Biomass derived carbon materials: Synthesis and application towards CO₂ and H₂S adsorption

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Abstract
Porous carbon materials derived from palm date seeds, guava seeds and winged beans are proposed as environmentally friendly and efficient adsorbents for CO₂ and H₂S adsorption. The feedstock is converted into hydrochar via hydrothermal carbonization (HTC), at 200°C, for several hours, and the textural properties are tuned using the chemical activation approach with KOH. The activated carbons (ACs) prepared in here are characterized by high surface areas, more than 2000 m² g⁻¹, and large pore volumes (1.23 cm³ g⁻¹). It is observed that a lower concentration of KOH results in a larger number of micropores, leading to improved gas uptake properties. The carbons obtained in here present sponge-like structure with particle sizes in the range of 5–100 µm. Their morphology is characterized by irregular particle shape with large conchoidal cavities and smooth surfaces. The samples display significant gas adsorption capacity, with 5.47 mmol g⁻¹ CO₂ uptake at 0°C, 1 bar and 4.36 mmol g⁻¹ at room temperature and atmospheric pressure. H₂S adsorption is achieved with more than 50% adsorption efficiency in 1 hour exposure time. Through this study we aim to add up to the eco-friendly and cost-effective materials, derived from biomass, suitable and efficient in CO₂ and H₂S adsorption.

KEYWORDS
biomass, chemical activation, gas capture, hydrothermal carbonization

1 | INTRODUCTION

Ever-increasing industrial activities and consumption have significant impact on the natural ecosystem. Excessive emissions of greenhouse and pollutant gases led to an intensification of the climate change around the world.¹ Since the pre-industrial revolution, the atmospheric concentration of CO₂ has increased with about 1.2°C, revealing the negative impact of the technology development on the ecosystem.² Many action plans, including Agenda 21 (1992), Kyoto Protocol (1997), Bali Road Map (2007), Copenhagen Accord (2009), Paris Agreement (2015), European Green Deal and UK, Japan, Korea and US 2050 Net Zero (2019) and China 2060 Net Zero (2020) target the diminution of the greenhouse effect and recently five scenarios for CO₂ emissions evolution...
have been reported by Climate Action Tracker. In short, the worst-case scenario predicts a warming of 4.8°C of the planet, by 2100, if no policies are considered. In parallel, in an ideal case, the average temperature will increase with only 1.5°C if a rapid reduction in the greenhouse gas effect will happen. Currently, based on the present policies, by 2100, the planet will be warmer with about 3.2°C, but if all countries will keep the targets established in the Paris agreement it is expected that the temperatures will increase with less than 2.8°C. The fifth scenario is called 2°C consistent and states for limiting the global warming by 2100 with only 2°C, but this requires an increase in the ambitions of the current policies.[3] Furthermore, to address toxic air pollution, sulphur-containing species should also be removed from the atmosphere.[4] H₂S has an offensive smell of rotten egg and a minimum threshold detection value of about 0.02 ppm.[5] The most common source of it is from the petroleum industry where can be a fatal poison. H₂S is present in caissons, tunnels, and mines, as a rock-gas constituent or dissolved in strata-water. For example, during the construction of the London tunnel under the river Thames, the gas was encountered, constituting an obstacle, causing delays in building process and adding up to the manufacturing cost. Decomposition of organic matter, including sewage, animal refuse, or algae (sargassum), after their massive beaching in the Caribbean, central America coasts or west coast of Africa represent other sources of H₂S.[6–9] Over the years, techniques like catalytic oxidation, membrane separation, biological methods and adsorption have been used towards CO₂ and H₂S capture.[10–13] Among all technologies, adsorption with activated carbons (ACs) is proposed as the most efficient and cost-effective way to diminish both CO₂ and H₂S atmospheric concentration. Although for CO₂ removal, the most common process consists of absorption with alkalinamine solvents, this methodology presents disadvantages of high energy consumption, the need of solvent regeneration, the equipment corrosion, and toxicity.[14] Regarding other solid adsorbents, different materials have been proposed over the years, including metal-organic frameworks (MOFs), polymeric membranes, covalent-organic frameworks (COFs), chemically modified porous materials, and carbonaceous materials.[15] Catalytic oxidation or claus process[16] is frequently used for H₂S removal, as it is a selective process. However, its high cost, complex reactor design and catalyst poisoning make this method less desirable.[17] In parallel, ACs are widely used in many fields, such as energy storage,[18] catalysis,[19] waste water treatment[20] and gas adsorption and separation,[21] due to their advantageous chemical and physical properties. Particularly, their high surface area and the flexibility in tuning the porosity during synthesis compounded with cost efficiency, make them the ideal choice for gas separation. Many research groups addressed this problem using ACs in the adsorption process. Porous carbon adsorbents for CO₂, derived from lotus leaf, have been reported.[22] Melamine was used as during the synthesis, with the purpose of doping nitrogen heteroatoms. The materials retained 5.89 mmol g⁻¹ at 0°C and 1 bar, and 3.87 mmol g⁻¹ at 25°C and 1 bar. Li et al.[10] proposed the synthesis of CO₂ adsorbents starting from biomass (date) and KOH activation. They obtained about 6.4 mmol g⁻¹ CO₂ uptake in standard conditions (STP, 0°C and 1 bar) and approximately 4.4 mmol g⁻¹ in normal conditions (RTP, 25°C and 1 bar), attributing the good results to the presence of narrow micropores (< 1 nm). Similar results have been reported by Rao et al.,[23] who conducted the CO₂ adsorption experiments on glucose/urea derived carbon treated with KOH. With a maximum CO₂ uptake of 4.26 and 6.7 mmol g⁻¹ at 25 and 0°C, respectively, the authors claimed that the adsorption process is governed by the volume of narrow micropores and the N content, concluding that the synergy between the two make these materials superior to other adsorbents. Hervy et al.[24] studied the H₂S removal from syngas using chars produced by the pyrolysis of waste materials, including: used wood pellets, food waste and coagulation-flocculation sludge. H₂S adsorption has been studied by Bagreev et al.[25–27] and Bandoz et al.[4,28] who focused their study on improving the H₂S uptake of waste derived adsorbents. As evidenced above, many studies relied on biomass feedstock as carbon precursor in their research and experimental work. The term biomass refers to basically any biological matter, including food waste,[29–31] household wastes,[32–34] agricultural waste,[35,36] also cereals.[12,37–39] The feedstock is usually selected considering various criteria: (i) the abundance of the feedstock in the desired region; the more abundant in the same region, the more robust and reproducible the process; (ii) the composition according to the target experiments; (iii) operational flexibility; in here parameters like solubility, transformation time are considered mostly, and finally (iv) costs of the precursor cumulated with operational costs. Considering the increased abundance of biomass and advantages such as high carbon content, the presence of other heteroatoms, including nitrogen,[31] sulphur,[30] phosphorus[32] and so on, operational versatility and cost effectiveness, results in an increasing amount of scientific research devoted to its applications. There are several strategies to turn biomass into carbonaceous materials. For example, direct pyrolysis of biomass in inert atmosphere[40,41] followed by activation. The activation step can be physical activation, using a reactive gas flow and high temperature,[32] whose role is to create porosity and enhance the surface area of the resultant carbon
materials. Besides this method, chemical activation can be used as well. For the latter, the biomass is mixed with compounds like KOH, ZnCl₂, H₃PO₄ followed by pyrolysis in inert atmosphere. Once the heat treatment is finished the activator substance is removed, leaving behind a highly porous structure, desirable in a wide range of applications. Another synthetic approach consists of hydrothermal carbonization (HTC) of biomass. The HTC step increases the carbon content and also enhances the surface functional groups, like oxygenated or nitrogen-containing functionalities, which render more efficient materials towards targeted applications. In this work we investigate the CO₂ and H₂S adsorption efficiency (AE) using ACs synthesized via HTC coupled with chemical activation. We believe that the combination of the two will render carbon materials with well-developed porous structure and large number of micropores, the key features for the application in gas adsorption. In this way, we aim to tackle the greenhouse gas emissions and add up to the cheap and eco-friendly biomass-derived materials, efficient for the removal of sulphur containing pollutants. The samples have been synthesized starting from renewable precursors, including palm date seeds (PDS), winged beans (WB) and guava seeds (GS), and have been chemically activated with KOH. Date palm seeds consist of 10.2% moisture, 1.2% ash, 16% protein and 72.6% carbohydrates; GS have 6.7% moisture, 1.2% ash, 11.2% protein, 23.7% carbohydrates and 57.2% dietary fiber and WB are made of 8.5% moisture, 3.9% ash, 27.8% protein, 41.9% carbohydrates and 17.9% fat. Considering the content of carbohydrates and proteins for all three biomass sources, we considered them good precursors for the synthesis of hydrochars as we anticipated they would yield high C and N content. In this way, three sets of materials have been synthesized, varying the salt concentration. In order to establish the exact chemical composition before and after HTC, elemental analysis (EA) has been performed on both raw biomass and the so obtained hydrochars. In addition, the samples have been further investigated via FTIR spectroscopy. \( N_2 \) sorption isotherms have been measured in order to determine the porosity of the ACs, and the efficient removal of the activator has been confirmed by TGA analysis. Surface morphology has been investigated by SEM and TEM microscopy, and XRD and XPS measurements have been used to further analyze the ACs. The adsorption capacity towards CO₂ and H₂S has been determined for all the samples synthesized in here.

2 | RESULTS AND DISCUSSION

2.1 | Materials characterization

HTC of biomass has been extensively reported in the literature for the production of carbonaceous materials, starting from different feedstock and using various additives to obtain the desired properties. For convenience, the corresponding porous carbon materials have been named with the abbreviation of the carbon precursor and the activator, followed by a number indicating the mass ratio between the hydrochar and the activator: that is, the sample derived from GS and activated with KOH in mass ratio 1:2 hydrochar to alkaline compound has been denoted GS_KOH_2. EA measurements on the raw biomass and on the hydrochars confirmed the high C content present in the biomass, which was increased after HTC (Table S1). Also, N was detected in the raw biomass, and in the hydrochars, in higher concentration.

The biomass sources and obtained hydrochars were further analyzed by FTIR spectroscopy (Figure S1A and S1B). The feedstock shows similar functional groups, according to their composition described above. The hydrochars’ FTIR spectra present the typical structure of the hydrothermal carbon.

Surface area and pore volume for ACs have been determined using BET and DFT calculations. The powders synthesized display high surface areas, between 836 and 2,335 m²g⁻¹, and large pore volumes, up to 1.54 cm³ g⁻¹. The resultant isotherms, displayed in Figure 1A, are a combination between type II and IV isotherms, according to IUPAC classification. Accordingly, PDS_KOH_1, PDS_KOH_2 and GS_KOH_1 present type IV isotherms with type H2 hysteresis loop. The shape of the isotherm is characteristic to mesoporous materials, in which the adsorption phenomenon is determined by the adsorbent – adsorptive interactions and by the interactions between the molecules in the condensed state. The hysteresis reveals the complex structure of the materials and can be attributed either to percolation in a narrow range of pore necks or to cavitation-induced evaporation. WB_KOH_1, WB_KOH_2 and GS_KOH_2 are described by type II isotherm and H4 type hysteresis loop. This type of isotherm suggests the formation of macroporous materials, and the shape is the result of unrestricted monolayer-multilayer adsorption up to high \( p/p^0 \).

The KOH activation may take place following one of the three proposed mechanisms, according to Wang and Kaskel: (i) the carbon structure is etched via the redox reactions occurring between the activator and the carbon; (ii) in the second mechanism \( H_2O \) and \( CO_2 \) are formed and positively contribute to the further development of porosity through the gasification of the carbon structure, this is analogous in nature to physical activation, (iii) during the whole redox reaction elemental K is generated, which is efficiently intercalated into the carbon matrix, resulting in an expansion of the carbon lattice. Overall, the development of large surface area and high porosity in KOH activation processes is due to a synergistic effect between chemical and physical activation enhanced by the intercalation of elemental K. The efficient removal of residual
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**FIGURE 1** A, N$_2$ adsorption-desorption isotherms for the ACs derived from PDS, GS and WB; (B) pore size distribution for the ACs synthesized by chemical activation; (C) micropore size distribution from CO$_2$ adsorption

KOH after activation-carbonization has been confirmed via TGA measurements. The TGA curves show 100% mass loss (Figure S2) corresponding to carbon decomposition, when measured in air, a clear indication that there is no inorganic matter, including residues of KOH or ash.

The microstructure and morphology of the KOH-treated ACs samples were analyzed by SEM microscopy (Figure 2). It can be observed that, independent of the biomass source, all six ACs are characterized by sponge-like structures, similar to what has been observed for other samples reported, with particle sizes between 5–100 µm and a morphology characterized by irregular particle shapes with large conchoidal cavities and smooth surfaces. It is also worth mentioning that the morphology does not seem to be highly affected by the variation in the KOH concentration.

This is corroborated by the XRD patterns (Figure S1C), which show profiles characteristic to carbon materials with an amorphous structure. TEM images for the samples prepared with 1:1 mass ratio hydrochar: KOH, are displayed in Figure 3 and show the multi-dimensional wormhole-like pore structure. The surface chemical composition and state of ACs has been evaluated via XPS analysis. Except PDS_KOH_1 and PDS_KOH_2, whose spectra show traces of nitrogen on the carbon surface, the rest seem to only have carbon and oxygen functionalities.

The analysis of C1s high-resolution spectra of GS_KOH_1 is shown in Figure 4A, and it can be divided into six peaks centered at 284.45 eV (C=C), 284.80 eV (C-C), 285.21 eV (C=O), 285.90 eV (C=O) 286.80 eV-COO and 288.03 eV (π-π* satellite), respectively. The same peaks have been identified in the C1s spectra for PDS_KOH_1 (Figure 4D), in addition to a peak assigned to C-N, centered at 285.37 eV. O1s spectra (Figure 4B and 4C) can be resolved into two peaks, positioned at 532.53 and 533.80 eV for GS_KOH_1 and 532.47 and 533.39 eV in case of PDS_KOH_1, can be assigned to the C=O and C-O bonds.[43] Additionally, the samples synthesized from palm-date seeds retain some nitrogen from the biomass, and the high-resolution N1s region for PDS_KOH_1 is displayed in Figure 4F, being composed of three peaks characteristic to pyridinic N (399.32 eV), pyrrolic N (400.05 eV) and quaternary N (400.94 eV). As a general trend, it has been observed that C1s and O1s spectra characteristic to ACs derived from GS_KOH_x and WB_KOH_x are resolved into the same peaks fitted at the same binding energies, as described above. The discrepancies between the binding energies, when it comes to PDS_KOH_x couple, can be assigned to the presence of nitrogen (Figure 4C). The variation of carbon functionalities as a function of the precursors and KOH
concentration is displayed in Figure 5. Along the AC samples it has been observed that the amounts of sp2 and sp3 C are approximately the same in all samples, and an increase in the KOH content results in an increase in the amount of surface-oxygenated groups. Similar behavior has been observed by Liu et al.\textsuperscript{[59]} during the synthesis of microporous nitrogen carbon derived wood fibers.

### 2.2 CO2 adsorption experiments

Owing their good textural properties, high number of micropores and the presence of nitrogen atoms, the biomass derived carbon materials have been tested for CO2 adsorption. The adsorptive properties have been determined both in standard conditions of temperature and pressure (STP) and at room temperature (RTP), the experimental outcomes being illustrated in Figure 6. The samples displayed good CO2 affinity, with adsorption capacities in between 3 and 5.5 mmol g\textsuperscript{-1} at 0\textdegree C and 1 bar. It has been observed that larger CO2 uptakes have been favored by a lower concentration of KOH, the maximum value determined in this study in STP, being 5.47 mmol g\textsuperscript{-1}, for PDS\_KOH\_1. The second-best value, 5.05 mmol g\textsuperscript{-1}, was obtained for GS\_KOH\_1. The results obtained at 25\textdegree C and 1 bar are in between 2.13 and 4.36 mmol g\textsuperscript{-1}, following the trend of an exothermic reaction (Figure 6C). The salt concentration has the same influence on the CO2 data acquired at room temperature. This behavior can be explained by the fact that a higher concentration of salts, used during chemical activation, is enhancing the pore expansion, and as a result the powders possess more mesopores. The change of the proportion of micropores and mesopores and its correlation with the gas uptake are displayed in Figure 6D. GS\_KOH\_1 shows a microporous structure, which would
FIGURE 4  A, D, C1s high resolution spectra for a. GS_KOH_1 and (D) PDS_KOH_1. B, E, O1s high resolution spectra for (B) GS_KOH_1 and (E) PDS_KOH_1; (C) XPS survey for the same samples and (F) N1s high resolution spectra for PDS_KOH_1

FIGURE 5  Percentage of carbon functional groups present in all samples ACs synthesized in this study

suggest that will have highest CO₂ uptake among the samples. However, the best adsorption capacity is registered for PDS_KOH_1, reaching as much as 5.47 mmol g⁻¹ with only 74% microporosity.

The good performance of this sample most likely comes from a synergetic effect between the textural properties and the presence of traces of nitrogen atoms. According to XPS data, PDS_KOH_1 retains about 1.15% nitrogen atoms from the parent biomass, meanwhile the GS_KOH_1, GS_KOH_2 or WB_KOH_1 and WB_KOH_2 have no nitrogen. Similar behavior has been reported by Rao et al.,[23] who ascribed the good gas – adsorption capacity to the synergy between porosity and nitrogen heteroatoms. In this way, the gas uptake variation for the undoped samples is directly proportional with the number of micropores (Figure 6D) and, consequently decreases with increasing the specific surface area and increasing the amount of activator. When no nitrogen is present on the carbon structure, the maximum CO₂ uptake, in standard conditions, reaches as much as 5.05 mmol g⁻¹, with 3.02 mmol g⁻¹ at room temperature. With the nitrogen incorporation, as in PDS_KOH_1 and 2, the CO₂ uptake is improved, retaining about 5.47 mmol g⁻¹, in standard conditions, and 4.36 mmol g⁻¹ at room temperature (Figure 6A and 6B). Even when the activator is in excess, PDS_KOH_2 adsorbs 4.16 mmol g⁻¹ at 0°C (Figure 6A), which is the highest value among these samples. Traces of nitrogen, especially the pyrrolic functionalities, have a positive impact towards CO₂ uptake due to their two lone pair electrons, which improve the electrical conductivity and creates defects providing enough space for gas diffusion.[60] The nitrogen incorporation does not change the trend among the samples, meaning that even if nitrogen facilitates the gas uptake the best performance is still obtained for the samples activated with less KOH, resulting in lower surface area and enhanced microporosity. The decrease in the CO₂ adsorption capacity moving from 0°C to 25°C can be easily explained, as the adsorption is accompanied by an exothermic effect, and in this case according to Le-Chatelier’s principle,
the magnitude of adsorption decreases by increasing temperature. The values obtained in this study for CO₂ adsorption experiments in STP and RTP are gathered in Table 2.

In order to compare and validate the results obtained for the CO₂ uptake on the samples synthesized in this study, three commercial activated carbon materials (NORIT PKI-3, NORIT SXRO-PLUS and NORIT GAC-830), having the specific surface area more than 1000 m² g⁻¹ have been tested using the exact same procedure as the homemade ACs. The highest gas uptake for the commercial samples was 3.73 mmol g⁻¹ in standard conditions of temperature and pressure. The values obtained at room temperature were even lower, following the trend of an exothermic process (Table 2). In order to determine the interactional strengths between CO₂ molecules and the surface of the
TABLE 2 CO$_2$ uptake and isosteric heats of adsorption for ACs synthesized in this study

| Sample       | CO$_2$ uptake [mmol g$^{-1}$] | STP | RTP | $Q$ [kJ mol$^{-1}$] |
|--------------|-------------------------------|-----|-----|---------------------|
| GS_HY        | 0.34                          | NA  | NA  |                     |
| WB_HY        | 0.15                          | NA  | NA  |                     |
| PDS_HY       | 0.26                          | NA  | NA  |                     |
| GS_KOH_1     | 5.05                          | 3.02| 26.23|
| GS_KOH_2     | 4.60                          | 2.67| 17.90|
| WB_KOH_1     | 3.06                          | 2.62| 18.62|
| WB_KOH_2     | 5.47                          | 4.36| 20.85|
| PDS_KOH_1    | 4.16                          | 3.17| 14.02|
| PDS_KOH_2    | 3.73                          | 1.90| 26.04|
| NORIT PK1-3  | 3.20                          | 1.84| 29.35|
| NORIT SXRO-PL | 3.73                       | 1.90| 26.04|
| NORIT GAC-830| 3.20                          | 2.20| 21.47|

Abbreviations: AC, activated carbons; PDS, palm date seeds; GS, Guava seeds; WB, winged beans.

ACs, isosteric heats of adsorption ($Q_{st}$) were calculated from the CO$_2$ adsorption isotherms at 0°C and 25°C, based on the Clausius-Clapeyron equation, they were determined by evaluating the slope of the plots of ln(P) versus 1/T at the same amount of gas adsorbed, where P and T are respectively the absolute temperature and pressure.$^{[61]}$

\[
\ln \frac{P_2}{P_1} = \frac{Q}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

(1)

The magnitude of isosteric heats of adsorption indicates that the adsorption takes places via physisorption, as the obtained values are in between 14.02 and 26.23 kJ mol$^{-1}$, at CO$_2$ loading lower than 0.85 mmol g$^{-1}$, significantly lower than the energy necessary to activate the C = O bonds (~749 kJ mol$^{-1})[^{[62]}$ The selectivity for CO$_2$ over N$_2$ for GS_KOH_1, WB_KOH_1 and PDS_KOH_1 has been studied by the ideal adsorbed solution theory (IAST). IAST is generally used to predict mixture adsorption equilibria using single-component adsorption isotherms.$^{[63]}$ The typical CO$_2$ and N$_2$ adsorption isotherms at 25°C for the aforementioned samples are shown in Figure 7. The values calculated from IAST, with bulk phase equilibrium partial pressure of 0.85 bar for N$_2$ and 0.15 bar for CO$_2$, are 30.02 (GS_KOH_1), 65.70 (WB_KOH_1) and 60.18 (PDS_KOH_1), respectively.

According to this set of data, the best performing sample of each couple shows high selectivity towards CO$_2$ and the selectivity among the series varies as follows: WB_KOH_1 > PDS_KOH_1 > GS_KOH_1. Table 3 compiles together some examples of biomass-derived carbon materials used for CO$_2$ adsorption, from literature.

### 2.3 H$_2$S adsorption experiments

Due to their large surface areas, high pore volumes, and based on the positive results obtained during CO$_2$ adsorption experiments, the ACs have been employed for H$_2$S adsorption. The experiments have been performed at room temperature, using a custom-made adsorption reactor made of Teflon, and the change in concentration has been monitored every 10 seconds, using a Drager sensing unit, as explained elsewhere.$^{[66]}$ Each sample has been measured three times for accuracy and to gauge reproducibility. Overall, all the samples showed good affinity towards H$_2$S, the adsorption capacity being in between 30 and 48 mmol g$^{-1}$, reaching about 50% AE. In addition, as a general trend it has been observed that the H$_2$S uptake is increasing with the number of micropores (Figure S3). In this way, the GS_KOH_x couple presents the highest gas retention within the series: 48 mmol g$^{-1}$ for GS_KOH_1 and 45 mmol g$^{-1}$ for GS_KOH_2. AE has an opposite behavior, with 43% AE for GS_KOH_2, and only 24% AE for GS_KOH_1. This variation can be explained with the difference in the number of micropores, as GS_KOH_1 possesses 18% more microporosity compared to GS_KOH_2, and this difference might cause a delay in reaching the saturation time of the first one. This is in good agreement with the breakthrough time values, listed in Table 4. It is obvious that it takes longer to saturate GS_KOH_1, about 76 minutes more than for GS_KOH_2, which implies a higher gas consumption and a lower AE, as the material is not able to adsorb all the gas that is passing through in the given time.

When evaluating the winged-beans samples, they present a similar behavior. With about 41 mmol g$^{-1}$ H$_2$S uptake, WB_KOH_1 has only a 23% efficiency. Furthermore, it took over 2 hours to saturate this sample, which implies that a high amount of gas remains unabsorbed in the atmosphere. But under the same conditions, WB_KOH_2 yields an almost 36 mmol g$^{-1}$ H$_2$S adsorption capacity, accompanied by more than 50% efficiency and less than 1 hour exposure time. It is therefore apparent that 9% difference in the microporosity content have a positive contribution on the WB_KOH_2 for the gas adsorption process. The H$_2$S uptake at 1 hour exposure time is depicted in Figure 8B, showing that GS_KOH_2 is the best performing specimen. When relating this to the adsorption capacity and AE (Figure 8A), it is evident that GS_KOH_2 presents a good balance between the two adsorption parameters, which makes this samples a desirable candidate for further applications. The PDS_KOH_x pair shows the smallest adsorption capacity among all six ACs and it also displays a slightly different adsorption behavior.

PDS_KOH_1 presents 35 mmol g$^{-1}$ H$_2$S uptake coupled with 34% AE and PDS_KOH_2 is only 24% efficient adsorbing 31 mmol g$^{-1}$ H$_2$S. Even though PDS_KOH_1 has a larger
concentration of micropores, compared to PDS_KOH_2, which could increase the saturation time and decrease the efficiency, the breakthrough time is only 85 minutes, 25 minutes less than that observed for PDS_KOH_2. This behavior is opposite to what was observed for the previous four samples prepared in the same series, and it may be due to traces of N\textsubscript{2} present in PDS_KOH\_x, which are completely undetectable in GS_KOH\_x and WB_KOH\_x. The parent hydrochars showed very poor adsorptive properties, reaching just over 1 mmol g\textsuperscript{-1} (Table 4). For a better understanding and validation of the H\textsubscript{2}S uptake data obtained on the samples synthesized in this study, three commercial activated carbon materials (NORIT PKI-3, NORIT SXRO-PLUS and NORIT GAC-830), all having specific surface areas over 1000 m\textsuperscript{2} g\textsuperscript{-1}, and thus comparable with the samples included in this study, have been tested using

### TABLE 3

| Ref. | Sample name | Carbon precursor | Carbonization conditions | Activation method | CO\textsubscript{2} uptake mmol g\textsuperscript{-1} |
|------|-------------|------------------|--------------------------|-------------------|-----------------------------------------------|
| [22] | LCM-550-3   | Lotus leaves     | 550°C, N\textsubscript{2} atmosphere | KOH               | 5.89, 3.67                                    |
| [64] | C-K-500     | Pineapple waste | 500°C, N\textsubscript{2} atmosphere | K\textsubscript{2}C\textsubscript{2}O\textsubscript{4} | 2.71, 2.22                                    |
| C-K-600 | Pineapple waste | 600°C, N\textsubscript{2} atmosphere | KOH               | 3.82, 3.16                                    |
| C-K-700 | Potato starch | 700°C, N\textsubscript{2} atmosphere | KOH               | 5.32, 4.25                                    |
| [65] | AA-0        | Potato starch    | 800°C, N\textsubscript{2} atmosphere | KOH               | –, 2.80                                       |
| AC-0  | Cellulose   | 800°C, N\textsubscript{2} atmosphere | KOH               | –, 2.80                                       |
| AS-2 M | Sawdust     | 800°C, N\textsubscript{2} atmosphere | KOH and melamine  | –, 2.20                                       |
| [52] | CMC-3       | Coca cola waste | High T°C, inert atmosphere | KOH               | 6.27, 5.20                                    |
| CMC-2 | Coca cola waste | High T°C, inert atmosphere | ZnCl\textsubscript{2} | 4.84, 3.00                                    |
| This work | PDS_KOH\_1 | Palm date seeds | 900°C, N\textsubscript{2} atmosphere | KOH               | 5.47, 4.36                                    |
| GS_KOH\_1 | Guava seeds | 900°C, N\textsubscript{2} atmosphere | KOH               | 5.05, 3.02                                    |
**Table 4** H₂S adsorption data for the ACs series and derived hydrochars

| Sample          | Breakthrough time [minutes] | Adsorption capacity [mmol g⁻¹] | AE [%] |
|-----------------|----------------------------|--------------------------------|--------|
| GS_HY           | 3.40                       | 1.52                           | 39     |
| WB_HY           | 3.20                       | 1.60                           | 43     |
| PDS_HY          | 2.70                       | 1.38                           | 40     |
| GS_KOH_1        | 166.30                     | 48.18                          | 24     |
| GS_KOH_2        | 89.67                      | 45.39                          | 43     |
| WB_KOH_1        | 145.67                     | 41.26                          | 23     |
| WB_KOH_2        | 58.17                      | 35.55                          | 52     |
| PDS_KOH_1       | 85.17                      | 35.12                          | 34     |
| PDS_KOH_2       | 110.39                     | 30.72                          | 24     |
| NORIT PK1-3     | 59.3                       | 21.3                           | 30.3   |
| NORIT SXRO-PLUS | 58.7                       | 17.7                           | 24.9   |
| NORIT GAC-830   | 54.8                       | 18.8                           | 29.2   |

Abbreviations: AC, activated carbons; PDS, palm date seeds; GS, Guava seeds; WB, winged beans; AE, adsorption efficiency.

**Figure 8**

(A) H₂S uptake and AE for the ACs prepared in this study and the commercial samples; (B) H₂S uptake at room temperature and atmospheric pressure for ACs for 1 hour exposure time; (C) comparison of H₂S uptake for all samples; (D) variation of breakthrough time and the H₂S uptake.

The exact same procedure as for the ACs synthesized in this study. The results showed an ordinary behavior, with lower gas uptakes than in the case of the custom-made samples. The maximum adsorption capacities towards H₂S for all the samples tested in this study are displayed in Figure 8C. Although GS_KOH_1 displays the highest H₂S uptake, the best performance is attributed to WB_KOH_2, which shows a good balance between rate of gas uptake in less than 1 hour and process efficiency. GS_KOH_2 and PDS_KOH_1 are also potentially good candidates for further applications, as they seem to adsorb considerably high amounts of gas in short exposure times (Figure 8D).
3 | CONCLUSION

CO₂ emissions are on the rise, with high gas generation coming from fossil fuel combustion and electricity generation. In parallel, sulphur containing pollutants represent a worrying problem, as they are toxic and corrosive, even in small concentration. Through this study we tried to add up to the present carbon-based materials used in gas sorption applications. In this way, ACs derived from biomass sources, such as PDS, guava seeds and WB have been successfully synthesized via HTC and chemical activation. EA confirmed the presence of C, N and O both in the precursors and the hydrochar and FTIR spectroscopy revealed the typical spectra of hydrothermal carbon. By varying the amount of KOH, samples with different porosity, surface area and morphology have been obtained. The N₂ adsorption-desorption isotherms showed the formation of micro-mesoporous materials, with surface areas in between 1682 and 2335 m² g⁻¹, and large total pore volume. XRD patterns showed the formation of amorphous carbon for the ACs prepared with KOH, and XPS analysis revealed that trace amounts of nitrogen heteroatoms were present in the samples derived from PDS. SEM and TEM microscopy revealed a sponge-like structure, with particle sizes between 5 and 100 µm, and presenting a morphology characterized by irregular particles shape with large conchoidal cavities and smooth surfaces. When used in gas adsorption tests, the powders showed good CO₂ affinity, with a maximum of 5.47 mmol g⁻¹ CO₂ uptake in STP and 4.36 mmol g⁻¹ in RTP. H₂S adsorption has been tested, as well, leading to more than 50% AE in less than 1 hour breakthrough time. Overall, the carbonaceous materials meet the criteria for CO₂ and H₂S capture in normal conditions of temperature and pressure. Furthermore, they have the advantage of not being obtained from precursors derived of fossil-fuels and being synthesized via an eco-friendly method, that is, HTC. Future work on the topic could be done to upgrade these powders for industrial applications, including biogas desulphurization and commercial filters for depollution.

4 | EXPERIMENTAL SECTION

4.1 | Materials

The carbon precursors were received from a local company in Guadalupe Islands, Phytobokaz. The biomass was washed with hot DI water several times in order to remove any traces of dust and other impurities and have been dried for few hours, until constant mass, prior to HTC experiments. KOH was purchased from Merck. Both N₂ and CO₂, research grade, used for post synthetic heat treatment were purchased from BOC Group. All chemicals were used as received.

4.2 | Synthesis

Prior to HTC, the feedstock has been carefully washed with DI hot water several times and dried in an oven at 60°C, for few hours. After the drying step, the biomass was crushed, as small as possible, followed by drying for another 3 hours at 60°C, until constant mass. In a typical synthesis, 5 g of biomass, was mixed with 50 mL of deionized water. The mixture was transferred in a stainless-steel autoclave and heated at 200°C for 48 hours. After HTC the samples were allowed to cool down to room temperature. The dark-brown precipitate obtained was separated by vacuum filtration, washed with DI until pH 7 and dried at 100°C, overnight. The resulted hydrochars were characterized by a lack of porosity, so in this regard further activation procedures have been used. The pristine samples have been denoted PDS_HY, GS_HY and WB_HY. KOH activation was performed at different mass ratios of hydrochar:KOH (1:1 and 1:2). In this way the calculated amounts of activating base were mixed with the corresponding mass of hydrochar by wet impregnation. The mixtures were stirred for about 2 hours and dried overnight, at 100°C, followed by further carbonization at 900°C, with 5°C min⁻¹ heating rate for 2 hours, in nitrogen atmosphere. After carbonization, the powders were washed with 6 M HCl, followed by water until neutral pH. In the end, the ACs were dried at 100°C for few hours, leading to PDS_KOH_x, GS_KOH_x and WB_KOH_x (where x corresponds to the mass ratio between pristine powder and KOH).

4.3 | Materials characterization

Surface area and pore size distribution were obtained with a Quanachrome Nova 4200e instrument, using N₂ adsorption-desorption isotherms measured at 77K. Prior to each measurement the samples were degassed overnight at 150°C under vacuum. The surface area related to the mesopores (S_BET), and micropores (S_DR), as well as the total pore volume (V_p) were determined from the N₂ adsorption isotherms as per IUPAC standards. The pore size distribution was obtained by fitting the N₂ isotherms in quenched solid DFT (QSDFT) for slit pores, provided by the Quanachrome NovaWin software.

Micrographs were acquired with a FEI Quanta 3D SEM and a JEOL JEM-2010 TEM. TGA was carried out on a Q500 TA instrument using a heating rate of 10°C min⁻¹ up
to 1000°C in air, to confirm the complete removal of inorganic phase.

FTIR spectra were acquired on a Bruker Tensor 27 FTIR spectrometer equipped with an ATR unit, in the 4,000-400 cm⁻¹ range, using 20 scans per minute.

XPS measurements were conducted on a Thermal Fisher Nexsa equipped with a 180° hemispherical analyzer using Al Kα1 (1,486.74 eV) radiation produced by a monochromatic X-ray source. The base pressure of the system was ca. 133.32 × 10⁻⁸ Pa rising to ca. 533.28 × 10⁻⁸ Pa under the analysis of these samples. Samples were mounted using conductive carbon tape and placed into the instrument chamber. The deconvolution and data analysis have been performed using the Avantage software.

Powder X-ray diffraction (PXRD) data was collected on a PANalytical X’Pert Pro diffractometer, using Cu Kα radiation (λ = 1.5418 Å).

4.4 CO₂ and H₂S adsorption experiments

The adsorptive properties of the herein synthesized carbons were measured towards CO₂ and H₂S adsorption. The CO₂ uptake has been determined using a volumetric method, with a Quantachrome Nova 4200e gas sorption instrument. A degassing step, at 150°C under vacuum for 16 hours, has been applied prior to the adsorption. All samples have been measured at 1 bar and 0°C (STP) and room temperature (RTP). The adsorption capacity was calculated using the formula below:

\[
\text{CO}_2 \text{uptake} = \frac{\text{Volume of gas adsorbed (cm}^3 \text{g}^{-1})}{\text{Molar volume (cm}^3 \text{mmol}^{-1})} \tag{2}
\]

as reported in our previous study.[66]

H₂S adsorption has been monitored, as reported in our previous study,[66] using a Drager X-am 5000 multi-gas monitor equipped with a H₂S sensor with infrared (IR) detection. The materials have been placed in an adsorption chamber, made of Teflon, connected to a 20 ppm H₂S in N₂ cylinder. The flow has been maintained constant, 0.2 L min⁻¹ using a Bronkhorst digital mass flow controller. The experiments were conducted under normal conditions (room temperature and 1 bar). Each measurement was preceded by blank tests. Based on the data collected from the multi-gas unit, breakthrough time was directly determined after each measurement. H₂S adsorption capacity and AE were calculated using the algorithm detailed elsewhere[66] and presented in the supplementary document.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

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