated carbon by using either physical or chemical activation processes (Bouchelta et al., 2008; Bouchelta et al., 2012; Al-Ghouti 2010; Al-Muhtaseb et al., 2008; El Nemr 2008). The lignocellulose composition of date seed biomass promote its use as an excellent precursor among the agricultural waste (Bouchelta et al., 2008). Bouchelta et al reported that the cellulose content of date seed was 42%, hemicellulose 25%, and lignin as 11%. However, a significant knowledge gap exist for the possible utilization of this biomass as economical biochar. Therefore, the overarching aim of this work was to find out whether date seed is a suitable precursor to prepare biochar adsorbent without activation. In this study, date seed biomass was characterized by using proximate and ultimate elementary analyses to evaluate its properties and to address factors affecting biochar characteristics. Biochar was prepared by using the slow pyrolysis process at various temperatures (350, 450, 550 and 650 ^{o}C) for 2 h.

The effect of pyrolysis temperature on mass yield, pH and porosity of the biochar were determined.

Experimental procedure

Date seeds biomass collection

Date palm fruits were obtained from the local Brisbane markets, Australia. The seeds were physically isolated from the date fruit by hand. Then, the seeds were soaked in tap water and washed several times with deionized water to remove of any remaining date flesh. The seeds were air dried at room temperature for 48 h and then dried in oven at 50 ^{o}C overnight.

Date seed biomass characterization

Characterization is an essential step to evaluate the physicochemical properties of biomass prior to the pyrolysis process. The biomass characterization was carried out by using proximate and ultimate analysis on dry seeds. Proximate analysis included the measurements of moisture content, ash content, volatile matter and fixed carbon. The moisture content was determined according to Sellaperumal (2012) method by measuring the loss in mass at 105 ^{o}C for 24 h. The volatile matter content was measured according to Saafi-Ben Salah et al., (2012) method by placing dry biomass inside a muffle furnace (Lenton furnace) at 350 ^{o}C for 3 h to measure mass loss due to volatilization of volatile components. Ash content was determined according to ASTM Standard Method Number E1755-01 by combusting the biomass at 650 ^{o}C for 6 h in open crucibles on a dry weight basis, while fixed carbon content was calculated as the residue remaining after volatile matter release has been expelled including the mineral matter originally present and non-volatile.

Bulk density was determined according to Mudoga et al., (2008) method by filling a 10-ml tube with dry adsorbent. The tubes were capped, tamped to reach a constant volume by tapping on a table, and weighed. Whereases, particle density was determined by using the method of volume displacement according to Khanmohammadi et al., (2015) by using water instead of kerosene. The pH of the biomass was measured by adding 1 g of powdered biomass to 20 mL of deionized water (1:20) and heated to 90 ^{o}C with continuous stirring for 20 min and was subsequently determined by using a pH meter (Ahmenda et al., 1997). Elemental analysis was performed to measure carbon (C), hydrogen (H), oxygen (O) and nitrogen (N) contents by using a Stable Isotope Analyser (SIA) (Eurovector EA 3000 elemental analyser). All measurements were carried out in triplicates at room temperature (23 ± 2 ^{o}C).

Biochar preparation

Thermal decomposition of the biomass was carried out using a bench-scale slow pyrolysis process in an oxygen deprived condition to convert the seeds biomass into stable biochar. For each experiment, about 100 g of dry biomass sample were placed in a ceramic dish and purged with nitrogen gas to provide a low-oxygen environment. The container was covered with aluminium foil with two small vents allowing only the evolved volatiles to escape. The biomass was pyrolysed inside a muffle furnace (Lenton furnaces). In this study, the evolved volatile was not collected or quantified. The pyrolysis temperature was increased to four terminal temperature levels (350, 450, 550 and 650 ^{o}C) and kept constant for a residence time of 2 h. The biochar was cooled in the furnace to room temperature and then placed inside a desiccator for 15 min. The mass yield was obtained from the final weight of the biochar as:

$$Mass\ yield\ \% = \frac{m_b}{m_f} \times 100 \qquad (1)$$

where, m_b and m_f are the mass of generated biochar and the feedstock respectively, (g).
All of the experiment results were presented as average value ± standard deviation of triplicate measurement unless otherwise stated.

Results and discussion

Biomass characteristics

Table 1 shows the physicochemical parameters of proximate and ultimate analyses of date seed biomass. The date seed biomass had low moisture content, high bulk density and high volatile content. The inorganic content of the biomass (i.e. ash content) was low. The pH of the biomass showed an acidity nature with a pH of 4.8.

Table 1. Physicochemical properties of date seed biomass

Parameter	**Value**
Moisture content %	8.95 ± 0.25
Ash content %	1.14 ± 0.04
Volatile content %	65.4 ± 3.5
Fixed carbon content %	24.87 ± 3.8
C %	28.3 ± 0.5
N %	0.7 ± 0.0
H %	7.53±1.43
O %	46.02±8.77
H/C ratio	2.65±0.07
O/C ratio	1.61±0.27
(N+O)/C	1.64±0.27
Bulk density, Kg/m^3	504
Particle density, $Kg/\ m^3$	667
Porosity %	25.0
pH	4.8± 0.3

The findings of this study were in general agreement with values reported in the literature which suggest that the moisture content of date seed is in the range of 5-10% while the ash content is in the range of 1-2% (Bouchelta et al., 2008; El May et al., 2012). El May et al., (2012) further reported a volatile content of 74%, fixed carbon of 17.5% and bulk density of 656 kg m^{-3}. The quantity of fixed carbon content in this study was 24.87% which is less than the ultimate carbon of 28.3%. That can be explained by the fact that some of the carbon might have been lost in the form of hydrocarbons as volatile compounds (Sellaperumal 2012). The high volatile content, high fixed carbon, lower ash content and high bulk density are good indicators of the suitability of date seeds as feed stock for preparation charred material (El May et al., 2012).

Biochar properties

Table 2 shows the experimental results for biochar production of date seed produced at various pyrolysis temperatures and a residence time of 2 h. The results showed that pyrolysis temperature had a significant influence on the productivity yield of date seeds - derived biochar being produced at slow pyrolysis process. The mass yields were 43.3%, 33%, 27% and 22% at pyrolysis temperatures of 350, 450, 550 and 650 ^{o}C, respectively. Figure 1 shows the trend of the biochar production yields in which the biochar mass yield was inversely related to pyrolysis temperature.

Table 2. The mass yield, pH and biochar density

	Biochar yield, %	**Bulk density, g L^{-1}**	**Particle density, g L^{-1}**	**Porosity, %**	**pH**
Biochar at 350 °C	43.31	0.510	0.687	25	6.60 ± 0.10
Biochar at 450 °C	33.18	0.500	1.000	50	7.10± 0.20
Biochar at 550 °C	27.18	0.490	1.333	63	8.00 ± 0.10
Biochar at 650 °C	22.13	0.475	2.000	76	9.10± 0.08

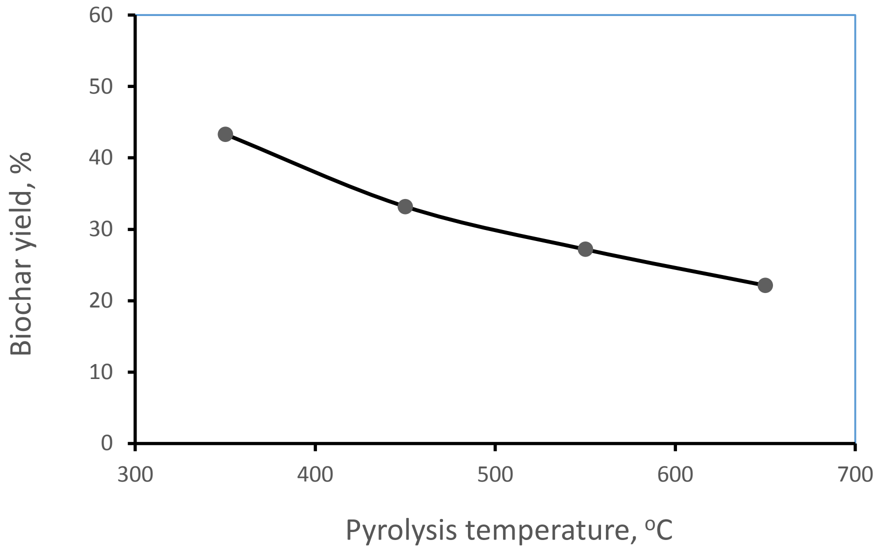

Figure 1. Biochar mass yield at different pyrolysis temperatures

These results are consistent with the results obtained for other types of biomass (Ates & Un 2013; Pellera et al., 2012; Wu et al., 2012; Brewer et al., 2014). Pellera et al., (2012) found that the biochar derived from rice husk, olive pomace, orange peel and compost biochars decreased with increasing pyrolysis temperature. The decrease of yield was 32.8% and 31.9% for rice husks, 39.3% and 26.7% for olive pomace, 39.6% and 32.8% for orange waste and 78.7% and 46% for compost at 300 °C and 600 °C respectively. Similar findings were reported by Ates & Un (2013) for hornbeam sawdust derived biochar, the mass yields obtained were 28% and 16.5% at temperature of 500 and 800 °C, respectively.

At higher temperatures, biochar showed high particle density, high porosity but the bulk density showed small differences between varying temperatures as shown in Figure 2. However, Claoston et al. (2014) stated that increasing pyrolysis temperatures produced high bulk density and an increase of porosity for rice husk and empty fruit bunch biochars. During the pyrolysis process, biomass porosity increased with increasing pyrolysis temperature. This can be attributed to volatilization processes and the loss of organic compounds, which creates more voids (Brewer et al., 2014). Brewer et al. (2014) found that particle density of wood derived biochar increased from 1344 kg/m^3 to 1742 kg/m^3 with an increase of pyrolysis temperature from 300 °C to 700 °C. Khanmohamadi et al., (2015) also reported that the solid density of biochar prepared from sewage sludge increased with increasing pyrolysis temperature while the bulk density decreased, as a result; the porosity increased.

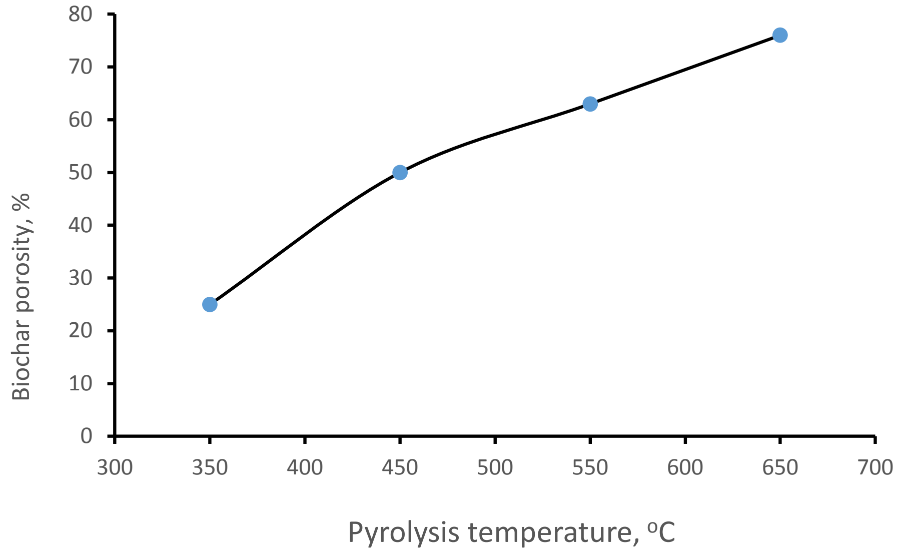

Figure 2. Porosity of biochar from date seed at different pyrolysis temperatures.

The pH values of the biochar is shown in Figure 3. The values increased with the pyrolysis temperature ranged from 6.6 to 9.1. These results were similar to other literature values that indicate most of derived biochar are alkaline (Claoston et al., 2014; Lehmann et al., 2011; Inyang et al., 2012; Kloss et al., 2012; Hossain et al. 2011). Kloss et al. (2012) found that the pH values of biochars derived from wheat straw, wood, spruce and needle mixture ranged from 6.9 to 9.2, which indicates a certain liming effect that may be achieved after biochar application. The findings of Claoston et al. (2014) indicated that rice husk and empty fruit bunch derived biochars produced at 300°C have acidic nature but that those produced at 650°C were alkaline. Yuan et al. (2011) stated that biochar produced from canola straw, corn straw, peanut and soybean straws at different pyrolysis temperatures had shown the alkalinity nature and pH of biochars increased with the pyrolysis temperature.

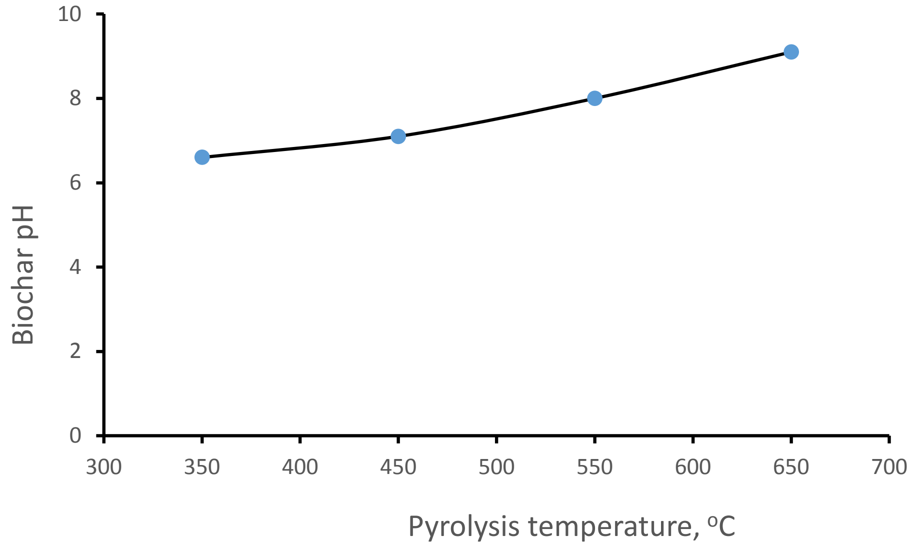

Figure 3. pH of biochar from date seed at different pyrolysis temperatures

Conclusions

In this work, date palm seed samples were characterized and used to prepare biochar at different pyrolysis temperatures (350, 450, 550 and 650 ^{o}C) and a residence time of 2 h. The physicochemical properties of biomass showed that date seed biomass have the potential to be successfully utilized as feedstock for biochar preparation. This was due to its high volatile content, high bulk density, low ash content and low moisture content. Regarding pyrolysis temperature, there were significant differences among biochar yields prepared at various temperatures. Biochar mass yield was inversely proportional to pyrolysis temperature. The biochar yields were of 43.3%, 33%, 27% and 22% at temperatures (350, 450, 550 and 650 ^{o}C), respectively. The alkaline nature of biochar prepared from date seed was expected to have high negatively charged surface functional groups. Furthermore, the highly porous structure makes it a suitable candidate for heavy metal ion removal from wastewater systems.

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