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Utilization of the UAE date palm leaf biochar in carbon dioxide capture and sequestration processes

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ABSTRACT

This paper evaluates the potential use of date palm leaf biochar as a climate change solution through CO₂ capture and sequestration. The pyrolysis of date palm leaf was performed at different temperatures 300 °C, 400 °C, 500 °C, and 600 °C. The physicochemical characteristics of the synthesized biochar were examined using Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), Fourier transforms infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), and X-ray diffraction analysis (XRD). Direct gas-solid interaction was carried out in an integrated Fluidized Bed Reactor (FBR), connected with a gas analyzer for maximum and effective mixing between the biochar and CO₂. LabView program was used as data acquisition for an instantaneous calculation of CO₂ adsorption. This study showed that the date palm biochar as porous carbon-based materials has high CO₂ adsorption capacity through physisorption and chemisorption progressions. The adsorption results showed a maximum CO₂ capture percentage of 0.09 kg CO₂/kg, 0.15 kg CO₂/kg, 0.20 kg CO₂/kg, and 0.25 kg CO₂/kg palm biochar synthesized at 300 °C, 400 °C, 500 °C, and 600 °C, respectively. This paper paid attention to the inexpensive technology applied in CO₂ sequestration, where fluidization provides well mixing of biochar particles with low operation cost.

1. Introduction

As the world develops daily, greenhouse gases produced by natural and human activities contribute to climate change. The world population is estimated to reach around 8.5 billion in 2030 and 9.7 in 2050 and continue to increase to 10.9 billion in 2100 (Desa, 2019). This projection and other projections show that the world population will increase, which means that the emissions of greenhouse gases (GHGs) from anthropogenic sources will increase too, accelerating climate change, making it worse. Carbon dioxide is one of the GHGs that shows exceptional persistence in the environment, and it has grown at a phenomenal rate due to human activities (Keller et al., 2018). CO₂ emissions produced from human activities such as burning fossil fuels and wastes store more infrared radiation, thus increasing the atmospheric temperature (Mfarrej, 2019). The increase in CO₂ concentration in the atmosphere has mainly resulted from using non-renewable energies, and there is a growth in the emission due to energy generation, industries, and transportation (Radhi and Harris, 2010).

It’s important to note that not all emissions reach the atmosphere. A percentage of carbon emissions are sequestered via carbon sinks. Carbon sinks are natural media that can sequester and store CO₂ from the atmosphere for a specific period (Ontl et al., 2020). Carbon dioxide is sequestered by carbon sinks such as oceans, soil, and forests, and the species living within the media exchange CO₂ with oxygen (Gorte, 2009; Metz et al., 2005). But, due to land use for agriculture and deforestation of forests, more carbon dioxide will be emitted into the atmosphere.

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 adsorbative materials is desirable (D’Alessandro et al., 2010; Osschatz and Antonietti, 2018).

The use of natural resources to capture and sequester CO₂ has been considered one of the main driving forces for solving global environmental issues such as global warming. Date palm trees are one of the ancient primary crops in Southwest Asia and North Africa, and they are very abundant in genera and species (Al-Alawi et al., 2017). They are highly adaptive is desert environments, where it is characterized by high temperature and scarce rainfall (Al-Yahyai and Al-Kharusi, 2012). Middle Eastern countries, including the UAE, Saudi Arabia, Iran, Egypt, and other countries, are known for their agricultural orientation to date.
palm tree cultivation. The UAE is one of the top ten date palm tree producers as it is part of the significantly contributed areas in the Middle East (Al-Alawi et al., 2017). The United Arab Emirates has approximately 40 million date palms, and 75% are in Abu Dhabi. Around 15 kg of biomass waste is produced by each tree every year, including dry leaflets, rachis, fronds, etc. A massive amount of palm dates, around 2 million tonnes, are produced and discarded every year from production (Ashraf et al., 2017).

The cultivation of palm trees in the UAE results in a large quantity of lignocellulosic waste, and about 20 kg per tree per year is transported to landfills. Branches, leaves, stem barks, and fronds are used in date palm tree waste (Chandrasekaran and Bahkali, 2013). They are the waste that is most commonly created. They are obtained by seasonal palm pruning, which is a farming method and is discarded without valorization. The large quantities of palm waste produced each crop season constitute a significant charge for farmers who always try to burn or transport them outside the oasis. Date palm waste biochar may also provide an economically and environmentally important tool for minimizing date palm waste. Therefore, the use of fronds from date-palm waste is a promising idea focused on economic and environmental considerations (Almi et al., 2015).

Biochar can minimize greenhouse gas emissions (GHG) from carbon dioxide sequestration strategies (Smith, 2016; Thomazini et al., 2015). Biochar is a black carbonaceous product of biomass when heated at temperatures greater than 250 °C in the absence of air or limited air (Lehmann and Joseph, 2015). Biochar is described as an alkaline soil amendment; it is mainly made up of carbon, along with trace amounts of minerals and organics, and is also resistant to biodegradation (Graber et al., 2010). About 40–75% of the carbon in biochar is in the form of complex organic matter, and this substance is not broken down easily by microorganisms (Tan et al., 2015). Moreover, biochar has an extensive surface area and is composed of numerous functional groups (Wang et al., 2009). Altering pyrolysis condition affects the composition of the biochar (Al-Wabel et al., 2013). The slower pyrolysis process is generally linked to increased nitrogen, sulfur, calcium, magnesium, phosphorus, more surface areas, and increased cation exchange capacities. This is due to the loss of biochar components that are easily decomposable and volatile, such as oxygen, hydrogen, nitrogen, total phosphorus, and sulfur, during the slow pyrolysis process (Lehmann and Joseph, 2015). Different temperatures during pyrolysis allow for chemical modifications to biochar. As the biomass gets dehydrated, aliphatic bonds are converted into aromatic bonds, consolidated into stable graphene structures (Zama et al., 2017).

At various temperatures and pressures, biochar demonstrated considerably high adsorption of CO₂ comparable to activated carbon (Kua et al., 2019; Zhang et al., 2015a). 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 (Chiang and Huang, 2017; Vijayaraghavan, 2019). Such physical and chemical characteristics of biochar are correlated to the kind of feedstock used and the thermochemical factors of the development of biochar (Sun et al., 2014). Furthermore, the conversion of waste biomass to biochar decreases possible emissions of methane and CO₂ from landfills and dumpsites. Numerous studies were conducted in that regard. Most studies have shown that as the pyrolysis temperature increases, the surface area of the biochar increases and gives more surface for adsorption (Zhao et al., 2017; Zhang et al., 2015b). Another study by (Chaves Fernandes et al., 2020) observed that the surface decreased as the temperature increased due to the formation of ash content, which reduced the microporous formation. Different temperatures can increase the biochar surface area depending on the conditions used and the pyrolyzed material.

The carbon storage in biochar is suggested to eliminate approximately 0.1–0.3 billion tons of CO₂ emission per year (Liu et al., 2015). Numerous studies have been performed over recent decades on the pyrolysis of various biomass feedstocks for different applications. Still, 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 (Jouiad et al., 2015). A study by (Tayade et al., 2012) stated that biochar mixed into the soil successfully reduced the concentration of atmospheric CO₂ and the same has been suggested for use in highly contaminated regions to minimize CO₂ emissions. However, according to the authors’ knowledge, there hasn’t been a study on conventional production of DPL waste biochar with CO₂ adsorption that doesn’t include soil application.

One of the main problems that researchers are trying to solve is the enormous amount of date palm waste, which is being thrown in the UAE and the other producing countries. Dates are considered one of the primary, stable food and industry production for locals while also connecting it to carbon dioxide capture and storage (CCS) technology for GHG emissions to address air pollution and climate change. Hypothesized that Date Palm Leaf (DPL) waste is a cost-effective source of biochar and can efficiently adsorb carbon dioxide and, in turn, can assist in CO₂ capture and storage management. This study compares the impact of different temperatures during pyrolysis on the biochar surface morphology through SEM. Second to characterize the DPL waste, Biochar through FTIR, XRD, SEM, EDX, then to determine the DPL waste biochar performance in adsorbing the CO₂ through the Gas-Solid analyzer technology, based on the fluidization method and to understand how the biochar properties affect the adsorption efficiency.

2. Materials and methods

2.1. Biochar preparation

Date Palm leaf (DPL) waste was collected from a farm in Abu Dhabi, United Arab Emirates. Around 10 kg of leaves were washed and then left to dry for 24 h under the thermal heat from the sun (Fig. 1a). To make the size less than half an inch, the DPL was ground (Fig. 1b). The DPL was sieved to obtain a particle size of about 0.15 mm and then were placed in a furnace to proceed with the pyrolysis process at 300 °C/min, showing the weight change with temperature using a thermogravimetric analyzer. Before Pyrolysis (Fresh sample) and after pyrolysis (different biochar samples were also analyzed using x-ray powder diffraction (XRD).

2.2. Biochar characterization test

In the present study, Thermogravimetric Analysis (TGA) is used to study the thermal stability of the isolated chemicals and measure the weight change with temperature using a thermogravimetric analyzer. Before Pyrolysis (Fresh sample) and after pyrolysis (different biochar 300, 400, 500, and 600 °C), samples were analyzed using PerkinElmer simultaneous thermal analyzer (STA)-600. The temperature has been heated up to 800 °C with a heating rate of 10–20 °C/min, showing the decomposition of the sample’s ingredients.

To classify the crystalline substance in phases and provide details about the unit cells’ dimensions (DPL300, 400, 500, and 600 °C), biochar and fresh sample were also analyzed using x-ray powder diffraction (XRD).

Biochar (DPL300, 400, 500, 600 °C, and Fresh Samples) were milled using a mortar and were prepared for SEM (Scanning electron microscopy) and EDX (Energy Dispersive X-ray) analysis. SEM coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) with INCAx-act (Oxford Instruments) is working at 20 kV. Before analysis with SEM-EDX, the samples were gold coated with a Balzer’s sputtering unit, which was used to cover the samples before placing them in the instrument. Samples were placed in the machine, and images were taken with...
different magnification.

To obtain the infrared spectrum of absorption of the biochar (300, 400, 500, and 600 °C and fresh samples), Fourier Transform Infrared Spectrometer (FTIR) is used by collecting high-spectral-resolution data over a wide spectral range using a small mortar (Agilent Tech, MOD-ELCary630). Analytical tool MicroLab was used to collect the data.

2.3. Carbon dioxide adsorption test

An integrated Fluidizing Bed Reactor (FBR) was used to achieve a direct gas-solid reaction (Fig. 2 (Mohamed et al., 2021)). The reactor has a dimension of 100 cm in length and 8 cm in diameter inside, fabricated with stainless steel. The bottom of the reactor has a distributor, which can install a mesh. The mesh size used for the current study is 30 μm. A mixed gas of 10% CO₂ and 90% air was connected to the inlet stream that enters the reactor from the bottom, and the gas flow rate is controlled by an automatic controlling valve that can operate the specified setpoint up to 50 L/min. The pressure difference across the bed while running experiments is calculated between the top and bottom of the reactor and measured instantaneously in the mm-H₂O unit. Other parameters such as pressure inside the reactor, the pressure difference across the reactor, the temperature at the bottom, the middle, and the temperature at the top of the reactor can be measured. In this study, the temperature was determined to be set at room temperature. The cylinder was filled with 300 g, and the height of the solid particle inside the reactor was measured to be 8 cm. The bed was operated slightly above minimum fluidization velocity with a flow rate of 1.6 L/min operated gas flow rate for a time as long as CO₂% rises and reaches a constant reading, estimated around 30 min to 1 h.

The fluidization is formed when a quantity of a solid biochar particulate is forced to behave as a fluid by the force of pressurized CO₂ gas through the particulate medium. This results in a medium with many properties and characteristics of the biochar as normal fluids, such as free-flow under gravity. It reduces the density of the medium without affecting its elemental nature. In the FBR, the increase in gas flow rate beyond minimum fluidization leads to instabilities with bubbling and channeling the gas. At higher flow rates, fluidization becomes more violent, and the movement of solids becomes more vigorous.

Supervisory Control and Data Acquisition, Software system (SCADA) were applied to achieve this control and measure their readings. Gas analyzer CAI-NDIR-600 series was used to measure the concentration of CO₂, in % volume, from the output stream of FBR. A hose is connected to the gas analyzer while running carbonation experiments showing instantaneous readings of CO₂ leaving the FBR. LabView program was used as data acquisition to calculate the amount of CO₂ consumed in FBR by subtracting the instantaneous reading shown on the gas analyzer from the fixed entrance concentration supplied by the gas mixture cylinder, 10% CO₂ balanced with air.

3. Results

3.1. Biochar characterisation

Different techniques were used for estimating the biochar quality. Fig. 3 illustrates the thermogravimetric data for the percentage mass loss during heating and the corresponding derivative of the mass loss for the five types of DPL biochar before and after the pyrolysis at different temperatures. The curves can be interpreted as indicative of the degradation stages of the main organic compounds in the biomass (i.e., hemicellulose, cellulose, and lignin) (Tonbul, 2008). At temperature 90 °C-100 °C, the degradation for all lignocelluloses was caused by moisture loss. The stage at temperature ~200 °C is characterized by a relatively thermal-stable stage with a limited mass loss. The fresh sample shows a major mass loss at ~210 °C-~520 °C, which is associated with the devolatilization and decomposition of the chemical constituents of the biomass (cellulose, hemicellulose, and lignin) (Tonbul, 2008). Table 1 indicates the percentage mass loss of DPL with the thermal decomposition. The total percentage mass loss for the fresh simple is around 60.67% and is widely believed as a result of hemicellulose 16.52%, cellulose 37.97%, and lignin 6.19% degradation. These results
are consistent with those obtained by other researchers (Yassir et al., 2019) and biochar at different temperatures using TGA analysis.

The thermal decomposition of Hemicellulose, Cellulose, and Lignin of fresh DPL samples are shown in Table 1.

Table 1

| Samples | Hemicellulose (210°C-295°C) | Cellulose (295°C-420°C) | Lignin (420°C-520°C) | Total mass loss % |
|---------|-----------------------------|-------------------------|---------------------|------------------|
| Fresh   | 16.52                       | 37.97                   | 6.19                | 60.67            |
| 300°C   | 0.91                        | 5.91                    | 9.07                | 15.88            |
| 400°C   | 0.73                        | 2.25                    | 4.68                | 7.66             |
| 500°C   | 0.22                        | 2.20                    | 4.12                | 6.54             |
| 600°C   | 0.27                        | 0.97                    | 1.33                | 2.57             |

Fig. 3. Thermogravimetric analysis of (a) mass loss and (b) derivative mass loss of date palm leaves at different pyrolysis temperatures.

Fig. 4 represents the X-ray diffraction (XRD) analysis of the synthesized biochar at different pyrolysis temperatures. The profiles of biochar samples pyrolyzed at 300°, 400°, 500°, and 600°C indicate the presence of insoluble CaCO3.

The morphology of the biochar was evaluated from SEM analysis. The surface of the fresh palm tree leaves is smooth and unified without internal pores, as shown in Fig. 5(a–c), which indicates the presence of cellulose, hemicelluloses, and lignin, which was turned into porous and non-crystalline after thermal treatment. Formation of the channels and development of the porous structure in the samples treated at 300°C, 400°C, 500°C, and 600°C is a clear indication of the loss of volatiles components during pyrolysis.

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Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the chemical composition of biochar by recording the infrared spectrum of fresh palm leaf samples and biochar at 300°, 400°, 500°, and 600°C.
Fig. 5. Scanning electron microscope (SEM) images of; (a–c) fresh date palm leaves and its derived biochar’s at different magnifications; (d–f) pyrolysis at 300 °C, (g–i) pyrolysis at 400 °C, (j–l) pyrolysis at 500 °C, from (m–o) pyrolysis at 600 °C.
The composition of the samples was recognized by analyzing the spectra with relative intensities, which indicate a different functional group. Fig. 8 illustrates the changes in biochar surface functions with pyrolysis temperature. It is observed a peak at 3300-3400 cm⁻¹ for biochar samples and fresh samples, which corresponds to the O–H stretching vibrations of hydrogen-bonded hydroxyl groups. Before pyrolysis (fresh sample), the strength of this peak was found to be high, dropping to the negligible intensity at 600 °C. We also notice the distinctive C–H stretching vibration of the alkyl structure of aliphatic groups at 2930 cm⁻¹ for the fresh sample but not for the biochar samples.

On the other hand, peaks between 1620 and 1400 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. The peak in the region of 1026 cm⁻¹ is typical of C–O stretching vibrations (which suggests the pyranose C–O structures from cellulose were preserved to some extent after pyrolysis) and the CNH₂ stretch of a primary aliphatic amine (Peterson et al., 2013). The band at 460 cm⁻¹ represented aromatic C-H deformation that indicates aromatic hydrogen and a greater degree of aromaticity of the samples.

FTIR-derived results clearly show that as the pyrolysis temperature increases compared to the fresh sample, the strength of all of these peaks decreases and becomes insignificant at the temperature of 600 °C. Biomass hydroxyl group breakage is known to take place between 120 °C and 200 °C (Elnour et al., 2019). Methylene, methoxyl, and aliphatic methyl groups break at about 400 °C, resulting in the reformation of functional groups such as carbonyl and carboxyl. But a moderate increase in temperature won’t impact either stable heteroaromatic or aromatic molecules. Phenolic and ether groups can be found in higher amounts when aliphatic compounds rearrange into aromatic structures. In addition, many C=C bonds collapse at high temperatures due to the availability of abundant energy. Because of this, the intensity of signals decreases with higher temperatures, as carbonization and production of graphite-like structures of the biochar cause a decline in the intensity of the signal (Li et al., 2018). In some cases, the biochar generated at higher temperatures showed lower (O/C) ratios because the biochar surface and its composition lack functional groups (Behazin et al., 2016).

Fig. 6. EDS spectrum and weight percent of quantitative elemental data representative of the biochar (a) at 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C.

Fig. 7. EDX analyses show the weight percent of the carbon and oxygen as the pyrolysis temperature increases.

3.2. Carbon dioxide adsorption on palm leaf biochar

The Carbon-based adsorbents were performed in the designed integrated fluidized bed reactor to enhance the physical and chemical adsorption of CO₂ on the different palm leaf biochar particles. Fig. 9a shows the instantaneous CO₂ concentration while running CO₂ adsorption experimentation. Fig. 9b shows the amount of CO₂ passed through the reactor. The gas analyzer readings provide the main calculations of CO₂ captured through the physical and chemical adsorption. They can be employed to get the instantaneous conversion of CO₂ within the reaction period. The carbon dioxide adsorption of DPL waste biochar was rapid at the start. Its speed reduced after 10 min and came at a plateau after 20–40 min, representing equilibrium. The area under the curve in Fig. 9a signifies the total captured CO₂ by the date palm leaf biochar placed into the reactor. The area under the curve in Fig. 9b represents the total carbon dioxide passed through the column cylinder.

Studying the relationships between pyrolysis conditions of different biochar and their resulting physical and chemical properties is necessary to control biochar properties for CO₂ adsorption. Carbon-based
adsorbents typically have CO$_2$ physisorption through van der Waals force on the surface of the materials (i.e., non-specific interactions determined by the surface area). CO$_2$ chemisorption, which has chemical reactions between absorbents and CO$_2$ gas, is available on metal oxides and amine-containing materials (D’Alessandro et al., 2010). In detail, two amine functional groups on biochar can chemically react with one CO$_2$ through zwiterion mechanisms, producing carbamate and ammonia pairs (Jung et al., 2019). Because the carbonaceous materials have the potential for CO$_2$ physisorption, their CO$_2$ adsorption capacity increases with increasing carbon percentage, as shown in Fig. 10.

4. Conclusions

The present study offered a new trend in carbon dioxide capture and storage for reducing CO$_2$ emissions in the atmosphere. Due to the vast amount of date palm waste in the UAE, mainly because it is not therapeutically useful and not a food crop, this study will utilize palm leaf waste, which contains the lignocellulose structures, to reduce the global climate issue resulted from the accumulation of greenhouse gases. Pyrolyzed date palm leaf waste at different temperatures 300\(^\circ\)C, 400\(^\circ\)C, 500\(^\circ\)C, and 600\(^\circ\)C was characterized and evaluated to achieve adsorption of 7, 9, 15, 20, and 25% of carbon dioxide, respectively. An integrated fluidized bed reactor (FBR) was used to ensure the maximum contact and interaction between date palm biochar and CO$_2$. A gas analyzer is installed at the outlet stream of the designed FBR reactor to measure the concentration of the captured CO$_2$. Results revealed superior adsorption efficiency over those in previously reported studies. The fluidized bed reactor enhanced the adsorption processes besides the synthesized biochar efficiency in adsorbing the CO$_2$ gas. The research team is looking forward to extending the research area to cover most agricultural wastes to the industrial scale and find an effective local solution to meet the sustainability goals for the future.

Author contributions

Conceptualization, IBS and ME; methodology, IBS, ME and SH; software, MS and SH; validation, IBS and ME; formal analysis, IBS, ME and FH; investigation, MS and SH; resources, FH and ME; data curation, IBS, ME, MS and SH; writing—original draft preparation, IBS and ME; writing-review & editing, IBS, ME and MS; visualization, IBS and ME; supervision IBS; funding acquisition, IBS.

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