Biochar from date palm waste, production, characteristics and use in the treatment of pollutants: A Review

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Abstract. In view of the continuously rising environmental problems and the increasing energy demand worldwide in general, the utilization of sustainable renewable energy and treatment methods have become a scientific and industrial move in the last few years. One of the most important energy sources, biomass constitute a precious source. The sustainable conversion of biomass products and the use of different agricultural and forestry-derived residues can play an important role in reducing pollution in many phases. Date palm Phoenix dactylifera L. is one of the most important fruit trees that is found in tropical, sub-tropical and arid regions of the world precisely those stretching from North Africa to the Middle East. There are about 120 million date palm trees in the world where each date tree generates around 20 kilograms of dry leaves annually while date pits account for almost 10% of date fruits. A varied range of physicochemical, biochemical and thermal technologies has been applied for sustainable application of date palm biomass. The present review elucidates the possible use of date palm waste and the efforts so far made in both producing biochar and its use in different treatment processes. The review also defines the future required solutions for the date palm waste problems.

Keywords
Date palm waste, renewable energy, activated carbon, biochar, fiber

Introduction
Date palm historical background
Date palm (Phoenix dactylifera) is one of the world’s earliest cultivated trees [Zaid and de Wet, 2002], it also has a history going back thousands of years. The date palm tree has a very rugged body; it can even grow after being damaged by fire along with the capability of surviving in harsh arid environments. Date palms and their culture are described in olden Babylonian and Assyrian writings, as well as the famous code of Hammurabi, which contained laws relating to date handling and sales. References linking to date palms are also found in ancient Egyptian, Syrian, Libyan, and Palestinian writings [Popenoe 1973]. Because of the history of the date palm tree and the wide spreading and exchange of date cultivars, the precise origin of the date is unidentified, but it most likely originated from the ancient Mesopotamia (southern Iraq) or western India [Wrigley, 1995]. The semi-arid and arid regions of
America are also sources of the date palm, with over 600,000 trees. In all, nearly 3% of the cultivable surface in the world is thought to be occupied by the date palm (Shah, 2014).

**Date palm tree production**

Years ago, Iraq was one of the largest producers of dates in the world. Many causes have negatively affected both the crop and the production process [Khieralla, 2015]. In pre-modern times, before the oil industry rising Africa and West Asia, there were less date palm trees in the world than it is today. There is also a global demand for dates that are increasing at a fast rate: it was 2.8 mmt in 1985 and became 5.4 mmt in 2001 and then 7.6 mmt in 2010 [FAO STAT, 2012]. Therefore, the amount of date palm farming is expected to increase in the years to come.

Table 1 shows the top ten producers of date fruit in 2013 [FAO STAT, 2013]. Egypt is the world leader in date production and cultivation. Following Egypt, Iran is the second largest producer of dates. The third largest producer of dates is Saudi Arabia, and then Algeria and Iraq follow. The date fruits contain carbohydrates, dietary fibers, protein, lipids, vitamins, and mineral matter [Al-Farsi et al., 2007; Elleuch et al., 2008; Hossain et al., 2014].

| Country          | Annual production (1000 metric tons) |
|------------------|-------------------------------------|
| Egypt            | 1502                                |
| Iran             | 1084                                |
| Saudi Arabia     | 1065                                |
| Algeria          | 848                                 |
| Iraq             | 676                                 |
| Pakistan         | 527                                 |
| Sudan            | 438                                 |
| South Sudan      | 432                                 |
| Oman             | 269                                 |
| United Arab Emirates | 245                               |

**Date palm tree waste**

The residue that used to be generated from date palm trees was utilized in different ways; dead leaves were used to make brooms, baskets, mats, etc. The trunk which is known for its great tensile strength was also used to make the jetty, pole, and light foot bridges. Some of the date palm residues were also used in making furniture [Barreveld, 1993]. The palm waste was useful and used then the date producing countries had a sharp economy change that leads to the replacement to the date palm waste products. The use of the residues became lesser along with the increase in the date palm cultivation. The handling and processing of date palm trees waste can affect the environment and cause some disposal problems. Incineration and composting are the typical processes used, but still, it is not proper to process these organic wastes, this is due to the nitrogen concentrations and a significant amount of solid grains and smoke that is released during the process (Tsai et al., 2007). Large quantities of date palm waste is generated. By now, it is one of the biggest types of lignocellulosic solid wastes in the world, exceeding 12 mmt per year [Al-Juhaimi et al., 2014]. It consists of the following parts [Figure 1]:
To utilize this worthy substance, advanced practical methods for the conversion of biomass like thermal processes is a suitable option for these lignocellulosic residues. Some works have been published in recent years regarding the date palm waste.

**Biochar**

Many different definitions for biochar have been cited, and the most detailed definition state that biochar is the porous carbonaceous solid produced by the thermochemical conversion of organic materials in an oxygen-depleted atmosphere that has physicochemical properties suitable for safe and long-term storage of carbon in the environment.

Biochar feedstock, the biomass is a complex heterogeneous structure composed of cellulose, lignin, and other organic (primarily C, H, N, S, and O) and inorganic components that can exceed 40% of dry weight (Vassilev et al., 2010). Biochar from solid agricultural residues has great attention from the scientific community [Demirbas, 2004; Ayanoglu and Aksoy, 2015; Demirbas et al., 2016] since it leads to useful products and simultaneously contributes to solving pollution problems arising from biomass accumulation [Rocha et al., 1999].

**Biochar production**

The conversion technologies for biomass can be separated into three categories: direct combustion, thermochemical processes and biochemical processes [Ok et al., 2016]. Specific examples include anaerobic digestion, (bio) gasification, and blending with fossil fuel sources (cofiring). Energy content of raw and thermochemically processed (e.g., pyrolysis and torrefaction) biomass can be used for direct combustion, co-firing with coal, or gasification (Pimchuai et al., 2010).

The pyrolysis process is a thermochemical process that is commonly used to convert biomass into bio-char and bio oil at temperature ranges of 300-600°C [Aladin et al., 2017]. Biochar can be produced on-farm by slow (1–20°C · min−1) pyrolysis of waste biomass (Brewer et al., 2009) typically at 350–700°C. The biochar property can be manipulated by altering pyrolysis parameters, especially the maximum heating temperature, heating rate, and feedstock [Ok et al., 2016]. Although other processing options (fast pyrolysis and gasification) are available for bioenergy production, slow pyrolysis produces biochars with lower mineral (compared to gasification) and higher fixed and recalcitrant carbon (compared to fast pyrolysis) components that are more suitable for carbon sequestration in soil.

![Figure 1: A date palm tree with its different components](image)
addition, mobile slow pyrolysis units are commercially available for on-farm use by farmers [Ok et al., 2016]. Figure 2 describes the different thermal conversion technologies and their products.

![Figure 2: Biochar production methods and different biochar yields obtained (Modified from Igalavithana et al., 2017)](image)

The thermal conversion process gives different products; biogas, bio-oil and biochar. The carbon-rich solid residue is the biochar. Many biomass components such as agricultural crop residues, forestry residues, wood waste, organic portion of municipal solid waste [MSW] or industrial solid waste (ISW), and animal manures have been proposed as feedstock for biochar production [Duku et al., 2011]. A typical pyrolysis system is shown below:

![Figure 3: Slow pyrolysis set-up for the production of biochar (Aladin et al., 2017)](image)

Lignocellulosic biomass has been examined as a sufficient carbon-neutral renewable source, which can decrease CO₂ emissions and atmospheric pollution. Thus, it can also be used to produce bio fuels and biomaterials [Bensidhom et al., 2018a]. In the Middle East, lignocellulosic biomass is found in “Date Palm residues,” where many of the country’s economy depends on the annual date production. Pyrolysis, which is thermal destruction of biomass in controlled conditions produce as mentioned useful products; “bio-oil,” gaseous “syngas” and solid fuels “biochar” [Fisher et al., 2002]. The process settings such as detention time, pyrolysis temperature, gas flow rate, etc. decide the final product characteristics [Bensidhom et al., 2018a].
Biochar characteristics
One of the most important properties of biochar is its relatively high organic C (Corg) content that is primarily stored in recalcitrant condensed aromatic rings with some reactive functional groups (Xu et al., 2012). This composition is fundamental to the concept of biochar as a means of C sequestration. In recent years, there has been considerable support for biochar use as a soil amendment to help mitigate climate change through increased C storage in soils and reductions in net carbon dioxide (CO₂) emissions. The biochar is also known to have a high BET surface area, which is suitable to be used as an adsorption media. Thus, it can be a treatment agent for many pollutants such as heavy metals.

Date palm waste biochar applications
Many types of research have studied the efficiency of date palm waste as biochar feedstock. [Ahmad et al., 2011] reviewed the different studies that concerned the date seed and its conversion to activated carbon along with its capability to remove different types of pollutants such as heavy metals, dyes, phenolic compounds, pesticides, and other pollutants. He suggested that date seed could be used as a water filter medium. Activated carbon from the date seed is perhaps one of the most widely used adsorbents since its adsorption capability has been determined and proven while it is a low-cost raw material [Girgis and El–Hendawy, 2002].

Tunisian date palm waste was evaluated by [Bensidhom et al., 2018b]. Rachis, leaflets and Empty Fruit Bunches were converted to biogas, bio-oil and biochar by using a fixed-bed reactor. The highest bio-oil yield was found from empty bunches sample (25.99 wt. %) while biochar showed highly porous substance. The syngas produced contained a significant amount of CH₄ and H₂ which give it good combustion properties.

The characteristics of date seed used as feedstock for biochar was studied by [Mahdi et al., 2016a] using proximate and ultimate elementary analyses. It was proved that the date seed biomass is highly volatile, had high bulk density and low ash content, which means that the biomass can be used as a proper source for biochar production. The moisture content was found 8.95% with a bulk density of 0.5 g/ml. For continuous work by the same author [Mahdi et al., 2016b] analyses of date seed biochar produced under different pyrolysis conditions were done to study the physicochemical properties of the biochar. Both detention time and pyrolysis temperature had a major influence on biochar characteristics.

The amount of biochar produced decreased with increasing pyrolysis temperature and detention time. The carbon contents of the biochar ranged from 63.7 to 82.2%. In addition, the pH values of the biochars were higher than the original feedstock. The FTIR spectra analyses assigned that the biochar had many surface functional groups such as alkene, ester, aromatic, ketone, alcohol, hydroxyl, ether, and carbonyl agreeing to the structure of date seeds, which mostly consist of cellulose, hemicellulose and lignin. Biochar produced from higher pyrolysis temperatures and longer detention times [i.e., 550°C and 3 h] gave higher adsorption capacity for MB 0.133 mM g⁻¹ [42.6 mg g⁻1] with a correlation coefficient of 0.99 which indicates monolayer adsorption.

The capability of date stone/seed as activated carbon studies was again reviewed by [Ahmed et al., 2016]. The effects of different factors like detention time, temperature, impregnation ratio, and type of activator on the porosity and yield of carbons of the biochar produced. According to the data collected in the review paper, it was concluded that the surface areas of date stone-carbons ranged between 490 to 1282 m²/g and yields from 17 to 47% with highest values obtained by chemical activation. Activated carbon derived from date seeds were applied to different contaminated media. The capability for removing heavy metals, dyes, pesticides, and phenols showed the following adsorption concentrations:1594.0, 612.1, 238.1 and 359.1 mg/g, respectively. This represents a promising option for solving environmental problems [Ahmed et al., 2016].
Many researchers had investigated the feasibility of biochars, produced from slow pyrolysis process of date palms and cotton stalks, as adsorbents for Co [II] and Ni [II] removal from polluted drainage water as was investigated by [Khalil et al., 2016]. The two biochars (i.e., date palms and cotton stalks) were characterized and investigated for Co [II] and Ni [II] removal from polluted main drain water. Similarly, activated carbon [A.C.] from the date palms residues was prepared by thermal analysis as adsorbent and used for comparison with the two biochars. The results indicated that the original product biochars from slow pyrolysis process might be used as inexpensive adsorbents for water distillation.

The ability of date seed biochar to adsorb lead was estimated in batch and column experiments by [Mahdi et al., 2018a]. The adsorption capacity of Pb²⁺ had a linear and positive connection with the temperature and time used in the pyrolysis process. Highest adsorption efficiency was found when using biochar prepared at 550°C for 3 hours. The concentration of lead absorbed depended considerably on initial lead concentration, pH of the solution and detention time. Langmuir and Freundlich isotherm models were a good fit [R² 0.97] for Pb²⁺ adsorption onto biochar. The ability to absorb Nickel and Copper were also studied by the same author [Mahdi et al., 2018b] in binary and ternary systems using the date seed biochar. The solution pH was found to strongly affect the adsorption process. The competitive adsorption for Cu²⁺ and Ni²⁺ arrangements behavior was well described by the modified Langmuir model. Furthermore, investigation of the adsorption capability, kinetics, and mechanisms of the same pollutant by the same biochar were considered by [Mahdi et al., 2018c]. In the metal ion adsorption, an interface between carboxyl and hydroxyl took place and played an important role. The adsorption process was found to be spontaneous. Due to the pH profile change during the batch process experiment, it gave lower adsorption capacity than in column experiments. The experiment suggests that regeneration for the biochar and recovery of the metal ion can be implemented.

Also, date palm feedstock and its derivate biochars were applied to heavy metal-contaminated soil in order to investigate their effect on different parameters such as; different types of carbon in the soil, a mobile fraction of heavy metals, pH and electrical conductivity [Al-Wabel et al., 2017]). Generally, it was found that changeable factors (temperature, rate, metal type) affect the reduction of metal availability. Therefore, enhancing metal phytostabilization of contaminated soils and plant growth should be considered in future researches.

Engineered biochar composites with silica and zeolite were synthesized by [Ahmad et al., 2017] via mechanical and chemical dealings to study the variations in physiochemical characteristics, possible recalcitrance and carbon stability of the produced samples. The original and engineered biochars where analyzed structurally, morphologically, and chemically to identify the difference in characteristics. Higher recalcitrance indices and Carbon sequestration capacities (64.17–95.59%) were found in the silica synthesized samples. This indicates that the silica particles affected the carbon and structural composition.

The silica was blended with the biochar and converted to amorphous material, which intensified a solid structure, producing C–Si bonding resulting in encapsulation of C particles by Si. This bonding protected the carbon particles during the thermal process.

Pyrolysis temperature efficiency on biochar derived from date palm was characterized by (Usman et al., 2015). The relation between the surface chemistry and elemental components was also considered. Carbon sequestration biochar was found at a temperature above 500 °C. However, biochar produced at lower temperatures do contain more functional groups and has lower pH values, this makes this biochar more suitable for soil with poor fertility and high pH. Our results suggest that the biochars derived from date palm waste may represent potential alternative materials for agronomic or environmental management.
In a continuous study by the same author (Usman et al., 2016), the capability of date palm biochar produced at different temperatures on the sorption of Cadmium in aqueous solution was studied. The kinetic reaction was described by the pseudo-second-order reaction, presenting the adsorption of cadmium into biochar as chemisorption as the rate-limiting step. High temperature, ion exchange between molecules, precipitation can be the reason for Cd sorption rather than surface complexation with oxygen-containing functional groups.

**Discussion**

Several studies [Bensidhom et al., 2018a; Mahdi et al., 2018a and Demirbas et al., 2017] showed that date palm waste could be characterized as high calorific values and high volatile content biomass materials and a noticeable HHV compared to other agricultural wastes. Hence, it could be concluded that date palm waste can be considered as a useful source and a valuable chemical product. FTIR analyses of biochar and bio-oil did by [Bensidhom et al., 2018a] showed that it consisted mainly of many aromatic and aliphatic components. The biogas as well was rich in CH₄, CO and H₂.

Many studies considered the pyrolysis temperature as a changeable factor, and it was proved that the biochar characteristics depended highly on it. Stability of the biochar carbons was effected directly by the temperature. The biochar can then be used as an adsorbent for removal of various pollutants from aqueous solution. The results suggest that date seed derived biochar can be a practical option for wastewater treatment [Mahdi et al., 2016]. The adsorption process has been found to be spontaneous due to the negative adsorption standard free energy changes. According to [Mahdi et al., 2018a] and the batch and column studies are done, biochar produced has the possibility to be an azy competent sorbent for lead ion removal. Among the different adsorbents studied in different papers, date palm waste like date seeds has given acceptable adsorption capability for removing of heavy metals [Mahdi et al., 2018b]. Indication of high ability to absorb Ni²⁺ and Cu²⁺ was also reported by [Mahdi et al., 2018c] by suggesting the date palm waste to be a promising low-cost alternative among treatment options.

**Future research**

According to the literature mentioned, some accepts had been mentioned for future work. Additional work could be concerning the improvement of the biochar properties like porosity, purity and surface functionalization.

It is believed that improvements and development of biochars might lead to improved filler-matrix interaction and hence, superior composite properties [Polouse et al., 2018].

Based on [Mahdi et al., 2018c] results, recommendations included the investigation in the following sectors: regeneration of biochar, adsorption/desorption cycles; the adsorption process under dynamic conditions and the economic cost of biochar applications. Furthermore, the structure of biochar, which is highly porous, making it an alternative for heavy metal removal in aqueous solutions [Mahdi et al., 2015]. According to an article of [Ghori et al., 2018], it was shown that more focus should be on improving the thermal properties including, electrical properties, thermal conductivity, dynamic mechanical analysis and modelling of date palm fibers reinforced polymer composites. In addition, different parts of the date palm should be used for biochar production and be compared with each other. In addition, the effect of date palm waste biochar on different pollutants (dye, heavy metals, phenols, etc.) in both wastewater and soil media should be considered. More research involving the mentioned factors should be considered.

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