Green Self-Activating Synthesis System for Porous Carbons; Celery Biomass Wastes as a Typical Case for CO2 Uptake with Kinetic, Equilibrium and Thermodynamic Studies

Mobin Safarzadeh Khowrsroshahi  
Iran University of Science and Technology (IUST)

Hossein Mashhadimoslem  
Iran University of Science and Technology (IUST)

Hosein Banna Motejadded Emrooz (✉ Motejadded@iust.ac.ir)  
Iran University of Science and Technology (IUST)

Ahad Ghaemi  
Iran University of Science and Technology (IUST)

Mahsa S Hosseini Naghavi  
Iran University of Science and Technology (IUST)

Research Article

Keywords: Self-activation, Synthesis system, Green synthesis, Activated carbon, CO2 uptake

Posted Date: January 3rd, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1175171/v1

License: ©  This work is licensed under a Creative Commons Attribution 4.0 International License.  
Read Full License
Green Self-Activating Synthesis System for Porous Carbons; Celery Biomass Wastes as a Typical Case for CO$_2$ Uptake with Kinetic, Equilibrium and Thermodynamic Studies

Mobin Safarzadeh Khowsroshahi$^1$, Hossein Mashhadimoslem$^2$, Hosein Banna Motejadded Emrooz$^*$,$^1$, Ahad Ghaemi$^*$,$^2$, Mahsa Sadat Hosseini$^1$

$^1$ Nanotechnology Department, School of Advanced Technologies, Iran University of Science and Technology (IUST), Narmak, 16846, Tehran, Iran
$^2$ School of Chemical, Petroleum and Gas Engineering, Iran University of Science and Technology (IUST), Narmak, 16846, Tehran, Iran

Abstract

A green self-activating synthesis system (SASS) has been introduced for porous carbons. In the presented system, there is no external support for the activation process, and the activating agents are the circulating gases released during the pyrolysis treatment. As a typical case, this system was used for the synthesis of hierarchical porous carbons from celery wastes in hydroponic greenhouses. Based on the adsorption-desorption results, the optimal porous carbons were synthesized at 700 °C, providing a surface area as high as 1126 m$^2$g$^{-1}$ and micropore volume of approximately 0.7 cm$^3$g$^{-1}$. X-ray photoelectron spectroscopy indicated the presence of graphitic nitrogen in the synthesized porous carbon structure. The synthesized porous carbons were applied as an adsorbent for CO$_2$ capture. CO$_2$ adsorption was performed at low and high pressures at various temperatures. Under low pressures (0-1 bar), the synthesized carbons adsorbed 5 mmolg$^{-1}$ at 0 °C and 2.03 mmolg$^{-1}$ at 25 °C. The adsorption capacity of the synthesized carbon at 25 °C and a relatively high pressure of 9.5 bar was 9.57 mmolg$^{-1}$. Based on the thermodynamic and kinetic models, it was clarified that the adsorption process can be regarded as physisorption with an adsorption enthalpy of 23.2 kJ.mol$^{-1}$. Additionally, the fractional-order kinetic model was found to be the best match in the kinetic curves. The synthesis system described herein represents a promising strategy for producing green porous carbon from various waste organic precursors.

Keywords: Self-activation; Synthesis system; Green synthesis; Activated carbon; CO$_2$ uptake
| Symbol | Definition |
|--------|------------|
| $A$    | Temkin model constant ($L \cdot mol^{-1}$) |
| $B$    | first virial coefficient |
| $C$    | Second virial coefficient |
| $f$    | subscripts refer to final condition |
| $i$    | subscripts refer to initial condition |
| $k_L$  | Langmuir model constant ($bar^{-1}$) |
| $k_f$  | Rate constant of adsorption for the Pseudofirst-order ($1/\text{min}$) |
| $k_F$  | Freundlich model constants [(mmol/g)-($bar^{-1}$)$^{1/n}$] |
| $k_s$  | Rate constant of adsorption for the first-order model (g-$\text{mmol}^{-1}$-$\text{min}^{-1}$) |
| $k_n$  | Rate constant of adsorption for the Fractional-order model ($1/\text{min}$) |
| $K_d$  | distribution coefficient |
| $m$    | mass of gas adsorbed (mg) |
| $M_w$  | molecular weight of gas (g-$mol^{-1}$) |
| $P$    | pressure ($bar$) |
| $P_e$  | equilibrium pressure ($bar$) |
| $P_0$  | saturated vapour pressure ($bar$) |
| $q$    | adsorption capacity (mmol/g) |
| $q_e$  | equilibrium adsorption capacity (mmol/g) |
| $q_m$  | maximum adsorption (mmol/g) |
| $q_t$  | adsorption capacity at specified time $t$ (mmol/g) |
| $R$    | universal gas constant ($8.314 \text{ J/mol K}$) |
| $R^2$  | Correlation coefficient (%) |
| $T$    | temperature (K), (C) |
| $t$    | time (s) |
| $w$    | mass of adsorbent (g) |
| $w_{ac-pick}$ | final weight after pickling |
| $w_{final}$ | final weight |
| $w_{initial}$ | initial weight |
| $Y$    | yield of AC |
| $Y_{ac-pick}$ | yield of AC after pickling |
1. Introduction

The increase in world population and the industrialization of many countries leads to an increase in demand for energy, which requires the combustion of fossil fuels to supply this energy. Despite many efforts to find a suitable alternative, these fuels are still cost-effective, convenient, and viable energy [1]. This has led to the production of excess carbon dioxide (CO$_2$) in the atmosphere and enhanced its concentration up to 450 ppm. It is anticipated that atmospheric CO$_2$ concentrations will increase to 950 ppm in the near future [2]. Rising carbon dioxide emissions as a greenhouse gas from widespread sources are one of the most important worries of recent decades. Therefore, to mitigate or separate this polar gas from other nonpolar gases, exclusive strategies must be used to reduce greenhouse effects, acid rain formation, and climate change. In addition, the presence of CO$_2$ in gaseous streams such as flue gases reduces the heating value and destroys transmission pipelines [3, 4]. The carbon capture and storage (CCS) approach consists of a set of
technologies for the uptake of CO$_2$ emissions from industries, followed by compression, transportation, and storage to execute a crucial function to decarbonize industry and deliver low carbon heat [5, 6]. Amine scrubbing, ionic liquid absorption, membrane separation, and solid adsorbent adsorption are the most common CO$_2$ capturing approaches [7]. Traditional CO$_2$ uptake techniques employ amine solutions, which have drawbacks including corrosion, a propensity for severe foaming, costly regeneration, and solid suspension, which reduce CO$_2$ solvent loading. Recently, a variety of solid physical adsorbents, such as fullerene (B40) [8], metal-organic frameworks (MOFs) [9], carbon nanotubes [10], zeolites [11], porous carbon (PC) [12], graphene [13], and others have been developed to substitute traditional alkanolamines [14]. Because of their exceptional characteristics, MOFs and porous carbons received much interest. Although, moisture-sensitive characteristics and extensive synthesis cycles obstruct MOFs use in many circumstances [15].

Owing to its low disposal cost, easy accessibility, thermal stability/conductivity, high specific surface area, insensitivity to moisture, ability to tune porosity, high adsorption, and easy regeneration due to weak interactions, porous carbons have attracted much attention as a promising CO$_2$ adsorbent for large-scale applications [6, 16]. The physisorption of CO$_2$ is influenced by intrinsic properties such as acidity-basicity on the carbon surface, hydrophobicity/hydrophilicity of the porous carbons, specific surface area, distribution and order of the porosities, the isosteric heat of adsorption value ($Q_{st}$), the presence of structural elements such as nitrogen, and the presence of micropores smaller than 1 nm [1, 17-21]. Furthermore, extrinsic parameters such as modifying the surface by heteroatom-doping, increasing pressure, and decreasing temperature play an important role in raising the quantity of adsorption [1, 22]. Meanwhile, porous carbon is suitable to moderate adsorption selectivity and separation for CO$_2$ over N$_2$ and CH$_4$ at low pressures (0.15
bar), owing to its higher quadrupole moment and acidic molecules unlike others [6, 14, 19]. Porous carbons are traditionally obtained by the pyrolysis of a variety of carbon-rich materials as precursors that can be artificial such as titanium carbide [23], sodium alginate [24], and melamine/polyaniline [25] or natural (biomass, cheap agricultural, and forestry wastes) such as rice husk [26], cornstalk [27], and tobacco rods [28] through different synthesis methods [16, 29]. The selection of an appropriate precursor for pyrolysis of porous carbon is important for the final product's porous texture, which is determined by several factors, including scalability, cost, availability, nonhazardous to nature, a high percentage of carbon in the precursor with low ash, and the presence of enough volatiles to produce porosity [17, 30, 31]. Due to the synthesis of heterogeneous micro-meso porous carbons, biomass is advantageous because it incorporates heterogeneous micro/nanostructures and morphology, leading to an oversized quantity of porosity and tunable pore size, resulting in high CO$_2$ sorption [32].

There are two widespread classical route methods to activate/pyrolyze a variety of carbonaceous biomass, generally known as chemical and physical activity that may consist of one (pyrolyzation of raw materials and activator) or two-step processes (carbonization and activation) [29, 31, 33]. Commercial porous carbons generated by physical gasification (air, N$_2$, O$_2$, NH$_3$, CO$_2$, or steam) have a limited CO$_2$ adsorption capability at ambient pressure, which makes them unsuitable for adsorption applications. As a result, microporosities must be introduced in such materials, resulting in a considerable increase in specific surface area. Because chemical activation may yield activated carbons with extraordinarily large surface areas, numerous publications have claimed that KOH activation produces porous carbons with significant CO$_2$ adsorption capability [16, 34, 35]. Even though physical activation is less expensive and has a lower environmental impact, chemical activation is preferred owing to the inclination to be mesoporous and tunable.
porosities of the final material. Nevertheless, chemical activation usually suffers from toxic gases generated during pyrolysis, process complexity, and corrosion of the devices and is not eco-friendly [16, 36-38]. In addition to the methods mentioned above, there are other methods for the synthesis of porous carbon such as molten salt etching, decomposable salt etching, template methods, and self-template methods that can be used for specific applications [39].

Due to the aforementioned drawbacks, a novel self-activation technique for porous carbon synthesis has been developed in recent years. Self-activation is a technique that uses the gases generated during the pyrolysis of biomass to activate the converted carbon, which saves money on activating chemicals and has a lower environmental effect than traditional activation methods [40]. In a previous study, a one-step self-activation technique under a N₂ atmosphere was used to create N-doped mesopore-dominant carbon materials using intrinsic hydroxyapatites as natural templates. As discussed, this method is not considered self-activation due to the use of inert gases and templates during the process [41, 42]. Moreover, few reports have focused on the preparation of porous carbons derived from biomass. Recently, Bommier et al. reported that cellulose-derived activated carbon under an argon atmosphere at 1100 °C for 2 h possessed specific surface areas, ranging from 98 m²g⁻¹ to values as high as 2600 m²g⁻¹ for use in an electrochemical capacitor [43].

Celery, as carbonaceous biomass that belongs to the Apiaceae family, is known for its wealthy cellulose. Owing to the high sturdiness inside the surroundings, celery can be cultivated broadly in most regions of the world with an excessive tonnage and ensure a lasting large-scale supply. It is frequently used in the food industry, resulting in a large number of byproducts, since nonedible and malformed sections of the celery must be removed to meet customer needs [36, 44]. Zhang et al. reported in a previous study that celery biomass waste is easily available for generating biochars that could be effective at removing heavy metal pollution [45]. Furthermore, Mohebali et
al. used celery residue modified with H$_2$SO$_4$ as a low-cost sorbent for the removal of methylene blue cationic dye [46].

Herein, a green, facile, low-cost, and efficient self-activating system has been introduced for the preparation of porous (activated) carbons. In this system, the circulating gases produced during the pyrolysis treatment of porous carbon precursors are the main activating agent of the precursors. Chopped celery wastes have been used as a typical precursor to accomplish the activation process. The morphology, structure, and mechanism of porosity formation at different temperatures as well as the chemical constitution of the resulting porous carbons, were characterized by field emission scanning electron and high-resolution transmission electron microscopy, Raman and Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), thermogravimetry-differential thermal analysis (DTA-TG) and N$_2$ adsorption-desorption analysis. The CO$_2$ adsorption behavior of the synthesized porous carbons was investigated at low (0-1 bar) and high pressures (2-9.5 bar). The results showed that the synthesized porous carbon has a high maximum CO$_2$ adsorption capacity of 5 mmolg$^{-1}$ at 1 bar, 0 °C, and 9.57 mmolg$^{-1}$ at 10 bar, and 25 °C. Eventually, based on the CO$_2$ adsorption behavior of the synthesized porous carbon, the kinetics and thermodynamics of the prepared adsorbent were determined.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade and employed as received without any further purification. Celery was collected from the waste of a hydroponic greenhouse (Tehran, Iran). To remove visible impurities from this biomass, it was washed several times before activation. Hydrochloric acid (37%) was purchased from Dr. Mojallali™ Company (Tehran, Iran),
and CO\textsubscript{2} (99.999\%) was supplied by Arman Gas Company (Tehran, Iran).

2.2. Self-activating system for preparation of porous carbon

The introduced self-activating system consists of a sealed chamber, a tubular electric furnace an air pump, and finally a condenser that is connected through pipes. Due to the sealing of the system, no gas is transmitted to the environment during the synthesis process. The gases created throughout the pyrolyzation of the feeding biomass circulate in a closed-loop channel with the assistance of an air pump positioned at the system and activation is combined into one step. The activation process is carried out with the aid of these gases. Therefore, there is no need for another activating agent. A condenser is also installed along the route of the gases, collecting a portion of the exhaust gases, and transforming them into liquid.

For the preparation of porous carbons, in the first step, collected celery was dried overnight at 80 °C to remove moisture. Afterward, it was vigorously ground into fine powders to the optimum micron size in a ball mill. 10 g of the dried celery powder was directly pyrolyzed in the self-activating system at 300, 600, 700 and 900 °C and maintained at final temperatures for 3 h. After cooling to room temperature, the obtained products were washed with 1 M HCl to remove the remaining impurities and then with deionized water until neutral pH. Finally, the green celery-derived porous carbons, hereafter named GC-PCs, were dried at 85 °C for 12 h.

The initial and final product yields were calculated by equations (1) and (2):

\[ Y (\%) = \frac{W_{\text{final}}}{W_{\text{initial}}} \times 100 \]  

(1)

\[ Y_{ac\text{-pick}} (\%) = \frac{W_{ac\text{-pick}}}{W_{\text{initial}}} \times 100 \]  

(2)

where Y demonstrates the yield of porous carbon after pyrolysis and \( Y_{ac\text{-pick}} \) displays the yield of porous carbon after acid pickling. \( W_{\text{initial}} \) and \( W_{\text{final}} \) specify the weight of the initial biomass weight.
and final weight of porous carbon and $W_{ac\text{-}pick}$ represents the final weight of porous carbon after pickling. GC-PCs derived at different temperatures were named C-T where $T$ is 300, 600, 700, and 900 (the pyrolyzation temperatures). A schematic of the green self-activating synthesis system and the process of preparing porous carbons for CO$_2$ capture is shown in Fig. 1.

![Fig. 1. Schema representing the production of porous carbon from celery in a self-activating system and its application for CO$_2$ capture](image)

### 2.3. Characterization

The physicochemical parameters of the synthesized samples were investigated quantitatively and qualitatively using various characterization methods. Micromeritics ASAP2020 (US) adsorption analyzers were employed to measure the N$_2$ adsorption-desorption isotherms at $-196 \, ^\circ\text{C}$. Before performing the adsorption-desorption analyses, samples were degassed under dynamic vacuum conditions to constant weight at a temperature of $150 \, ^\circ\text{C}$ for 6 h. The total surface area was calculated using the multipoint Brunauer–Emmett–Teller (BET) technique. The Barrett–Joyner–Halenda (BJH) technique is equipped to calculate the mesopore surface area, pore volume,
and pore diameter. The t-method is used to calculate the micropore surface area and pore volume, whereas the Dubinin–Astakhov (DA) technique is used to determine the micropore diameter. Raman spectroscopy was conducted on a Takram micro-Raman spectrometer (Teksan™, Iran). FTIR spectroscopy was accomplished on a Perkin–Elmer Spectrometer in the range of 500–4000 cm$^{-1}$ using the potassium bromide (KBr) disc method. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an Al Ka source (XPS Spectrometer Kratos AXIS Supra). High-resolution transmission electron micrographs were obtained on a 300-kV FEI (US) TITAN microscope (HR-TEM). Thermogravimetric and differential thermal analyses (DTA/TG) in argon and air atmospheres were conducted on a Q600 (US) TA. Field emission scanning electron microscopy (FESEM) was observed on a Nanosem 450 microscope. Powder X-ray diffraction (XRD) patterns between 10 and 80 (~2θ) degrees were collected on a Philips (Holland) PW1730 diffractometer with Cu-Kα radiation ($\lambda=0.154$ nm).

2.4. CO$_2$ adsorption-desorption

The CO$_2$ uptake behavior of the prepared porous carbons was investigated at low and high pressures. Low-pressure CO$_2$ adsorption isotherms of the synthesized porous carbon were measured at 0 and 25 °C on an ASAP 2020 (US) Micromeritics between 0 and 1 bar. To evaluate the high-pressure CO$_2$ capturing behavior of the synthesized porous carbon, a fixed bed adsorption reactor was constructed to evaluate the CO$_2$ adsorption-desorption performance of GC-PC adsorbents. Pure CO$_2$ and N$_2$ were utilized as feeds in the studies to investigate the GC-PC surface adsorption ability. 1g of GC-AC was loaded in the cylindrical reactor of the instrument, and the reactor was then fully sealed. To assess the amount of gas adsorption, N$_2$ was introduced into the device compartment as a purge gas. To eliminate moisture and all preadsorbed CO$_2$, GC-PC was preheated under pure N$_2$ gas at 110 °C for 30 minutes before being placed under vacuum for
another 40 minutes. Experiments were conducted for 60 minutes at temperatures of (25, 35, and 45 °C) and pressures of (2-9.5 bar). The CO$_2$ pressure and temperature were stabilized thanks to the mixing tank in the passage, and the stable gas was then delivered to the adsorbent reactor. The reactor's heat is provided by electric heat tracing, and the temperature and pressure fluctuations of CO$_2$ are recorded in real-time by the computer.

3. Results and discussions

3.1. Characterization

The differential thermal and thermogravimetric analysis method (DTA/TG) was accomplished in air and argon atmospheres to follow the mass change of celery from 25 °C to 1000 °C, (Fig. 2). This analysis provides crucial details about the decomposition behavior that occurs as the temperature rises, allowing the mechanism and temperatures of the reaction to be determined [47-49]. As shown in Fig.2 (a,b), in the first step, for both atmospheres, the TG % curves show an ~9-15% mass loss up to 200 °C due to the evaporation of physically adsorbed molecular bound water. The second step at ~200-500 °C corresponds to the decomposition of the organic components, hemicellulose, cellulose, and lignin, while the third step of mass loss at 500-800 °C corresponds to the combustion of lignin residues. Hemicelluloses are the first to decompose and degrade from 220 to 315 °C. Cellulose is made up of glucose with a glycosidic bond and decomposes at temperatures ranging from 315 to 400 °C. Eventually, the behavior of phenolic compounds such as lignin covered an extraordinarily broad decomposition temperature range of 500 to 850 °C. The exothermic peaks at approximately 350 °C in the DTA curves of Fig.2 (a) can be due to the combustion of residual hemicellulose through the formation and emission of volatile compounds. Furthermore, an exothermic peak at ~450 °C corresponds to carbon matrix
combustion as well as cellulose and lignin decomposition. A similar exothermic peak can be found in Fig. 2 (b) from which it can be inferred that celery combustion takes place in an argon (inert) atmosphere. This means that there is enough oxygen in the celery constituents from which the combustion reaction can take place [31, 50].

![Fig. 2. Thermogravimetric and differential thermal analysis results of celery waste in air (a) and argon (b) atmospheres from 25 °C to 1000 °C](image)

The structure, crystallinity, and textural properties of the pyrolyzed celery wastes are demonstrated in Fig. 3. Porosity formation is impacted significantly by a variety of factors, including active-site clustering or fusion, carbon skeletons, inorganic impurities, and gas diffusion. The internal structure of carbon is thought to be the most essential of these characteristics. X-ray diffraction patterns display the formation of turbostratic carbon with a structural ordering intermediate between the amorphous carbon phase and crystalline graphite phase, as seen in Fig. 3 (a) [51]. There is only one broad signal for C-Raw and C-300 at approximately 23° which corresponds to amorphous carbons. For C-600, in addition to the peak at 23°, there is one additional peak at approximately 31° which can be attributed to the (003) planes of graphitic carbons. The peak corresponds to the (003) planes vanishing at higher temperatures, owing to a steady rise in disordered carbons [52]. X-ray diffraction patterns of C-700 and C-900 display only two broad Bragg reflections at about 22-23° and 42-44°, which correspond to the (002) and (100/101)
turbostratic planes of graphitic carbons, respectively (JCPDS X-ray Powder Diffraction Database No. 75-1621). This is an indicator of amorphous graphitic carbon which is possibly formed during carbonization. The lower proportion of crystallinity in these two cases may be attributed to the broader intensities for the peak occurring at 22-23°. Broadening of these peaks implies a very small crystallite size and hence the development of a nanostructured skeleton. These results indicate that when the temperature rises, the porosity of graphitic carbons gradually increases until the structure collapses [53-56]. The (002) peak moves towards higher diffraction angles as the activation temperature rises from 300 to 900 °C. The change in peak location indicates a decrease in the interlayer distance, and the increased intensity correlates to greater translational ordering in porous carbons pyrolyzed at more elevated temperatures [51]. The lack of any sharp peak in the XRD plots for acid-washed samples indicates that the synthesized compounds are to some extent amorphous in nature, and it also confirms that there are no left-over inorganic residues after acid pickling [57, 58].

Raman analysis was employed to investigate the crystallinity and graphitization level of the synthesized porous carbons. The Raman spectroscopy results of C-700 and C-900 (See Fig. 3 (b)) show D-band peaks at approximately 1345 cm⁻¹ and G-band peaks at around 1603 cm⁻¹, indicating the presence of a carbon lattice defect with a distorted structure (sp3) and some order-layered graphite with vibration sp2 hybridized carbon atoms, respectively. Moreover, the presence of a 2D-band around 2873 (cm⁻¹) is a sign of a local graphene-like structure [16, 59-63]. The integrated intensity ratio of the D and G bands (I_d to I_g) can be used to evaluate the surface graphitization, higher of which shows lower graphitization level. For C-700 and C-900, these ratios are 0.95 and 0.98, respectively, which is sign of an intermediate amorphous-crystalline structure. According to the results, the quantity of graphitization in these two samples is very little different.
from each other. C-900 is carbonized at a higher temperature and has a higher I_d to I_g ratio than C-700 which is compatible with the XRD results. While a higher temperature was appropriate for the graphitization stage, high temperatures in combination with a reactable (corroding) atmosphere which is the case in the introduced system can destroy a portion of the synthesized carbon structure and reduce the graphitization level [14, 64-66].

Nitrogen adsorption-desorption analysis results of the pyrolyzed celery wastes in Figs. 3(c-e) and Table 1, demonstrate the activation strength of the introduced self-activating system. The specific surface area, mean pore diameter, and total pore volume of the celery wastes pyrolyzed at 300 and 600 °C are 1.7 m².g⁻¹, 53.5 nm, 0.02 cm³.g⁻¹, and 9.75 m².g⁻¹, 11.7 nm, 0.03 cm³.g⁻¹, respectively, which confirms that these two pyrolyzed celery wastes are not porous in nature. Conversely, as the activation temperatures increase, the mesopore volumes of porous carbons increase as seen by the much higher N₂ adsorption. From the DTA-TG results of celery wastes in an argon atmosphere, Fig. 2 (b), it can be deduced that the combustion of the carbonaceous components of celery results in mass losses of approximately 30% and 70% at 300 and 600 °C, respectively. This accompanies the production of gases such as CO₂, CO, H₂, and H₂O. Based on the following reactions, all of these gases have activating potential on the carbon precursors [61, 67].

\[
\begin{align*}
H₂O(ℓ) & \rightarrow H₂O(g) \quad (3) \\
C(ℓ) + H₂O(g) & \rightarrow CO(g) + H₂(g) \quad (4) \\
2C(ℓ) + O₂(g) & \rightarrow 2CO(g) \quad (5) \\
CO₂(g) + H₂(g) & \rightarrow CO(g) + H₂O(g) \quad (6) \\
C(ℓ) + CO₂(g) & \rightarrow 2CO(g) \quad (7)
\end{align*}
\]

The specific surface area, mean pore diameter, and pore volume of the synthesized carbons
at 300 and 600 °C in Table 1 confirm that at these pyrolyzation temperatures, the gaseous activating agents have no significant effect on the activation of celery biomass. On the other hand, celery wastes pyrolyzed at 700 and 900 °C possess a specific surface area, mean pore diameter, and total pore volume of 1126 m².g⁻¹, 2.5 nm, 0.69 cm³.g⁻¹ and 1169 m².g⁻¹, 2.7 nm, 0.84 cm³.g⁻¹, respectively. Therefore, these temperatures are high enough for the activation of celery. Based on the TG results, at 700°C about 75%, 5% greater than that at 600 °C, and at 900 °C about 90% of the initial weight of the biomass was lost. Therefore, combustion of the carbon precursor which takes place up to 600 °C cannot have a direct effect on the activation of the biomass. When the activation temperature increases (≥700 °C) the standard Gibbs free energy change of reactions (4) and (7) becomes negative. Therefore, CO₂ and H₂O, which are the combustion reaction products of celery biomass can react with the carbon atoms and, in fact, etch the surface of carbon layers. This etching process results in porosity formation and increases in the specific surface area. During self-activation, two situations may occur: (1) pore expansion and (2) pore combination. The narrow boundaries between the pores are removed, allowing the pores to merge. The specific surface area is enhanced by pore expansion during the self-activation process, but at high temperatures (≥700 °C) it is unchanged due to pore combination. At higher temperatures, the pore combination mechanism seems to dominate the whole process. As a result, as shown in the XRD plots, the order of the structure does not increase with increasing temperature, contrary to expectations [68-70]. It can thermodynamically be concluded that temperatures lower than about 705 °C are not high enough to effectively initiate the aforementioned reactions of carbons with the combustion product gases. Pyrolyzation at ≥850 °C is high enough to effectively initiate reaction (6) [70]. In this reaction, CO₂ reacts with H₂, which is the product of carbonization treatment and reaction (4). On the other hand, H₂O which is one of the products of this reaction can be helpful for the activation
process in reaction (4). The dual effect (both positive and negative) can be regarded as the reason for the approximately same activation response of C-700 and C-900. This can also be inferred from the TG result of celery in the argon atmosphere (See Fig. 2 (b)). Circulation and transfer of the gases to atmospheric temperature (approximately 25 °C) hinders the increase in the pressure of the hot reaction chamber. This, in turn, prevents the stopping of the activation reactions, especially reactions (4), (5), and (7) [68, 70]. Another important beneficial role of the circulation process is the possibility of saving the large amounts of the activation gases produced during the carbonization process at low temperatures (T≤700 °C). The amounts of the activating gases can be inferred from the TG result of celery in the argon atmosphere, Fig.2 (b). These gases can participate in the activation process at T≥700 °C. In conventional self-activating processes, the active gases produced at low temperatures are exhaust gases [36, 43, 59]. Therefore, they do not have a considerable role in the activation process but are also harmful to the environment. Based on the BJH and MP plot results in Fig.3 (d, e), C-700 has mesopore and micropore volumes of 0.27 cm³g⁻¹ and 0.42 cm³g⁻¹, and C-900 has mesopore and micropore volumes of 0.41 cm³g⁻¹ and 0.43 cm³g⁻¹, respectively. Moreover, based on BJH pore size distributions, porous carbons are composed of microspores (1–2 nm), small mesopores (2–5 nm), and large mesopores-macropores (10–60 nm). Therefore, both of these porous carbons can be regarded as hierarchical [71, 72].
Fig. 3. XRD (a), Raman (b), N$_2$ adsorption/desorption isotherms (c), MP plots (intensity of pores smaller than 2 nm) (d), and Barrett-Joyner-Halenda (BJH) pore size distribution curves (e) of GC-PCs.
Table 1. Detailed textural properties of GC-PCs at different activation conditions

| Sample ID | Yield (%) | Total BET specific surface area (m²g⁻¹) | Average pore diameter (nm) | Total pore volume (cm³g⁻¹) | Mesoporous volume (cm³g⁻¹) | Microporous volume (cm³g⁻¹) | Mesoporous surface area (m²g⁻¹) | Microporous surface area (m²g⁻¹) |
|-----------|-----------|-----------------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|--------------------------------|--------------------------------|
| C-300     | 45        | 1.75                                    | 53.9                      | 0.02                      | 0.02                      | 0.002                     | -                              | -                              |
| C-600     | 33        | 9.72                                    | 11.7                      | 0.03                      | 0.02                      | 0.005                     | -                              | -                              |
| C-700     | 20        | 1126.2                                  | 2.5                       | 0.69                      | 0.27                      | 0.42                      | 113.6                          | 1012.6                         |
| C-900     | 18        | 1169.6                                  | 2.6                       | 0.84                      | 0.41                      | 0.43                      | 181.7                          | 987.9                          |

In addition to the carbon atoms, intrinsic heteroatoms, such as nitrogen and oxygen which are normally the constituents of the initial structure of the precursors can affect and generally improve the properties of the synthesized porous carbons. Additionally, the functional groups containing the mentioned elements can greatly affect the behavior of the final product for various applications, including CO₂ adsorption. The surface chemistry of porous carbons is a function of their acidity, electronegativity, and hydroxyl groups [67, 73-75]. The surface chemical characteristics of the synthesized carbons are illustrated in Fig.4. The surface functional groups of the synthesized carbons collected from Fourier transform infrared (FTIR) spectroscopy are shown in Fig.4. (a). Similar peaks can be detected in all synthesized carbons at ~3420 (cm⁻¹), 2925 (cm⁻¹), and 2856 (cm⁻¹), which are consistent with the O-H stretching vibrations of hydroxyl groups, asymmetric and symmetric C-H methylene, and methyl groups in aliphatic CH, CH₂, and CH₃ from lignin, respectively [73, 76, 77]. The 1730 (cm⁻¹) band is caused by the stretching of C=O bonds in ketone, aldehyde, lactone, and carboxyl groups. The band at approximately 1632 cm⁻¹ can be associated with the stretching of the C=C aromatic ring stretching vibrations caused by polar functional groups [49, 52, 77]. The -CH₂= and C-O tensile vibration bands in ether, phenol, and alcohol are responsible for the peaks at 1467 and 1095 (cm⁻¹), respectively [49, 52, 78]. As the pyrolyzation temperatures increased, the total intensity of the peaks decreased and the hydrophobic
properties of the synthesized carbons increased. Moreover, the number of acidic functional groups in the carbon decreased while the number of alkaline surface groups increased. Due to the relatively high pyrolyzation temperatures, many functional groups decompose to form volatile CO and CO$_2$ and move away from the structure. This is caused by the heterogeneity of acidic groups at high temperatures. Basic types, on the other hand, increase as the temperature rises. These groups can form during the cooling process. As a result, CO$_2$ and CO formation in porous carbons (C-700, C-900) was confirmed by the detection of minor peaks at around 1900-2300 (cm$^{-1}$) in the FTIR spectra [49, 52, 79]. The pyrolysis temperature of 900 °C used for C-900 degraded the functional groups that were originally comprised within the raw celery biomass material. Therefore, the bonds of carboxyl, alcohol, and ether groups that formed the lignocellulosic structure were fractured. This is due to the elimination of oxygen-containing functional groups and the high degree of graphitization at high temperatures [77]. On the other hand, the surface of C-700 synthesized carbons is highly aromatic and contains many oxygenated functional groups such as phenolic and carboxylic acid groups, which add a negative charge to the surface. All of these functional groups can increase the CO$_2$ adsorption capacities of these porous synthesized carbons [55]. X-ray photoelectron spectroscopy (XPS) analysis was used to determine the chemical bonding states, elemental compositions, and atomic percentage of C-700. The carbon, nitrogen, and oxygen peaks and quantities can be seen in Fig.4 (b-e) and Table 2, respectively. From the survey analysis in Fig.4 (b) and Table 2, C, O, and N atomic percentages of C-700 synthesized porous carbons are 93.7, 4.8 and 1.5, respectively. C1 s (93.7%), and O1 s (4.8%) peaks can be seen at around 285, and 533 eV, respectively. N1 s (1.49%) peak can also be observed at around 401.5 eV [59, 62, 80]. The deconvoluted spectra of C1 s in Fig. 4 (c) indicate that there are three peaks at 285, 287, and 289.6 eV, corresponding to sp2 C-C (graphitic carbon) bonds, C-O
(phenolic) bonds and C=O (carboxyl) bonds, respectively. Two peaks in the deconvoluted O1 s spectrum of Fig. 4 (d), centered at 533 and 534.5 eV, can be attributed to the C-O, and O=C-O groups [55, 81]. Both of these forms of oxygenated groups give a negative charge or basic character to the surface of porous carbons. This helps to anchor mildly acidic CO2 molecules by acid-base interactions [55]. For N1 s, [Fig.4 (e)], there is one detectable graphitic nitrogen (N-Q) bond centered at 402 eV [19, 82].

**Table 2.** The carbon, nitrogen, and oxygen peaks and quantities of GC-PC (C-700)

| Sample ID | C (at %) | O (at %) | N (at %) | Peak area (C) | Peak area (O) | Peak area (N) |
|-----------|----------|----------|----------|--------------|--------------|--------------|
| C-700     | 93.7     | 4.8      | 1.5      | 21264        | 1100         | 340          |

![Graph showing the transmission and binding energy of different samples](image)

![Graph showing the C 1s, N 1s, and O 1s peaks with their corresponding intensities and binding energies](image)

![Cumulative fit peaks for C 1s, C-C, C-O, and C=O](image)
The surface morphology and crystalline analysis of C-700 are shown in Fig.5. From the field emission scanning electron microscopy micrographs, Fig.5 (a-c), well-developed meso sized porosities and a cauliflower-like structure of the synthesized carbons can be inferred. High-resolution transmission electron microscopy micrographs of C-700 in Fig.5 (d-f) display a fairly disordered and amorphous carbon matrix that consists of plenty of wormhole-like pore structures, Fig. 5 (d). Additionally, the micropore structure of the synthesized porous carbon can clearly be detectable in HR-TEM micrographs. Some (002) lattice fringes with a distance of 0.35 nm between two adjacent planes can be detected in Fig. 5 (e) and the yellow square in Fig. 5 (f), which is to some extent larger than that of the bulk graphite planes. This can be attributed to the presence of functional groups and nitrogen and oxygen-doped atoms in the porous carbon structure [83]. The edges of these graphitic layers are distinctly crystalline, and the crystallinity in-plane was fine, which confirmed the Raman spectroscopy results in Fig. 3 (b). Another characteristic of the graphitic layers is that they appear to adhere to the surface of porous carbon, creating an ultrathin conductive layer on the surface of the disordered carbon matrix. Besides, the amorphous-crystalline intermediate structure in Fig. 5 (f) verifies the formation of a turbostratic carbon structure as claimed in the X-ray diffraction pattern analysis of this synthesized carbon, Fig.3 (a).
Fig. 5. FE-SEM micrographs of the heterogeneous surface showing the cauliflower-like texture of carbons (a), (b) and (c), HR-TEM micrographs of turbostratic carbon matrix with plenty of wormhole-like micro-mesopores and some clear graphite crystallites (d), (e), and (f) of C-700

3.2. CO$_2$ adsorption performance

The CO$_2$ adsorption efficiency of C-700 was obtained under 1 bar at 0 °C and 25 °C, respectively, as shown in Fig.6. The CO$_2$ adsorption capacity at 1 bar was 5 mmol g$^{-1}$ at 0 °C and
2.03 mmolg\(^{-1}\) at 25 °C, which is comparable to that of other biomass-derived porous carbons. This sample was chosen for adsorption testing based on the adsorption-desorption findings, which showed a higher microporous surface area (1012.61 m\(^2\) g\(^{-1}\)) than C-900. The non-activated samples (C-300, 600) were extremely nonporous and had a very low specific surface area, so CO\(_2\) adsorption was not performed on them. CO\(_2\) uptake increases with increasing pressure without indicating adsorption saturation at both temperatures, indicating an adsorbents can sustain increased CO\(_2\) uptake at higher pressures. The overall output pattern revealed that higher loadings occur at lower temperatures, indicating that the exothermic nature physisorption process. Moreover, isotherms display almost no adsorption-desorption hysteresis, indicating that this adsorption mechanism is physically invertible. The appearance of oxygen-nitrogen-containing groups on carbon surfaces (without any external source) and micropores, which may increase the carbon materials affinity for CO\(_2\) due to acid-base interactions and pole-pole interactions, are the key factor determinants of CO\(_2\) adsorption by porous materials [57, 80, 84-86]. Physisorption mechanism created by van der Waals and quadrupole nature of the CO\(_2\) molecule interactions between the gas and the surface molecules at the walls of the carbon pores. Owing to this mechanism, interaction is so weak and regeneration does not necessitate additional energy [67, 87].
3.3. The effect of temperature on \( \text{CO}_2 \) adsorption

Another variable that has a significant impact on \( \text{CO}_2 \) adsorption capacity is temperature. The C-700 behavior and the quantity of \( \text{CO}_2 \) adsorption capability are revealed in Fig. 7. Figure 7 shows the \( \text{CO}_2 \) adsorption on GC-PC as determined using an experimental setup over 75 minutes at various isotherm temperatures. The observed \( \text{CO}_2 \) adsorption capacity findings for GC-PC in the temperature range of 25 °C – 55 °C show that the decrease in adsorption temperature can enhance \( \text{CO}_2 \) adsorption capacity at lower temperatures. Due to the Boltzmann equation, the increase in interaction is due to a rise in the kinetic energy of the solid/gas molecules engaged in the adsorption process, which generates increased molecular interaction and decreases the efficient adsorption surface. At high temperatures, the interactions between the sorbent and the sorbate weaken, and repulsion becomes more desirable, resulting in a shift in equilibrium in the opposite direction of the adsorption process. As the adsorption temperature rises, molecular activity rises as well, intensifying the struggle for limited adsorption sites. As a result, the repulsions between molecules increase, resulting in a decrease in the quantity of adsorption. Therefore, the lowest
temperature is the most favorable of the adsorption capacity obtained throughout the adsorption process and at 10 bar pressure and 25 °C, the maximum adsorption on the GC-PC adsorbent is 9.57 (mmolg⁻¹) [88-90].

Fig. 7. Temperature effect on the CO₂ adsorption capacity of GC-AC under 10 bar for 75 min.

3.4. Kinetic adsorption and equilibrium isotherms

3.4.1. Kinetic modeling

To assess their adsorption performance and comprehend the total mass transfer in CO₂ capture, kinetic studies of adsorption on the produced porous carbon are necessary. Furthermore, adsorption kinetics are required for the logical design and modeling of gas-treatment facilities. Moreover, to estimate the capacity and rate of CO₂ adsorption in adsorbents, kinetic models can be used. As a result, research into CO₂ adsorption kinetics is critical. Micropores, mesopores, the surface area of the adsorbent, and the form of different kinetics all play a key role in gas adsorption by porous materials. The physical and chemical structure of the adsorbent also affects the mechanism, according to a review and study of the uptake kinetics [91]. We explored different
theoretical kinetic models for the kinetic study, including pseudo-first-order, pseudo-second-order, Elovich, and fractional order, models (Eqs. 8-11).

\[ q_t = q_e (1 - e^{-k_f t}) \]  

\[ q_t = \frac{q_e^2 k_s t}{1 + q_e k_s t} \]  

\[ q_t = \frac{1}{\beta \ln(\alpha \beta)} + \frac{1}{\beta \ln t} \]  

\[ q_t = q_e - \left( q_e^{(1-n)} + \left( \frac{n-1}{m} \right) k_n t^m \right)^{\frac{1}{1-n}} \]

where \( q_e \) and \( q_t \) (mmol.g\(^{-1}\)) are the adsorptive capabilities at equilibrium and at time \( t \) (minutes), respectively, and \( k_f \) and \( k_s \) are the rate constants (1.min\(^{-1}\)). The rate constant for the fractional-order is \( k_n \), whereas the model constants are \( m \) and \( n \). Reversible adsorption with equilibrium between the gas and solid surface is depicted in the pseudo-first-order kinetic model based on the chemisorption process as the adsorption controlling factor, whereas the pseudo-second-order kinetic model was based on the hypothesis that chemical adsorption was the rate-controlling step. The fractional-order kinetic model represents the complexity of the reaction mechanism that could involve more than one reaction pathway. This means that this model is capable of calculating the CO\(_2\) capture occurring by both physisorption and chemisorption mechanism [92-94]. Since predicting kinetic parameters is complex, a typical method is to adjust experimental data to a series of models and then choose the best model [95]. The kinetic parameters are mentioned in Table 3, and the fractional-order kinetic model was found to be the best match based on correlation coefficient values (\( R^2 \)) in the range of 0.9915 to 0.9979 at 25 °C, 35 °C, 45 °C, 55 °C under 10 bar. This model is based on the assumption that the rate of sorption is influenced by the \( n^{th} \) power.
of the driving force, and the $m^{th}$ power of the sorption time. The best CO$_2$ adsorption kinetic model was also fitted to the experimental data, and the GC-PC kinetic curves are presented in Fig. 8.

Table 3. Calculated parameters of CO$_2$ adsorption kinetic models and fitting comparison at 10 bar for C-700

| Kinetic models    | Parameters     | 25 °C   | 35 °C   | 45 °C   | 55 °C   |
|-------------------|----------------|---------|---------|---------|---------|
| Pseudo-first-order| $q_e$ (mmol/g) | 9.131   | 7.225   | 6.449   | 5.715   |
|                   | $k_f$ (l/min)  | 0.011   | 0.003   | 0.005   | 0.005   |
|                   | $R^2$          | 0.8291  | 0.8761  | 0.9462  | 0.9258  |
| Pseudo-second order| $q_e$ (mmol/g) | 9.397   | 7.737   | 6.754   | 5.987   |
|                   | $k_s$ (l/min)  | 0.0021  | 0.00065 | 0.001517| 0.001594|
|                   | $R^2$          | 0.9445  | 0.9425  | 0.9841  | 0.9708  |
| Elovich           | $\alpha$ (mmol/g.min) | 211.303 | 0.480058| 5.5873  | 5.9924  |
|                   | $\beta$ (g/mmol) | 0.714   | 0.994   | 0.705   | 0.624   |
|                   | $R^2$          | 0.9753  | 0.9937  | 0.9501  | 0.9571  |
| Fractional-order  | $q_e$ (mmol/g) | 10.887  | 8.837   | 6.664   | 5.872   |
|                   | $k_n$ (l/min)  | 0.001   | 0.0938  | 0.0438  | 0.0906  |
|                   | $n$            | 2.9136  | 0.6121  | 0.9741  | 0.662   |
|                   | $m$            | 0.6071  | 0.2619  | 0.4791  | 0.3549  |
|                   | $R^2$          | 0.9937  | 0.9979  | 0.9935  | 0.9915  |
Fig. 8. CO₂ adsorption capacity of C-700 and corresponding desirable kinetic models at 25 °C.

3.4.2. Equilibrium adsorption isotherms

The adsorption mechanism and expression of surface attributes throughout the adsorption process may be predicted using an adsorption isotherm analysis, which is highly essential. Adsorption isotherms are essential in improving the use of carbon as an adsorber because they represent how adsorbates interact with porous carbon. In Fig. 9, the CO₂ adsorption isotherms were plotted using the Langmuir, Freundlich, Dubinin Radushkevich (D-R), and Temkin equations at 25 °C and pressures ranging from 2 to 9.5 bar. The findings showed that increasing the uptake pressure increased the rate of CO₂ adsorption. Monolayer adsorption occurs on a finite number of energetically equivalent adsorbent sites, according to the Langmuir isotherm. For adsorption on an energetically heterogeneous adsorbent surface, the Freundlich isotherm can be used. The Dubinin Radushkevich equation may also be used to examine liquid-phase adsorption data. The quantity adsorbed corresponding to each adsorbate concentration is considered to be a Gaussian function of the Polanyi potential in this equation for liquid-phase adsorption. This result is based on the notion that adsorption occurs by pore volume filling rather than the layer-by-layer
development of a film on the pore walls. Because of adsorbent-adsorbate interactions, the Temkin isotherm also describes adsorption on heterogeneous surfaces, albeit with the assumption that the adsorption heat of the molecules in the layer drops linearly rather than logarithmically with coverage [96]. Table 4 shows the experimental results and related R^2 correlation coefficients for all coefficients of isotherm parameter models.

Table 4. Isotherm models of CO\textsubscript{2} adsorption at 10 bar for GC-PC.

| Models               | Parameters | 25 °C   | 35 °C   | 45 °C   | 55 °C   |
|----------------------|------------|---------|---------|---------|---------|
| Langmuir             | q\textsubscript{m} | 678.8   | 17276.2 | 2607.6  | 1204.4  |
|                      | k\textsubscript{L} | 0.179   | 0.002   | 0.013   | 0.027   |
|                      | R^2        | 0.9994  | 0.9990  | 0.9946  | 0.9621  |
| Freundlich           | k\textsubscript{F} | 142.4   | 38.081  | 38.115  | 37.54   |
|                      | n          | 2.022   | 1.019   | 1.103   | 1.205   |
|                      | R^2        | 0.9947  | 0.9990  | 0.9954  | 0.9652  |
| Dubinin Radushkevich | q\textsubscript{m} | 452.134 | 386.462 | 332.446 | 277.624 |
|                      | \lambda    | 1.439   | 2.894   | 2.730   | 2.400   |
|                      | \Theta      | 0.589   | 0.416   | 0.428   | 0.456   |
|                      | R^2        | 0.9913  | 0.9597  | 0.9475  | 0.9052  |
| Temkin               | A           | 1.364   | 0.524   | 0.537   | 0.590   |
|                      | B           | 167.227 | 205.937 | 173.749 | 137.668 |
|                      | R^2        | 0.9994  | 0.9837  | 0.9774  | 0.9421  |

The adsorption isotherm formula calculated from Eq.

\[ q_e = q_m k_L P (1 + k_L P) \] (12)

\[ q_e = k_F P_e^{1/n} \] (13)

\[ q_e = q_m e^{-\lambda \omega^2} \] (14)

\[ q_e = B log(A) + B log(C) \] (15)

where \(q_e\) is the value of CO\textsubscript{2} adsorption capacity (mmolg\textsuperscript{-1}), \(q_m\) is the max adsorption value of CO\textsubscript{2} (mmolg\textsuperscript{-1}), \(P\) is the equilibrium pressure (bar), and \(K_F\) is the Freundlich model constant ((mmol.g\textsuperscript{-1}). (bar\textsuperscript{-1})\textsuperscript{1/n}), and \(n\) is the Freundlich isotherm constant indicating the adsorption intensity.
Moreover, λ is the D-R model constant \((\text{mol}^2 \text{J}^{-2})\), \(\omega\) is the Polanyi potential \((\text{J.mol}^{-1})\), A is the Temkin model constant \((\text{L.mol}^{-1})\), B is the first virial coefficient \((B=\text{RT} \cdot b_T^{-1})\); \(b_T^{-1} \text{J.mol}^{-1}\). Values decreased as the temperature was increased, indicating an exothermic \(\text{CO}_2\) adsorption behavior. While all of the isotherm models agreed well with the experimental results, the Langmuir isotherm model had the highest correlation coefficient \((R^2)\) values when fitted to the data. The main assumption in this equation is that the solid adsorber surface is homogeneous. The Langmuir model, which is the most widely used isotherm model for gas sorption on solids, is premised on the theory of dynamic equilibrium between the rates of gas adsorption on a solid and desorption from the solid surface. Adsorption is considered to be limited to a single layer. Therefore it is used to represent single gas capture behavior owing to the facility. The following are the most important assumptions of this theory: 1) molecules are trapped at a definite number of well-defined localized sites; 2) the sorption is monolayer; 3) each site may store one sorbate molecule and the adsorbed molecules will not transfer to another adsorption site; 4) every sorption site has the same adsorption energy (i.e. there are specific and energetically equivalent numbers of adsorption sites), indicating that the sorbent surface is homogeneous; 5) there is no interaction among molecules adsorbed on neighboring sites; and 6) the adsorption system is in dynamic equilibrium, with a sorption rate equal to the desorption rate [97]. Furthermore, two isotherm models developed by D-R and Temkin have useful data allocated to the energy parameters, where \(\omega\) is the mean adsorption free energy and \(b_T\) is the heat of adsorption. The normal physisorption of \(\text{CO}_2\) adsorption is shown by average \(\lambda\) values in the 1-2 (kJmol\(^{-1}\)) range [93]. The Freundlich constant, \(n\), in the range of 1 to 2, illustrates the desirability of physisorption based on the findings of Table 4. According to the results, the adsorption process is multi-layer, with \(\text{CO}_2\) adsorbed and penetrated in the surface and inner layers of C-700. According to the nonlinear \(R^2\) values derived in Table 4 and by the nonlinear regression
method, Langmuir > Freundlich > D-R > Temkin was the order of effectiveness of the stated isotherms in the explanation and prediction of the adsorption behavior [89, 98]. Fast adsorption kinetics are one of the most significant features anticipated in a good sorbent, because the effectiveness of a sorbent in dynamic processes and its capacity to endure huge sorbate fluxes are linked to its rate of sorption. Indeed, even if the equilibrium adsorption capacity is quite high, the adsorbent cannot be employed in industrial applications if the adsorption rate is too low.

**Fig. 9.** Comparison isotherm models and GC-PC experiment of CO₂ at 25 °C

### 3.4.3. Thermodynamic modeling

Aside from the isotherm parameters, thermodynamic parameters such as the standard Gibbs free energy change ($\Delta G^0$), the standard enthalpy change ($\Delta H^0$), and the standard entropy change ($\Delta S^0$) can be used to determine the nature of adsorption (i.e., the nature of the sorbent-sorbate interactions), whether physisorption and chemisorption. Thermodynamic data only describe a system's final state (i.e., its equilibrium adsorption capacity), whereas kinetics are concerned with how the system changes over time, with a focus on the rates of change. The laws of thermodynamics are used to calculate the mentioned parameters using the following equations. The adsorption enthalpy was evaluated using the Van't Hoff equation, Eq. 14, and from the
unification of two equations, Eq. 16 and Eq. 19 [99]:

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \] (16)

\[ \Delta G^0 = -RT \ln K_d \] (17)

\[ \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \] (18)

\[ K_d = \left( P_i - P_e \right) \left( \frac{V}{W} \right) \] (19)

where \( R \) is the gas constant [8.314 (J.mol\(^{-1}\)K\(^{-1}\))], \( T \) is the absolute temperature (°K), enthalpy (\( \Delta H^0 \)) is the slope, and entropy (\( \Delta S^0 \)) is the intercept that they are obtained from the plotting of \( \ln K_d \) against 1/T. Equations 12 and 13 were used to calculate the standard Gibbs free energy change of adsorption [93]. Table 5 shows the results of the estimated CO\(_2\) thermodynamic parameters. In terms of \( \Delta H^0 \), a negative or positive value indicates whether a process is exothermic or endothermic. Since the total energy adsorbed in bond breaking is less than the total energy released in bond formation between gas molecules and the surface of the sorbent in the negative form, the process is characterized by a release of energy in the form of heat to its surroundings. In the positive situation, however, the process is distinguished by the adsorption of energy in the form of heat from its surroundings. The physisorption process was represented by a value of less than 20 (kJ.mol\(^{-1}\)), whereas the chemisorption process was represented by a value of more than 40 (kJ.mol\(^{-1}\)) [99]. \( \Delta S^0 \) is a representation of the randomized and organized gas-solid interfaces, with \( \Delta S^0 > 0 \) representing more randomness and \( \Delta S^0 < 0 \) representing less randomness [90]. The Van't Hoff plot of the equilibrium constant of GC-PC adsorbent used for the estimation of \( \Delta S^0 \) and \( \Delta H^0 \) of the CO\(_2\) adsorption reaction in the temperature range from 298 °K to 328 °K is plotted in Fig. 10. The negative values of Gibbs free energy change (\( \Delta G^0 \)) and (\( \Delta S^0 \)), indicates that the adsorption process is exothermic and spontaneous [98]. Figure 11 depicts the percentage changes in CO\(_2\) adsorption as a function of temperature on the GC-PC adsorbent. This physisorption process is confirmed by
the fact that the percentage of adsorption capability for CO$_2$ rises as the temperature drops.

![Fig. 10. CO$_2$ Experimental Van’t Hoff plot on C-700](image)

![Fig. 11. CO$_2$ adsorption variation percentage vs. temperature on C-700](image)

| Table 5. Thermodynamic parameters of the GC-PC in CO$_2$ adsorption at 10 bar. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\Delta H$ (kJ/mol) | $\Delta S$ (kJ/mol K) | 25 °C | 35 °C | 45 °C | 55 °C |
|---------------------|---------------------|------|------|------|------|
| -23.208             | -0.05               | -8.313 | -7.814 | -7.314 | -6.8146 |

3.5. CO$_2$ isosteric heat of adsorption and regeneration
To determine the affinity of the guest adsorbate for the adsorbent, the Clausius-Clapeyron equation was used to compute the isosteric heat of adsorption (Q_{st}) based on the pure component adsorption isotherms at three temperatures (298, 308, and 318 °K). Figure 12 (a) depicts the isosteric heat of CO_{2} adsorption in the range of 33–44 kJ.mol^{-1}. The slopes of the straight lines may be utilized to determine the Q_{st} value after graphing lnP_{CO_{2}} vs. 1/T at a set specified adsorbed quantity of CO_{2}[100].

\[ \frac{-Q_{st}}{R} = \left( \frac{\partial \ln p}{\partial T} \right)_{n} \tag{20} \]

The computed value of Q_{st} (45 kJ.mol^{-1}) for the C-700 sorbent is less than 80 (kJ.mol^{-1}), implying that CO_{2} adsorption is physical and similar to other adsorbents utilizing porous carbon. The Q_{st} value declined quickly and became steady as the surface coverage and CO_{2} loading rose. This variability in Q_{st} can be ascribed to an energetically heterogeneous surface for CO_{2} capture [101]. The higher values of Q_{st} at the beginning of the sorption process can be correlated to CO_{2} adsorption on strong binding sites and the filling of ultrafine micropores. The Q_{st}, conversely, drops as the surface coverage rises. This is due to weaker interactions between restricted CO_{2} in larger pores and the surface [102].

The reusability of C-700 was investigated by repeating ten CO_{2} adsorption cycles with regeneration. As seen in Fig. 12(b), for the CO_{2} adsorption isotherms, there is no discernible decrease in the measured CO_{2} uptake over ten cycles. Aside from high CO_{2} capture, the adsorbent's ability to be recycled is a critical requirement for practical applications implying that celery can be used as a high-performance reusable sorbent for CO_{2} capture applications [1, 103]. One of the most important factors to consider is adsorbent reuse for economic reasons. The adsorbent potential does not change significantly after each cycle, as seen in Fig. 12(b). GC-PC can be used in manufacturing applications as a low-cost and cost-effective adsorbent due to the benefits of the
regeneration process.

Fig. 12. Isosteric heat of CO\textsubscript{2} adsorption C-700 (a), Recycling performance of C-700 for CO\textsubscript{2} adsorption at 0 °C and 25 °C within ten repeated cycles (b)

3.6. Comparison of various adsorbents

The adsorption capacities of GC-PC used in this study are compared to those of a variety biomass precursor-derived porous adsorbents previously used for CO\textsubscript{2} capture, as shown in Fig. 13. As shown, GC-PC has significantly higher adsorption capacities than many other adsorbents previously mentioned. The findings of this research can be used to develop a novel CO\textsubscript{2} capture GC-PC synthesis adsorbent that is both effective and high-performing [60, 103-111].
Fig. 13. Comparison performance of different precursor biomass porous carbons for CO$_2$ uptake at 273 K and 1 bar

4. Conclusions

In this work, a green self-activating synthesis system was introduced for the preparation of porous carbon from waste carbon precursors. As a typical case, hierarchically porous carbon was synthesized from celery waste. This system is environmentally friendly, simple, cost-effective, and a one-step self-activating method. During pyrolysis, the activating reagents are the gaseous pyrolyzation products of the precursors, resulting in the synthesis of porous carbon without the need for an additional activator. Achievement specific surface areas as high as about 1170 m$^2$g$^{-1}$ confirm the proper performance of the designed activating system. Based on the observed characteristics, the CO$_2$ capture capacities of the best sorbent were evaluated. The celery precursor activated at 700 °C validates an important perspective for CO$_2$ capture. At low temperature and pressure, the synthesized porous carbons adsorbed 5 (mmolg$^{-1}$) at 0 °C and 2.03 (mmolg$^{-1}$) at 25 °C under 1 bar. Adsorption experiments in the temperature range of 25 °C to 55 °C under pressures
up to 10 (bar) were conducted with an adsorption duration of 75 minutes. The CO₂ adsorption kinetics on the porous carbon closely followed the fractional-order kinetic model. After comparing experimental adsorption effects by models, the Langmuir, fractional-order, and pseudo-second-order isotherm models were well equipped with adsorption isotherm and kinetic adsorption models, respectively. The Langmuir isotherm equation matched the equilibrium results very well, and the maximal adsorption potential for CO₂ was found to be 9.57 (mmolg⁻¹) at 298 °K and 10 bar. Adsorption was a possible, spontaneous, and physisorption process, as shown by the negative values of thermodynamic parameters. The physisorption process was reported by enthalpy 23.2 (KJ.mol⁻¹). The effectiveness of porous carbon was very successful after 10 cycles of regeneration. The produced porous carbon could be promising for industrial CO₂ adsorption technologies based on improved adsorbents, compared to the other biomass adsorbents investigated, due to its high-performance efficiency and high-efficiency regeneration.

**Declaration of Competing Interest**

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

**Acknowledgement**

This research work was conducted under the kind support of the advanced technologies department of Iran University of Science and Technology.

**AUTHOR INFORMATION**

* Corresponding Authors

* Tel.: +98 21 73225804; +98 21 73225812; +98 21 77240496

Email corresponding author: Motejadded@iust.ac.ir (H.B.M. Emrooz); aghaemi@iust.ac.ir (A. Ghaemi).
References

1. Ma, X., et al., Heteroatom-doped porous carbons exhibit superior CO2 capture and CO2/N2 selectivity: Understanding the contribution of functional groups and pore structure. Separation and Purification Technology, 2021. 259: p. 118065.

2. Singh, G., et al., Emerging trends in porous materials for CO2 capture and conversion. Chemical Society Reviews, 2020. 49(13): p. 4360-4404.

3. Bhattacharya, M. and M.K. Mandal, Synthesis of rice straw extracted nano-silica-composite membrane for CO2 separation. Journal of Cleaner Production, 2018. 186: p. 241-252.

4. Yave, W., A. Car, and K.-V. Peinemann, Nanostructured membrane material designed for carbon dioxide separation. Journal of Membrane Science, 2010. 350(1-2): p. 124-129.

5. Bui, M., et al., Carbon capture and storage (CCS): the way forward. Energy & Environmental Science, 2018. 11(5): p. 1062-1176.

6. D'Alessandro, D.M., B. Smit, and J.R. Long, Carbon dioxide capture: prospects for new materials. Angewandte Chemie International Edition, 2010. 49(35): p. 6058-6082.

7. Zhang, W., Y. Bao, and A. Bao, Preparation of nitrogen-doped hierarchical porous carbon materials by a template-free method and application to CO2 capture. Journal of Environmental Chemical Engineering, 2020. 8(3): p. 103732.

8. Dong, H., et al., B40 fullerene: an efficient material for CO2 capture, storage and separation. Current Applied Physics, 2015. 15(9): p. 1084-1089.

9. Panda, D., et al., Lab cooked MOF for CO2 capture: a sustainable solution to waste management. Journal of Chemical Education, 2020. 97(4): p. 1101-1108.

10. Adeniran, B. and R. Mokaya, Low temperature synthesized carbon nanotube superstructures with superior CO2 and hydrogen storage capacity. Journal of Materials Chemistry A, 2015. 3(9): p. 5148-5161.

11. Fang, H., et al., First principles derived, transferable force fields for CO2 adsorption in Na-exchanged cationic zeolites. Physical Chemistry Chemical Physics, 2013. 15(31): p. 12882-12894.

12. Mashhadimoslem, H., et al., Biomass derived hierarchical porous carbon for high-performance O2/N2 adsorption; a new green self-activation approach. RSC Advances, 2021. 11(57): p. 36125-36142.

13. Ai, N., et al., Facile synthesis of macroalgae-derived graphene adsorbents for efficient CO2 capture. Process Safety and Environmental Protection, 2021. 148: p. 1048-1059.

14. Li, K., et al., Pine cone shell-based activated carbon used for CO2 adsorption. Journal of Materials Chemistry A, 2016. 4(14): p. 5223-5234.

15. Srinivas, G., et al., Exceptional CO2 capture in a hierarchically porous carbon with simultaneous high surface area and pore volume. Energy & Environmental Science, 2014. 7(1): p. 335-342.

16. Emrooz, H.B.M., M. Maleki, and A. Rahmani, Azolla-derived hierarchical nanoporous carbons: From environmental concerns to industrial opportunities. Journal of the Taiwan Institute of Chemical Engineers, 2018. 91: p. 281-290.

17. Sun, H., B. Yang, and A. Li, Biomass derived porous carbon for efficient capture of carbon dioxide, organic contaminants and volatile iodine with exceptionally high uptake. Chemical Engineering Journal, 2019. 372: p. 65-73.

18. Singh, V.K. and E.A. Kumar, Measurement and analysis of adsorption isotherms of CO2 on activated carbon. Applied Thermal Engineering, 2016. 97: p. 77-86.
19. Saha, D. and M.J. Kienbaum, "Role of oxygen, nitrogen and sulfur functionalities on the surface of nanoporous carbons in CO2 adsorption: a critical review." Microporous and Mesoporous Materials, 2019. 287: p. 29-55.

20. Shou, W., et al., "Ordered Mesoporous Carbon: Fabrication, Characterization, and Application as Adsorbents," in Dekker Encyclopedia of Nanoscience and Nanotechnology. 2015, CRC Press. p. 1-14.

21. Hossein Mashhadimoslem, M.V., Mobin Safarzadeh, Ahad Ghaemi, Farnoush Fathalian, and Ali Maleki, "Development of Predictive Models for Activated Carbon Synthesis from Different Biomass for CO2 Adsorption Using Artificial Neural Networks." Industrial & Engineering Chemistry Research, 2021.

22. Raganati, F., R. Chirone, and P. Ammendola, "CO2 capture by temperature swing adsorption: working capacity as affected by temperature and CO2 partial pressure." Industrial & Engineering Chemistry Research, 2020. 59(8): p. 3593-3605.

23. Presser, V., et al., "Effect of pore size on carbon dioxide sorption by carbide derived carbon." Energy & Environmental Science, 2011. 4(8): p. 3059-3066.

24. Ma, X., et al., "A novel activating strategy to achieve highly porous carbon monoliths for CO2 capture." Journal of Materials Chemistry A, 2014. 2(13): p. 4819-4826.

25. Park, J.M. and S.H. Jhung, "Remarkable adsorbent for removal of bisphenol A and S from water: Porous carbon derived from melamine/polyaniline." Chemosphere, 2021. 268: p. 129342.

26. Zhang, W., et al., "Direct carbonization of rice husk to prepare porous carbon for supercapacitor applications." Energy, 2017. 128: p. 618-625.

27. Wang, H., et al., "Combined grand canonical Monte Carlo and finite volume method simulation method for investigation of direct air capture of low concentration CO2 by 5A zeolite adsorbent bed." International Journal of Heat and Mass Transfer, 2018. 126: p. 1219-1235.

28. Zhao, Y.-Q., et al., "Hierarchically porous and heteroatom doped carbon derived from tobacco rods for supercapacitors." Journal of power sources, 2016. 307: p. 391-400.

29. He, S., et al., "Facile preparation of N-doped activated carbon produced from rice husk for CO2 capture." Journal of Colloid and Interface Science, 2021. 582: p. 90-101.

30. Manocha, S.M., "Porous carbons." Sadhana, 2003. 28(1-2): p. 335-348.

31. González-García, P., "Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications." Renewable and Sustainable Energy Reviews, 2018. 82: p. 1393-1414.

32. Pal, A., K.A. Rocky, and B.B. Saha, "Thermodynamic analysis of promising biomass-derived activated carbons/CO2 based adsorption cooling systems." Journal of CO2 Utilization, 2021. 46: p. 101457.

33. Pérez-Mayoral, E., et al., "New and advanced porous carbon materials in fine chemical synthesis. Emerging precursors of porous carbons." Catalysts, 2019. 9(2): p. 133.

34. Emrooz, H.B.M., et al., "Adsorption mechanism of a cationic dye on a biomass-derived micro-and mesoporous carbon: structural, kinetic, and equilibrium insight." Biomass Conversion and Biorefinery, 2020: p. 1-12.

35. Zhang, C., et al., "Enhancement of CO2 capture on biomass-based carbon from black locust by KOH activation and ammonia modification." Energy & Fuels, 2016. 30(5): p. 4181-4190.

36. He, J., et al., "One-step large-scale fabrication of nitrogen doped microporous carbon by self-activation of biomass for supercapacitors application." Journal of Energy Storage, 2019. 21: p. 94-104.

37. Rodríguez-Reinoso, F. and M. Molina-Sabio, "Activated carbons from lignocellulosic materials by chemical and/or physical activation: an overview." Carbon, 1992. 30(7): p. 1111-1118.
38. Kosheleva, R.I., A.C. Mitropoulos, and G.Z. Kyzas, *Synthesis of activated carbon from food waste*. Environmental Chemistry Letters, 2019. **17**(1): p. 429-438.
39. Yin, J., et al., *Synthesis strategies of porous carbon for supercapacitor applications*. Small Methods, 2020. **4**(3): p. 1900853.
40. Xia, C. and S.Q. Shi, *Self-activation for activated carbon from biomass: theory and parameters*. Green Chemistry, 2016. **18**(7): p. 2063-2071.
41. Wang, H., et al., *Mesopore-dominant nitrogen-doped carbon with a large defect degree and high conductivity via inherent hydroxyapatite-induced self-activation for lithium-ion batteries*. RSC Advances, 2018. **8**(22): p. 12204-12210.
42. Dai, J., et al., *Facile synthesis of porous carbon sheets from potassium acetate via in-situ template and self-activation for highly efficient chloramphenicol removal*. Journal of Alloys and Compounds, 2018. **732**: p. 222-232.
43. Bommier, C., et al., *Self-activation of cellulose: A new preparation methodology for activated carbon electrodes in electrochemical capacitors*. Nano Energy, 2015. **13**: p. 709-717.
44. Sowbhagya, H., *Chemistry, technology, and nutraceutical functions of celery (Apium graveolens L.): an overview*. Critical reviews in food science and nutrition, 2014. **54**(3): p. 389-398.
45. Zhang, T., et al., *Efficient removal of lead from solution by celery-derived biochars rich in alkaline minerals*. Bioresource technology, 2017. **235**: p. 185-192.
46. Mohebali, S., D. Bastani, and H. Shayesteh, *Methylene blue removal using modified celery (Apium graveolens) as a low-cost biosorbent in batch mode: Kinetic, equilibrium, and thermodynamic studies*. Journal of molecular structure, 2018. **1173**: p. 541-551.
47. Demiral, İ., C. Samdan, and H. Demiral, *Enrichment of the surface functional groups of activated carbon by modification method*. Surfaces and Interfaces, 2021. **22**: p. 100873.
48. Xu, H., et al., *Adsorption of Cr (VI) from aqueous solutions using novel activated carbon spheres derived from glucose and sodium dodecylbenzene sulfonate*. Science of The Total Environment, 2021. **759**: p. 143457.
49. Doğan, M., et al., *Activated carbon synthesis from tangerine peel and its use in hydrogen storage*. Journal of the Energy Institute, 2020. **93**(6): p. 2176-2185.
50. Luo, J., et al., *A comparative study of lignocellulosic nanofibrils isolated from celery using oxalic acid hydrolysis followed by sonication and mechanical fibrillation*. Cellulose, 2019. **26**(9): p. 5237-5246.
51. Ruz, P., et al., *Structural evolution of turbostratic carbon: Implications in H2 storage*. Solid State Sciences, 2016. **62**: p. 105-111.
52. Sahu, A., S. Sen, and S.C. Mishra, *Economical way of processing activated carbon from Calotropis gigantea and its suitability for application in Lithium/Sodium ion batteries*. Diamond and Related Materials, 2020. **108**: p. 107931.
53. Du, W., et al., *Nitrogen-doped hierarchical porous carbon using biomass-derived activated carbon/carbonized polyaniline composites for supercapacitor electrodes*. Journal of Electroanalytical Chemistry, 2018. **827**: p. 213-220.
54. Zhu, X.-L., et al., *Activated carbon produced from paulownia sawdust for high-performance CO2 sorbents*. Chinese Chemical Letters, 2014. **25**(6): p. 929-932.
55. Singh, G., et al., *A combined strategy of acid-assisted polymerization and solid state activation to synthesize functionalized nanoporous activated biocarbons from biomass for CO2 capture*. Microporous and Mesoporous Materials, 2018. **271**: p. 23-32.
56. Bakti, A. and P. Gareso, *Characterization of active carbon prepared from coconuts shells using FTIR, XRD and SEM techniques*. Jurnal Ilmiah Pendidikan Fisika Al-Biruni, 2018. **7**(1): p. 33-39.
57. Singh, G., et al., *Convenient design of porous and heteroatom self-doped carbons for CO2 capture*. Microporous and Mesoporous Materials, 2019. **287**: p. 1-8.
58. Du, J., et al., Waste chrysanthemum tea derived hierarchically porous carbon for CO2 capture. Journal of Renewable and Sustainable Energy, 2017. 9(6): p. 064901.
59. Yu, S., et al., Self-template and self-activation synthesis of nitrogen-doped hierarchical porous carbon for supercapacitors. Journal of Power Sources, 2018. 405: p. 132-141.
60. Huang, G.-g., et al., Activated carbons prepared by the KOH activation of a hydrochar from garlic peel and their CO2 adsorption performance. New Carbon Materials, 2019. 34(3): p. 247-257.
61. Niu, J., et al., Porous carbon electrodes with battery-capacitive storage features for high performance Li-ion capacitors. Energy Storage Materials, 2018. 12: p. 145-152.
62. Wang, A., et al., Cleanly synthesizing rotten potato-based activated carbon for supercapacitor by self-catalytic activation. Journal of Cleaner Production, 2021. 283: p. 125385.
63. Zhou, M., et al., Oil tea shell derived porous carbon with an extremely large specific surface area and modification with MnO2 for high-performance supercapacitor electrodes. Applied Materials Today, 2017. 7: p. 47-54.
64. Smith, L.M., et al., EFFECT OF WOOD SPECIES ON THE PORE VOLUME AND SURFACE AREA OF ACTIVATED CARBON DERIVED FROM THE SELF-ACTIVATION PROCESS. Wood and Fiber Science, 2020. 52(2): p. 191-207.
65. Liu, Y., et al., Biomass-derived hierarchical porous carbons: boosting the energy density of supercapacitors via an ionothermal approach. Journal of Materials Chemistry A, 2017. 5(25): p. 13009-13018.
66. Alsaedi, A. and B. Ahmad, The preparation of CuO@ ZnO core-shell materials as high-stability anodes for lithium-ion batteries. Int. J. Electrochem. Sci, 2019. 14: p. 8973-8985.
67. Singh, G., et al., Biomass derived porous carbon for CO2 capture. Carbon, 2019. 148: p. 164-186.
68. Hunt, J., et al., Microwave-specific enhancement of the carbon–carbon dioxide (Boudouard) reaction. The Journal of Physical Chemistry C, 2013. 117(51): p. 26871-26880.
69. Jiang, C., et al., Activated carbons prepared by indirect and direct CO2 activation of lignocellulosic biomass for supercapacitor electrodes. Renewable Energy, 2020. 155: p. 38-52.
70. Gaskell, D.R. and D.E. Laughlin, Introduction to the Thermodynamics of Materials, Sixth Edition. 2017: CRC Press.
71. Kueasook, R., et al., Green and facile synthesis of hierarchically porous carbon monoliths via surface self-assembly on sugarcane bagasse scaffold: influence of mesoporosity on efficiency of dye adsorption. Microporous and Mesoporous Materials, 2020. 296: p. 110005.
72. Deng, S., et al., Superior CO2 adsorption on pine nut shell-derived activated carbons and the effective micropores at different temperatures. Chemical Engineering Journal, 2014. 253: p. 46-54.
73. Mistar, E.M., T. Alfatah, and M.D. Supardan, Synthesis and characterization of activated carbon from Bambusa vulgaris striata using two-step KOH activation. Journal of Materials Research and Technology, 2020. 9(3): p. 6278-6286.
74. Xing, X., et al., Preparation and analysis of straw activated carbon synergetic catalyzed by ZnCl2-H3PO4 through hydrothermal carbonization combined with ultrasonic assisted immersion pyrolysis. Waste Management, 2019. 89: p. 64-72.
75. Kim, B., et al., Spent coffee derived hierarchical porous carbon and its application for energy storage. Journal of Porous Materials, 2020. 27(2): p. 451-463.
76. Rao, L., et al., Nitrogen enriched porous carbons from d-glucose with excellent CO2 capture performance. Chemical Engineering Journal, 2019. 362: p. 794-801.
77. Li, Z., et al., Adsorption of congo red and methylene blue dyes on an ashitaba waste and a walnut shell-based activated carbon from aqueous solutions: Experiments, characterization and physical interpretations. Chemical Engineering Journal, 2020. 388: p. 124263.
78. Wazir, A.H., I.U. Wazir, and A.M. Wazir, *Preparation and characterization of rice husk based physical activated carbon*. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2020: p. 1-11.

79. Shin, S., et al., *A study on the effect of heat treatment on functional groups of pitch based activated carbon fiber using FTIR*. Carbon, 1997. 35(12): p. 1739-1743.

80. Li, D., et al., *Improving low-pressure CO2 capture performance of N-doped active carbons by adjusting flow rate of protective gas during alkali activation*. Carbon, 2017. 114: p. 496-503.

81. Sun, B., et al., *Waste-cellulose-derived porous carbon adsorbents for methyl orange removal*. Chemical Engineering Journal, 2019. 371: p. 55-63.

82. Wang, L., et al., *Nitrogen-doped hierarchical porous carbon for supercapacitors with high rate performance*. Microporous and Mesoporous Materials, 2019. 279: p. 439-445.

83. Zheng, B., et al., *Ultrafast ammonia-driven, microwave-assisted synthesis of nitrogen-doped graphene quantum dots and their optical properties*. Nanophotonics, 2017. 6(1): p. 259-267.

84. Rao, L., et al., *N-doped porous carbons from low-temperature and single-step sodium amide activation of carbonized water chestnut shell with excellent CO2 capture performance*. Chemical Engineering Journal, 2019. 359: p. 428-435.

85. Ogungbenro, A.E., et al., *Synthesis and characterization of activated carbon from biomass date seeds for carbon dioxide adsorption*. Journal of Environmental Chemical Engineering, 2020. 8(5): p. 104257.

86. Zhu, M., et al., *Preparation of pineapple waste-derived porous carbons with enhanced CO2 capture performance by hydrothermal carbonation-alkali metal oxalates assisted thermal activation process*. Chemical Engineering Research and Design, 2019. 146: p. 130-140.

87. Bottani, E.J. and J.M. Tascón, *Adsorption by carbons*. 2011: Elsevier.

88. Singh, J., H. Bhunia, and S. Basu, *Adsorption of CO2 on KOH activated carbon adsorbents: Effect of different mass ratios*. Journal of environmental management, 2019. 250: p. 109457.

89. Taheri, F.S., et al., *High CO2 adsorption on amine-functionalized improved mesoporous silica nanotube as an eco-friendly nanocomposite*. Energy & Fuels, 2019. 33(6): p. 5384-5397.

90. Taheri, F.S., A. Ghaemi, and A. Maleki, *High efficiency and eco-friendly TEPA-functionalized adsorbent with enhanced porosity for CO2 capture*. Energy & Fuels, 2019. 33(11): p. 11465-11476.

91. Wu, D., et al., *Nitrogen/oxygen Co-doped porous carbon derived from biomass for low-pressure CO2 capture*. Industrial & Engineering Chemistry Research, 2020. 59(31): p. 14055-14063.

92. Niu, M., et al., *Amine-impregnated mesoporous silica nanotube as an emerging nanocomposite for CO2 capture*. ACS applied materials & interfaces, 2016. 8(27): p. 17312-17320.

93. Wang, X., Q. Guo, and T. Kong, *Tetraethylenepentamine-modified MCM-41/silica gel with hierarchical mesoporous structure for CO2 capture*. Chemical Engineering Journal, 2015. 273: p. 472-480.

94. Baysal, M., et al., *Preparation of high surface area activated carbon from waste-biomass of sunflower piths: Kinetics and equilibrium studies on the dye removal*. Journal of environmental chemical engineering, 2018. 6(2): p. 1702-1713.

95. Singh, V.K. and E.A. Kumar, *Comparative studies on CO2 adsorption kinetics by solid adsorbents*. Energy Procedia, 2016. 90: p. 316-325.

96. Hu, Q. and Z. Zhang, *Application of Dubinin–Radushkevich isotherm model at the solid/solution interface: a theoretical analysis*. Journal of Molecular Liquids, 2019. 277: p. 646-648.

97. Zhou, J., et al., *Measurements and modelling of CH4 and CO2 adsorption behaviors on shales: Implication for CO2 enhanced shale gas recovery*. Fuel, 2019. 251: p. 293-306.

98. Rashidi, N.A., S. Yusup, and A. Borhan, *Isotherm and thermodynamic analysis of carbon dioxide on activated carbon*. Procedia engineering, 2016. 148: p. 630-637.
99. Raganati, F., et al., *Isotherms and thermodynamics of CO2 adsorption on a novel carbon-magnetite composite sorbent*. Chemical engineering research and design, 2018. 134: p. 540-552.

100. Zhang, P., et al., *A new choice of polymer precursor for solvent-free method: Preparation of N-enriched porous carbons for highly selective CO2 capture*. Chemical Engineering Journal, 2019. 355: p. 963-973.

101. Wang, Y., et al., *Nitrogen and oxygen codoped porous carbon with superior CO2 adsorption performance: a combined experimental and DFT calculation study*. Industrial & Engineering Chemistry Research, 2019. 58(29): p. 13390-13400.

102. Balou, S., S.E. Babak, and A. Priye, *Synergistic effect of nitrogen doping and ultra-microporosity on the performance of biomass and microalgae-derived activated carbons for CO2 capture*. ACS Applied Materials & Interfaces, 2020. 12(38): p. 42711-42722.

103. Zhang, X., et al., *Microporous carbon nanoflakes derived from biomass cork waste for CO2 capture*. Science of the Total Environment, 2020. 748: p. 142465.

104. Wang, R., et al., *Promising porous carbon derived from celtuce leaves with outstanding supercapacitance and CO2 capture performance*. ACS applied materials & interfaces, 2012. 4(11): p. 5800-5806.

105. Hong, S.-M., et al., *CO2 capture in the sustainable wheat-derived activated microporous carbon compartments*. Scientific reports, 2016. 6(1): p. 1-10.

106. González, A., et al., *Sustainable biomass-based carbon adsorbents for post-combustion CO2 capture*. Chemical engineering journal, 2013. 230: p. 456-465.

107. Parshetti, G.K., S. Chowdhury, and R. Balasubramanian, *Biomass derived low-cost microporous adsorbents for efficient CO2 capture*. Fuel, 2015. 148: p. 246-254.

108. Wang, Q., et al., *Influence of CO2 exposure on high-pressure methane and CO2 adsorption on various rank coals: implications for CO2 sequestration in coal seams*. Energy & Fuels, 2015. 29(6): p. 3785-3795.

109. Chen, T., et al., *CO2 adsorption on crab shell derived activated carbons: contribution of micropores and nitrogen-containing groups*. Rsc Advances, 2015. 5(60): p. 48323-48330.

110. Li, D., et al., *Production of highly microporous carbons with large CO2 uptakes at atmospheric pressure by KOH activation of peanut shell char*. Journal of Porous Materials, 2015. 22(6): p. 1581-1588.

111. Wei, H., et al., *Granular bamboo-derived activated carbon for high CO2 adsorption: the dominant role of narrow micropores*. ChemSusChem, 2012. 5(12): p. 2354-2360.