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Date palm waste pyrolysis into biochar for carbon dioxide adsorption

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Abstract

Mitigation of CO₂ is a very popular research currently, it is ultimately beneficial to find new ways that are sustainable, low cost and gas emission friendly. Therefore, with biochar's characteristics and properties it has great potential to be used as a CO₂ capture and storage media. The objectives of reducing palm waste by using the low-cost, sustainable method for reducing and storing CO₂, characterize the DPL biochar through FTIR, XRD, SEM, EDX, and then evaluate the efficiency of the date palm leaf waste biochar in adsorbing CO₂ through the Gas–Solid analyzer technology. Date palm leaf was set in pyrolysis process at 500°C peak at a 10°C per min rate for 5 h. The peaks of maximum intensity are approximately 1000 to 1500 cm⁻¹; two peaks are approximately 1110 and 1600 cm⁻¹ as the transition rises when the peaks are wider and shorter. Carbonyls, Alkenes, Alkynes, and others were found in feature groups, but the maximum area with O-H and C-H bonds and vibration picks is reduced and nearly non-existent. Biochar showed porous and heterogeneous structures with various magnifications, which give a greater amount of surface for adsorption. XRD analysis indicated that cellulose could progressively be decreased. The weighing of each component was 83.56% for Carbon, 12.43% for Oxygen, 1.12% for Potassium, 1.64% for Calcium, 0.83% for Phosphorus and 0.4% for Magnesium. The presence of these metals gives a strong CO₂ attraction. The area value was found to have been approximately 3.117, reflecting the total CO₂ obtained by the date palm leaf biochar. This shows that 300 gr of DPL biochar have been consumed by just one third of CO₂. Date palm leaf of biochar's shows a carbon dioxide adsorption efficiency of 20% and measured CO₂ adsorption per g of biochar DPL of 0.017 g at 500 °C pyrolysis temperature and conditions set.

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1. Introduction

Consequently, in the entire carbon capture and storage (CCS) process, high costs of the CO₂ capture phase have been described as one of the key obstacles to the realistic implementation of CCS. Therefore, the production of efficient and inexpensive CO₂ adsorptive materials is desirable [1,2]. Biochar has the ability to minimize greenhouse

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gas emissions (GHG) from Carbon dioxide sequestration strategies [3,4]. Biochar are carbon-rich biomaterials produced at high temperatures with low to no oxygen through the process of pyrolysis.

Biochar are widely recognized as biomaterials that are cheap, renewable and sustainable. Biochar can be generated at considerably lower temperatures from a variety of waste products, such as agriculture waste, food waste, and sewage [5,6]. At various temperatures and pressures, Biochar demonstrated considerably high adsorption of CO₂ comparable to activated carbon [7,8]. The implementation and potential of biochar to adsorb CO₂ is dependent on properties such as surface area, surface charge, pH, porosity, mineral composition, pore size, pore volume, biochar surface basicity, hydrophobicity and functional groups [9,10]. Such physical and chemical characteristics of biochar are correlated to the kind of feedstock used and to the thermo-chemical factors of the development of biochar [11]. Furthermore, the conversion of waste biomass to biochar decreases possible emissions of methane and CO₂ from landfills and dump sites. The carbon storage in biochar is suggested to eliminate the emission of approximately 0.1 to 0.3 billion tons of CO₂ per year [12]. Numerous studies have been performed over recent decades on the pyrolysis of various biomass feedstocks for different applications, but only a few have investigated the potential and characteristics of date palm leaf waste. Two forms of lignocellulosic biomass date palm fronds (*Phoenix dactylifera*) and rhodes grass (*Chloris gayana*) were turned into biochar and compared in a study [13]. Another study stated that biochar mixed into soil was successful in reducing the concentration of atmospheric CO₂ and that biochar is suggested for use in highly contaminated regions to minimize CO₂ emissions [14]. However, according to authors knowledge there has not been a study on conventional production of date palm leaf waste biochar with CO₂ adsorption that does not include soil application.

One of main problems that we are trying to find solution is the huge amount waste of date palm that is being thrown in UAE and by the way in other date producing countries. Dates are one of major and stable food and industry production for locals, while connecting it to greenhouse gases (GHG) emissions and carbon dioxide capture and storage (CCS) technology to address air pollution and climate change. Hypothesized that Date Palm Leaf (DPL) waste is a cost-effective source of biochar and is able to efficiently adsorb carbon dioxide and in turn assist in CO₂ capture and storage management. This research is trying to find reliable answers of questions: (1) How biochar composition and size affect CO₂ adsorption? (2) Is DPL waste biochar a good media for CO₂ adsorption? (3) How much is the DPL waste biochar efficiency in holding CO₂? And so the aim of this study is to clear the objectives where help reduce date palm waste and transform it into a usable form, use a low cost and renewable method to assist in CO₂ emission reduction and storage, to characterize the DPL waste Biochar through FTIR, XRD, SEM, EDX, then determine the DPL waste biochar performance in adsorbing the CO₂ through the Gas–Solid analyzer technology provided and to understand how the biochar properties affect the adsorption efficiency.

2. Materials and methodology

2.1. Biochar preparation

Dried Date Palm tree leaves were collected from a farm in the United Arab Emirates, Abu Dhabi. Around 10 kg of leaves were washed and then left to dry for 24h under the sun heat, after being put into a grinder for a size of less than half an inch. The grinded DPL was then placed in two furnaces and proceed the pyrolysis process at 500 °C peak with 10 °C per min for 5 h, then let cool for 1 to 2 h before collection and weighing. Temperatures around 500 °C were found as optimal temperatures for the development of biochar with wide surface area, high porosity, stable carbon content and high electrical conductivity [15].

2.2. FTIR test

A Fourier Transform Infrared Spectrometer (FTIR) (Agilent Tech, MODEL Cary630) was used to obtain the infrared spectrum of absorption of the DPL500, by collecting high-spectral-resolution data over a wide spectral range. Analytical tool; Micro-Lab was used to collect the data.

2.3. X-ray powder diffraction (XRD)

Shimadzu LabX 6000 model is a quick analytical technique mainly used to classify a crystalline substance in phases and can provide details on the dimensions of unit cells.

2.4. SEM-EDX

Two to three grams of DPL biochar sample were milled using mortar and prepared for SEM and EDX analysis. Scanning electron microscopy coupled with TESCAN VEGA (LMU) SEM energy dispersive X-ray spectroscopy (SEM-EDS) with INCAX-act (Oxford Instruments) EDS attachment working at 20 kV. Prior to analysis with SEMEDXX, the samples were gold coated with a Balzers sputtering unit.

2.5. CO₂ adsorption test

Biochar was loaded inside a vertical cylinder and 181.38 g of biochar measured to be 8 cm elevation level. The temperature was determined to be set in room temperature with 1.6 L/min operated gas flow rate for time as long as CO₂ % is rising and reaches a constant reading, estimated around 30 to 1 h. A device was connected to the output stream and it can measure the percentage concentration of CO₂ that is leaving (unreacted). Nitrogen was used to flow in the cylinder for a duration of 30 min for calibration.

3. Results & discussion

Fourier Transform Infrared Spectroscopy (FTIR) is used to identify the chemical composition of biochar by recording the infrared spectrum of respective samples. The compositions of the sample can be recognized by analyzing the spectra with relative intensities which indicates different functional group. In Fig. 1, It is observed that the peaks with highest intensity are around 1000 to 1500 cm⁻¹, with two peaks being at ~1110 and 1600 cm⁻¹ as transition gets higher after where peaks are broader and weaker. Function groups detected were Carbonyls, Alkenes, Alkynes and others, however the peak area presenting O-H bond and C-H stretching and vibration peaks are decreased and almost non-existent. The stretching band of hydrogen-bonded hydroxyl groups began to slowly decrease during the rising temperature of pyrolysis. Due to higher mass loss during thermal decomposition and gas product evolution, this was predicted. It was claimed that a FTIR biochar spectra showed a decrease in H-bonded hydroxyl groups at 350° and 500 °C. This was due to the development of the biomass dehydration reaction as the temperature of pyrolysis increased [16,17].

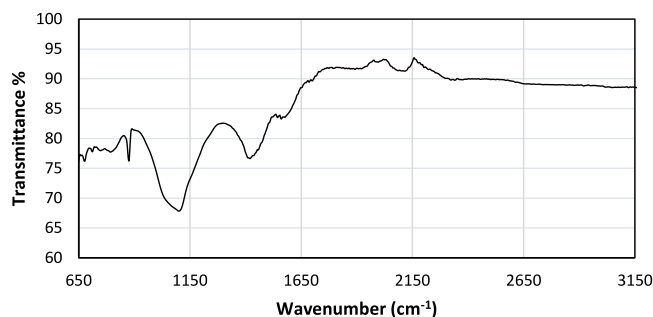


Fig. 1. FTIR spectroscopy of DPL biochar transmittance (%) vs wavenumber (cm⁻¹).

On the other hand, peaks between 1630 and 1520 cm⁻¹ area display a C=C ring stretching due to the presence of aromatic C=C stretching and C=O stretching of possible conjugated ketones (1600 cm⁻¹). In the sample, the aromatic groups give rise to C=C stretching at 1605 cm⁻¹ and aromatic forms of C-H deformation at 856 cm. In the sample, the aromatic groups give rise to C=C stretching at 1605 cm⁻¹ and aromatic forms of C-H deformation at 856 cm. suggesting that the peaks may be the presence of C-O stretching vibration of C=O stretching of aromatic rings at around 1400 cm⁻¹ and 1600 cm⁻¹ (1426 cm⁻¹, 1606 cm⁻¹) respectively. A peak of C-O stretching is also presented in the sample at 1110 cm⁻¹, and a triple CC bond around 2000–2170 cm⁻¹ peak at 2120 cm⁻¹. It is proved that the presence of oxygen-containing acid-containing functional groups such as hydroxyl groups, carboxyl groups and carbonyl groups also increase the adsorption of CO₂ on carbonaceous surfaces by facilitating the bonding of hydrogen between CO₂ molecules and carbonyl groups [18,19].

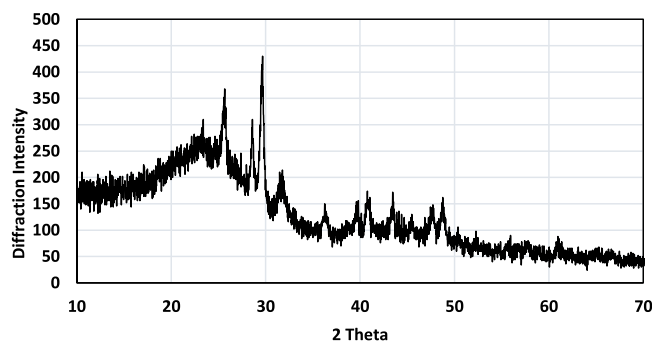


Fig. 2. XRD analysis graph of DPL biochar sample diffraction intensity vs 2Theta.

A major part, of the biomass sample include cellulose, hemicellulose and lignin. Such compounds are polymeric and somewhat amorphous. To find out whether any other crystalline phase was presented, XRD analysis was performed. The date palm leaf waste (DPL) sample was found to have 10 peaks of 2theta: 25.6, 29.4, 30, 31.9, 36.3, 40.6, 41, 43, 48, and 48.9 (Fig. 2). The biochar structure, determined by X-ray diffraction, was basically amorphous in nature, but contained strongly conjugated aromatic compounds with some local crystalline structure. Strong cellulose peaks of around 60, 53, 40, and 25 have been reported to gradually lose strength and become wider with increasing charring temperatures of 100° to 300 °C, suggesting a gradual decrease in cellulose. In addition, mineralization and oxidation have been reported to decrease in tested maize biochars at higher temperatures [20]. Komnitsas and Zaharaki [21] show that characteristic amorphous peaks of cellulose, which is one of the structural components of the primary cell wall of green plants, are detected before pyrolysis in the analysis of raw materials before and after biomass pyrolysis. After pyrolysis, however the amplitude of these peaks was decreased. Peaks of residual inorganic phases such as calcite, quartz, whewellite, halite, and thermonatrite are evident in non-modified biochar.

The samples were gold coated with a Balzer's sputtering device prior to analysis with SEMEDX. The surface morphology of the Date Palm biochar as shown in Fig. 3 show irregular and porous surfaces. SEM images of Biochar at different magnifications showed porous and heterogeneous structure which offers more surface area for the adsorption process. Carbon dioxide adsorption occurs between gas molecules and the solid phase (biochar) through van der Waals forces, which are correlated with the particular surface area, pore size, and pore volume of the biochar [22]. Through physical adsorption, a biochar with larger surface area offers more active CO₂ adsorption sets, and so a higher biochar surface area results in a correspondingly larger adsorption capacity.

A study conducted to determine the effect of the pyrolysis temperature on the volume of the pore showed that the volume of the micropore and the total volume of the pore of the biochar increased as the temperature rose from 400 to 500 °C and a reverse trend was observed when the temperature increased above 500 °C. The coming together of neighboring pores will enlarge the pores when the temperature is higher than 500 °C while reducing the volume of the pore. A decrease in pore volume with an increase in heating rate from 10 to 50 °C per minute was noted by authors [23]. When the process heating rate is poor, there is enough time for pyrolysis products/volatile organic matter to disperse from the biochar particles. Nevertheless, the time for discharge of volatile organic matter decreases with the rise in heating rate, resulting in the accumulation of volatiles inside the particles and blocking the pore entrance.

Using SEM-EDX to calculate the intensity of the K-line across the sample (Fig. 4), the elemental distribution of carbon and oxygen in DPL sample was investigated. Carbon was detected with around 2 cps per eV, and oxygen comes after it. It is generally expected for biochar to have carbon as highest intensity element because carbonization due to pyrolysis [24].

The EDX analysis showed the presence of different compounds on the biochar produced surface (Table 1), the elemental weight of each ingredient was 83.56 percent for carbon, 12.43 percent for oxygen, 1.12 percent for potassium, 1.64 percent for calcium, 0.83 percent for phosphorus, and 0.4 percent for magnesium. The findings revealed that along with high carbonization, volatilization of organics was improved by rising the pyrolysis temperature [25]. The presence of alkali metals and alkaline earth metals such as K, Ca, and Mg will improve

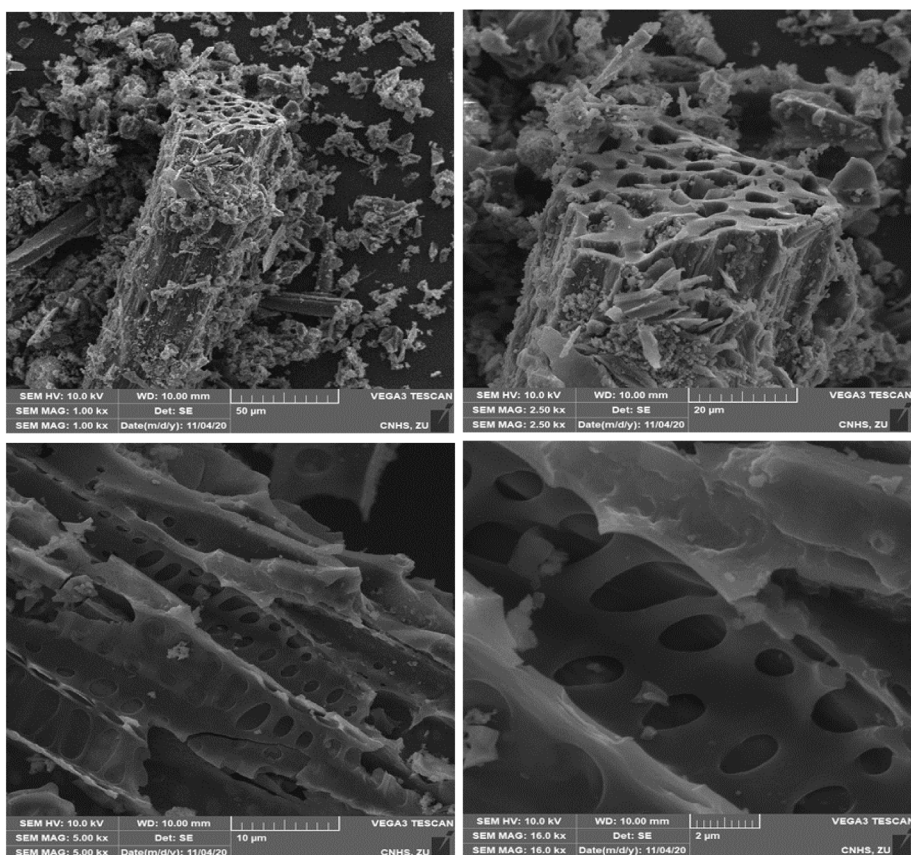


Fig. 3. SEM analysis image for DPL biochar at different magnifications.

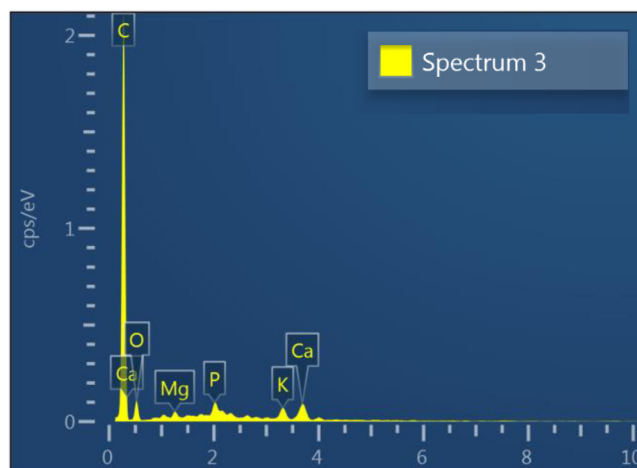
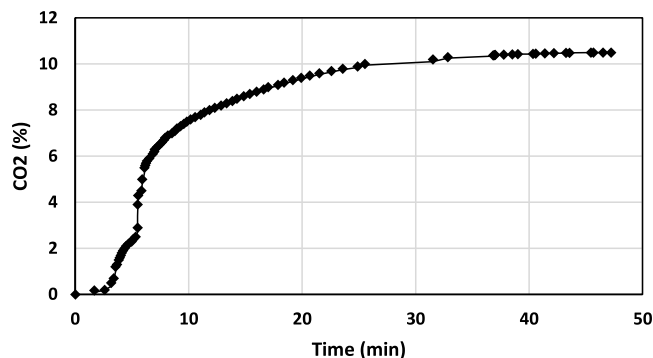
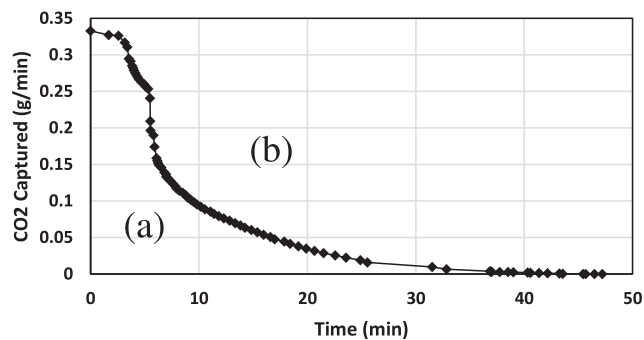


Fig. 4. Elemental composition graph of keV vs cps per keV through EDX analysis.

the acid-based development of sites with a high CO_2 attraction [26]. The existence of alkaline metals and alkaline earth metals can thus increase the ability of biochar CO_2 adsorption. MgO was produced when the temperature was above 400°C when biochar was loaded with Mg , and the outcome was the stimulated CO_2 adsorption through the interaction between CO_2 and O_2 [27]. Biochar with hydrophobic and non-polar properties may be limiting the

Table 1. Elemental composition by weight percentage through EDX analysis.

Elements	Weight (%)
Carbon (C)	83.56
Oxygen (O)	12.43
Potassium (K)	1.12
Calcium (Ca)	1.64
Phosphorus (P)	0.83
Magnesium (Mg)	0.41
Total	100

**Fig. 5.** Line graph show the CO₂ (%) detected by the gas analyzer in minutes time recorded.**Fig. 6.** Graph showing the amount of CO₂ captured (a) and the amount of CO₂ passed through (b).

competition of H₂O molecules, facilitate the ability of CO₂ adsorption. The low H/C and O/C ratios indicate a high degree of chemically stable aromaticity and fixed carbon [28].

The graph shown in Fig. 5 presents the data of increasing carbon dioxide percent over time in minutes, which was recorded manually and plotted in excel. Recorded time where CO₂ passed through was around 47 min with reached maximum value and unchanged through time 10.5% CO₂ flowed. Another observe from the line graph indicates a flow in the beginning was strong and passed through the cylinder between biochar particles. This can help in understanding and predict the efficiency of the biochar at reacting with CO₂ and adsorbing them.

The carbon dioxide adsorption of date palm leaf waste biochar was rapid at the start and its speed reduced after 5 min, and came at a plateau after 40 min, representing it was at equilibrium and there is no more carbon dioxide passing through. Both areas under the curve were calculated shown in the graph above (Fig. 6), the area (b) shown has an area value of 15.7 signifying that total amount of carbon dioxide that passed through the column cylinder. However, (a) was found to be a value was around 3.117, which represents the total captured CO₂ by the date palm leaf biochar. This indicated that only one third of CO₂ was adsorbed by 183 grams of DPL biochar. Therefore, date palm leaf biochar at 500 °C pyrolysis temperature and conditions set shows a carbon dioxide adsorption efficiency

of 20 percent, and calculated amount of CO₂ adsorbed per gram of DPL biochar is 0.017 grams. It should be noted that during the adsorption test the temperature was observed to increase for 2 degrees above room temperature due to pressure and possible reactivity inside.

The feedstock can be treated either before pyrolysis or after pyrolysis, in order to make the desired changes to biochar. Chemical modification, physical modification, element impregnation, etc. can be known as biochar modification [29]. Potential biochar adsorbents should be chemically and thermo-stable and have high CO₂ adsorption capability and selectivity for use in industrial processes that emit fire gas at high temperatures [30]. The biochar must have a wide region, high volumes of pore, suitable functional surface groups, high aromatics, and sufficient elementary composition to achieve this objective [31]. Also, looking at future applications of biochar with CO₂ adsorption, from field sites to CO₂ adsorption tests that do not include that integration of soils.

4. Conclusion

Using the low-cost, sustainable method of reducing and storing CO₂, the aims of reducing palm waste define the DPL biochar through FTIR, XRD, SEM, EDX and then assess the efficiency of the date palm leaf waste biochar through the Gas–Solid analyzer technology in adsorbing CO₂. Findings show that date palm leaf (DPL) waste showed great characterizations as a biochar pyrolyzed at 500 °C for 5 h, meaning that could be a good material for other source of studies and employed in different uses.

However, from the analysis of results discussed for CO₂ adsorption it is safe to claim that raw DPL biochar has potential and is able to efficiently adsorb 20% of carbon dioxide. It is suggested to that reduce the flow rate and temperature can be changed to see how DPL efficiency would improve. Also, modifications can be suggested to boost its performance to 50 or even 60% possibly. It is also recommended to conduct more tests such as TGA, calculate the surface area, and pore volume, and other methods available to extract an even better understanding of the DPL waste biochar. Moreover, to estimate the possible potential of the date palm leaf waste with accuracy. It is also concluded that the date palm waste was successfully turned into useful material helping in the management of such waste will be very useful.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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