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Sustainable synthesis of activated porous carbon from lignin for enhanced CO₂ capture: A comparative study of physicochemical activation routes

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Abstract

A sustainable and readily available material-lignin protobind 2400 was upcycled to activated porous carbon (APC) compatible with post-combustion CO₂ capture. The effectiveness of the novel two-step physicochemical activation using KOH + CO₂ and ZnCl₂ + CO₂ was compared with that of the respective physical (only CO₂) and chemical activation (only KOH or ZnCl₂). The effect of carbonization conditions (N₂ or CO₂ purging) on the resulting APC properties and CO₂ adsorption performance was studied. The maximum BET surface area of 1480 m²/g and the best CO₂ adsorption capacity of 5.68, 3.66, and 2.67 mmol/g were observed at 0, 25, and 40 °C/1 bar, respectively. From the precursor to the final product, the APC yield falls within the range of 14.5-40.8 wt.%. The APC derived from lignin exhibited better CO₂/N₂ selectivity. The isosteric heat of adsorption for all the APCs remained below 40 kJ/mol, which suggested a lower energy requirement during the regeneration. The excellent reusability with fluctuations of only 0.51% in the amount of CO₂ adsorbed over ten consecutive adsorption/desorption cycles, highlights the APC's outstanding recyclability.

Keywords: Carbon capture, Activated porous carbon, Physicochemical activation, Waste valorization

Nomenclature

| | |
|--------------|---|
| GHGs | Greenhouse Gases |
| CCUS | Carbon Capture, Utilization, and Storage |
| APC | Activated Porous Carbon |
| BET | Brunauer-Emmett-Teller |
| <i>L</i> | Lignin Protobind 2400 |
| NLPH | Normal Litres per Hour |
| <i>L X-Y</i> | Lignin prtobind 2400 based activated porous carbon, where <i>X</i> represents gas purged during carbonization and <i>Y</i> denotes activating agent used; <i>X</i> = <i>N</i> indicates N ₂ purging, <i>X</i> = <i>CD</i> indicates CO ₂ purging; <i>Y</i> = <i>K</i> denotes KOH |



activation, $Y = CD$ denotes CO_2 activation, $Y = Z$ denotes ZnCl_2 activation, $Y = ZCD$ denotes $\text{KOH} + \text{CO}_2$ activation, $Y = ZCD$ denotes $\text{ZnCl}_2 + \text{CO}_2$ activation

| | |
|--------------------------|--|
| SD | Standard Deviation |
| SEM | Scanning Electron Microscopy |
| TEM | Transmission Electron Microscopy |
| HR-TEM | High-resolution Transmission Electron Microscopy |
| NLDFT | Non-local Density Functional Theory |
| S_{BET} | Specific BET surface area, m^2/g |
| S_{micro} | Micro-pore area using t-plot method, m^2/g |
| φ_{micro} | Micro-porosity ($S_{\text{micro}}/S_{\text{BET}}$) $\times 100$, % |
| R_{avg} | Average pore radius, nm |
| V_{T} | Estimated at a relative pressure $P/P_0 = 0.99$, cm^3/g |
| V_{micro} | Micropore volume estimated using t-plot method, cm^3/g |
| f_{micro} | Percentage of micro-pore volume ($V_{\text{micro}}/V_{\text{T}}$) $\times 100$, % |
| q_{st} | Isothermic heat of adsorption, kJ/mol |

1 Introduction

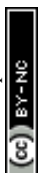
Climate change is closely tied to the continuous increase in anthropogenic greenhouse gases (GHGs) emissions and poses a significant threat to human existence. The energy sector, driven by hefty dependence on fossil fuels, is accountable for 72% of GHGs, with CO_2 contributing 76% to the overall GHGs emissions.¹ Despite a noteworthy increase in renewables, fossil fuels are projected to maintain a substantial global dependence of 74% by 2040, underscoring the critical need to decarbonize the energy sector.² This highlights the significance of CO_2 as the most crucial greenhouse gas (GHG) contributing to catastrophic events, such as climate change associated with global warming, increased ocean acidity, and rising sea levels. The World Meteorological Organization's report highlights that the socioeconomic consequences of climate change are worsening, with unprecedented GHG concentrations pushing global temperatures perilously closer to critical levels.³ The primary aim of the Paris Climate Change Agreement is to achieve a 40% reduction in GHG emissions by 2030.⁴ To address the immediate challenges posed by the escalating levels of global CO_2 concentration, there is an ongoing exploration of carbon capture, utilization, and storage (CCUS) as a potential short-term solution to curb the release of this specific greenhouse gas. Fundamentally, carbon capture involves the application of technologies to either directly extract CO_2 from the air/atmosphere or to capture it during the formation process (large point source). Specifically, the removal of CO_2 from a flue gas stream is termed post-combustion CO_2 capture, which can be a cost-effective approach for addressing emissions from current coal and gas-fired power plants, as well as coal-intensive industries, such as cement, oil refineries, chemicals, and steel.⁵ Approximately one-third of the existing coal and gas-fired power plants have been constructed in the last decade. Retrofitting these facilities with post-combustion CO_2 capture enables them to remain operational, thereby avoiding the expenses associated with early phase shutdowns.⁶



Several methods such as amine absorption, membrane separation, cryogenic distillation, and physical adsorption have been developed for CO₂ capture from industrial flue gases. The adsorption-based method, utilizing solid adsorbents such as porous aluminosilicate or zeolites, metal organic frameworks, silica gel, and activated porous carbons (APCs) offers excellent performance and energy efficiency compared to other separation techniques.^{7,8} In this context, APCs present numerous advantages over other CO₂ adsorbents. Their affordability, well-developed pore structure, exceptional thermal and chemical stability, heightened efficiency under humid conditions, straightforward surface functionalization, and lower energy requirements during regeneration highlight their significance as CO₂ adsorbents coupled with commendable multi-cyclic stability.^{9,10} Presently, large-scale production of APCs predominantly relies on carbon-intensive precursors, such as coal, as well as carbon-neutral alternatives, such as wood and coconut shells.¹¹ Researchers are exploring economically viable and efficient replacements to mitigate the environmental impact of this sector and fortify the supply chain.¹²

On the other hand, lignin stands as the Earth's second most abundant naturally occurring complex organic material. Lignocellulosic wastes (forest and agricultural waste) and pulp paper mills are two potential sources of lignin, generating 225 and 130 Mt of lignin per annum, respectively.¹³ Projections indicate that this figure will surge by 225 Mt per year by 2030, driven by the increasing annual production of lignin as a by-product of bioethanol production mandated by the Renewable Fuel Standard (RFS) program aimed at 60 billion gallons of biofuel.¹⁴ Hence, the development of cost-effective valorisation technologies is crucial to ensure the long-term stability and vitality of biorefineries. Traditionally regarded as a low-value waste by-product, recent studies have demonstrated its potential in producing high-value commodities.¹⁵⁻¹⁹ Despite an expanding body of research on the conversion of lignin into commercial commodities, a large fraction of lignin produced by the paper industry is currently incinerated as a low-value fuel for electricity and heat generation (with a value of < \$50/dry ton).^{20,21} Less than 2% is used to produce specialty chemicals and other value-added products. The advancement of value-added lignin-derived co-products holds the potential to enhance the profitability of second-generation biorefineries and the paper industry by valorising their lignin by-products.

Physical and chemical activation are the most common and extensively studied techniques for producing APCs. Their individual effects on the performance and properties of APCs prepared from a wide range of carbonaceous materials have been investigated extensively. A hybrid synthesis route of physicochemical activation that simultaneously utilize both physical and chemical activating agents is less explored. Previously, some researchers investigated the effect of physicochemical activation on other applications, such as Cu adsorption²², dye (i.e., crystal violet) removal²³, and CH₄ storage²⁴. The effect of physicochemical activation on the CO₂ adsorption performance is even less studied among other applications of APCs. Previous studies have reported the preparation of APC via physicochemical activation using ZnCl₂ + CO₂²⁵ and KOH + CO₂^{26,27} for CO₂ adsorption. However, these studies lacked a comparison of the effectiveness of physicochemical activation with the respective physical and chemical



reagents used. In our previous study, we compared the CO₂ adsorption performance of APCs derived through physicochemical activation of pine sawdust with those derived through chemical activation (using only KOH) and physical activation (using only CO₂).²⁸ Physicochemical activation (KOH + CO₂) resulted in APCs with 68% and 586% more BET surface area compared to APCs derived using only KOH and only CO₂ activation, respectively. However, the CO₂ adsorption capacity of physicochemically activated carbon was 26.5% lower than that of APCs produced using only KOH and 53.3% higher than that of APCs produced using only CO₂ activation. However, a limitation of this study was that it tested only one combination of physical and chemical activating reagents. The results may be significantly different for different combinations and feedstocks.

In this study, the combined effects of chemical activating agents (such as KOH and ZnCl₂) and a physical activating agent (CO₂) on the textural properties and CO₂ adsorption performance of the resulting APC were investigated. In addition, we compared the effectiveness of physicochemical activation with that of individual chemical and physical activating agents. The effect of carbonization conditions on APC performance was also studied. Lignin protobind 2400, a sustainable material, was used as a precursor to derive APC for CO₂ capture applications.

2 Experimental

2.1 Feedstock and material

Lignin protobind 2400 (*L*) was purchased from ALM Private Limited, Hoshiarpur, Punjab, India. The chemical and thermal properties of *L* were reported previously.²⁹ KOH pellets (P250-3) with a purity of $\geq 85.0\%$, anhydrous ZnCl₂ with a purity of $\geq 98.0\%$, and 1 N HCl solution (SA48-1) from Fisher Scientific were used.

2.2 Synthesis of activated porous carbon

A horizontal fixed-bed annealing furnace (Carbolite GERO, GLO 10/11-1G) was used for carbonization and activation. More details on the furnace used have been published elsewhere.²⁸ APCs were produced by direct activation as well as two-step activation. KOH, ZnCl₂, CO₂, and their combinations were used as the activating agents. Based on the type of activating agent used, the activation can be classified into three categories: (i) physical activation using CO₂, (ii) chemical activation utilizing KOH and ZnCl₂, and (iii) physicochemical activation using KOH + CO₂ and ZnCl₂ + CO₂. Figure 1 illustrates the methodology followed during the APC preparation. The precursors were dried in a hot-air oven at 80 °C for 24 h, prior to carbonization and/or activation. Lignin protobind 2400 was carbonized at 600 °C, with a heating rate of 7.5 °C/min of a heating rate and a residence time of 1.5 h in an N₂ atmosphere (at 50 NLPH). The reactor was allowed to cool down naturally and the resulting biochar was labelled as *L N*. Pore formation via CO₂ mainly occurs via Boudouard reaction, which activates above 700 °C.³⁰ Considering the poor thermal



conductivity of the feedstock used and the heat transfer limitations of the reactor housing, all activation experiments were performed at 800 °C. Direct physical activation of lignin protobind 2400 was performed at 800 °C, 7.5 °C/min of a heating rate, 1.5 h of a residence time in a CO₂ atmosphere (at 75 NLPH). The reactor was cooled naturally, and the resulting biochar was labelled *L CD*. For all CO₂ related activations, the precursors were heated from room temperature to 800 °C in an N₂ environment (at 50 NLPH). After achieving 800 °C, N₂ purging was stopped, and CO₂ was purged (at 75 NLPH) throughout the holding time of 1.5 h and until the reactor temperature dropped below 700 °C during the natural cool-down cycle. From 700 °C to room temperature N₂ was purged.

Directly activated APC (i.e., *L CD*) and biochar (i.e., *L N*) were pulverized in a ball mill (Fritsch, Pulverisette 5) for 1 h and sieved through 300 μm mesh. Prior to chemical and physicochemical activation, 25 g of the pulverized precursor was impregnated with 50 g of KOH or ZnCl₂, and 150 ml of deionized water was added. The slurry was stirred for 24 h at 500 RPM followed by overnight drying in a hot-air oven at 105 °C. The dried and impregnated samples were activated at 800 °C, with a heating rate of 5 °C/min for 1.5 h. Adhering KOH or ZnCl₂ was removed from the derived APCs via hot water washing, followed by acid soaking in 0.1 M HCl, and then further hot water washing until a neutral pH was achieved. The washed APCs were dried at 105 °C for 24 h, labelled, and stored. The yield was calculated based on the initial and final weight differences. The combined yield of the carbonization and activation steps was considered as the APC yield.

L X-Y denotes the lignin protobind 2400 based activated porous carbon. Where *X* denotes the type of purging gas used during carbonization: *X = N* indicates carbonization was executed in N₂ and *X = CD* indicates carbonization was performed in CO₂ atmosphere. *Y* denotes the type of activating agent used in the two-step activation process: *Y = K* indicates KOH used as an activating agent, *Y = CD* denotes CO₂ used as an activating agent, *Y = Z* means ZnCl₂ is used as an activating agent, *Y = KCD* means KOH + CO₂ is used as the activating agent, and *Y = ZCD* is ZnCl₂ + CO₂ used as the activating agent. For example, *L N-KCD* represents lignin protobind 2400 based activated carbon derived via a two-step activation method from lignin protobind 2400 biochar prepared in a N₂ atmosphere, followed by activation using KOH + CO₂ as an activating agent. The details of the characterization protocol have been explained elsewhere.^{28,31}



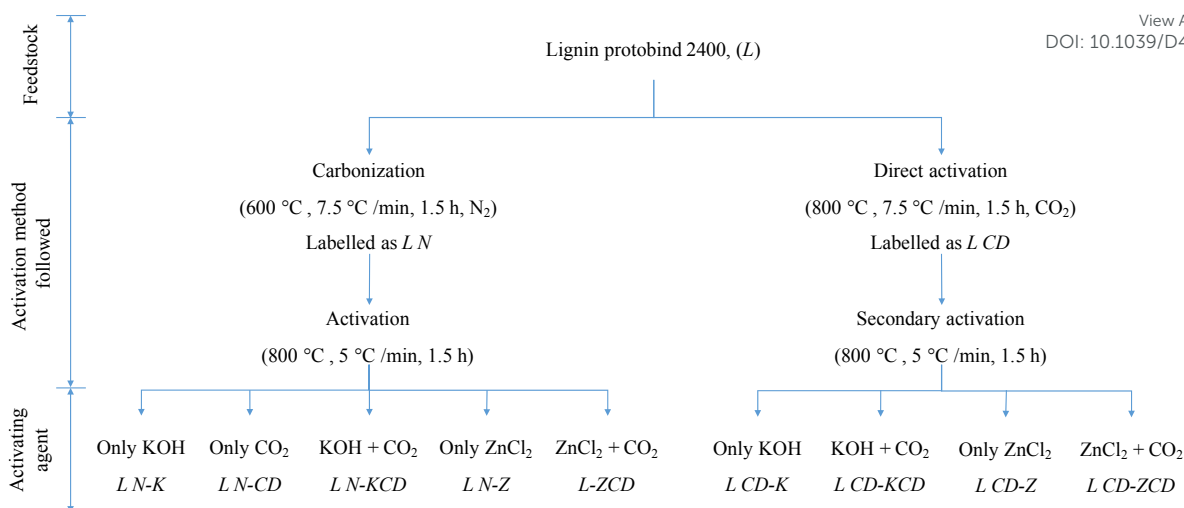


Figure 1. Methodology followed during the synthesis of activated porous carbon. ($L X-Y$, where X represents gas purged during carbonization and Y denotes activating agent used; $X = N$ indicates N_2 purging, $X = CD$ indicates CO_2 purging; $Y = K$ denotes KOH activation, $Y = CD$ denotes CO_2 activation, $Y = Z$ denotes $ZnCl_2$ activation, $Y = KCD$ denotes KOH + CO_2 activation, $Y = ZCD$ denotes $ZnCl_2$ + CO_2 activation).

3 Result and discussion

3.1 Composition and structural characterization

The elemental compositions of lignin protobind 2400, biochar, and APCs are listed in Table 1. Carbonization significantly increased the carbon content and reduced the hydrogen and oxygen content. Chemical activation using KOH and physical activation using CO_2 produced APC with slightly higher carbon content than biochar. However, chemical activation using $ZnCl_2$ and physicochemical activation ($KOH + CO_2$ and $ZnCl_2 + CO_2$) significantly reduced the carbon content compared to biochar. Similar trends were observed during physicochemical activation (using $KOH + CO_2$) of pine sawdust.²⁸ Compared to the feedstock, the reduced H/C molar ratio for the biochar and APCs indicated that the aromatization reaction was dominant during carbonization and activation.

Table 1. Elemental composition of the feedstock, biochar, and activated porous carbons.

| Material | C, wt.% | H, wt.% | N, wt.% | O ^a , wt.% | H/C | C/O | H/O |
|---------------|-----------|-----------|-----------|-----------------------|------|-------|------|
| <i>L</i> | 63.03 | 6.20 | 1.23 | 29.54 | 1.18 | 2.85 | 3.36 |
| | SD = 0.23 | SD = 0.01 | SD = 0.00 | SD = 0.22 | | | |
| <i>LN</i> | 84.84 | 2.45 | 1.13 | 11.58 | 0.35 | 9.77 | 3.39 |
| | SD = 0.09 | SD = 0.01 | SD = 0.98 | SD = 0.95 | | | |
| <i>LN-K</i> | 85.05 | 0.32 | 0.68 | 13.95 | 0.05 | 8.13 | 0.37 |
| | SD = 0.30 | SD = 0.03 | SD = 0.02 | SD = 0.27 | | | |
| <i>L CD-K</i> | 87.25 | 1.02 | 0.78 | 10.95 | 0.14 | 10.62 | 1.49 |
| | SD = 0.63 | SD = 0.01 | SD = 0.01 | SD = 0.62 | | | |



| | | | | | | | |
|-----------------|--------------------|-------------------|-------------------|--------------------|------|------|------|
| <i>L N-CD</i> | 86.17 SD = 1.79 | 1.15 SD = 0.10 | 1.12 SD = 0.13 | 11.56 SD = 1.95 | 0.16 | 9.94 | 1.50 |
| <i>L CD</i> | 85.91 SD = 1.05 | 0.79 SD = 0.09 | 1.30 SD = 0.15 | 12.00 SD = 1.27 | 0.11 | 9.55 | 1.05 |
| <i>L N-KCD</i> | 81.86 SD = 1.41 | 0.51 SD = 0.16 | 1.22 SD = 0.22 | 16.41 SD = 1.77 | 0.07 | 6.65 | 0.50 |
| <i>L CD-KCD</i> | 81.10 SD = 1.14 | 1.16 SD = 0.03 | 1.20 SD = 0.01 | 16.53 SD = 1.13 | 0.17 | 6.54 | 1.12 |
| <i>L N-Z</i> | 76.24 SD = 6.36 | 0.84 SD = 0.15 | 0.66 SD = 0.02 | 22.25 SD = 6.53 | 0.13 | 4.57 | 0.61 |
| <i>L N-ZCD</i> | 76.11 SD = 4.67 | 0.93 SD = 0.13 | 0.61 SD = 0.04 | 22.35 SD = 4.80 | 0.15 | 5.93 | 0.90 |
| <i>L CD-Z</i> | 80.22 SD = 1.55 | 1.01 SD = 0.09 | 0.74 SD = 0.02 | 18.03 SD = 1.65 | 0.15 | 5.93 | 0.90 |
| <i>L CD-ZCD</i> | 80.37 SD = 2.81 | 1.06 SD = 0.13 | 0.67 SD = 0.05 | 17.90 SD = 2.94 | 0.16 | 5.99 | 0.95 |

^a by differences

SD = Standard deviation

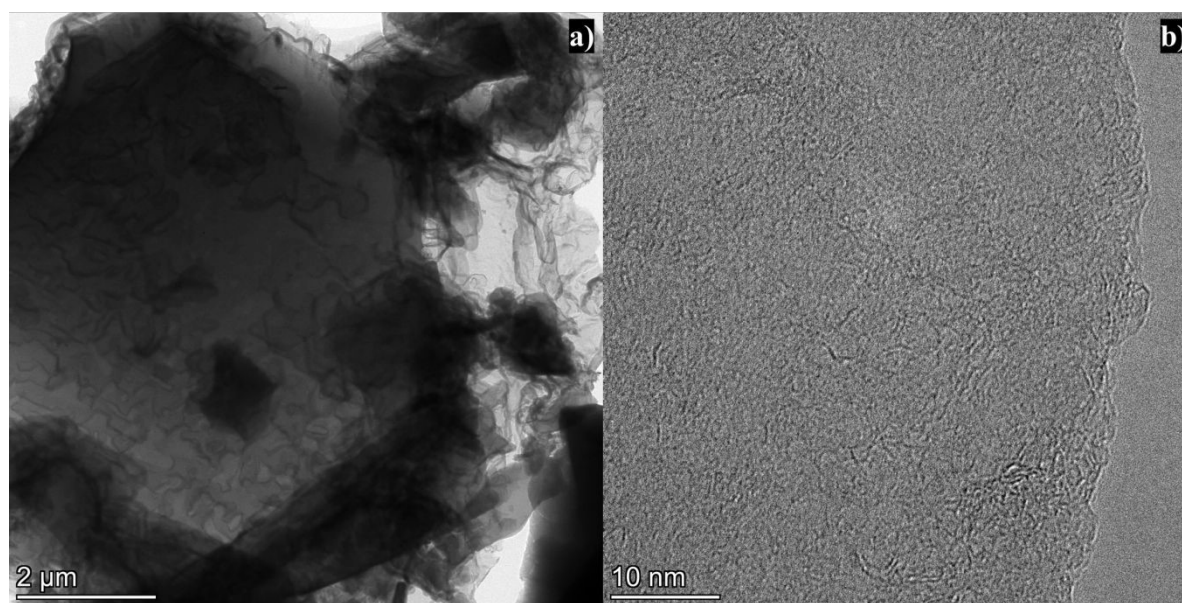


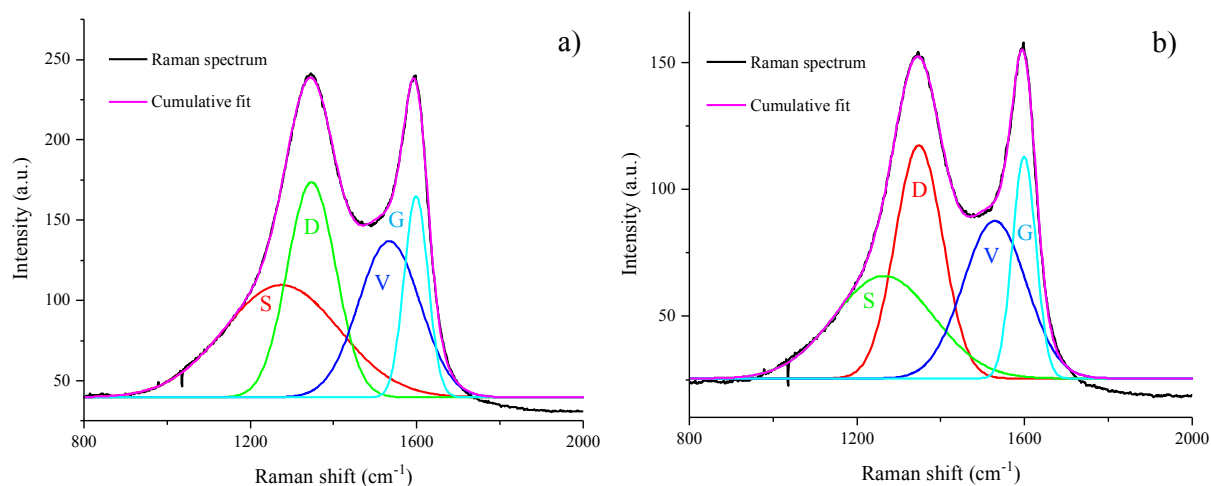
Figure 2. (a) Transmission electron micrograph and (b) High-resolution transmission electron micrograph of *L N-K*.

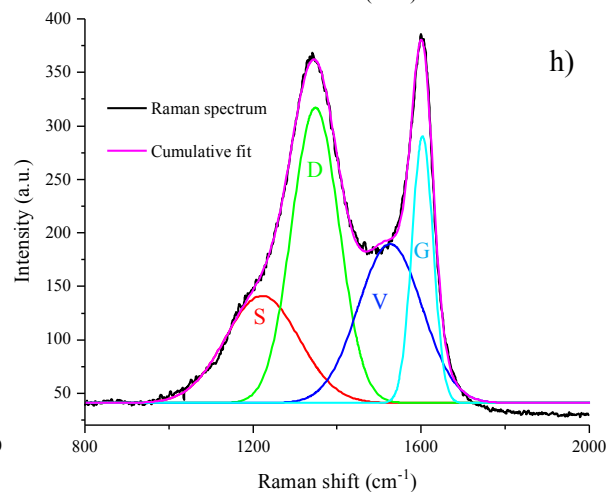
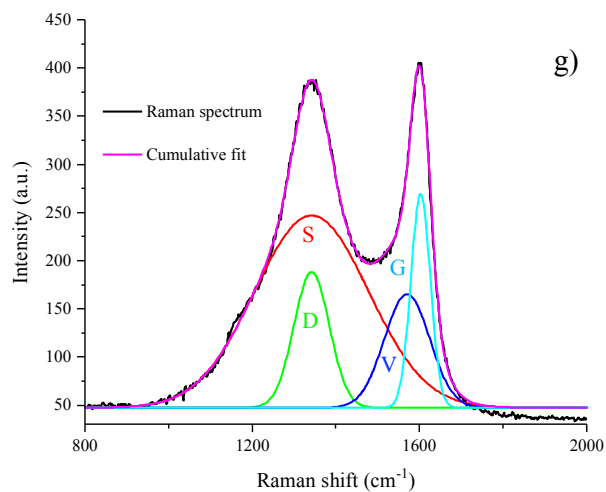
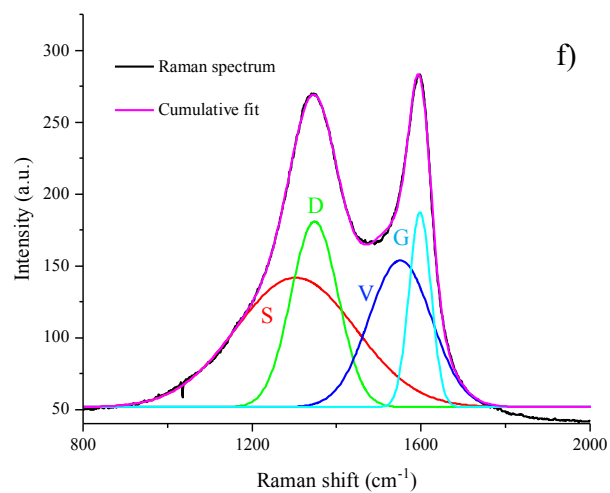
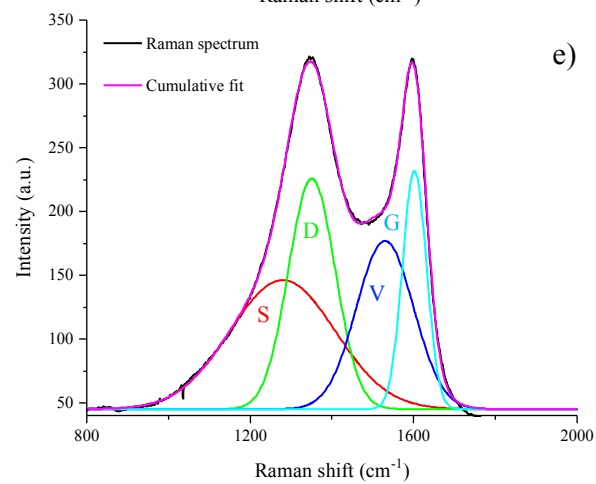
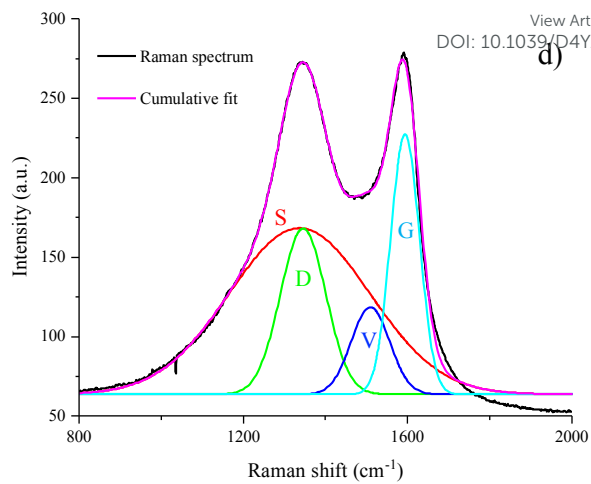
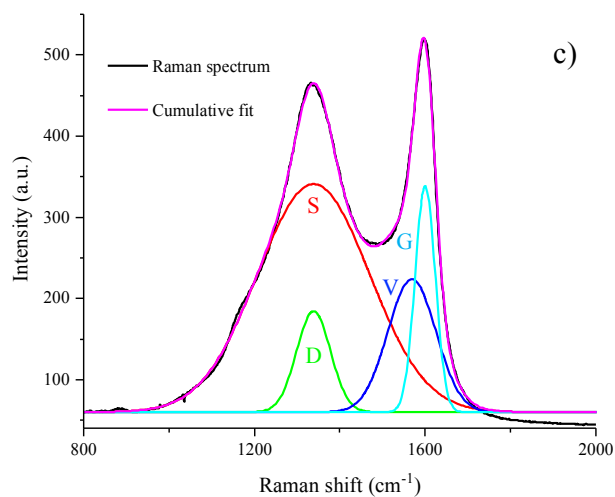
Scanning electron microscopy (SEM) was utilized to investigate the morphology of the lignin protobind 2400 based APCs. SEM micrographs of all lignin-based APCs are presented in Figure S1, indicating a blocky and sharp edge morphology. Random cracks and cavities were observed on the external surface. The porous structure and detailed morphology of *L N-K* were further investigated using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM). As portrayed in Figure 2a, the overlapping of multiple carbon sheets resulted in a relatively dense TEM image. The HR-TEM image of *L N-K* depicted in Figure 2b shows disordered worm-like micropores randomly distributed on the



surface of *L N-K*, indicating a microporous nature, which was further confirmed by N_2 adsorption isotherms.

Raman spectra were recorded to evaluate crystallographic disorders in carbon structure. Only the key features of the Raman spectra within the Raman shift range of 800–2000 cm^{-1} are highlighted in Figure 3. Two broad overlapping peaks were deconvoluted using the Fourier–Gaussian peak-fitting method. The first peak, a maxima occurring at $\sim 1300 \text{ cm}^{-1}$, represents a defect or disorder in the carbon structure originating from local defects (D-band). The second peak at $\sim 1600 \text{ cm}^{-1}$ can be attributed to the graphitic crystallites of sp^2 hybridized carbon (G-band). The I_D/I_G ratio is the intensity ratio of the D and G peaks, which quantifies the degree of graphitization. This signifies the ratio of disordered carbon structure to ordered carbon structure. A lower I_D/I_G ratio indicates a more ordered or crystalline carbon structure. Figure 3k portrays the I_D/I_G ratios of all ten APCs. Physical activation resulted in the most ordered carbon structure morphologically, which is consistent with a previous study using different feedstocks.²⁸ Chemical or physicochemical activation leads to pronounced deformation of the aromatic rings, which reduces the degree of graphitization. During activation, ZnCl_2 was more reactive towards the aromatic rings of biochar produced in a CO_2 atmosphere than in a N_2 atmosphere. This can be inferred from the higher I_D/I_G ratio for *L N-Z* than for *L CD-Z* and *L N-ZCD* than for *L CD-ZCD*. Conversely, KOH was more reactive towards aromatic rings of biochar produced in a N_2 atmosphere than in a CO_2 atmosphere. The higher I_D/I_G ratio for *L N-K* than for *L CD-K* and *L N-KCD* than for *L CD-KCD* support this statement.





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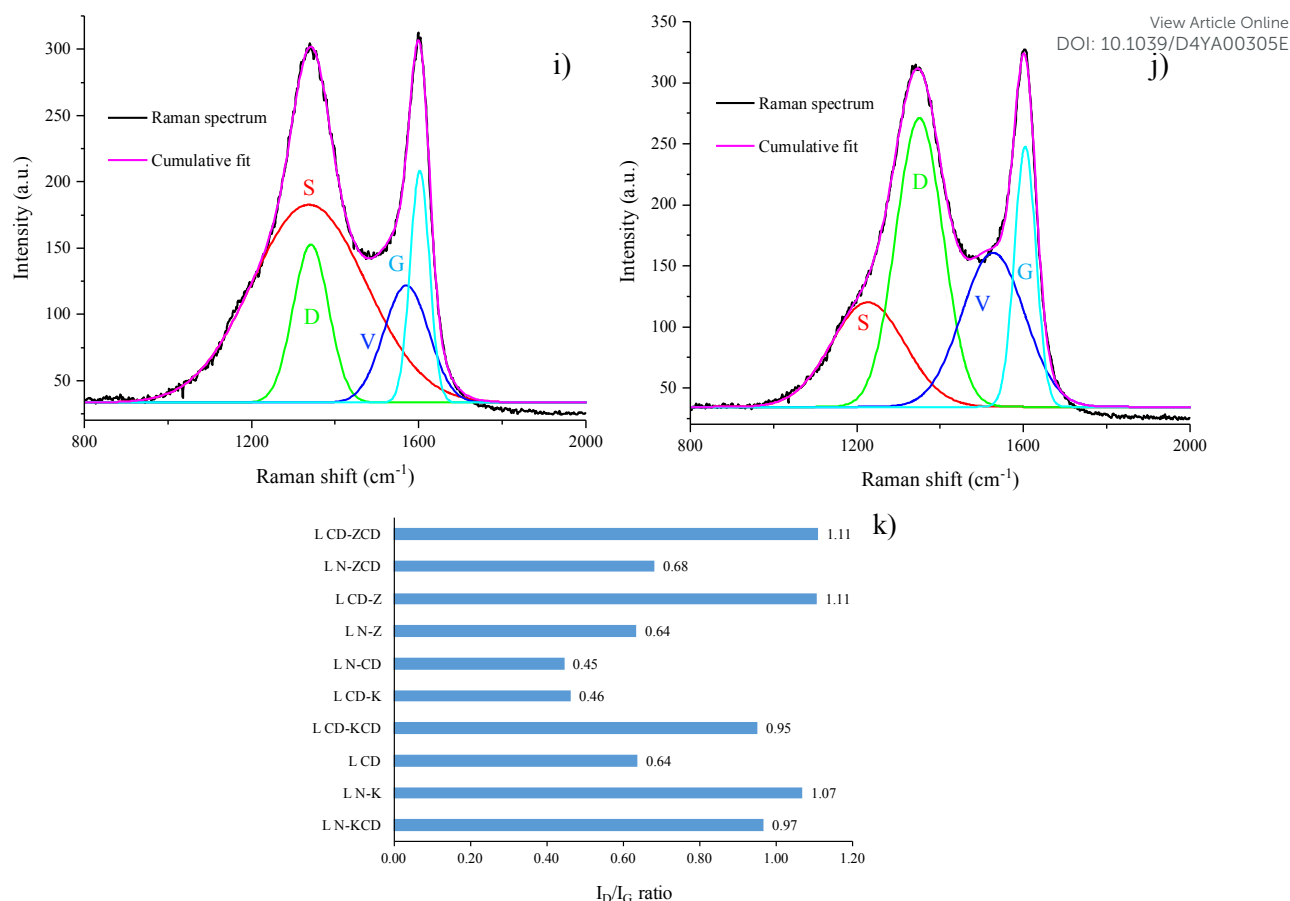
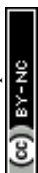


Figure 3. Curve fitting of Raman Spectra (a) *L N-K*, (b) *L CD-K*, (c) *L N-CD*, (d) *L CD*, (e) *L N-KCD*, (f) *L CD-KCD*, (g) *L N-Z*, (h) *L CD-Z*, (i) *L N-ZCD*, (j) *L CD-ZCD*, (k) I_D/I_G ratio.

3.2 Textural properties

The textural properties of the carbonaceous adsorbent significantly affect its CO₂ adsorption performance. Therefore, to evaluate the porosity, N₂ adsorption isotherms were recorded at -196 °C up to a relative pressure of 1.0 bar. Figure 4a shows the N₂ adsorption isotherms of lignin-based APCs prepared using a wide range of activating agents. For all the samples, a steep rise in N₂ adsorption was observed at $P/P_0 < 0.05$. The rise ranged from 65 to 333 cc/g, which could be attributed to micropore filling due to better adsorbent-adsorbate interactions at lower pressures.^{32,33} Thereafter, beyond $P/P_0 = 0.05$, the N₂ adsorption increased gradually, except for *L N-KCD*. For *L N-KCD*, N₂ adsorption continued to rise exponentially up to a P/P_0 of 0.45 and achieved plateau. For all the samples, hysteresis at $P/P_0 > 0.4$ suggested a type IV isotherm according to IUPAC classification. The existence of hysteresis is linked to the capillary condensation of N₂. Hysteresis is a characteristic of mesoporous adsorbents and confirms the presence of micro and mesopores.^{34,35} The pore size distribution curve presented in Figure 4b (and Figure S2) further confirms the microporous and mesoporous nature of all APCs. The figure illustrates pore width maxima occurring at 8.4/9.7/11.1/19.0 Å for *L N-K*, 9.7/12.1/19.8 Å for *L CD-K*, 8.4 Å for *L N-CD*, 19.0 Å for *L CD*, 8.1/9.2/11.6 Å for *L N-KCD*, 9.2/19.0 Å for *L CD-KCD*, 8.4/9.7/19.0 Å for *L N-Z*, 9.7/19.0 Å for *L CD-Z*, 8.4/9.7/19.0 Å for



L N-ZCD and 8.4/9.2/19.0 Å for *L CD-ZCD*. For all the APCs, the pore diameter of ~8 Å available in the pore size distribution curves was large enough to accommodate CO₂ with a kinetic diameter of 3.3 Å.³⁶ This is crucial for efficient CO₂ capture. Pore width maxima centred at 19 Å were common in *L CD* and APCs derived from the secondary activation of *L CD*, such as *L CD-Z* and *L CD-ZCD*. This indicated the absence of a pore-widening effect during secondary chemical activation using ZnCl₂ and physicochemical activation using ZnCl₂ + CO₂. In contrast, the secondary chemical activation of *L CD* using KOH resulted in pore widening, and the maxima shifted to 19.8 Å. The pore size distribution curves suggested that the secondary activation of *L CD* via both chemical and physicochemical activation resulted in the formation of additional micropores.

Table 2 lists the yields and key textural properties of the *L*-based APCs. The conversion yield of the raw biomass to APC ranged within 14.5–40.8 wt.%. The highest S_{BET} of 1480 m²/g and maximum total pore volume of 0.737 cm³/g were obtained for the APC produced via the physicochemical activation of *L N* using KOH+CO₂. In contrast, the chemical activation of *L N* using KOH promoted the formation of micropores, achieving a micro-porosity (ϕ_{micro}) as high as 97.74%. Physicochemical or chemical treatment of *L N* led to better porosity than the identical treatment of *L CD* did. For example, chemical activation of *L N* using KOH resulted in S_{BET} of 1108 m²/g, which is considerably higher than that for the chemical activation of *L CD* using KOH. This could be attributed to the relatively higher processing temperature of *L CD* (i.e., 800 °C), leading to the formation of a sturdy aromatic structure, which could be less susceptible to further activation. For *L N*, combined physical and chemical activation (using KOH + CO₂ and ZnCl₂ + CO₂) produced better porosity than physical activation (using CO₂) and chemical activation (using KOH and ZnCl₂) alone. Compared to KOH activation, physicochemical activation with KOH + CO₂ increased the S_{BET} by 33% and the total pore volume by 31%. However, S_{BET} and total pore volume were improved by ~12% and 10%, respectively, for physicochemical activation using ZnCl₂ + CO₂ compared to activation with ZnCl₂ only. A similar trend was reported in.^{24,28,37} For lignin-based APCs, the percentage of micropore volume (f_{micro}) ranged from 81 to 93%, indicating the dominance of micropores. Micropores are desired for better CO₂ capture.



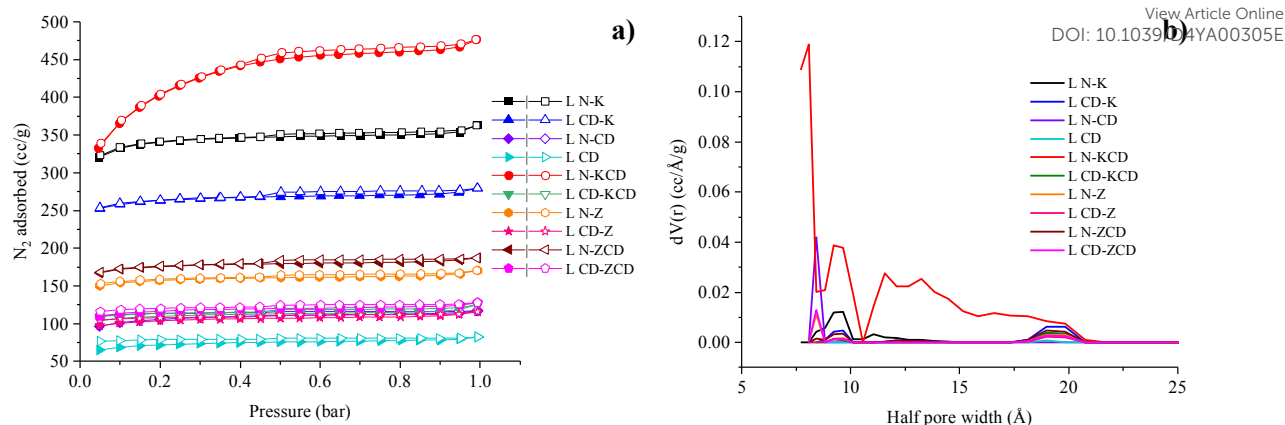


Figure 4. (a) N_2 adsorption/desorption isotherms of lignin-based activated porous carbons at $-196\text{ }^\circ\text{C}$ (solid symbols represent adsorption and hollow symbols indicates desorption), (b) pore size distribution from NLDFT method using N_2 isotherms at $-196\text{ }^\circ\text{C}$.

Table 2. Yield and textural properties of activated carbons derived from lignin protobind 2400 at varied conditions.

| | Yield, wt. % | S_{BET} , m^2/g | S_{micro} , m^2/g | ϕ_{micro} , % | R_{avg} , nm | V_{T} , cm^3/g | V_{micro} , cm^3/g | f_{micro} , % |
|-----------------|--------------|--|--|---------------------------|-----------------------|---|---|------------------------|
| <i>L N-KCD</i> | 14.54 | 1480 | 1383 | 93.45 | 0.995 | 0.737 | 0.597 | 81.00 |
| <i>L N-K</i> | 28.96 | 1108 | 1083 | 97.74 | 1.014 | 0.562 | 0.515 | 91.64 |
| <i>L CD</i> | 40.82 | 269 | 257 | 95.53 | 0.946 | 0.127 | 0.107 | 84.25 |
| <i>L CD-K</i> | 35.28 | 844 | 826 | 97.87 | 1.024 | 0.432 | 0.400 | 92.59 |
| <i>L N-CD</i> | 35.36 | 399 | 385 | 96.49 | 0.908 | 0.181 | 0.159 | 87.84 |
| <i>L CD-KCD</i> | 30.09 | 353 | 338 | 95.75 | 1.093 | 0.193 | 0.163 | 84.46 |
| <i>L N-Z</i> | 38.93 | 504 | 491 | 97.42 | 1.045 | 0.264 | 0.237 | 89.77 |
| <i>L CD-Z</i> | 31.82 | 334 | 322 | 96.40 | 1.071 | 0.180 | 0.155 | 86.11 |
| <i>L N-ZCD</i> | 37.19 | 564 | 551 | 97.70 | 1.026 | 0.290 | 0.266 | 91.72 |
| <i>L CD-ZCD</i> | 31.82 | 377 | 364 | 96.55 | 1.051 | 0.198 | 0.175 | 88.38 |

S_{BET} = Specific BET surface area

S_{micro} = Micro-pore area using t-plot method

ϕ_{micro} = Micro-porosity, % = $(S_{\text{micro}}/S_{\text{BET}}) \times 100$

R_{avg} = Average pore radius

V_{T} = Estimated at a relative pressure $P/P_0 = 0.99$

V_{micro} = Micropore volume estimated using t-plot method

f_{micro} = Percentage of micro-pore volume, % = $(V_{\text{micro}}/V_{\text{T}}) \times 100$

3.3 CO_2 adsorption characteristics

CO_2 and N_2 adsorption isotherms were recorded at 0, 25 and 40 $^\circ\text{C}$ up to 1 bar (Table 3). CO_2 uptake values at 0.1-0.15 bar are also listed in the Table 3. Low-pressure CO_2 uptake at 0.1-0.15 bar is vital as it represents the realistic partial pressure of CO_2 in the flue gas.³⁸ Figure



5a-c demonstrates CO₂ adsorption isotherms at three different temperatures. At 1 bar, saturation in terms of CO₂ uptake was absent for *L N-K*, *L CD-K* and *L N-KCD*, indicating more CO₂ uptake at elevated adsorption pressure. It was consistent over the range of tested adsorption temperatures. The absence of hysteresis indicated that CO₂ adsorption followed Type I isotherms, which further advocates the microporous nature of the APCs.

Despite having higher S_{BET} for physicochemical activated APC (i.e., *L N-KCD*), it indicated lower CO₂ adsorption capacity than chemically activated APC (i.e., *L N-K*). It indicates non-linearity between S_{BET} and CO₂ adsorption capacity, which was commonly observed.^{7,28,39,40} Conversely, combined physical and chemical activation using ZnCl₂ + CO₂ slightly improved CO₂ uptake compared to individual physical or chemical activation using CO₂ or ZnCl₂, respectively. APCs derived via chemical activation using KOH resulted in the highest CO₂ adsorption capacity. The maximum CO₂ adsorption capacity of 5.68 mmol/g at 0 °C/1 bar was observed for *L N-K*. At lower adsorption pressure, *L CD-K* exhibited better CO₂ adsorption than *L N-K*. However, CO₂ adsorption capacity of *L N-K* starts surpassing that of *L CD-K* above adsorption pressure of 0.5 bar. The observation was consistent over the range of adsorption temperature studied. This could be attributed to the superior microporosity of *L CD-K* as micropores are likely to get occupied first at lower adsorption pressure. Two-step physical activation yield slightly better CO₂ adsorption performance than one-step physical activation. Energy penalty during two-step physical activation is yet to be justified by a marginal increase in CO₂ adsorption. From a better CO₂ uptake perspective, the performance of the type of activating agents can be ranked as: KOH > KOH + CO₂ > ZnCl₂ + CO₂ > ZnCl₂ > CO₂. Table 4 compares the CO₂ adsorption capacity of APCs derived from various biomass precursors.

A linear relationship between CO₂ uptake and textural properties (i.e., S_{BET} , S_{micro} , ϕ_{micro} , R_{avg} , V_{T} , V_{micro} , and f_{micro}) is presented in Figure S3 to better understand the parameters affecting the CO₂ adsorption performance of APC. No clear trend was observed between any of the textural properties and CO₂ uptake. It implied that CO₂ adsorption on the APC surface is affected by multiple parameters.⁴¹

3.4 Selectivity and heat of adsorption

For practical on-field gas separation applications, better CO₂ uptake along with higher CO₂/N₂ selectivity is desired. A CO₂/N₂ volume ratio of 15:85 was assumed, and ideal adsorption solution theory was applied to determine CO₂ over N₂ selectivity at 0, 25, and 40 °C/1 bar. Adsorption isotherms of single component were fitted into Langmuir-Freundlich isotherm model Eq.(1) and resulting parameters were fitted to Eq.(2).

$$Q = \frac{q_{\text{sat}} * k * c^n}{1 + k * c^n}$$

Equation 1



$$S = \frac{q_{CO_2}/q_{N_2}}{p_{CO_2}/p_{N_2}}$$

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Equation 2

where, S is CO_2/N_2 selectivity, q is the amount of i^{th} gas adsorbed and p is the relative pressure of the i^{th} gas.

Table 3 lists CO_2/N_2 selectivity for all the APCs, which ranged within 11.9-20.4. A clear trend between selectivity and adsorption temperature was absent. Higher polarizability, quadrupole moment, critical temperature, and lower kinetic diameter for CO_2 than N_2 , favoured better adsorption of CO_2 on the APC surface.⁴² Also, being an electrophilic molecule, CO_2 strongly interacts with heteroatom-containing functional groups of APCs.

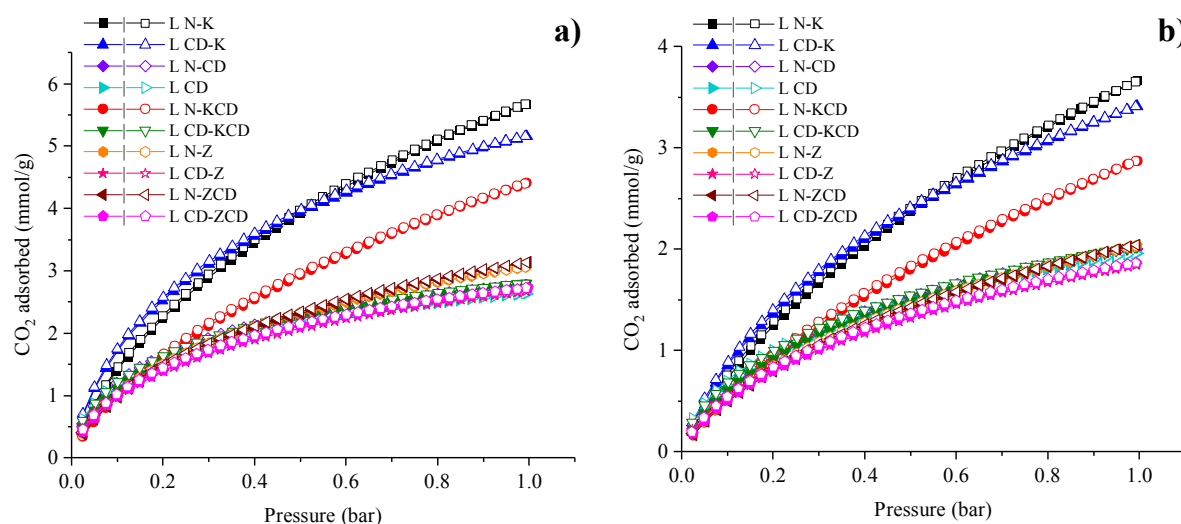
Isosteric heat of adsorption (q_{st}) measures the strength of adhesion between adsorbent and adsorbate, which is linked to ease of regeneration of the adsorbent. Table 3 lists q_{st} values of all the APCs at lower CO_2 loading, which ranged within ~20-33 kJ/mol. The q_{st} value is inversely proportional to the energy required during the regeneration of the adsorbent. For all the APCs, $q_{\text{st}} < 40$ kJ/mol indicated that adsorption predominantly occurred via physisorption through dipole-quadrupole interaction between CO_2 and APC surface. Secondary activation of biochar prepared in CO_2 indicated higher CO_2/N_2 selectivity and q_{st} than that of biochar prepared in the N_2 atmosphere. The observation was consistent for all the tested combination of activating agents considered in the study. For example, $L N-K$ vs. $L CD-K$, $L N-KCD$ vs. $L CD-KCD$, $L N-Z$ vs. $L-CD Z$ and $L N-ZCD$ vs. $L CD-ZCD$. CO_2 carbonization/activation may have modified the surface chemistry of the material or introduced functional groups, leading to stronger interactions with CO_2 molecules. This enhanced interaction can result in a higher heat of adsorption. The similar trend observed for APCs derived from pine sawdust indicates this effect is not much more feedstock sensitive.²⁸ Figure 5d represents variation in q_{st} with CO_2 loading. The elevated q_{st} observed at the minimum CO_2 loading may be explained by a preference for occupying ultrafine pores and/or the adhesion of CO_2 to surface heterogeneity. As CO_2 loading increases, the diminishing trend in the isosteric heat of adsorption can be ascribed to the saturation of strong binding sites. For most of the APCs, a consistently strong correlation with increasing CO_2 loading suggests uniformity in adsorption sites in terms of binding energy. The moderate q_{st} value indicates convenient regeneration, supporting their suitability for multi-cycle CO_2 adsorption applications. Multi-cyclic CO_2 adsorption at 0 °C was executed for the best-performing APC in terms of CO_2 adsorption i.e., $L N-K$ up to 10 cycles. As indicated in Figure 6, a fluctuation of 0.51% in amount of CO_2 adsorbed was observed during 10 consecutive adsorption/desorption cycles. The remarkable stability and reusability of $L N-K$ for CO_2 adsorption could be attributed to non-destructive uptake and release. However, its stability towards the actual flue gas scenario has yet to be tested.

As of 2023, approximately 40 commercial CO_2 capture facilities are actively operating worldwide, with a total annual capture capacity exceeding 45 Mt of CO_2 . Despite the announcement of over 50 upcoming capture facilities scheduled to commence operations by



2030, declared since January 2022, the current project pipeline only represents roughly one-third of the anticipated requirement for achieving net-zero emissions by 2030. Noteworthy advancements have also been observed in the application of CCUS within the industrial sector. In 2022, several new projects were commissioned, encompassing the integration of CCUS into sectors such as iron, steel, fertilizer, and other chemical production processes. Projections indicate that approximately 25 biomass and waste-fired combined heat and power plants could be responsible for capturing around 30 Mt of CO₂ by the year 2030. Considering the ongoing project pipeline, it is anticipated that by 2030, the annual capture capacity, derived from both new constructions and retrofits, could reach around 90 Mt of CO₂ from hydrogen production, approximately 80 Mt from power generation, and roughly 35 Mt from various industrial facilities, including cement and steel production.⁴³

In the wider spectrum, utilization of APC for post-combustion CO₂ capture presents invaluable benefits such as compatibility to current energy systems, easy scalability, and steady operation. APC can be employed in packed-bed adsorption systems, known for their simplicity and straightforward scalability. APC derived from green and renewable sources can effectively capture CO₂ emissions from industries heavily reliant on coal, including cement, chemical, oil refineries, and steel. As per the technical report from the National Energy Technology Laboratory (NETL), an adsorbent proves practical and economically viable for CO₂ capture if it demonstrates an isothermal CO₂ adsorption capacity exceeding 3 mmol/g at 25 °C and 1 bar.⁴⁴ The *L N-K*, as indicated, exhibits an isothermal CO₂ adsorption capacity of 3.66 mmol/g at 25 °C and 1 bar, signifying its suitability for commercial operations. Along with CO₂ capture applications, the conversion of lignin into a stable form of APC restricts the release of carbon into the atmosphere.



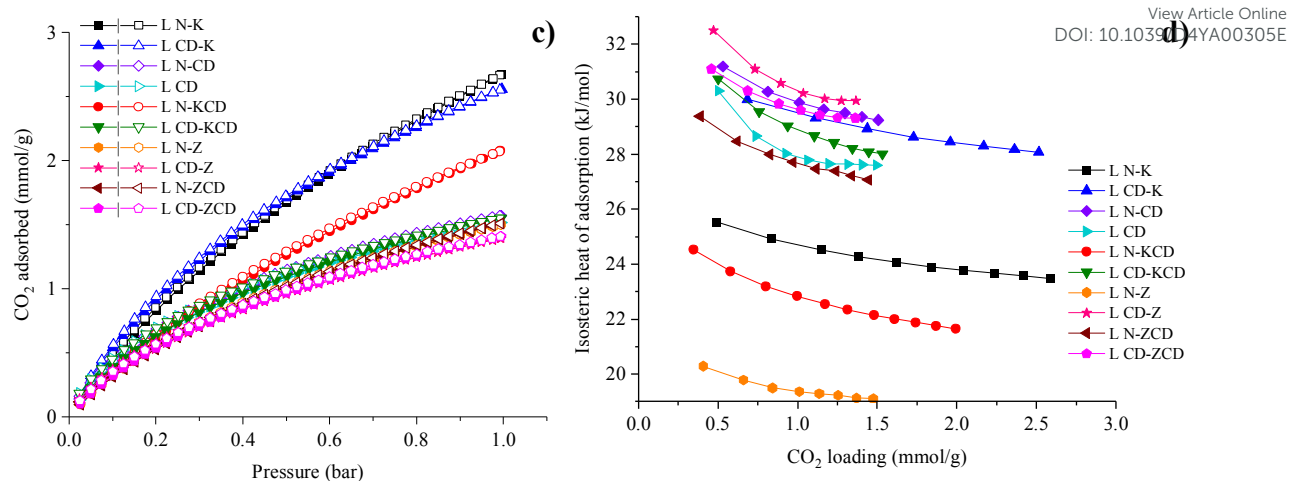


Figure 5. CO₂ adsorption isotherms at (a) 0 °C, (b) 25 °C, and (c) 40 °C (solid symbols represent adsorption, and hollow symbols indicate desorption), and (d) isosteric heat of CO₂ adsorption.

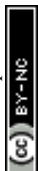




Table 3. Gas adsorption performance of activated carbons at 0, 25, and 40 °C.

| Sample | CO ₂ adsorption capacity, mmol/g | | | | | | N ₂ adsorption capacity, mmol/g | | | <i>q_{st}</i> (kJ/mol) | CO ₂ /N ₂ selectivity | | |
|-----------------|---|-------|-------|----------------|-------------|-------------|--|-------|-------|--------------------------------|---|-------|-------|
| | 1 bar | | | 0.1 (0.15) bar | | | 0 °C | 25 °C | 40 °C | | 0 °C | 25 °C | 40 °C |
| | 0 °C | 25 °C | 40 °C | 0 °C | 25 °C | 40 °C | | | | | | | |
| <i>L N-K</i> | 5.68 | 3.66 | 2.67 | 1.38 (1.84) | 0.72 (1.00) | 0.46 (0.66) | 0.88 | 0.52 | 0.34 | 25.53 | 13.52 | 12.56 | 12.50 |
| <i>L CD-K</i> | 5.16 | 3.41 | 2.56 | 1.73 (2.17) | 0.85 (1.12) | 0.54 (0.73) | 0.75 | 0.46 | 0.30 | 29.99 | 18.51 | 16.09 | 16.14 |
| <i>L N-CD</i> | 2.77 | 2.00 | 1.57 | 1.16 (1.40) | 0.61 (0.79) | 0.40 (0.54) | 0.50 | 0.29 | 0.18 | 31.20 | 18.20 | 18.10 | 20.39 |
| <i>L CD</i> | 2.64 | 1.96 | 1.52 | 1.07 (1.31) | 0.61 (0.79) | 0.39 (0.53) | 0.47 | 0.28 | 0.18 | 30.31 | 17.69 | 17.88 | 18.79 |
| <i>L N-KCD</i> | 4.40 | 2.87 | 2.08 | 0.99 (1.31) | 0.52 (0.73) | 0.34 (0.48) | 0.66 | 0.40 | 0.26 | 24.53 | 12.97 | 11.86 | 11.97 |
| <i>L CD-KCD</i> | 2.80 | 2.02 | 1.55 | 1.11 (1.34) | 0.61 (0.78) | 0.39 (0.53) | 0.47 | 0.28 | 0.17 | 30.74 | 18.21 | 18.58 | 19.92 |
| <i>L N-Z</i> | 3.06 | 2.03 | 1.50 | 1.00 (1.26) | 0.51 (0.67) | 0.32 (0.44) | 0.49 | 0.29 | 0.17 | 20.29 | 16.45 | 15.15 | 17.17 |
| <i>L CD-Z</i> | 2.67 | 1.84 | 1.39 | 0.97 (1.20) | 0.50 (0.66) | 0.32 (0.43) | 0.44 | 0.26 | 0.16 | 32.51 | 17.71 | 16.50 | 17.82 |
| <i>L N-ZCD</i> | 3.14 | 2.04 | 1.51 | 0.97 (1.24) | 0.50 (0.65) | 0.31 (0.43) | 0.48 | 0.29 | 0.18 | 29.38 | 16.53 | 14.57 | 15.84 |
| <i>L CD-ZCD</i> | 2.73 | 1.87 | 1.41 | 0.98 (1.21) | 0.51 (0.67) | 0.33 (0.44) | 0.45 | 0.27 | 0.17 | 31.10 | 17.46 | 16.13 | 17.17 |

Table 4. Comparison of CO₂ adsorption performance of activated porous carbon derived via chemical activation of various biomass precursors.

| Precursor (P) | Activating agent (AA) | Impregnation ratio (P:AA) | Carbonization (C) & activation conditions (A) (T) (°C)/residence time (min.) | Yield (wt.%) | <i>S</i> _{BET} (m ² /g) | <i>V_t</i> (cm ³ /g) | CO ₂ adsorption conditions | | CO ₂ adsorption capacity (mmol/g) | <i>q_{st}</i> (kJ/mol) | Selectivity (CO ₂ /N ₂) ^e | Ref. |
|---|--------------------------------|---------------------------|--|--------------|---|---|---------------------------------------|---------|--|--------------------------------|---|------|
| | | | | | | | T (°C) | P (bar) | | | | |
| Bamboo shoot shells ^b | CaCl ₂ | 1:1 | C ^c -600/120 A-700/120 | - | 541 | 0.24 | 0/25 | 1/1 | 3.14/2.39 | 35.0 | - | 45 |
| Bamboo shoot shells + urea ^b | K ₂ CO ₃ | 1:3 | C ^c -500/120 A-800/- | - | 1958 | 0.83 | 0/25 | 1/1 | 7.52/3.60 | 33.0 | 14.0 | 46 |
| Chitosan ^a | KOH | 3:2 | A-700/60 | - | 1506 | 0.64 | 0/25 | 1/1 | 6.91/4.40 | 32.5 | 21.0 | 47 |



| | | | | | | | | | | | | |
|------------------------------------|--|-------|--------------------------------------|-------|------|------|---------|-------|----------------|------|------|----------------------|
| Coconut shells ^b | K ₂ S ₂ O ₃ | 1:1 | C ^c - A-700/60 | - | 1188 | 0.47 | 0/25 | 1/1 | 5.31/3.59 | 35.0 | 20.0 | 48 |
| Coconut shells ^b | K ₂ S ₂ O ₈ | 1:1 | C ^c -500/120 A-750/120 | - | 581 | 0.26 | 0/25 | 1/1 | 3.77/2.56 | 39.0 | 17.0 | 49 |
| Coconut shell ^b | KOH | 1:3 | C ^c -500/120 A-600/60 | - | 1172 | 0.44 | 0/25 | 1/1 | 6.04/4.23 | 37.0 | 22.0 | 50 |
| Corn cob ^b | KOH | 1:3 | C ^d -230/480 | 16.3 | 2716 | 0.71 | 15 | 1 | 4.50 | 24.1 | - | 51 |
| | ZnCl ₂ | 1:3 | A-600/60 | 18.9 | 1567 | 0.48 | 15 | 1 | 3.64 | 17.7 | - | |
| | H ₃ PO ₄ | 1:3 | | 17.3 | 2314 | 0.59 | 15 | 1 | 2.95 | 9.3 | - | |
| Cotton bolls ^b | KOH | 1:2 | C ^c -500/60 A-700/90 | 23.3 | 1381 | - | 25 | 1 | 5.14 | - | - | 52 |
| Garlic peel ^b | KOH | 1:2 | C ^d -200/1440 A-800/60 | - | 1262 | 0.70 | 0/25 | 1/1 | 4.33/2.82 | - | - | 53 |
| Lotus seeds ^b | KOH | 1:3 | C ^c -600/120 A-800/120 | - | 2230 | 0.96 | 0/25 | 1/1 | 6.80/3.10 | 30.4 | - | 54 |
| Macadamia nutshell ^b | KOH | 1:1.7 | C ^c -500/120 A-771/150 | - | 1417 | 0.75 | 0/25/40 | 1/1/1 | 6.58/3.94/3.15 | 27.0 | - | 55 |
| Slash pine ^a | KOH | 1:4 | A-580/120 | 19.5 | 1185 | 0.35 | 0/15 | 1 | 4.93/3.86 | 39.7 | - | 56 |
| Pine sawdust ^b | KOH | 1:2 | C ^c -600/90 A-800/90 | 19.89 | 1319 | 0.66 | 0/25/40 | 1/1/1 | 6.35/3.82/2.81 | 24.9 | 11.8 | 28 |
| Lignin protobind 2400 ^b | KOH | 1:2 | C ^c -600/90 A-800/90 | 28.96 | 1108 | 0.56 | 0/25/40 | 1/1/1 | 5.68/3.66/2.67 | 25.5 | 12.6 | Present study |

^a Direct activation

^b Two-step activation

^c Pyrolytic carbonization

^d Hydrothermal carbonization

^e at 25 °C

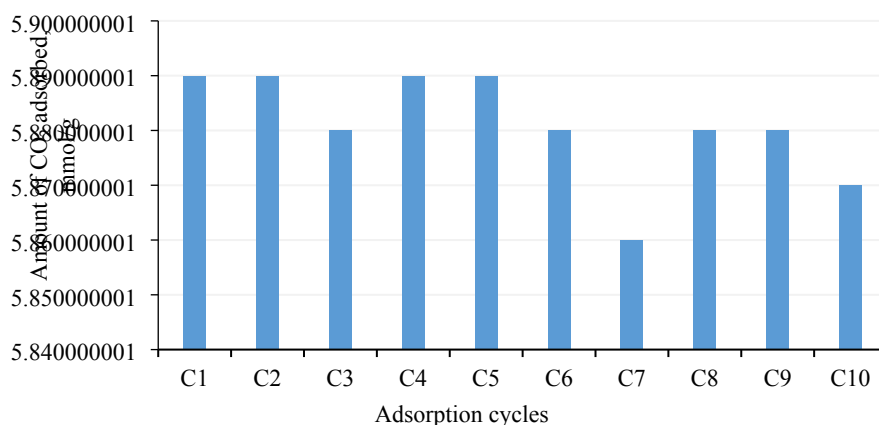


Figure 6. Multi-cyclic CO₂ adsorption performance of *L N-K* at 0 °C.

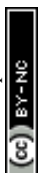
4 Conclusion

Lignin protobind 2400 was converted to a value-added product, activated porous carbon (APC) using combined activating agents KOH + CO₂ and ZnCl₂ + CO₂. Also, the effectiveness of the combined physicochemical activation with individual chemical and physical activating agents was compared. Although KOH + CO₂ activation improved BET surface area by 33% compared to only KOH activation, CO₂ uptake for KOH + CO₂ activation decreased by 23%, compared to only KOH activation. On the other hand, physicochemical activation using ZnCl₂ + CO₂ slightly improved BET surface area as well as CO₂ uptake compared to only ZnCl₂ and only CO₂ activation. From a better CO₂ uptake perspective, the performance of the type of activating agents can be ranked as: KOH > KOH + CO₂ > ZnCl₂ + CO₂ > ZnCl₂ > CO₂. Secondary activation of biochar carbonized in the N₂ atmosphere offered better BET surface area and increased CO₂ uptake compared to that of biochar carbonized in the CO₂ atmosphere. Considerably, higher CO₂/N₂ selectivity and isosteric heat of CO₂ adsorption were observed for APC derived from secondary activation of biochar carbonized in a CO₂ environment than in N₂ environment. The combination of better CO₂ adsorption capacity, lower heat of adsorption, reasonably good CO₂/N₂ selectivity, and excellent reusability/stability of lignin-based APC supported its utilization for post-combustion CO₂ capture.

Declaration of Competing Interest

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

CRedit authorship contribution statement



Himanshu Patel: Methodology, Validation, Formal analysis, Investigation, Writing – original draft. **Amar Mohanty:** Conceptualization, Resources, Supervision, Investigation, Validation, Writing – review & editing. **Manjusri Misra:** Conceptualization, Methodology, Funding acquisition, Project administration, Resources, Supervision, Investigation, Validation, Writing – review & editing.

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Data for this article, including Raw/processed/metadata files are available at 'Open Science Framework' at https://osf.io/kqfuy/?view_only=7cda4a7a86174137b9f1ecc2548dc5ce.

