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Tuning Microporosity in *Pterospermum acerifolium* derived Activated Carbons for CO₂ capture: Influence of KOH and H₃PO₄ activation on Adsorption Performance

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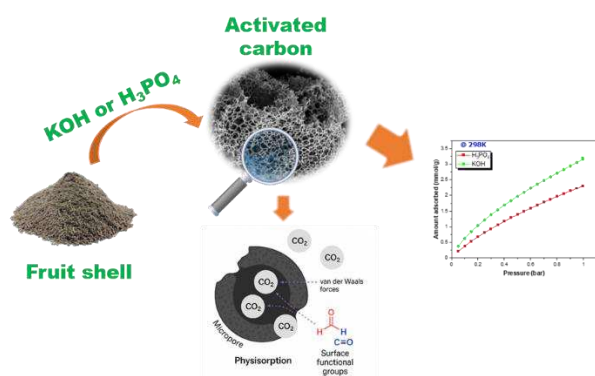
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Abstract

Sustainable carbon-based adsorbents derived from under-utilized biomass are gaining increasing attention for CO₂ capture owing to their tunable pore structure and surface chemistry. In this study, *Pterospermum acerifolium* were prepared via H₃PO₄ and KOH activation and comparatively evaluated to elucidate structure performance relationships. Ultimate analysis, Thermogravimetric analysis, Transmission Electron Microscopy and X-Ray Spectroscopy analysis were carried out for activated carbons to understand its physicochemical properties. At 298K and 1 bar, the KOH-activated carbon achieved a CO₂ uptake of 3.35mmol/g, exceeding that of the H₃PO₄-activated carbon. Equilibrium data were best described by the Sips model, while kinetics analysis followed pseudo-first order behaviour, indicating physisorption dominance. Furthermore, KOH-activated carbon retained approximately 96% of its initial capacity after 20 cycles and achieved 18.53 mmol/g at 30°C and 30 bar. These findings highlight the critical role of activation strategy in tailoring pore structure and optimizing CO₂ adsorption performance of biomass-derived activated carbons.

Keywords: Activated carbon, CO₂ adsorption, Sustainable adsorbents, Physisorption, Sips model



1. Introduction

The greenhouse effect plays a pivotal role in maintaining Earth's climatic stability by trapping infrared radiation through naturally occurring greenhouse gases (GHGs), forming a "blanket" that sustains conditions favourable for life. However, the rapid rise in anthropogenic GHG emissions principally carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), water vapor, and fluorinated gases has significantly intensified global warming and disrupted the planet's energy balance [1]. To quantify the relative contribution of individual GHGs to climate forcing, the Intergovernmental Panel on Climate Change (IPCC) introduced the concept of Global Warming Potential (GWP) in 1990, identifying CO₂ as the dominant contributor due to its long atmospheric lifetime and continuously increasing concentration. Since the onset of the Industrial Revolution, global CO₂ emissions have increased dramatically from approximately 6 billion tonnes in 1950 to nearly 20 billion tonnes by 1990 and continue to rise, reaching a record concentration of 430 ppm in 2025, corresponding to nearly a 15% increase over the past two decades (NOAA, NASA, IEA). Anthropogenic activities such as fossil fuel combustion, industrial operations, and transportation have surpassed natural emission rates, with fossil fuel-based power generation alone accounting for nearly 33–40% of total CO₂ emissions [2].

In response, carbon capture, utilization, and storage (CCUS) technologies have emerged as essential strategies for large-scale mitigation of CO₂ emissions from major industrial sectors, including thermal power, cement, and steel production. Four primary CO₂ capture pathways—chemical looping combustion (CLC) [3], oxyfuel combustion [4], pre-combustion [5], and post-combustion [6] have been extensively investigated. Among these, post-combustion capture is regarded as the most adaptable and technologically mature, allowing retrofitting in existing facilities without substantial modification [7]. Within these frameworks, various CO₂ separation techniques have been developed, including absorption [8], adsorption [9], membrane separation [10], cryogenic distillation [11], and hydrate-based processes [12]. Chemical absorption using amine-based solvents such as monoethanolamine (MEA) [13], diethanolamine (DEA) [14], and piperazine [15] remains the most established approach for post-combustion capture; however, it suffers from high regeneration energy demands, solvent degradation, and corrosion issues. In contrast, adsorption-based processes have garnered increasing attention due to their low energy consumption, ease of regeneration, and environmental compatibility.

A wide range of porous adsorbents, including metal organic frameworks (MOFs) [16], zeolites [17], and carbonaceous materials have been explored for CO₂ capture. Although MOFs and zeolites exhibit exceptionally high surface areas, high thermal stability and tunable structures, their high synthesis cost and poor moisture stability restrict their practical application. Carbon-based sorbents, such as activated carbon and biochar, overcome many of these drawbacks owing to their chemical robustness, cost-effectiveness, hydrophobicity, and superior regeneration characteristics, rendering them among the most promising candidates for sustainable CO₂ capture and climate change mitigation.

Activated carbon, a highly porous and versatile carbon-based adsorbent, is widely recognized for its exceptional surface area, tunable pore structure, and chemical stability, making it effective material for CO₂ capture [18]. Biomass-derived activated carbon, produced from renewable sources such as agricultural or lignocellulosic residues [19][20], offers a sustainable and low-cost alternative to fossil-based precursors while contributing to carbon neutrality. Activation via physical (steam or CO₂) or chemical (KOH, H₃PO₄, ZnCl₂) [21][22][23] methods generate a well-developed pore network and abundant surface functionalities that promote efficient CO₂ adsorption via physisorption and weak chemisorption. The ability to tailor pore characteristics and surface chemistry through controlled synthesis further enhances the performance of biomass-based activated carbons, for scalable and environmentally benign CO₂ capture applications.

Recent investigations on biomass-derived activated carbons have demonstrated their considerable promise for CO₂ adsorption by revealing how textural and chemical properties govern performance. For instance, walnut shell-derived activated carbons prepared via microwave steam activation exhibited specific surface areas of 570-690 m² g⁻¹ and pore volumes of 0.26-0.34 cm³ g⁻¹, with adsorption behaviour dominated micropores (< 0.8 nm) at ambient pressure and by larger pores (1.6-2.4 nm) at elevated pressure [24]. In another study, rice-husk-derived activated carbons produced through a two-step KOH activation achieved specific surface areas exceeding 2000 m² g⁻¹ and displayed enhanced CO₂ uptake, highlighting the role of KOH activation in generating narrow micropores favourable for CO₂ binding [25][26]. More broadly, a recent review summarizing biomass-based carbon materials reported maximum CO₂ adsorption capacities exceeding 20 mmol g⁻¹ under high pressures for activated carbons derived from feedstocks such as coffee grounds or mesquite wood [27]. Collectively, these studies indicated that high CO₂ adsorption performance associated with

large micropore volume (particularly ultra-micropores <0.8 nm), large specific surface area, appropriate pore-size distribution extending into the mesopore range for high-pressure adsorption, and suitable surface chemical functionality (e.g., heteroatom doping) to enhance CO₂ binding strength.

Despite these instances, the practical application of biomass-derived activated carbons remains constrained by the need to optimize activation conditions that simultaneously balance surface area, pore structure, and surface functionality for efficient and regenerable CO₂ adsorption. Previous studies have largely focused on individual activation routes, while systematic comparisons between activation agents particularly H₃PO₄ and KOH regarding their influence on textural, chemical, and thermodynamic characteristics toward CO₂ adsorption remains limited. Moreover, systematic investigations integrating physicochemical characterization (ultimate analysis, TGA, XPS) with adsorption isotherm, kinetic, thermodynamic, and regeneration studies are still scarce for *Pterospermum acerifolium*-based activated carbons.

The novelty of the present work lies in extending the application of developed sustainable adsorbent using *Pterospermum acerifolium*, a biomass resource which offers a pathway for environmental remediation and greenhouse gas mitigation. Accordingly, this study aims to evaluate two *Pterospermum acerifolium*-derived activated carbons, using H₃PO₄ and KOH, with the objective of elucidating the relationship between activation chemistry, pore architecture, and surface functionality on CO₂ adsorption performance. The adsorption behaviour is analyzed using equilibrium isotherms and kinetic models, while thermodynamic parameters are employed to access feasibility and spontaneity of adsorption. In addition, cyclic adsorption-desorption studies are conducted to examine the stability and regenerability of the adsorbents. This comprehensive investigation provides insights into optimizing activation strategies for the development of cost-effective, high-performance, and sustainable carbon-based materials for CO₂ capture.

2. Experimental Section

2.1 Preparation and characterization of activated carbon

Pterospermum acerifolium fruit capsules are indigenous to Southeast Asian countries and are abundantly available within the campus of National Institute of Technology Rourkela, Odisha. Owing to wide availability and cost effectiveness of this biomass, it has been employed as a precursor for activated carbon production using with chemical activation with

H₃PO₄ and KOH as activating agents. Box-Benhken Design (BBD) statistical tool was utilized to optimize the synthesis parameters namely impregnation ratio, activation temperature and activating time based on responses variables including yield percentage and iodine value. The detailed synthesis procedure, optimization strategy and preliminary tests conducted to access the suitability of the precursor have been reported in earlier studies [28].

Previous investigations on prepared activated carbons included extensive physicochemical characterization using proximate analysis, Thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) surface area analysis, RAMAN spectroscopy, and Field Emission Scanning Electron Microscope (FESEM) [28]. In addition to these analyses, the present work further evaluates the activated carbon using ultimate analysis and X-ray photospectroscopy (XPS) to gain deeper insights into bulk elemental composition and surface chemical characterization.

Ultimate analysis was carried out using CHNS analyzer (Flash Smart V CHNS/O, Thermofisher Scientific) to determine the carbon, hydrogen, nitrogen, and sulfur contents of activated carbons, providing information on material purity and chemical nature of the activated carbon. Surface chemical states and elemental composition were investigated using XPS (PHI 5000 Versa Prob II, FEI Inc), enabling identification of surface functional groups and heteroatom incorporation resulting from the activation process. The synthesised activated carbons subsequently were employed for CO₂ adsorption in BELSORP-max II (Microtrac BELCorp). The physisorption of CO₂ was evaluated at ambient room temperature (298K). Prior to adsorption measurements, all samples were degassed at 200°C for 5 hours to remove physically adsorbed moisture and gases.

2.2 Volumetric CO₂ adsorption measurements

Determination of amount of carbon dioxide adsorbed on the activated carbon was performed using volumetric method, as illustrated in figure 1. Fabricated setup consisted of a high pressure reference cell, sample cell and interconnecting stainless steel pipes. Preceding adsorption analysis, the activated carbon samples placed in the sample cell were oven dried at 150°C for 4 to 5 hours to remove inherent moisture. Stainless steel fittings and bolts were used to secure the system and connect the flow lines. Two pressure gauge were installed in the system, one for monitoring the pressure in the reference cell and the other for measuring the pressure in sample cell. The entire assembly was immersed in a thermostatic bath to

maintain a constant temperature in both the cells. The setup was leak-tested before each experiment to ensure system integrity.

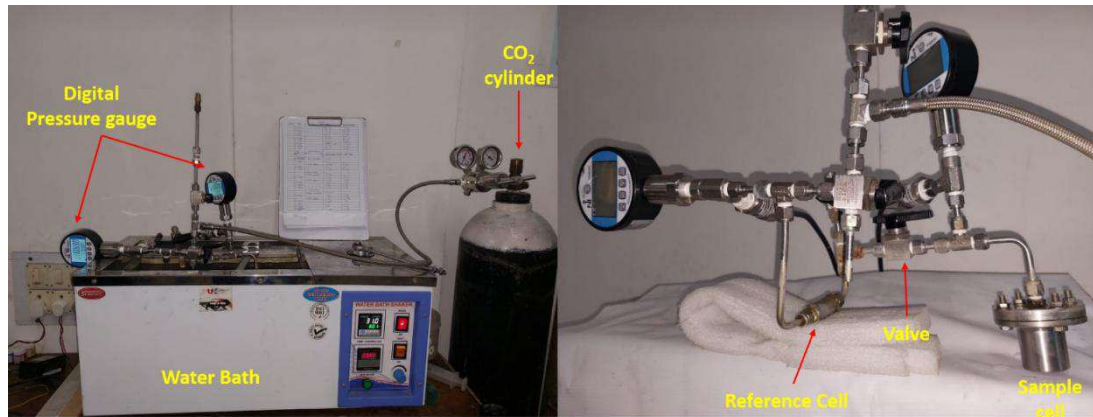


Figure 1 Volumetric gas adsorption set up with the detailed view and labelling

Dead volume (void volume) of the adsorption system was determined experimentally using helium gas. Helium, being a non-adsorbing gas, inert gas can invade into every accessible pore volumes of the AC without undergoing adsorbed. Dried AC was loaded into the sample cell, which was then sealed and evacuated under vacuum. Subsequently, a known amount of helium gas (0.5 to 2 bar) was introduced for void volume determination. The volume of sample cell, reference cell and void volume were calculated using the following relationships. The volume of the sample cell V_S was calculated using equation 1

$$V_S = \frac{b}{b-a} \times V_B \quad \text{Eq. (1)}$$

where, a and b are constants without iron balls placed in sample cell and with iron balls present in sample cell respectively; V_B is the volume of iron balls placed in the cell, P_{S1} and P_{S2} are helium pressure in sample cell before and during equilibrium, P_{r1} and P_{r2} are reference cell pressure due to helium injection before and at equilibrium. Z_{r1} , Z_{r2} , Z_{S1} and Z_{S2} are compressibility factor at varying pressure and temperatures at reference cell and sample cell respectively.

The volume of the reference cell V_r was calculated using equation 2

$$V_r = \frac{ab}{b-a} \times V_{IB} \quad \text{Eq. (2)}$$

The void volume (V_0) was calculated using pressure recorded for reference and sample cell.

$$V_0 = \frac{\frac{P_{r1}}{Z_{r1}} \frac{P_{r2}}{Z_{r2}}}{\frac{P_{S2}}{Z_{S2}} \frac{P_{S1}}{Z_{S1}}} \times V_r \quad \text{Eq. (3)}$$

The total moles transferred to the reference cell were evaluated by equation 4:

$$n_{total} = \frac{P_r V_r}{Z_r R T} \quad \text{Eq. (4)}$$

where R is real gas constant, T is the operating temperature

CO₂ gas was initially introduced in the reference cell and allowed to stabilize before being transferred to the sample cell by opening the connecting valve. The total moles transferred to reference cell were calculated using equation 5

$$n_r = \frac{\frac{P_{r1}}{Z_{r1}} - \frac{P_{r2}}{Z_{r2}}}{R \times T} \times V_r \quad \text{Eq. (5)}$$

The moles transferred to sample cell were calculated as equation 6

$$n_s = \frac{\frac{P_{s2}}{Z_{s2}} - \frac{P_{s1}}{Z_{s1}}}{R \times T} \times V_s \quad \text{Eq. (6)}$$

where Z represents the compressibility factor of helium and CO₂ gases

The amount of adsorbed gas was evaluated using equation 7

$$\Delta n_{ads} = \frac{1}{X} \left[\left(\frac{P_{r1}}{Z_{r1}} - \frac{P_{r2}}{Z_{r2}} \right) \frac{V_r}{RT} - \left(\frac{P_{s2}}{Z_{s2}} - \frac{P_{s1}}{Z_{s1}} \right) \frac{V_0}{RT} \right] \quad \text{Eq. (7)}$$

where X is mass of activated carbon, V_r is the reference cell volume and V_0 is the void volume of the sample cell

The net amount of adsorbed gas was calculated as equation 8

$$n_{adsorbed} = n_{injected} - n_{void} \quad \text{Eq. (8)}$$

Desorption experiments were conducted by closing the reference cell valve and opening the valve and equilibrium pressures were recorded for the desorbed gas from both cells.

Adsorption experiments were conducted for optimized activated carbon by varying temperature (303K, 313 K and 323K), pressure (1 to 3 bar), and adsorbent dosage (20mg, 40mg, 80mg and 100mg).

2.3 Adsorption Isotherm Models

The equilibrium behavior of CO₂ adsorption on the activated carbon was analyzed using the Langmuir, Freundlich and Sips isotherm models. The Langmuir model assumes monolayer adsorption on a homogeneous surface and provides insight on the maximum adsorption capacity and adsorbate-adsorbent affinity. The Freundlich model accounts for surface heterogeneity and describes multilayer adsorption. To bridge the limitations of these individual models, the Sips model which is a combined form of Langmuir and Freundlich is employed, which effectively describes adsorption behavior on heterogeneous surfaces at low pressures while converging to Langmuir behavior at higher pressures. These models

collectively help interpret the distribution of adsorption sites and the nature of the adsorbent-adsorbate interactions. The model equations are summarized in table 1.

Table 1 Isotherm models for carbon dioxide adsorption

Isotherms models	Nonlinear equation
Langmuir	$q_L = \frac{q_m P K_L}{1 + b C_e}$
Freundlich	$q_F = K_F P^{1/n}$
Sips	$q_S = \frac{q K P^n}{1 + K P^n}$

3. Adsorption Kinetic Models

The adsorption kinetics describes the rate of CO₂ uptake on AC surface as a function of parameters such as temperature, pressure, porosity and surface functional groups. In the present study, the adsorption kinetics were evaluated using pseudo-first order model, pseudo-second order model, intraparticle diffusion model and Elovich model as summarized in Table 2.

Table 2 Kinetic mechanism for carbon dioxide adsorption

Kinetic models	Equation	Kinetic mechanism
Pseudo first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	Adsorption rate is proportional free active sites.
Pseudo second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	Chemisorption governs the adsorption rate.
Intraparticle	$q_t = k_{id} t^{0.5} + C$	Investigates the internal diffusion of carbon dioxide on overall adsorption rate
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	It illustrates the chemisorption on the carbon surface.

2.4 Thermodynamic analysis

Thermodynamic analysis was performed to evaluate the spontaneity, feasibility, and energetics of the CO₂ adsorption process. Parameters including enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) help determined to access whether adsorption proceeds via physisorption or chemisorption. The isosteric heat of adsorption (E_{iso}), derived from the Clausius–Clapeyron equation, reflects the interaction strength between CO₂ molecules and the activated carbon surface. Typically, values in the range of 20-40 kJ mol⁻¹ indicate physisorption, while significantly higher values suggest chemisorption. The isosteric heat of adsorption was calculated using equation 9

$$E_{\text{iso}} = -R \left(\frac{dP}{d\frac{1}{T}} \right)_{\theta} \quad \text{Eq. (9)}$$

Thermodynamic parameters were determined from Van't Hoff Equation as expressed in equation 10 and 11.

$$\ln K = \frac{-\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R} \quad \text{Eq. (10)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{Eq. (11)}$$

3. Results and discussion

3.1 Physicochemical characterization of Activated carbon

3.1.1 Ultimate Analysis

Table 3 Ultimate analysis of prepared activated carbon

H₃PO₄-activated carbon (w/w) %		KOH activated carbon(w/w) %	
Carbon	69.69	Carbon	76.878
Hydrogen	2.39	Hydrogen	2.043
Nitrogen	0.19	Nitrogen	1.014
Oxygen	27.72	Oxygen	20.064

Table 3 represents the ultimate analysis of the H₃PO₄-AC and KOH-AC. The H₃PO₄-AC exhibited a carbon content of 69.69 wt% along with 2.39 wt% hydrogen, 0.19 wt% nitrogen, and 27.72 wt% oxygen. The relatively high oxygen content indicates the presence of abundant oxygen-containing surface functional groups, which are typically introduced during phosphoric-acid activation. These functionalities enhance surface polarity and may promote the adsorption of polar or weakly acidic gases. The moderate carbon content reflects the

partial retention of heteroatoms due to the dehydrating and cross-linking effects of H_3PO_4 during activation, leading to the formation of a highly functionalized carbon matrix.

In contrast, the KOH-activated carbon showed a higher carbon content of 76.878 wt%, with 2.043 wt% hydrogen, 1.014 wt% nitrogen, and 20.064 wt% oxygen. The increased carbon fraction indicates more extensive devolatilization and aromatization during high-temperature KOH activation, resulting in a more carbon-rich and structurally ordered framework. The lower oxygen content compared to the H_3PO_4 -activated sample reflects fewer oxygenated surface groups, which is characteristic of KOH activation due to strong etching and pore-forming reactions that remove volatile oxygen species [29]. The slightly higher nitrogen content may originate from nitrogen retention or incorporation during carbonization. Overall, the ultimate analysis demonstrates that KOH activation produces a more carbon-dense adsorbent with reduced heteroatom content, which can influence adsorption behavior and surface chemistry [30].

3.1.2 Thermogravimetric Analysis (TGA)

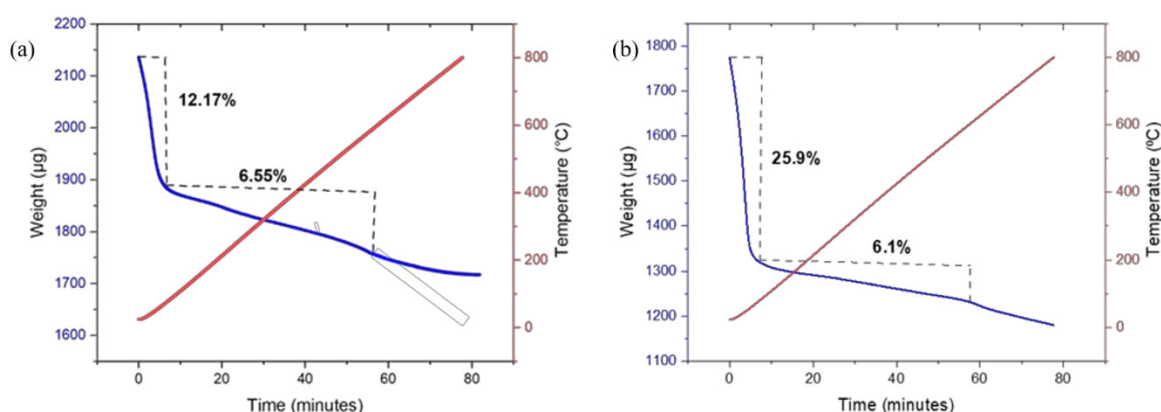


Figure 2 Thermogravimetric analysis graphs of H_3PO_4 and KOH activated carbons

The TGA profile of H_3PO_4 -AC and KOH-AC are shown in figure 2. The initial weight loss below $\sim 120^\circ\text{C}$ corresponds to the removal of physically adsorbed moisture. The major weight loss between ~ 150 – 350°C is attributed to hemicellulose degradation, partial cellulose breakdown, and decomposition of phosphate esters formed during acid impregnation [31]. A broader weight loss region between 350 and 600°C is associated with cellulose and lignin decomposition, accompanied by aromatisation and char formation promoted by H_3PO_4 through dehydration and cross-linking mechanisms [32]. Beyond 600°C , gradual mass loss reflects the breakdown of highly condensed aromatic structures and residual phosphorus

species. The high final char yield indicates enhanced thermal stability and effective pore development resulting from phosphoric acid activation [33][34][35].

The TGA profile of the KOH activated carbon reveals (figure 2b) approximately 25.9% which is attributed to the evaporation of the moisture bound to the carbon surface. Physically adsorbed moisture is removed up to approximately 150°C. Minimal weight loss is observed up to 600°C, indicating the presence of thermally stable surface functional groups such as carbonyl and phenolic moieties. Significant decomposition of carbon skeleton begins beyond 700°C. Overall, the relatively flat TGA curve indicates high thermal stability of KOH-AC at elevated temperature.

3.1.3 Transmission Electron Microscopy

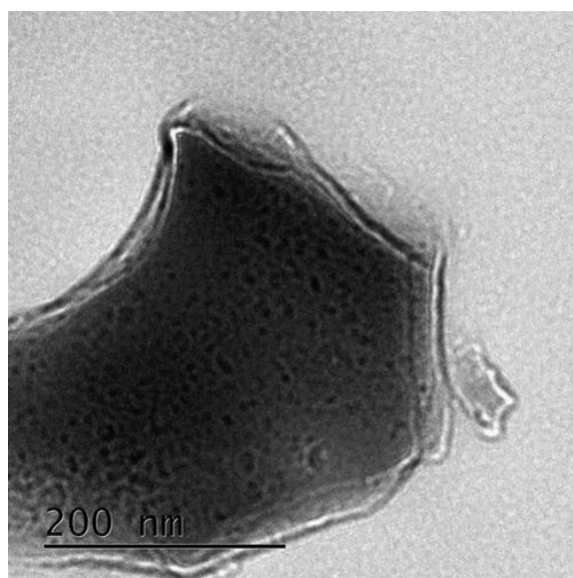


Figure 3 TEM image of KOH activated carbon

The nanoscale visualization of the KOH activated carbon was examined using TEM as shown in figure 3. The image reveals a disordered and predominantly amorphous carbon structure, characteristic of chemically activated carbon. The presence of extensive microporosity, along with presence some mesopores formed during the carbonisation and activation process is evident. The interconnected nanochannels represented by i.e., the light regions corresponding to pore spaces between disordered carbon sheets, confirm the development of a porous network conducive to gas adsorption.

3.1.4 X-ray Photoelectron Spectroscopy

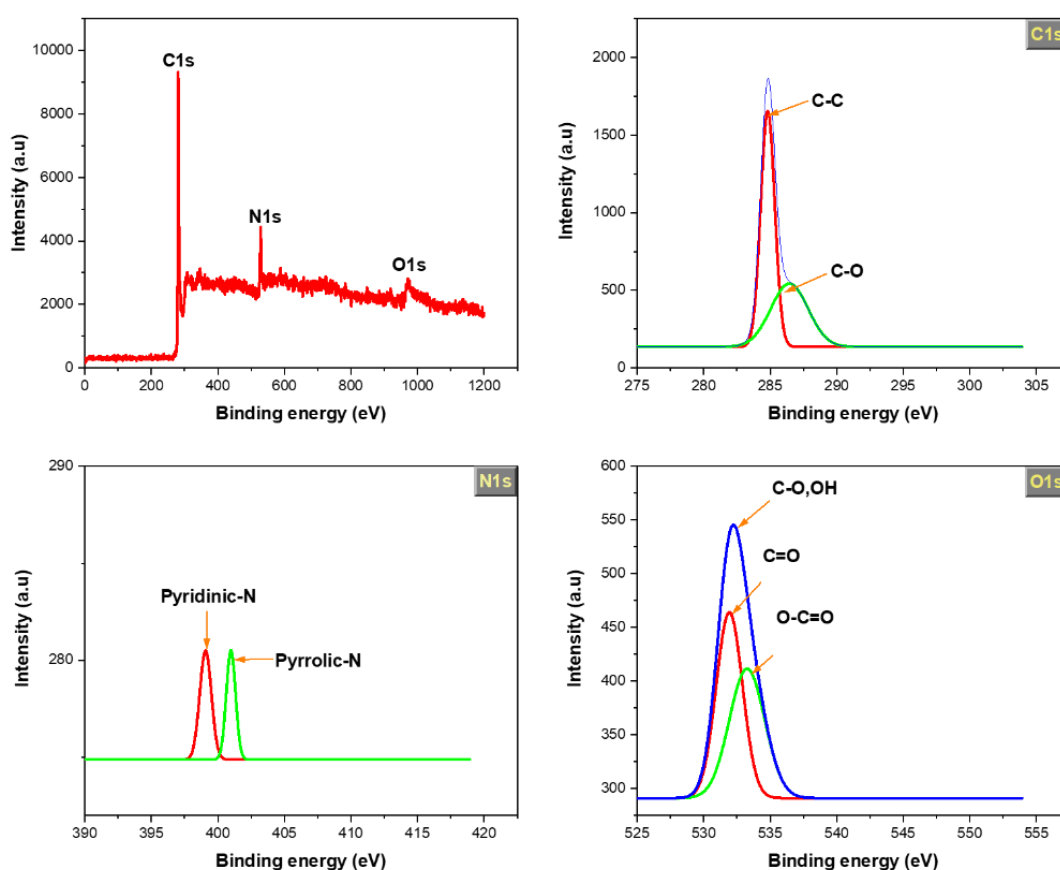


Figure 4 XPS graph of overall spectra and individual elemental analysis

XPS was employed to investigate the surface chemical composition and functional groups of the AC, as shown in figure 4. CO₂ capture performance is closely related to surface chemical properties, and XPS provides insight into the elemental states and bonding environment present on the carbon surface of composition [36]. The survey spectra confirm the presence of carbon, oxygen, nitrogen. As reported previously, higher activation temperatures results in increased surface carbon content and nitrogen concentration [37].

Table 4 XPS quantitative analysis

C1s	N1s	O1s
91.44%	1.83%	6.73%

Quantitative XPS analysis (table 4) shows surface composition of 91.44% carbon, 1.83% nitrogen and 6.73% oxygen. The deconvoluted C1s spectrum for KOH carbon exhibits peaks corresponding to C-C/C=C (284.9 eV), indicative of graphitic carbon, and C-O species

associated with alcohols, ethers, or phenolic groups. N1s spectrum reveals two peaks at binding energies 401.9 eV and 399.1 eV assigned to pyrrolic-N and pyridinic-N respectively [38,39]. Previous studies by Chen et. al. [40] demonstrated that the role of N species enhanced CO₂ adsorption through favourable interactions with acidic CO₂ molecules. In particular, pyrrolic N exhibit weak acidic properties hence the interaction of acid base is impossible with CO₂ molecules. However, some studies by researchers inclined towards the favourable aspect of pole-pole interactions among the N species CO₂ entity for adsorption mechanism [36, 37].

Moreover, the deconvoluted O1s spectra are assigned to three sub peaks in the figure 7.8. The peaks 531.9 eV, 532.3 eV and 533.4 eV links to the existence of C=O (carbonyl groups), C-O/OH (hydroxyl group ether or ester) and O-C=O (carboxylic acid oxygen) respectively [43]. The carbonyl group exhibited strong interaction forces through formation of the electron transfer complexes [44]. According to Liu et. al. [45], the presence of OH group and the bonding formed with CO₂ molecules, despite being weak, significantly increase CO₂ capture capacity. The overall basicity of the carbon surface attributed to trapping of CO₂ molecules at lower pressure and temperature.

3.2 CO₂ Adsorption Performance

3.2.1 Effect of activating agents

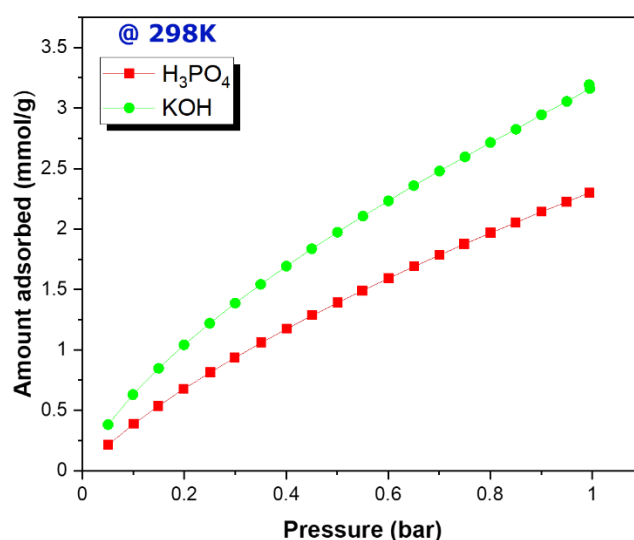


Figure 5 Adsorption capacity of different activated carbons for 1 bar pressure at 298K

The CO₂ adsorption capacities of H₃PO₄ and KOH-AC were evaluated at 298K and 1 bar using a Quantachrome AUTOSORB iQ equipment as shown in figure 5. Prior, to adsorption

measurements, the samples were outgassed at 200°C for 6 hours. The results demonstrate a clear dependence of CO₂ uptake on the activating agent KOH AC indicated experimental adsorption capacity of 3.35 mmol/g followed by H₃PO₄ AC (2.3mmol/g). The disparity in adsorption capacities of activated carbon arise from the basic character of the KOH adsorbent as compared to H₃PO₄ and our findings are in accordance with the previous studies. One more attribute contributing to higher CO₂ retention capacity can be higher surface area of KOH activated carbon (1509.04 m²/g) and microporous volume of 0.804 cm³/g as found in our previous work [46]. Hence, CO₂ adsorption capacity of adsorbents are deduced in the order of KOH > H₃PO₄ – AC.

3.2.2 Effect of temperature

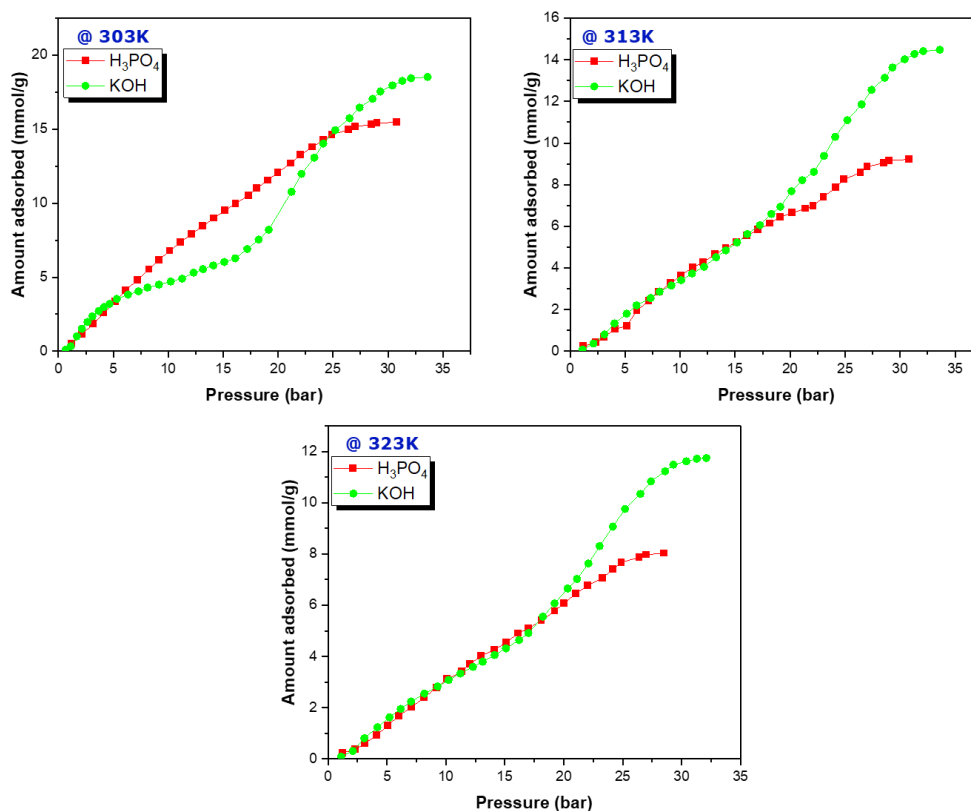


Figure 6 Adsorption capacity of different activated carbons at varying temperature

The influence of temperature (303K, 313K, and 323K) on CO₂ adsorption capacity for different activated carbon are illustrated in figure 6. An increase in temperature resulted in a decrease in CO₂ adsorption capacity for all ACs, including the exothermic nature of the adsorption process.

The increase in vapour pressure and energy level of molecules adsorbed, the uptake capacity decreases with rise in temperature [47]. As, van der Waals forces are responsible for physisorption of CO₂ molecules on the surface which is effective at lower temperature. With increase in thermal energy, the CO₂ molecules are likely to desorb resulting in lower adsorption capacity due to easy break of van der Waals bond. Mohammed Alhassan et al studied CO₂ adsorption using *Jatropha curcas* shell activated carbon and observed similar results of decreases in uptake value at higher temperature [48]. The above mentioned phenomenon is well-established for physisorption-dominated systems. The magnitude of this decline varies depending on the activation route and resulting pore architecture. KOH-AC exhibited a more pronounced reduction in CO₂ uptake with temperature compared to other adsorbents. This behavior can be due to the predominance of ultramicropores generated during KOH activation where CO₂ adsorption is governed by strong confinement and enhanced adsorbent-adsorbate potential overlap.

At lower temperature, these narrow pores facilitate high CO₂ uptake; however, with increasing temperature, the increased kinetic energy of CO₂ molecules weakens the confinement induced interactions, leading to a sharper decline in adsorption capacity. Furthermore, the basic surface functionalities and residual alkali species introduced during KOH activation promote strong quadrupole-dipole interactions with CO₂ at lower temperature, which are more sensitive to thermal disruption. Consequently, the temperature dependence of CO₂ adsorption in KOH-AC reflects the combined influence of its activation chemistry, pore size distribution and structural chemistry.

3.2.3 Influence of bulk density variation of activated carbon in a fixed sample cell

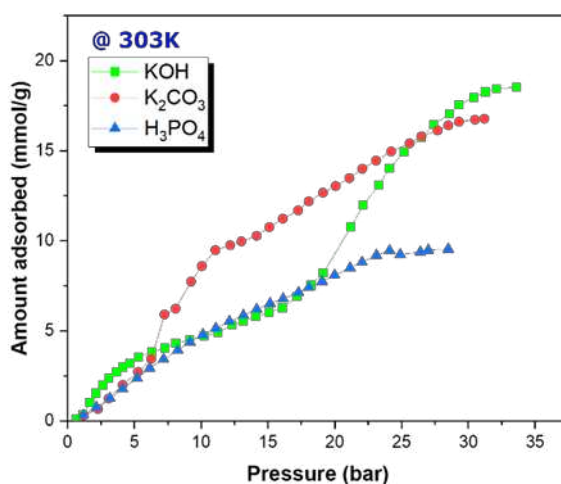


Figure 7 Adsorption capacity of different activated carbons at varying bulk densities

In the present study, the adsorption sample cell volume was maintained constant for all experiments. Consequently, the mass of AC loaded into the adsorption cell varied depending on the bulk density, particle packing behavior and textural characteristics of each adsorbent. Accordingly, approximately 1800mg of $\text{H}_3\text{PO}_4\text{-AC}$, 1000mg of $\text{K}_2\text{CO}_3\text{-AC}$ and 700mg of KOH-AC were required to completely fill the adsorption cell. Figure 7 illustrates the differences in adsorption uptake observed among the AC at full cell loading. Although an increase in adsorbent mass generally enhances the number of available adsorption sites, a decline in adsorption capacity was observed for $\text{K}_2\text{CO}_3\text{-AC}$ and $\text{H}_3\text{PO}_4\text{-AC}$ under complete cell filling condition. This reduction can be attributed to particle aggregation and inefficient packing at higher loadings, which hinder effective gas diffusion and result in the partial blockage or inaccessibility of active adsorption sites, particularly within the microporous network. As a result, the effective utilisation of the internal pore structure is reduced, leading to a lower apparent adsorption capacity despite the higher mass of adsorbent present. In contrast, the comparatively lower mass requirement for KOH-AC indicates a lower bulk density and more efficient packing, which facilitates improved accessibility of adsorption sites and minimizes pore blockage effects within the confined adsorption cell volume [49].

3.2.4 Effect of adsorbent dosage

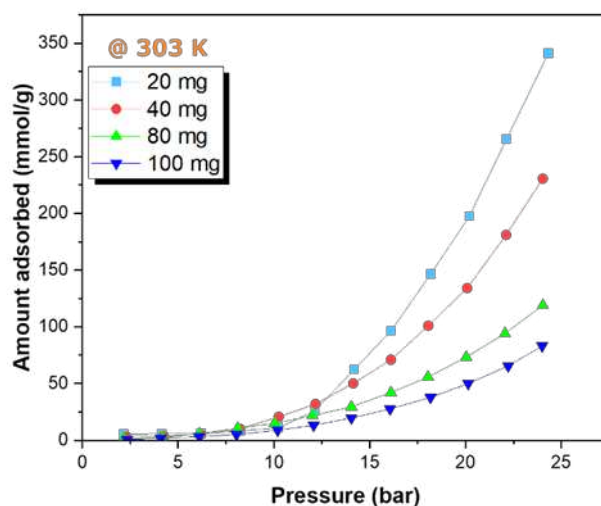


Figure 8 Adsorption capacity of KOH activated carbon at varying dose

The figure 8 represents the different adsorbent dose for the study of CO₂ adsorption capacity at 303K. It illustrates the increase of adsorption efficiency with comparative decrease of amount of carbon. 20mg of activated carbon reveals higher uptake capacity of 341.29mmol/g followed by 40mg, 80mg, and 100mg of carbon. This trend is inversely proportional to number of free sites accessible for CO₂ binding resulting in decrease in efficiency for adsorption. The excessive accumulation of activated carbon in the system prevents the diffusion of CO₂ into the active sites due to agglomeration of particles thereby lowering CO₂ uptake [50,51]. A comparable behaviour is mirrored by commercial granular activated carbon modified using NaOH for CO₂ adsorption studied by Karbalaei Mohammed et al [49].

3.2.5 Adsorption isotherm

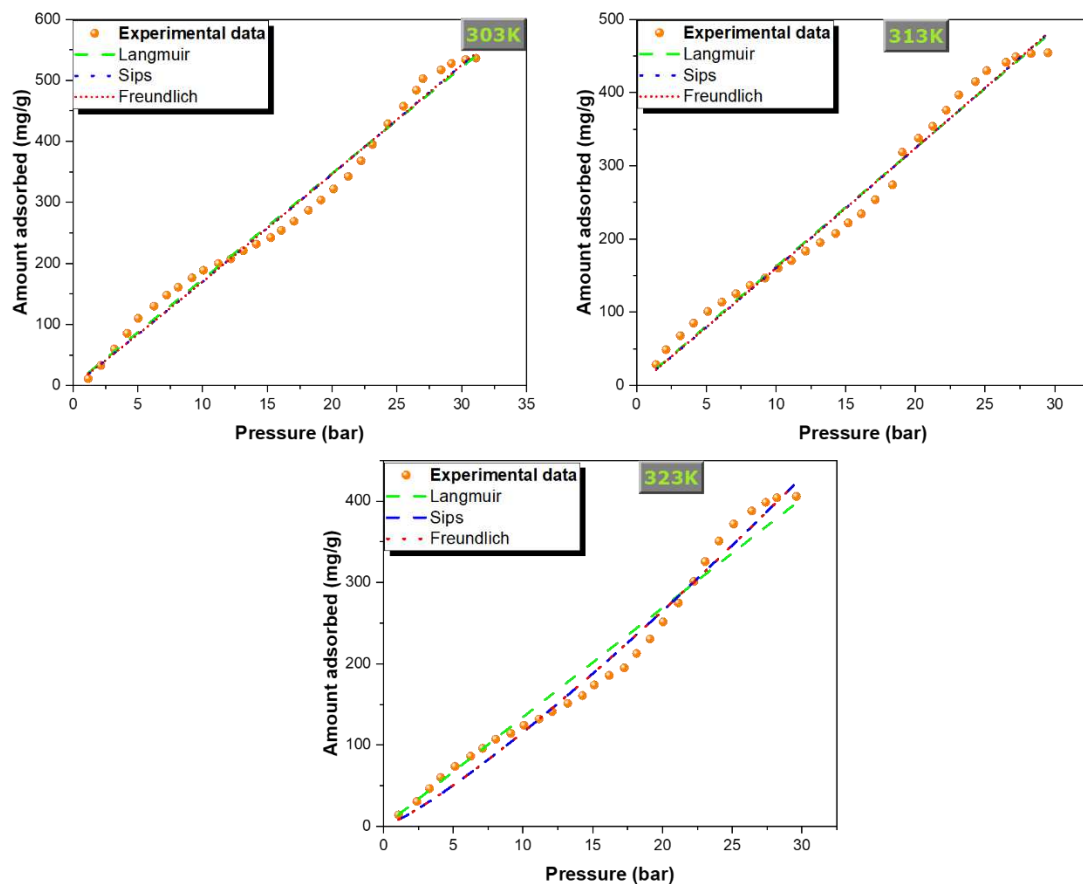


Figure 9 Adsorption isotherms at varying temperature

Isotherms discuss the equilibrium performance of adsorbents when temperature is constant. The experimental data presented in Figure 9 were fitted to Langmuir, Freundlich and Sips model. Using the squared statistics, the model with the best fit with experimental data are

found. The calculated adsorption parameters and correlation coefficient (R^2) of all the isotherms at 303K, 313K, and 323K for the adsorption of CO_2 onto KOH AC are summarized in Table 5. Statistical investigation and highest R^2 (closer to 1) values allowed the choice of the model with minimum discrepancies between the experiment and model data of the CO_2 adsorption on activated carbon. According to the graphs in figure 6.5 the adsorption uptake increases with the rise of pressure and on the other hand an increase in the temperature leads to the CO_2 adsorption reduction which points to an exothermic process due to decrease of binding forces between adsorbate and adsorbent with elevated temperature. The experimental results matched well with Sips with almost highest R^2 values. With decrease in equilibrium constant value (K) in temperature range 303K to 323K, indicated the lower affinity of CO_2 at highest temperature. On the basis of findings in table 5, the Freundlich constant 'n' is within the range of 0.8 to 1.4 demonstrating the attractiveness of physisorption [52]. According to the results (Freundlich model) it is multilayer adsorption and illustrates the heterogeneity nature of the adsorbent surface [53]. Freundlich model described the adsorption of CO_2 on microporous activated carbon and pore size distribution. The 3-parameter model, Sips equation successfully matched for CO_2 gas adsorption for three temperatures. It captures both high pressure and low pressure behaviour accurately and $n > 1$ exhibits high surface heterogeneity of the carbon material [54].

Table 5 Isotherm modelling parameters at varying temperature

Models	Parameters	Temperature		
		303K	313K	323K
Langmuir	q_m	2475921.93	1458086.97	5647241.45
	K_L	7.02153×10^{-6}	1.1128×10^{-5}	2.37964×10^{-6}
	χ^2	389.57	297.03	477.56
	RMSE	19.73	17.23	21.85
	R^2	0.98517	0.98499	0.96978
Freundlich	K_f	16.01251	15.48662	7.42534
	n_f	0.97	0.98	0.84
	χ^2	381.49	294.83	277.91
	RMSE	19.53	17.17	16.67
	R^2	0.98548	0.98511	0.98241
Sips	q_s	1325614.22	742111.32	1162770.21

	K_s	1.20612×10^{-5}	2.08373×10^{-5}	6.37215×10^{-6}
	n_s	1.02683	1.01579	1.19392
	χ^2	395.2929	306.29	288.69
	RMSE	19.88	17.50	16.99
	R^2	0.98547	0.9851	0.98241

3.2.6 Isosteric heat of adsorption and thermodynamic analysis

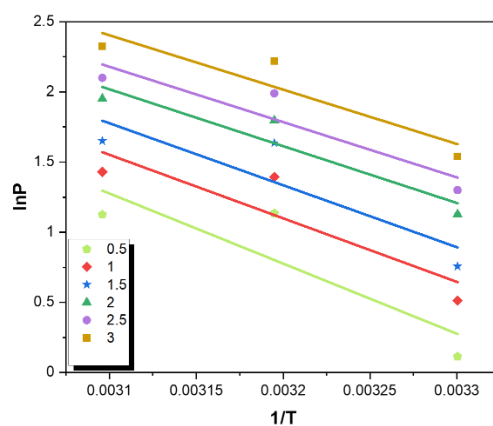


Figure 10 Adsorption isotherms

The isosteric heat adsorption values were calculated using $\ln P$ vs $1/T$ for surface coverage 0.5 – 8 as illustrated in figure 10 and 11. The calculated adsorption heat values ranged from 41 – 7 kJ/mol and decreased with increasing surface coverage, indicating weaker interactions between CO_2 molecules and activated carbon. This trend suggests that the strongest adsorption sites are occupied at low surface coverage.

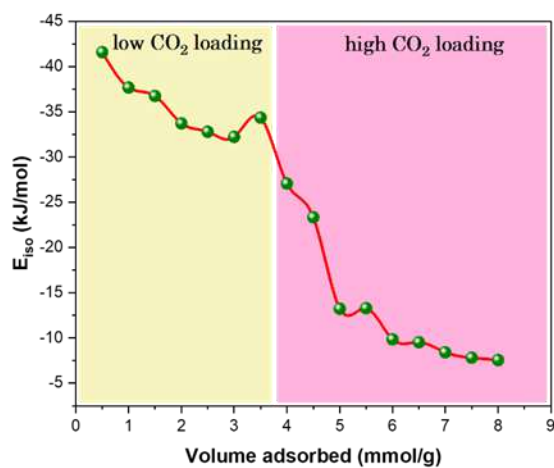


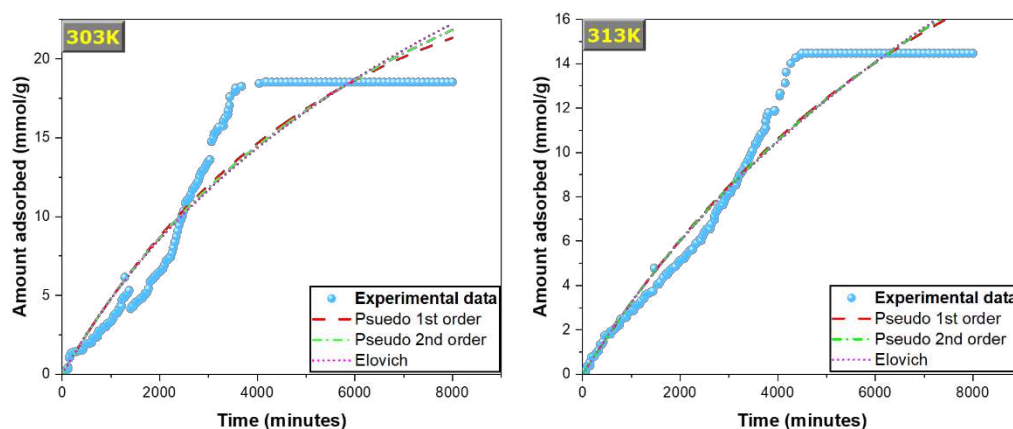
Figure 11 Isosteric heat of adsorption with varying surface coverage

Table 6 Thermodynamic parameters

ΔH (kJ/mol)	ΔS (J/molK)	ΔG (kJ/mol)		
		303K	313K	323K
-25.25	-63.31	-6.07	-5.44	-4.81

Thermodynamics parameters derived from van't Hoff analysis are presented in Table 6. The Freundlich isotherm was fit to the experimental data and was considered for the calculation of thermodynamic attributes. The enthalpy was observed to be negative and in the range of 20-40 kJ/mol indicating the release of heat during adsorption i.e; exothermic reaction. The negative value of entropy reflects the decrease in the randomness of CO₂ molecules with increase in pressure or loading implying the adsorption of CO₂ molecules into the micro and mesopores. Till -20 kJ/mol is the range of the Gibbs free energy for spontaneous physisorption. These parameters values are consistent with the previous findings.

3.2.7 Adsorption Kinetics



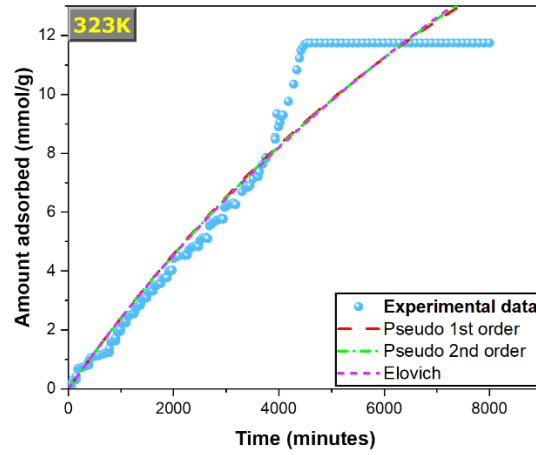


Figure 12 Kinetic models at varying temperatures

One of the most important properties for an effective adsorbent is the rate of reaction of the adsorbate onto the adsorbent surface, hence adsorption kinetic is quite essential. For the determination of CO₂ adsorption kinetics on the carbon surface various models are taken into account. Pseudo 1st order, Pseudo 2nd order, Elovich and Intraparticle diffusion model (figure 12). The brief description about the model parameters are furnished in table 7. Pseudo 1st order represents the physisorption, i.e, reversible interaction between the CO₂ gas and activated carbon whereas Pseudo 2nd order model is based on the assumption of chemisorption where there is strong interaction between the adsorbent and CO₂ [55]. The Elovich model incorporates the surface and bulk diffusion of CO₂ molecules in carbon entity. Furthermore, Webber Morris Intraparticle Diffusion model for the assessment of CO₂ adsorption mechanism. IPD is represented in linearized equation 12

$$q_{ID} = K_{id}\sqrt{t} + C \quad \text{Eq. (12)}$$

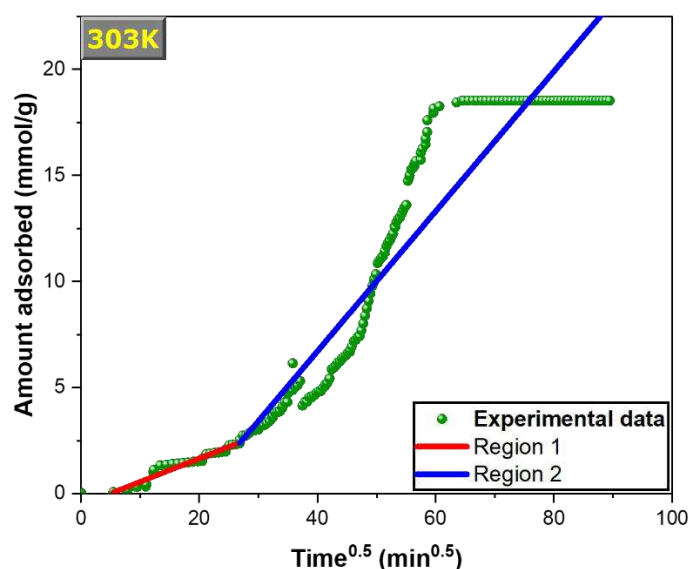


Figure 13 Intraparticle diffusion model at 303K

Notably, according to R^2 , pseudo 1st order model fits better with the experimental data. In the current work, the sorption process was found to follow physisorption phenomenon based on thermodynamics analysis which now aligns with the kinetic pseudo 1st order model indicating physisorption interaction [56–58]. To obtain deeper insight into CO₂ adsorption mechanism the plot of q_{id} (mmol/g) vs $t^{0.5}$ (min^{0.5}) was assessed and resulting curve exhibited multilinear profile in two distinct regions (figure 13). The intra particle diffusion is sole rate-limiting step, if the plot passes through origin. The linear regression of three region segmentation of plot and individual fitting were summarized in table 8. In Region I, the slope was 0.10957 with an intercept of -0.53428 , and the correlation coefficient (R^2) was 0.93, indicating a strong linear relationship. This stage likely represents the rapid surface adsorption phase, where the adsorbate molecules quickly occupy the readily available active sites on the adsorbent surface. In Region II, the slope increased to 0.32974 with a more negative intercept of -6.47321 , and the R^2 value decreased slightly to 0.87. This stage is attributed to the gradual intraparticle diffusion of adsorbate molecules into the pores of the adsorbent, which becomes the rate-controlling step. The non-zero intercepts in both regions suggest that intraparticle diffusion is not the sole rate-limiting mechanism and that film diffusion may also contribute to the overall adsorption kinetics [42,59]. Governing the bulk of CO₂ transport into traps of carbon material. The intercepts confirms that IPD is not rate-limiting step instead it is an overall involvement of film diffusion, intraparticle diffusion and equilibrium stabilization.

Table 7 Kinetics modelling parameters at varying temperatures

Models	Parameters	Temperature		
		303K	313K	323K
Pseudo 1st order	a	26.96	24.62	23.48
	b	1.95892×10^{-4}	1.40995×10^{-4}	1.08524×10^{-4}
	X^2	3.54	1.04	0.71
	RMSE	1.88	1.02	0.84
	R^2	0.91754	0.95353	0.95323
Pseudo 2nd order	q_e	44.36	42.24	42.01
	K_2	2.73116×10^{-6}	1.9698×10^{-6}	1.44976×10^{-6}
	χ^2	3.79	1.09	0.73
	RMSE	1.95	1.05	0.86
	R^2	0.9121	0.95122	0.95169
Elovich	A	0.00548	0.00357	0.00257
	B	0.0555	0.05578	0.05344
	χ^2	4.02	1.15	0.76
	RMSE	2.006	1.07	0.87
	R^2	0.90637	0.94897	0.95034

Table 8 Intraparticle diffusion model parameters at 303K

Parameters	Region I	Region II
Intercept	-0.53428	-6.47321
Slope	0.10957	0.32974
R^2	0.93	0.87

3.3 CO₂ adsorption mechanism

Taking into account the surface chemistry, pore size, isotherm models, kinetic models and thermodynamic parameters of the interaction among the adsorbent and adsorbate the cumulative interaction pathway. Based on characterization results, it was evident that the activated carbon has rich microporous structure and heteroatom functional groups. The process of CO₂ adsorption involves two main mechanisms that are closely linked to pore size.

Micropores are more conducive to adsorb CO₂ molecules. The narrow pore size distribution and extensive surface area are found to be critical for CO₂ adsorption at lower pressure range [60]. Micropores possess a highly developed surface area due to their narrow structure, which enhances the coverage of carbon surfaces and increases the amount of CO₂ adsorbed. Ultrafine micropores (<1 nm) filling exhibits a strong ability to accommodate CO₂ molecules through condensation. The confined dimensions of these pores create elevated vapor pressures within them, enabling pore filling to occur even at relatively low bulk pressures. Within these narrow spaces, CO₂ undergoes a phase transition from the gaseous state to a condensed form, thereby promoting efficient utilization of the micropore volume [61]. Also, the presence of some nitrogen/oxygen functional groups are assumed to attract acidic CO₂ molecules. Enhanced basicity of the carbon bind the electron deficient CO₂ molecules via Lewis acid base interaction [62]. Second dominant mechanism is accountable for CO₂ capture on adsorbent surface is physisorption. Yahia et al (2025) explained similar mechanism using argan press cake activated carbon for CO₂ study [61]. Intermolecular interactions such as van der Waals force are attributable for CO₂ uptake alongside lower temperature which favors the physical adsorption. As the pressure rises, the rate of adsorption also increases until the active sites i.e pore saturation is not reached. Accordingly it can be inferred that the process is fast, reversible and thermally manageable as compared to other studies.

3.4 Cyclic stability and Comparative performance

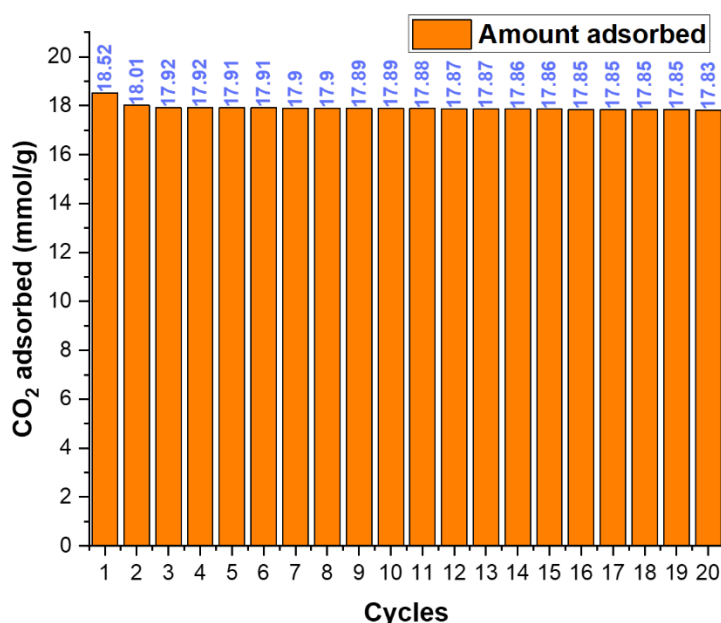


Figure 14 Cyclic adsorption and desorption test for 20 cycles

To monitor the long term durability of the microporous activated carbon which is considered pre-requisite for practical application, the cyclic adsorption – desorption study was carried out at 30°C and presented in figure 14 upto 20 cycles the stability was assessed and the results revealed that the adsorbent retained approx. 96% of its initial CO₂ uptake after the aforementioned cycles. This confirms the suitability of the adsorbent after consecutive adsorption cycles under controlled conditions due to the robust and thermally stable pore structure, surface functional groups and predominance of physisorption [61] enabling an efficient regeneration process without any structural degradation. The present investigation aligns with existing literature.

The comparison of the present studied activated carbons with other activated carbons are mentioned in table 9. It is observed that CO₂ adsorption capacity of Bayur fruit activated carbon at 25°C and 1 bar pressure shows comparable results with respect to activated carbon prepared from different precursors. However, Bayur fruit activated carbon exhibits much higher adsorption capacity 18.53 mmol/g at 30°C and 30 bar pressure with respect to other activated carbons mentioned in table 9. Thus, Bayur fruit activated carbon produced from KOH activation can be good alternative to capture CO₂ at both lower pressure (1 bar) and high pressure (30 bar).

Table 9 Comparison of CO₂ adsorption study using different activated carbons

Precursor	Activating agent	Adsorption Capacity	Temperature (°C)	Pressure (bar)	Reference
Waste tea	melamine	3.56 mmol/g	0	0.97	[63]
		2.69 mmol/g	25	0.99	
Carpet + KOH	KOH	8.41 wt%	25	1	[64]
		3.37 wt%	70	1	
Bio-oil residue	Urea +K ₂ CO ₃	6.22 mmol/g	0	1	[65]
Rice husk	KOH	3.5 mmol/g	25	1	[53]
Commercial AC	-	3.37 mmol/g	0-60	0-1	[66]
<i>Nauclea diderrichii</i>	KOH	2.8mmol/g	0	1	[20]

		3.2 mmol/g	25		
Bayur fruit	KOH	3.35 mmol/g	25	1	Present study
	H₃PO₄	2.3 mmol/g			
Pine Cone	H ₃ PO ₄	4.5-7 mmol/g	25-45	16	[67]
AC	Chitosan + TETA	12-16mmol/g	20-40	40	[68]
Pistachio shells	N ₂	3.28 mmol/g	25	0-6	[69]
Bamboo	H ₃ PO ₄	6.2 mmol/g	25	30	[70]
Corn cobs	KOH	20.73 mmol/g	30	16	[71]
Bayur fruit	KOH	18.53 mmol/g	30	30	Present study
	H₃PO₄	15.47 mmol/g			

4. Conclusion

This work elucidates the adsorption pathway-dependent influence of H₃PO₄ and KOH activation on the structural and surface properties of *Pterospermum acerifolium* derived AC and their corresponding CO₂ adsorption behaviour. KOH activation resulted in a more carbon-rich matrix (76.878 wt% carbon) with reduced oxygen content (20.064 wt%) compared to H₃PO₄ activation indicating enhanced pore development. XPS confirmed the presence of surface nitrogen and oxygen functionalities, including pyridinic-N, pyrrolic-N, carbonyl, hydroxyl, and carboxyl groups, which contribute the superior CO₂ adsorption capacity of the KOH-AC (3.35 mmol/g at 298K and 1 bar) relative to the H₃PO₄ activated sample (2.3 mmol/g) is attributed to its higher specific surface area (1509.04 m²/g), greater micropore volume (0.804 cm³/g), and favourable surface functionalities.

Temperature- dependent adsorption (303-323K) confirmed the exothermic and predominantly physisorption-driven nature of the process. The Sips model best described equilibrium data, while pseudo-first order and kinetics and isosteric heat values (41-7 kJ/mol) further supported physisorption dominance. The adsorbent retained approximately 96% of its initial capacity after 20 cycles at 30°C and achieved 18.53 mmol/g at 30°C and 30 bar. Overall, the results

highlight the strong potential of biomass-derived activated carbon as a sustainable and efficient adsorbent for CO₂ capture, supporting its applicability in advanced gas separation and environment remediation systems.

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Author contribution

Experimentation, analysis and interpretation of data, writing of manuscript are done by AS. SM was involved in conceptualization, reviewing, editing and correction of manuscript.

Data Availability

All data generated or analyzed during this study are included in this article.

Competing Interest

The authors declare that they have no known competing interest that could have appeared to influence the reported work.

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