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Biomass-derived activated carbons from date pits and spirulina for CO₂ and water vapor adsorption: A comparative uptake ratio study

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Keywords: activated carbon, adsorption, isotherm, water vapor

Abstract: Increasing emissions of greenhouse gases, such as CO₂, cause a rise in the average temperature of the Earth's climate system. It is well established that ZnCl₂ activation or treatment is one of the most widely used methods for maximizing CO₂ adsorption capacity. However, water vapor co-adsorption during CO₂ capture processes can result in higher regeneration energies. This study aims to evaluate the effectiveness of ZnCl₂-activated carbons coated with a thin layer of vinyltrimethoxysilane to increase the CO₂/H₂O uptake ratio. Date pits and *Spirulina* were used separately to produce activated carbons. The CO₂ adsorption capacities of the samples were investigated using thermogravimetric analysis with 15% CO₂ in nitrogen, while the water vapor uptake at 10, 50, and 95% relative humidity (RH) was investigated using Dynamic Vapor Sorption. Partial reductions in specific surface area and pore volume occurred after silane modification. However, heat treatment of the coated samples at 450 °C, which moderated the coating layer on the surface and reopened some of the blocked pores, increased the CO₂/H₂O uptake ratio, especially for the activated carbon derived from date pits (DPZHC), to 3.01 at 10% RH. Therefore, this sample is a promising candidate for co-adsorption processes. Although the study was conducted under controlled conditions, the adsorbent's stability and its ability to regenerate and be reused still need to be determined.

Introduction

Human activities, especially over the last few decades, have significantly increased atmospheric pollutant concentrations, leading to an increase in the Earth's average surface temperature. Greenhouse gases, particularly carbon dioxide (CO₂), are emitted from industrial processes and contribute significantly to global warming (Mashkhool et al. 2021). However, CO₂ can be captured using various technologies. Among the wide variety of adsorbents, including silica, zeolites, polymers, metal-organic frameworks (MOFs), and activated carbons that have been extensively investigated for CO₂ capture, carbon-based materials derived from different precursors exhibit high CO₂ uptake capacities and stability during adsorption-desorption cycling (Reddy et al. 2021). Limited CO₂ adsorption selectivity in the presence of water vapor is one of the main obstacles to the widespread use of conventional activated carbon in CO₂ capture technologies. Therefore, the development of well-designed carbon-based materials with controlled properties has become essential for efficient environmental applications.

Chemical and physical treatments have been used to modify the surface chemistry of carbon materials and tailor their adsorption properties. For instance, enlarged micropores with small amounts of mesopores can be obtained using potassium hydroxide (KOH) (Oumabady et al. 2021), sodium hydroxide (NaOH) (Borisut et al. 2025), and zinc chloride (ZnCl₂) (Möller et al. 2023). Due to its acidifying properties, zinc chloride plays an important role in activating carbonaceous precursors and improving the adsorption capacity of the resulting carbon materials by promoting dehydration and bond cleavage in biomass, facilitating aromatization and crosslinking of the carbon matrix. Furthermore, subsequent acid washing dissolves zinc species and removes them from the carbon matrix, creating voids that develop into micropores and mesopores (Li et al. 2020). These processes strengthen the internal pore network and increase surface accessibility for adsorption, making the activated carbon more effective.

Two biomass precursors were selected in this study: date pits and *Spirulina*. Their selection was based on carbon



Fig 1. Spirulina powder and Date pits powder

density, cost, abundance, CO₂ adsorption potential, and their fundamentally different biochemical compositions. Date pits are lignocellulosic materials rich in cellulose, hemicellulose, and lignin, whereas *Spirulina* is a protein-rich microalga containing nitrogenous functional groups that may lead to differences in the surface chemistry and adsorption behavior of the resulting carbons. Water vapor is the third most abundant component of flue gas after nitrogen and carbon dioxide. The presence of water is generally detrimental to CO₂ capture using activated carbons, especially at low relative pressures, where water and gas molecules compete for active sites. In general, for most CO₂ capture processes, water vapor in a gas stream increases the energy demand. Water molecules (diameter $\approx$ of 0.275 nm) adsorb first onto the functional groups, which represent the primary active sites. These sites typically occur at the edges and corners of basal planes and interact with water molecules through hydrogen bonding, forming a water layer on the activated carbon surface. Subsequently, as the relative humidity (RH) increases, water clusters form around the initially adsorbed water molecules, which themselves become secondary adsorption sites.

Once a critical cluster size is reached, the clusters possess sufficient dispersive interaction energy to fill the carbon pores (Duan et al. 2023). At equilibrium, water isotherms on the pore surface typically exhibit a V-type topology, which is relatively rare. This is due to the hydrophobic nature of activated carbons, which has been shown to be strongly dependent on relative humidity (Zheng et al. 2023). Therefore, studying water adsorption is important for evaluating sorbent performance in CO₂ capture. Querejeta et al. (2016) reported that moisture strongly influenced the adsorption performance of activated carbons derived from biomass under post-combustion CO₂ capture conditions. Surface post-treatments can increase water vapor adsorption capacity by altering pore accessibility and surface chemistry. Liu et al. (2018) confirmed that adsorption processes are strongly affected by moisture. They investigated the sorption equilibria and kinetics of CO₂ and H₂O on KOH-treated activated carbon and reported that the adsorption capacity for H₂O was higher than that for CO₂. The main objective of this study was to evaluate the adsorption performance of modified activated carbons toward CO₂ and water vapor separately and to assess their relative affinity using a CO₂/H₂O uptake ratio. Laboratory-scale adsorption experiments were conducted using thermogravimetric analysis and a dynamic vapor sorption instrument.

Materials and methods

Materials

Spirulina powder (*Spirulina Hawaiiiana*) was purchased from Cyanotech, USA, and used as the algal raw material for the preparation of activated carbon. The powder was dried at 105 °C for 5 h to remove moisture and then cooled to room temperature. Dates were collected from local markets in Basra, Iraq, and the pits were manually separated from the fruit. The pits were first washed several times with potable water followed by distilled water, and then dried and cooled using the same procedure as that applied to the *Spirulina* powder. The dried pits were subsequently crushed and sieved to obtain particles with diameters in the range of 1.0-1.4 mm.

Methods

Carbonization

The carbonization process was conducted separately for each dried powder by heating it to 550 °C at 5 °C/min under nitrogen (N₂), maintaining this temperature for 60 min and then cooling to room temperature. The resulting carbonized samples derived from date pits and *Spirulina* were designated DP and SP, respectively. ZnCl₂ (purity $\geq$ 98%) was purchased from Sigma-Aldrich (UK).

Activation of Materials

The following steps were carried out for chemical activation:

- 1- The SP carbon was mixed with ground ZnCl₂ at a mass ratio of 1:1 (m/m).
- 2- Approximately 5 g of the mixture was placed in a ceramic pot and loaded into a quartz tube of a horizontal tube furnace (Elite Thermal Systems Ltd., UK). The system was purged with nitrogen (N₂ gas (1 bar, 1 L/min) for 30 min to remove residual air and moisture. The samples were then heated to 650 °C at 5 °C/min for over 60 min under continuous nitrogen flow, followed by cooling to room temperature.
- 3- To remove residual ZnCl₂ and achieve neutral pH, the resulting activated carbon was treated with 1 M hydrochloric acid and subsequently washed repeatedly with distilled water. The washed samples were then dried in an oven at 110 °C for 6 hours. The final activated carbon derived from *Spirulina* was labelled SPZ. The same procedure was applied to the date pit-derived carbon, yielding DPZ.

Modification of Activated Carbon

The surface modification was performed according to the experimental protocol described by Albazzaz (2020) and consisted of three stages: oxidation, reduction, and hydrophobization. First, the oxidation step was conducted by adding 2.5 g of DPZ to 250 mL of 15% w/w H_2O_2 solution. The mixture was subsequently washed with distilled water, dried at 100 °C for 24 hours, and then heated at 450 °C for 3 hours under N_2 gas. The second stage, reduction, was performed by dissolving 2.5 g of the $NaBH_4$ in 250 mL of anhydrous methanol. The sample was submerged in the mixture for 12 hours, then diluted with 250 mL of water and boiled for 3 hours. The sample was then removed from the solution, washed with water, and dried in a vacuum oven at 100 °C for 24 hours. Finally, the hydrophobization step was conducted by partially dissolving vinyltrimethoxysilane (VTMOS) in toluene at a volume ratio of 1:10 (VTMOS:toluene:v/v), followed by the addition of a few drops of water to induce the hydrolysis of the alkoxysilane molecules. The sample was placed in an extraction thimble and loaded into the main chamber of a Soxhlet extractor connected to a distillation flask and a reflux condenser. The distillation flask was heated to the boiling point of toluene (110.6 °C), and the condensation reaction was allowed to proceed via Soxhlet extraction for 3 hours to achieve hydrophobization. The resulting coated activated carbon derived from date pits was labelled DPZH. The same procedure was applied to SPZ, producing the hydrophobized sample SPZH.

Calcination

To moderate the thickness of the coating layer, the two samples, DPZH and SPZH, were separately subjected to thermal treatment under N_2 (1 bar, 100 mL/min). The process was conducted using thermogravimetric analysis (TGA) (Q500, TA Instruments Incorporated) at 450 °C for 1 hour, a temperature identified by the referenced study as optimal for CO_2 adsorption. TGA is an integrated thermal weight-change analysis instrument. It is equipped with standard mass flow controllers to measure the amount and rate of change in the weight of a material as a function of temperature or time, and operates in the temperature range from ambient to 1000°C. It has an isothermal temperature accuracy of ± 1 °C, an isothermal temperature precision of ± 0.1 °C, a weighing capacity of 100 mg, a sensitivity of 0.1 μ g and a precision of $\pm 0.01\%$. The resulting samples were labelled DPZHC and SPZHC.

Textural Characterization of the Samples

The textural properties of the samples, including the specific surface area and pore volume, were characterized using N_2 and CO_2 sorption isotherms. Surface area and porosity data were measured using both experimental techniques and models applied to the isotherms, such as the BET and Non-Local Density Functional Theory (NLDFT) models.

Experimental Procedure

The textural properties of the samples (DP, DPZ, DPZH, DPZHC SP, SPZ, SPZH, and SPZHC) were characterized using a Micromeritics Accelerated Surface Area and Porosimetry Analyzer (ASAP 2420, Micromeritics Corporation) with N_2 (at -196 °C) and CO_2 (at 0 °C) as adsorbates. Before the measurements, approximately 0.2 g of each sample was

weighed into a sample tube and degassed under high vacuum (<0.013 mbar) at 120 °C for 6 hours to remove adsorbed moisture and gases. The surface area was calculated using the BET model from N_2 adsorption isotherm data over the relative pressure range of 0.01-0.10, yielding positive BET 'C' parameters. The cumulative pore volumes (V_{total}) were calculated using a non-local density functional theory (NLDFT) carbon slit pore model through a combined analysis of N_2 adsorption isotherms at -196 °C (over a relative pressure range of 0.00001 to 0.99850) and CO_2 adsorption isotherms at 0 °C (over a relative pressure of 0.00006 to 0.03498) using Microactive Software V5.0.

Fourier Transform Infrared (FTIR) Spectroscopy analysis

Fourier transform infrared spectroscopy (FTIR) analysis was performed using a Perkin Elmer Spectrum 100 instrument in the mid-infrared range (4000–400 cm^{-1}) at a resolution of 2 cm^{-1} . Each spectrum represents the average of 16 scans acquired in transmittance mode. Using a mortar, 0.0015 g of the sample was mixed and ground with 0.25 g of potassium bromide (KBr). The obtained powder was loaded into a circular die and subjected to high pressure (100 MPa) for 10 seconds. The sample was then dried in a drying oven at 100 °C overnight under vacuum and left to cool to ambient temperature under vacuum. After that, the sample was analyzed using an FTIR spectrophotometer.

CO_2 and H_2O Adsorption Measurement

CO_2 Adsorption Measurement

The samples were analyzed using a TGA to determine the amount of CO_2 adsorbed. Approximately 20 mg of a sample was placed in a platinum pan and heated to 150 °C at a rate of 20 °C/min under a flow of N_2 (1 bar, 100 mL/min) for 30 minutes to remove any moisture and/or pre-adsorbed CO_2 . After drying, the sample was cooled to the adsorption temperature of 25 °C under the same N_2 flow rate. The gas was then switched to simulated flue gas (15:85 v/v CO_2 : N_2 , 1 bar, 100 mL/min), and the sample was held isothermally for 1 hour. The sample's weight change at the point of gas switch-over was taken as the baseline, and the subsequent increase in mass during exposure to the simulated flue gas was used to calculate CO_2 uptake. From this, the adsorption kinetics at t_{60} , t_{80} , and t_{90} were calculated for the samples by determining the time taken to reach 60, 80, and 90% of the CO_2 equilibrium capacity, based on the net weight gain recorded during the adsorption period. The experiment was repeated for all other samples. Since N_2 is assumed to be non-adsorbing under the experimental conditions, the observed mass increase after gas switching was attributed solely to CO_2 adsorption.

H_2O Adsorption Measurements

Dynamic vapor sorption (DVS) measurements were carried out using a DVS Adventure analyzer (Surface Measurement Systems Ltd., London, UK). The balance head and reaction chamber were purged with dry nitrogen before sample loading. The flow of nitrogen is automatically controlled to keep the head of the sensitive recording microbalance dry inside the controlled temperature chamber, thereby preventing the condensation of vapor in connections and ensuring accurate

uptake measurements. The uptake was calculated by dividing the difference between the temporal mass measured and the mass of adsorbent after the drying process (before the start of adsorption process) by the mass of the adsorbent after the drying process. An optical vapor pressure sensor and an RTD temperature probe fixed beside the sample pan (which contained 10 mg of the sample) were used to measure the test conditions in DVS. The weights of samples measured by the microbalance were transmitted directly to a PC microcomputer for recording and analysis. The six samples were dried at 150 °C for 12 hours, and the adsorption process was then conducted at 25 °C.

Results and discussion

Characterization of Activated Carbon

Table 1 summarizes the specific BET surface areas (SBET) and pore volumes, including micropore volumes, for all samples. The SP sample exhibited the lowest SBET value, 198 m²/g, which is typical for carbonized *Spirulina platensis* (Yu et al. 2022). SPZ showed a well-developed porous structure, where the intercalation of ZnCl₂ led to an increase in specific surface area to 796 m²/g, the total pore volume to 0.59 cm³/g, and a micropore volume to 0.34 cm³/g, increasing from 0.26 cm³/g for SP. In addition, the textural properties of carbonized date pits (DP) developed after the activation process. The SBET values for DP and DPZ were 613 and 1,214 m²/g, respectively, while the micropore volume and total pore volume increased from 0.31 to 0.54 and from 0.48 to 0.87 cm³/g, respectively. These results suggest that the modification treatments drastically altered the pore texture of the activated carbon, driven by the chemical activation (ZnCl₂) of the carbon network, and are consistent with those previously reported by Bouchemal and Addoun (2009), where the specific surface area and total pore volume of the activated carbon prepared from date pits increased to 1,322 m²/g and 0.81 cm³/g, respectively, after activation by ZnCl₂ at 600 °C. After VTMO

modification, a significant decrease in the BET surface area and pore volume of the coated samples (DPZH and SPZH) was observed.

This trend is consistent with reports in the literature, which indicate that chemical treatments may partially reduce porosity without drastically altering the pore structure, as silane modification can create a thin layer on the external surface, leading to partial blockage of pore entrances while preserving the overall pore architecture of the activated carbon (Pustahija et al. 2024). On the other hand, the effect of heat treatment was very clear on the two coated samples. The surface area increased and approached its pre-modification value, accompanied by increases in micropore and total pore volume. This trend is consistent with results reported in the literature, which indicate that heat treatment of coated activated carbons increases specific surface area and pore volume (Albazzaz, 2020).

SBET is the specific surface area obtained using the BET model from the N₂ isotherm in the relative pressure range of 0.01 - 0.10 P/Po. V_{micro}, V_{meso}, and V_{total} are pore volumes corresponding micropores, mesopores, and total pores up to 100 nm, respectively, determined using NLDFT with a carbon slit-pore model applied to combined N₂ and CO₂ isotherms.

Scanning Electron Microscopy of Samples

The morphologies of the six samples were examined using a Quanta 600 scanning electron microscope (SEM) on the micrometer scale. The SEM images in Fig. 2 (a-f) were acquired at magnifications ranging from 1000× to 1500×, with a constant scale bar of 50 µm. The SEM image of DP shows a relatively smooth surface with limited pore development. Most of the visible pores are shallow and spherical, reflecting the natural structure of the biomass, which has not yet been significantly altered. The hemicellulose and lignin in the date pits were partially decomposed during the carbonization process, but this did not yield a well-developed porous network.

Table 1: Texture properties of activated carbon samples.

	SBET (m ² /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	V _{macro} (cm ³ /g)	V _{total} (cm ³ /g)
DP	613	0.31 (65%)	0.13	0.04	0.48
DPZ	1214	0.54 (62%)	0.23	0.09	0.87
DPZH	789	0.34(63%)	0.12	0.08	0.53
DPZHC	1177	0.46 (64%)	0.19	0.07	0.72
SP	198	0.26 (40%)	0.07	0.02	0.35
SPZ	796	0.34 (58%)	0.20	0.05	0.59
SPZH	423	0.28(72%)	0.07	0.04	0.39
SPZHC	752	0.31 (70%)	0.09	0.04	0.44

The DPZ sample reveals a highly porous structure characterized by rough, irregular, and heterogeneous pores of varying sizes, including micro-, meso-, and macropores. Additionally, some ZnCl_2 residue, which may not have been removed during repeated washing, appears as light or white particles due to its higher electron density than carbon. After the VTMO coating, many small pores disappeared from the surface of the DPZH sample, while others were partially closed by the coating material, which covered the remaining residue of the chemical activating agent. Despite this, the overall pore structure remained clear, indicating the coating layer did not have a major effect on the underlying pore structure. Calcination of the DPZH sample removed a large portion of the VTMO and reopened many pores. On the other hand, the SEM image of SP shows a compact and weakly porous structure with a rough surface. This morphology is consistent with the recent literature, which reports that low porosity typically forms on the *Spirulina* surface after carbonization due to its high protein content (Mushtaq and Alzurfi, 2023). Conversely, the SPZ sample exhibits a highly porous structure with irregularly shaped pores. Distinct crevices are apparent on the porous surface, indicating pores of various sizes, including mesopores

and macropores. Some ZnCl_2 residues are more clearly visible on the carbon surface. The image of SPZH shows changes in the surface structure after VTMO-coating. The large cavities disappeared from the SPZH sample, resulting in a low-level pore network. The bright, light-colored edges indicate the presence of a coating or surface effects caused by VTMO that were not present in the DPZH sample. A notable reduction in the number and size of pores was observed, resulting in a smoother, more uniform surface. Some pores remained scattered across the surface, indicating that the coating process successfully reduced porosity.

The effect of heat treatment was very clear in the coated sample, where many pores reopened, and the surface morphology of SPZHC was similar to that observed before modification. The same effects of coating materials and calcination on pore size were observed by Albazzaz (2020), who found that VTMO coated most pores in the activated carbon, especially the large cavities, and that calcination at 450°C reopened most of them, suggesting that the VTMO coating collapsed on the surface.

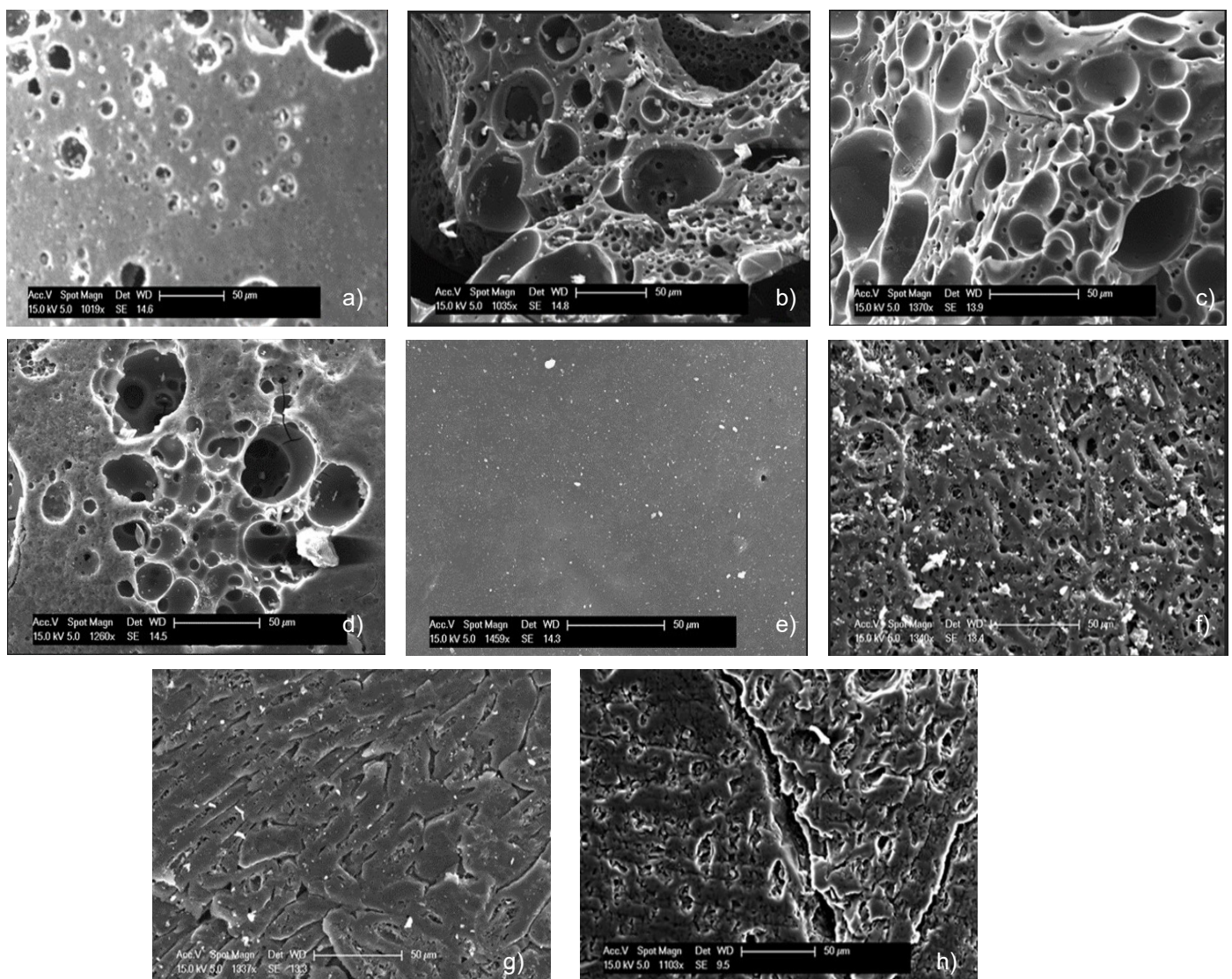


Fig 2. SEM images of carbon (a) DP, (b) DPZ, (c) DPZH, (d) DPZHC, (e) SP, (f) SPZ, (g) SPZH, and (h) SPZHC

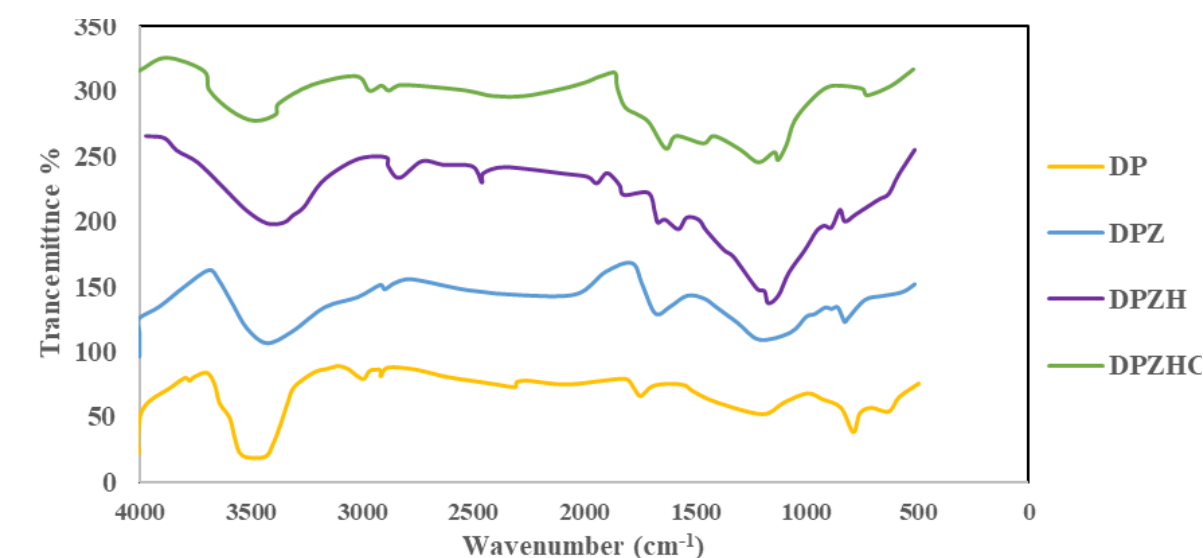


Fig 3. FTIR spectra of DP, DPZ, DPZH and DPZHC.

Fourier Transform Infrared Spectroscopy (FTIR)

In this work, FTIR spectroscopy was performed on samples derived from date pits, which exhibited higher specific surface area and pore volume, to evaluate the effects of carbonization, activation, and VTMOs grafting on the carbon surface, as well as the effect of heat treatment on the chemical structure of VTMOs. As shown in Figure 3, DP and DPZ exhibited a broad band in the 3,650–3,200 cm⁻¹ wavelength range; the broader band with a gradual decrease was observed in the coated sample DPZH. This is possibly due to the O-H stretching vibration of surface hydroxyl groups (Yang and Yuan, 2025). However, the broad band decreased considerably after heat treatment, possibly indicating the removal of some hydroxyl groups from the DPZHC sample. Another large absorption band was observed in the DPZH spectrum in the 1,450-900 cm⁻¹ region, with a maximum at about 1,170 cm⁻¹, possibly due to the stretching vibrations of Si–O–Si and Si–O–CH₃ groups, confirming the successful incorporation of silane-based coating species onto the carbon surface (Albazzaz, 2020). As a result of heat treatment, the intensity of this band decreased to a weak shoulder, reflecting a reduction in the characteristic absorption features in DPZHC, and a new band appeared at

1,126 cm⁻¹. Finally, the bands appearing below 800 cm⁻¹ in DP and DPZ may be attributed to out-of-plane bending vibrations of aromatic C–H bonds. In conclusion, the effectiveness of the activation and coating processes was confirmed by FTIR analysis. The DPZH sample exhibited the most pronounced chemical modification, indicating a successful transformation from hydrophilic to hydrophobic surface characteristics. Heat treatment significantly altered the chemistry of the coated sample by removing some hydroxyl groups.

Measurement of the Kinetic Adsorption of CO₂

Dry simulated flue gas (15% CO₂) at a flow rate of 100 mL/min was used to evaluate the kinetics of CO₂ adsorption for all samples using TGA. Overall, the kinetics were relatively fast, with most samples approaching equilibrium within 10 minutes (Fig. 4).

Detailed adsorption kinetics at t_{60} , t_{80} , and t_{90} are further reported in Table 2. As expected, and because they contain high proportions (40% and 72%) of the total pore volumes, the microspores offer sufficient active sites for adsorbate molecules (CO₂). Therefore, less than 2.5 minutes was sufficient to attain 60% of equilibrium uptake for all samples. For instance, DP

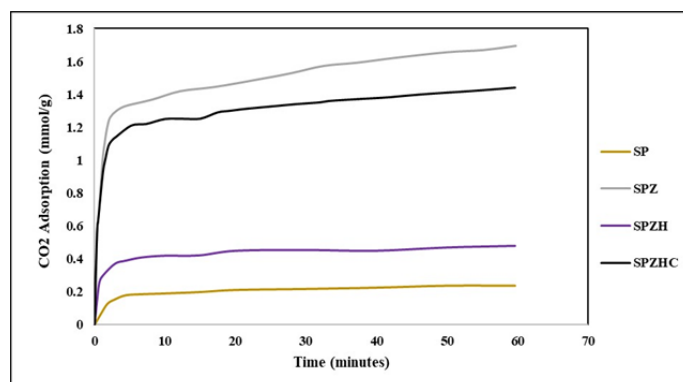
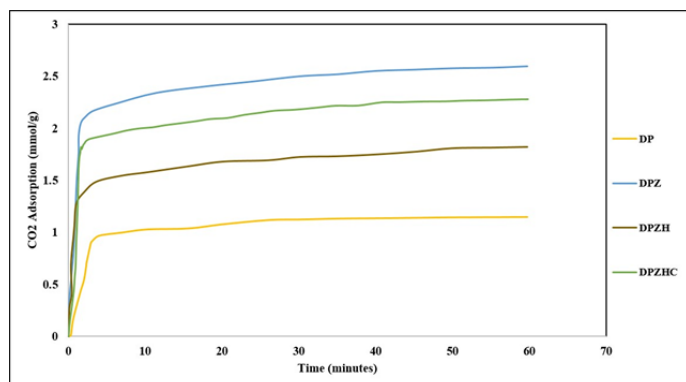


Fig 4. SCO₂ adsorption (a) for the DP, DPZ, DPZH, and DPZHC samples (b) for the SP, SPZ, SPZH, and SPZHC using TGA in 15% CO₂ and 85% N₂ at 25 °C

and SP attained 60% of equilibrium at 2.3 and 2.42 minutes, respectively. These outcomes confirm the results obtained by Kretzschmar et al (2021), which showed that a short contact time (~3 minutes) is sufficient to achieve high adsorption capacity for carbonized materials. After activation, the CO₂ adsorption performance of ZnCl₂-activated carbons (DPZ and SPZ) was markedly enhanced, and the adsorption kinetics were faster in reaching 60% of equilibrium. This can be attributed, first, to the activation process, which led to significant mesopore development, facilitating rapid diffusion into the micropores and increasing their volume (see Table 1). This effect not only improved accessibility but also provided abundant high-energy adsorption sites that are rapidly saturated with CO₂ molecules (Meng and Park 2014). Second, oxygen-containing functional groups (such as carboxyl and hydroxyl groups) were formed due to changes in surface chemistry. These groups interact strongly with CO₂ molecules, thereby accelerating adsorption (Liu et al. 2018).

In the first stage of adsorption, which accounts for 60-80% of the total adsorption within the micropores, uptake is driven by van der Waals forces between carbon dioxide molecules and the pore walls. These interactions occur more rapidly than those in the second stage, when adsorption approaches equilibrium. This explains the longer time required to reach 90% of total adsorption for all samples. On the other hand, except for the DPZH sample, which required a relatively long time to achieve 90% of the equilibrium (15.6 minutes), the two coated samples attained 60, 80, and 90% of equilibrium in shorter times compared to DPZ and SPZ. The effect of heat treatment was very clear in the time required to reach equilibrium for the two calcined samples. These results are superior to those reported in a previous study using zeolite calcined at 600 °C and a syngas flow rate of 0.5 L/min containing 15% of CO₂, where the adsorbent required 30, 32.5 and 38 minutes to reach 60%, 80%, and 90% of the total adsorption capacity (1.9452

mg CO₂ / kg adsorbent $\approx 4.42 \times 10^{-5}$ mmol CO₂/g adsorbent), respectively (Maceiras et al. 2025).

Gravimetric Measurement of Water Vapor Adsorption

DVS was used to determine the adsorption isotherm data for H₂O on all samples. As shown in Fig. 5, the samples exhibited a type IV isotherm according to the IUPAC classification (Thommes et al. 2015).

Water molecules showed preferential adsorption on the DPZ and SPZ (<20% RH). The high adsorption of H₂O on the DPZ can be attributed to the abundance of high-density hydrophilic surface functional group, which increased during the washing process, and to the greater volume of micropores after ZnCl₂ activation, where residual Zn²⁺ and Cl¹⁻ species are removed and oxygen-containing functionalities such as –OH and –COOH are formed or increased (Möller et al. 2023; Li et al. 2020; Li et al. 2023). In addition, the precursor material (date pits) is rich in lignin and cellulose, which promotes the development of oxygen-containing functional groups on the activated carbon surface (Al-Harrasi et al. 2025). On the other hand, as reported in the literature, *Spirulina platensis* contains nitrogen and sulphur. Therefore, after activation, the surface may remain more heterogeneous, with the presence of –N and –S groups in addition to oxygen-containing groups (–O), which promote the hydrophilicity of the SPZ surface (Xie et al. 2022). In general, the adsorption in this range for both samples can be considered minor or initial water uptake. By increasing the relative humidity to 60%, the adsorbed water molecules may serve as secondary adsorption sites for cluster formation. The critical size of these clusters may enable them to possess sufficient dispersive energy to fill the carbon pores (Jia et al. 2022). Consequently, this region exhibited the highest water uptake rate, characterized by a gradual yet more pronounced increase in adsorption compared with other regions.

Table 2: Comparison of CO₂ equilibrium capacity and adsorption times (or kinetics) of CO₂ under dry conditions for all samples using TGA in 15% CO₂ and 85% N₂ at 25 °C

Sample	Adsorption time of CO ₂ (minutes)			CO ₂ equilibrium capacity(mmol/g)
	t ₆₀	t ₈₀	t ₉₀	
DP	2.30	7.25	21.09	1.62
DPZ	1.61	2.87	11.41	2.56
DPZH	1.09	2.1	15.6	1.81
DPZHC	1.51	2.82	12.51	2.52
SP	2.42	10.01	23.42	0.24
SPZ	1.42	9.87	21.51	1.71
SPZH	0.85	3.24	15.12	0.48
SPZHC	1.21	5.02	21.09	1.60

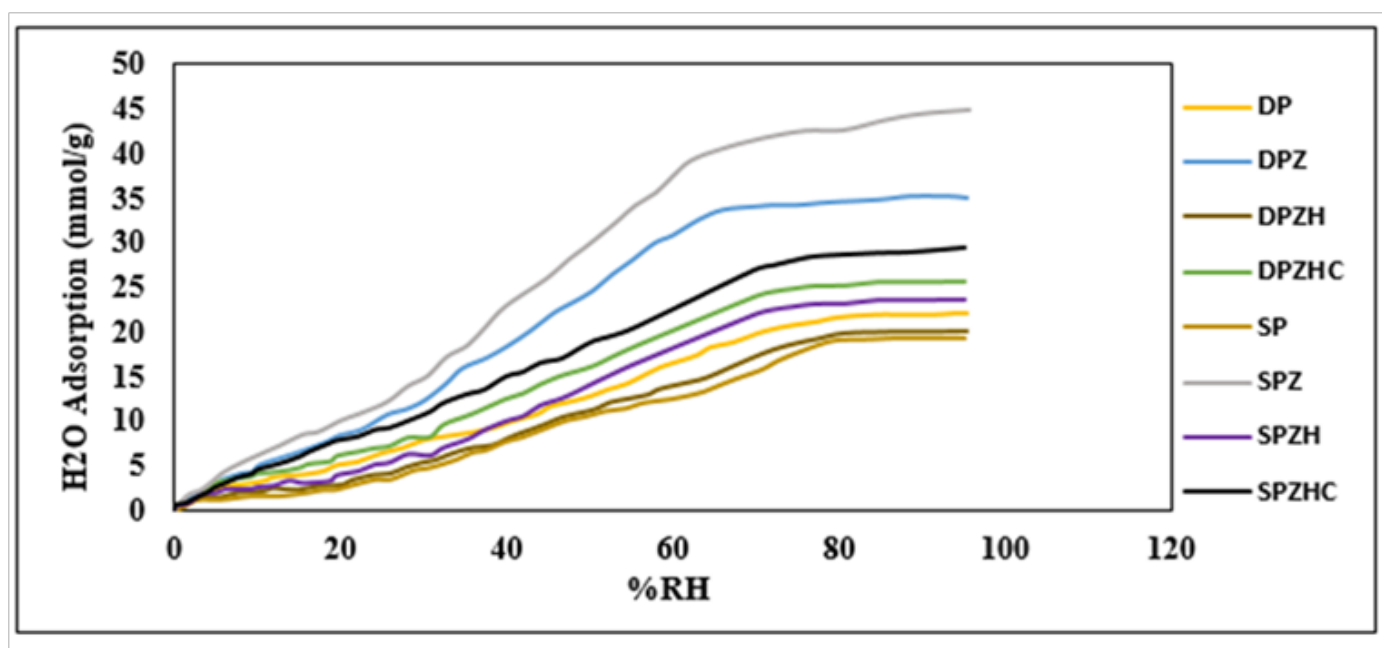


Fig 5. Water vapor adsorption isotherms of the samples using DVS in 100% N₂ at 25 °C (desorption omitted for clarity).

At higher relative humidity (RH >60%), both DPZ and SPZ exhibited higher water adsorption capacities owing to their advanced microporous structures. There was a clear difference in adsorption capacity between the two isotherms, with SPZ sample showing higher performance. This can be attributed to the nitrogen- and oxygen-containing functional groups in *Spirulina platensis*, which increase surface polarity and promote stronger interactions with water molecules. These observations are consistent with a previous study reporting that heteroatom co-doping (N, S, and O) enhances surface polarity, increases the density of active sites, and promotes hydrogen-bonding interactions with water molecules (Zhang et al., 2019). At high relative humidity (95% RH), the H₂O uptakes for DPZ and SPZ were 42.61 and 33.38 mmol/g, respectively, indicating that *Spirulina platensis* is more affected by ZnCl₂ activation than date pits, and that water uptake depends more on the surface chemistry than on its porosity. These results are consistent with those previously reported by Bai et al. (2020). As expected, water vapor adsorption declined markedly due to effectiveness of the coating on the DPZH and SPZH surfaces. In contrast, the calcination process increased the amount of water vapor adsorbed on the DPZHC and SPZHC samples.

The kinetic H₂O sorption profiles of the samples at 10%, 50%, and 95% RH were obtained using DVS. At less than 10% RH, both carbonized samples (DP and SP) showed low adsorption capacities (<1.5 mmol/g) and required less than 60 minutes to reach equilibrium (Figs. 5(a) and 6(a)). This is likely due to their low surface area (613 and 198 m²/g) and limited micropore volumes (0.31 and 0.26 cm³/g). The DPZ sample reached equilibrium after 60 minutes. In contrast, the SPZ sample showed a higher affinity for water molecules and required approximately 120 minutes to reach equilibrium despite having a lower total pore volume and surface area. On the other hand, the water absorption of the coated samples (DPZH and SPZH) ranged from 1.4 to 2 mmol/g. This may be due to the closure of some pores during the coating process.

A decrease in the BET surface area and pore volume of the coated samples was shown in Table 1. The samples submitted to heat treatment after coating with VTMOs showed higher values.

At moderate humidity (50% RH) and high relative humidity (95% RH), DPZ surpassed SPZ in water uptake (Figs. 6(b, c) and 7(b, c)) because of its larger surface area (1,214 m²/g) and higher micropore volume (0.33 cm³/g), which provide more accessible microporous sites and more substantial capillary condensation effects within these pores. Except for DPZH, which showed high water adsorption, the other samples maintained the expected relative values during adsorption and desorption. The heat-treated samples recorded intermediate values between those of the activated and carbonized samples across all relative humidities.

These differences in the time required to reach equilibrium for activated carbons derived from date pits and *Spirulina* can be principally attributed to their different textural properties, particularly the abundance of narrow micropores. In general, the presence of small pores can retard diffusion and lead to much longer equilibration times, although the adsorption rate is fast at low relative humidity. It is important to note that the absence of a large difference in the time required to reach equilibrium at 60%, 80%, and 95% RH for each sample (Figs. 6 and 7) is consistent with literature reports (Martins et al., 2015; Jia et al., 2017). Previous studies have shown that, with increasing relative humidity, an increase in the adsorption capacity of an adsorbent may not always lead to an increase in the adsorption rate, as diffusion limitations may occur within micropores. Therefore, the adsorption capacity increases as the pores are filled at elevated RH.

Table 3. demonstrates the differences in H₂O adsorption of the samples at 10%, 50%, and 95% RH for 10 minutes (typical residence time in fluidized bed sorbents). All values were obtained from the two figures above.

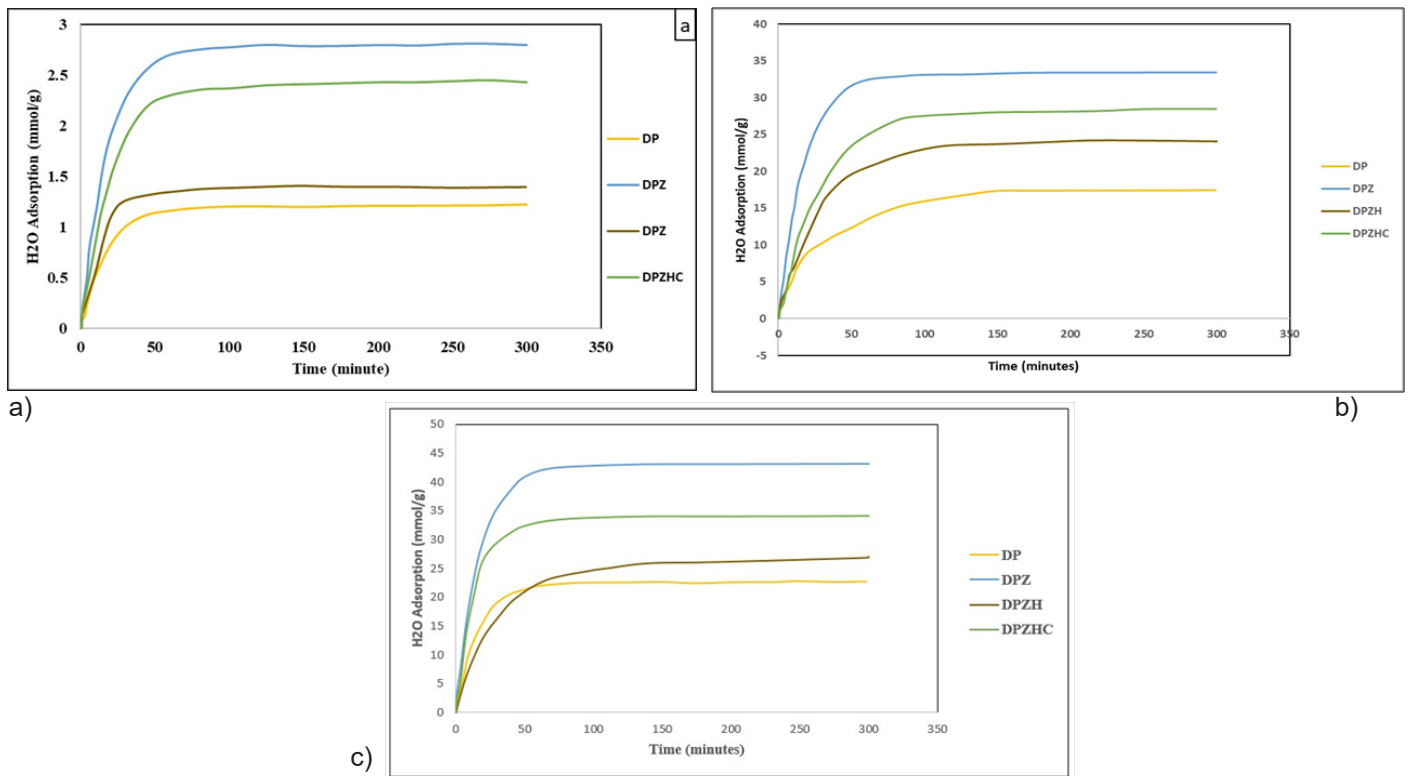


Fig 6. H₂O uptake DP, DPZ, DPZH, and DPZHC samples using DVS in 100% N₂, (a) 10% RH, (b) 50% RH, and (c) 95% RH at 25 °C.

CO₂/H₂O uptake ratio

The adsorption performance ratio of the CO₂ to H₂O is calculated as follows:

$$S (\text{CO}_2/\text{H}_2\text{O}) = \text{Adsorption CO}_2 (\text{mmol/g}) / \text{Adsorption H}_2\text{O} (\text{mmol/g})$$

In this work, the uptake ratio of the samples was evaluated after 10 minutes under typical post-combustion flue gas conditions. At 10% RH, the $S_{\text{CO}_2/\text{H}_2\text{O}}$ ratios of DPZ and SPZ were 1.9 and 2.09, respectively, compared with 1.84 and 0.57 for DP and SP, as shown in Table 4. The CO₂/H₂O uptake

ratios of the coated samples were lower than those recorded for the modified samples. The differences in CO₂ adsorption between DPZ and DPZHC were 13%, whereas those between SPZ and SPZHC were 5%. The differences in H₂O adsorption were higher than these values: 15% between DPZ and DPZHC and 37% between SPZ and SPZHC, as shown in Table 4.

The highest CO₂/H₂O values were observed for the heat-treated samples (DPZHC: 3.01; SPZHC: 2.46), indicating that the thickness of the coating layer played a significant role in determining CO₂ and H₂O adsorption.

Table 3: H₂O uptake of the samples at different RHs after 10 minutes

Sample	H ₂ O adsorption (mmol/g)		
	10% RH	50% RH	95% RH
DP	0.50	5.4	10.2
DPZ	1.12	14.6	20.3
DPZH	0.61	7.5	10.1
DPZHC	0.83	11.9	16.3
SP	0.28	4.2	10.2
SPZ	0.62	9.0	26.6
SPZH	0.34	5.1	7.2
SPZHC	0.49	6.5	18.1

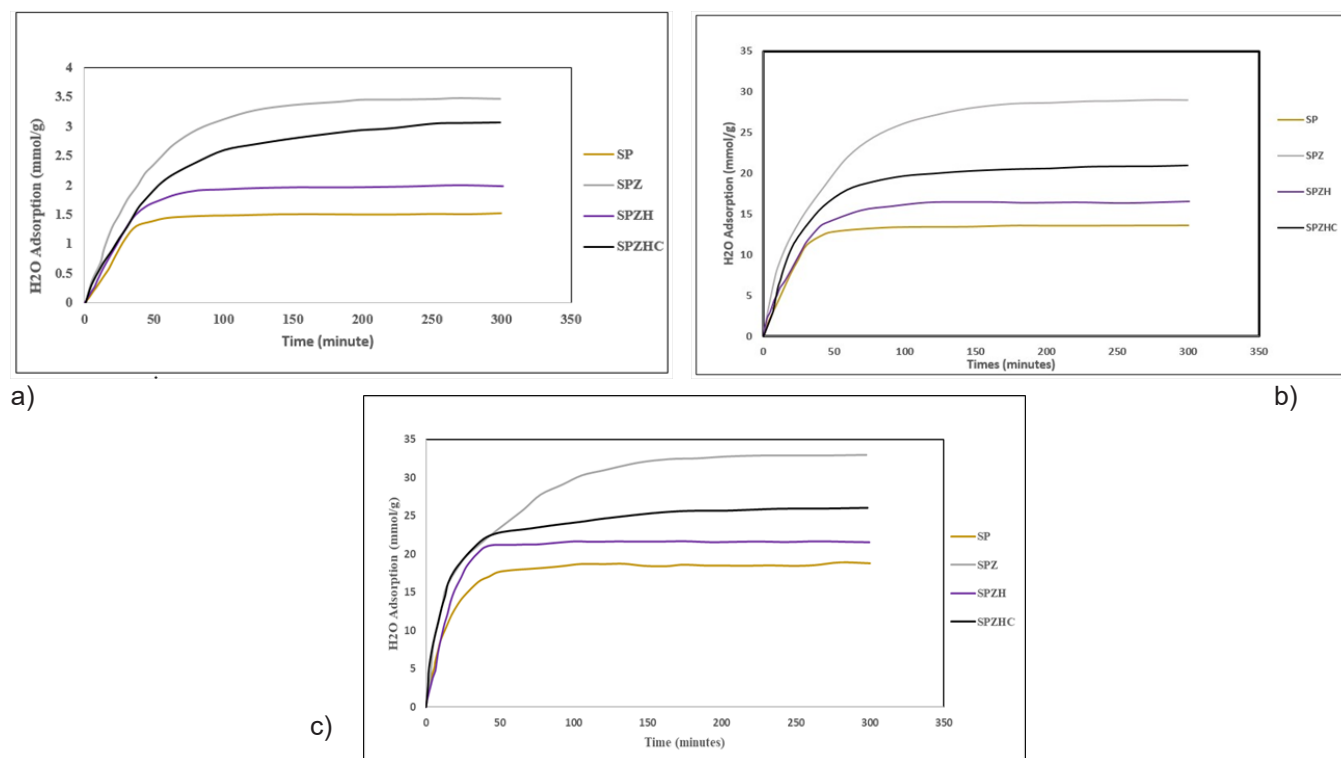


Fig 7. H₂O uptake SP, SPZ, SPZH, and SPZHC samples using DVS in 100% N₂, (a) 10% RH, (b) 50% RH, and (c) 95% RH at 25 °C.

The differences in CO₂/H₂O uptake were not significant among all samples at 50% and 95% RH (Table 4). Based on the previous results, the highest CO₂/H₂O ratio was observed for DPZHC, suggesting that it is a promising adsorbent for co-adsorption processes.

CO₂ adsorption capacities were collected from the literature and measured under different experimental conditions. H₂O adsorption is expressed qualitatively (e.g., low, moderate,

high) because it strongly depends on relative humidity and temperature, making direct numerical comparison difficult. Additionally, most literature values are based on equilibrium measurements, whereas the present study reports kinetic adsorption ($t = 10$ min); therefore, direct comparison should be made with caution.

Table 4: CO₂ and H₂O adsorption capacities at 10% RH, 50% RH, and 95% RH, and the CO₂/H₂O ratio of the samples after 10 minutes.

Samples	CO ₂ adsorption (mmol/g)	At 10% RH		At 50% RH		At 95% RH	
		H ₂ O uptake (mmol/g)	S _{CO₂/H₂O}	H ₂ O uptake (mmol/g)	S _{CO₂/H₂O}	H ₂ O uptake (mmol/g)	S _{CO₂/H₂O}
DP	1.03	0.56	1.84	6.72	0.15	10.61	0.1
DPZ	2.31	1.21	1.9	14.31	0.16	19.89	0.12
DPZH	1.57	0.52	1.23	6.95	0.23	8.49	0.18
DPZHC	2.01	0.93	3.01	11.23	0.18	16.31	0.12
SP	0.19	0.33	0.57	4.51	0.04	8.21	0.02
SPZ	1.32	0.63	2.09	8.33	0.16	13.92	0.09
SPZH	0.42	0.40	1.67	4.92	0.09	6.82	0.06
SPZHC	1.26	0.52	2.46	6.57	0.19	10.42	0.12

Table 5: Comparison of the CO₂ and H₂O adsorption performance of this study with that of previously reported adsorbents. CO₂ uptake is reported in mmol/g, while H₂O adsorption is presented qualitatively due to its dependence on relative humidity (RH).

Adsorbent	CO ₂ uptake (mmol/g)	H ₂ O uptake	Selectivity/ uptake ratio (basis -dependent)	Basis of measurement
Activated carbon	1-3 (reported range)	moderate	moderate	equilibrium isotherm (batch)
Zeolite 13X	3-5 (equilibrium)	Very high	high	equilibrium adsorption
KOH-activated carbon	2-5	moderate	moderate-high	equilibrium adsorption
activated alumina	0.2-1	Very high	low	equilibrium adsorption
amine-functionalized carbon	2-4	low-moderate	high	equilibrium adsorption
Biomass-based carbon	0.5-2.5	moderate-high	low-moderate	equilibrium adsorption
DPZHC	2.01	0.93 mmol/g, at 10%RH	3.1 (Moderate to moderately high)	kinetic of adsorption (non equilibrium, t = 10 min)

Conclusions

One of the main challenges that CO₂ capture technology faces today is the efficiency of adsorbents, such as activated carbons, for CO₂ adsorption in the presence of water vapor. Water molecules strongly compete with CO₂ for the adsorbent's active sites because of their higher polarity and smaller size. Therefore, the CO₂/H₂O uptake ratio is an important parameter for evaluating the relative adsorption affinities of the prepared adsorbents toward CO₂ and water vapor under independent adsorption conditions, and for identifying promising materials for applications in humid environments.

The results of this study establish that both VTMOs-activated carbon produced from date pits and *Spirulina platensis*, synthesized through thermal treatment at 450 °C and designated as DPZHC and SPZHC, respectively, exhibit high CO₂/H₂O selectivity. The DPZHC sample exhibited higher CO₂ adsorption performance and hydrophobic properties, with CO₂/H₂O selectivity exceeding 3 at 10% RH. It is important to note that, as relative humidity increases to 50% and 95%, the CO₂/H₂O values become very low and approach zero, indicating that water vapor adsorption increases significantly with increasing relative humidity across all samples, and that the coating layers are not sufficiently thick. This study indicates that activated carbons, with their distinct structural characteristics, including high specific surface area, micro- and mesoporosity, and a thin VTMOs coating, can be used as hydrophobic adsorbents in CO₂ capture technology.

The CO₂/H₂O uptake ratio at higher relative humidities (50% and 95%) did not vary significantly across all samples, indicating that the adsorption sites on the adsorbents are mainly occupied by water molecules. Multilayer adsorption of water dominates the surface, blocking most of the active sites that would otherwise adsorb CO₂. Under the studied conditions, the relative CO₂/H₂O uptake is highly sensitive to surface modification and differences in porosity. This study also demonstrates that date pits and *Spirulina platensis* byproducts can serve as cost-effective sorbents for CO₂ removal from flue gas. Further investigations are needed to develop applications

for these adsorbents and to address operational challenges at the pilot scale.

Acknowledgement

The authors would like to thank the Department of Chemical Engineering at the University of Basra, Iraq, for their technical support throughout this work.

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