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Article

Sustainable Development of Sawdust Biochar as a Green and Promising Material for CO₂ Capture Technologies

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Abstract: The study investigates the synthesis of highly porous ZnCl₂-activated biochars derived from sawdust via controlled pyrolysis at 300 °C and 500 °C, aimed at enhancing CO₂ adsorption performance. The effects of pyrolysis temperature and chemical activation on particle size distribution, surface area, and pore structure are systematically analyzed. Particle size analysis has revealed that higher pyrolysis temperature and ZnCl₂ activation significantly reduced both median and mean particle sizes, resulting in finer and more uniform biochar morphology. BET analysis has demonstrated a substantial increase in specific surface area and micropore volume upon ZnCl₂ activation, particularly at 500 °C, where the activated biochar (S500ZC) has exhibited a high surface area of 717.60 m²/g and a micropore area of 616.60 m²/g. CO₂ adsorption isotherms are recorded at 25 °C confirmed that both thermal treatment and activation markedly enhanced adsorption capacity, with the highest uptake of 35.34 cm³/g achieved by S500ZC. The adsorption performance has followed the order: S300NZC < S300ZC < S500NZC < S500ZC, closely correlating with microporosity and surface textural development. The findings highlight the potential of ZnCl₂-activated biochars as cost-effective, environmentally friendly, and efficient sorbents for scalable CO₂ mitigation technologies.

Keywords: biochar; CO₂ storage; Porosity; BET surface area; carbon capture and storage (CCS); chemical activation; microporosity

1. Introduction

Emissions of carbon dioxide (CO₂) from human activities, especially the burning of fossil fuels and diverse industrial processes, are largely acknowledged as a significant factor in climate change [1,2]. Several studies have indicated that atmospheric CO₂ levels have been consistently rising since the industrial revolution, leading to global temperature increases, ocean acidification, and ecological disturbances [3,4]. The ongoing dependence on coal, oil, and natural gas, particularly in electricity generation, transportation, and heavy industries like cement and steel production, has resulted in a significant rise in greenhouse gas emissions [5]. Global climate organizations and scientific entities have consistently highlighted that, without urgent and ongoing mitigation actions, the effects of increasing CO₂ levels will become progressively more severe [6,7]. This critical scenario highlights the necessity for efficient approaches to control and lower CO₂ emissions in different sectors.

Technologies for carbon capture and storage (CCS) have become an essential method to tackle these issues [7]. CCS consists of capturing CO₂ at its origin, compressing and transporting it, and then either storing it in geological formations or using it in industrial applications [8]. It is commonly seen as a vital instrument in the collection of strategies designed to reach net-zero emissions. Among the different CO₂ capture techniques, post-combustion capture is the most commonly applicable,

especially for modifying existing fossil fuel-powered plants [9,10]. Nevertheless, traditional technologies like amine-based solvents, while efficient, face various drawbacks such as significant energy use for regeneration, corrosion problems, deterioration after multiple cycles, and environmental issues related to solvent disposal [11,12]. These limitations have prompted investigations into other solid sorbents capable of providing significant CO₂ absorption, selectivity, thermal and chemical resilience, along with minimal regeneration expenses.

Biochar, a carbon-rich porous substance produced from the thermal transformation of biomass in low-oxygen environments, has gained growing interest as an eco-friendly material for CO₂ adsorption [13–15]. Generated from diverse organic materials like agricultural byproducts, forestry waste, livestock manure, and sewage sludge, biochar provides a sustainable, affordable, and eco-friendly choice for carbon sequestration [1,16]. The pyrolysis method not only prevents waste from entering landfills but also produces a stable carbon-rich material that can remain in the environment for hundreds to thousands of years. The inherent stability of carbon in biochar makes it a vital resource for sequestering carbon [17,18]. Moreover, the physicochemical characteristics of biochar, like elevated surface area, adjustable porosity, and surface functional groups, can be modified to improve its engagement with CO₂ molecules [19–21].

In contrast to traditional sorbents like zeolites and metal–organic frameworks (MOFs), which often involve intricate synthesis and high costs, biochars can be created through comparatively straightforward and scalable methods. Biochar characteristics can be modified by choosing appropriate feedstocks and altering pyrolysis conditions like temperature, heating rate, and duration [22]. Moreover, chemical activation (e.g., using KOH, ZnCl₂, H₃PO₄) and surface functionalization (e.g., nitrogen doping, amine grafting) are commonly utilized to further improve the adsorption capacity and selectivity of biochars for CO₂ [23]. Such changes usually lead to a rise in microporosity and the addition of basic functional groups that positively interact with acidic CO₂ molecules [24]. Certain engineered biochars have shown CO₂ adsorption capabilities surpassing 2 mmol/g under ambient conditions, positioning them as rivals to commercial activated carbons and various solid adsorbents [11].

An additional important benefit of biochar is its sustainability and circularity. Using waste biomass as a raw material, biochar production promotes the concepts of waste valorization and circular economy [25]. Additionally, combining biochar-based CO₂ capture with renewable or low-emission energy systems can yield synergistic environmental advantages, especially when the pyrolysis process is fine-tuned for energy recovery and co-product creation. In some instances, the production of biochar may actually be deemed carbon-negative, based on the lifecycle emissions and the applications at the end of its use [18]. Nonetheless, challenges persist in comprehending the relationships among structure, properties, and performance that dictate CO₂ adsorption, along with the need for standardized methods to assess and compare biochars created under varying conditions. Additional studies are required to enhance activation techniques, boost adsorption kinetics and selectivity, and guarantee the durability of biochars in real-world operating circumstances.

This research utilizes waste sawdust as a biomass precursor for biochar creation, which were pyrolyzed at temperatures of 300 °C and 500 °C to examine how thermal processing affects the structural characteristics and CO₂ adsorption capacities of the produced biochars. Pyrolysis temperatures of 300 °C and 500 °C are chosen to investigate the influence of thermal treatment on the physicochemical characteristics of biochars derived from wood. A temperature of 300 °C represents low-temperature pyrolysis, generally leading to biochars that have a higher yield and increased concentration of oxygen-containing surface functional groups. These features can improve CO₂ adsorption via physisorption and surface interactions. Conversely, 500 °C signifies a moderate pyrolysis environment that fosters the formation of microporous structures, enhanced surface area, and elevated carbon levels as a result of intensified devolatilization and aromatization. Comparing these two temperature regimes allows for an assessment of how the degree of carbonization and the development of porosity impact CO₂ uptake efficiency.

Zinc chloride (ZnCl_2) has been utilized as a chemical activating agent before pyrolysis to improve the porosity and surface reactivity of the biochars. ZnCl_2 is a commonly utilized Lewis acid recognized for its dehydrating characteristics and its capacity to aid in the decomposition of cellulose and hemicellulose elements during pyrolysis. This activation procedure encourages the creation of a more porous configuration with a greater number of micropores and an expanded surface area, both of which are essential factors for enhancing gas adsorption. Additionally, ZnCl_2 activation can create advantageous surface functional groups and improve the availability of adsorption sites, rendering it an appropriate and efficient option for boosting the CO_2 capture ability of biochars derived from biomass. This study seeks to enhance the development of sustainable and effective biochar-based adsorbents for carbon capture methods, providing an eco-friendly and economical strategy for reducing CO_2 emissions.

2. Materials and Methods

2.1. Production of Biochar

In this study, sawdust collected from a woodworking shop in Ansan, South Korea, is used as the raw biomass for biochar production. The biomass is oven-dried at 105°C for 48 hours to remove inherent moisture and is then ground using an electric grinder (Cuckoo Electronics, Seoul, South Korea) to obtain a uniform particle size. The ground biomass is divided into two portions: one is subjected to chemical activation using a 1 M aqueous ZnCl_2 (DUKSAN Reagents, South Korea) solution, while the other is kept unmodified to serve as a control. For the activation, 1 kg of biomass is mixed with 1 L of ZnCl_2 solution and kept for 12 h at room temperature to ensure proper impregnation.

Both the activated and non-activated biomass samples are pyrolyzed at two different temperatures, 300°C and 500°C , in an electric muffle furnace (Model MSF-22, Lab House, Gyeonggi-do, South Korea). The temperature is increased at a constant heating rate of $10^\circ\text{C}/\text{min}$ and then held isothermally at the target temperature for 1 h to complete carbonization. After pyrolysis, the ZnCl_2 -activated biochars are thoroughly washed with deionized water to remove residual ZnCl_2 and subsequently dried. The resulting biochars are labeled based on their pyrolysis temperature and activation status: S300NZC (300°C , non-activated), S300ZC (300°C , ZnCl_2 -activated), S500NZC (500°C , non-activated), and S500ZC (500°C , ZnCl_2 -activated).

2.2. Characterizations

The particle size distribution of the biochars is analyzed using a laser scattering particle size distribution analyzer (LA-960, HORIBA, Kyoto, Japan). The surface morphology and elemental composition are examined using a field emission scanning electron microscope (FE-SEM, SU5000, Hitachi) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. To identify surface functional groups, Fourier-transform infrared spectroscopy (FT-IR; UATR Two, PerkinElmer, Shelton, CT, USA) is employed.

The pore structure and specific surface area are determined by nitrogen adsorption-desorption analysis using the Brunauer-Emmett-Teller (BET) method on an accelerated surface area and porosimetry system (ASAP 2460, Version 3.01, Micromeritics, Norcross, GA, USA). Prior to analysis, the biochar samples are degassed at 150°C for 6 h. Measurements are conducted at -195.850°C across a relative pressure (P/P_0) range of 0.0 to 1.0.

To assess the CO_2 capture capacity, CO_2 adsorption-desorption measurements are carried out using a CO_2 adsorption isotherm analyzer (TriStar II Plus, Version 3.03, Micromeritics, Norcross, GA, USA), also based on the BET method. Before testing, the samples are degassed under vacuum at 110°C for 10 h. The analysis is performed at a constant bath temperature of 25°C over a relative pressure (P/P_0) range from 0.0 to 0.016.

3. Results

3.1. Particle Size Distribution of Biochar

The particle size distribution of the synthesized biochar samples, as summarized in Table 1, reveals significant changes influenced by both pyrolysis temperature and ZnCl₂ activation. These factors play a critical role in modifying the physical morphology of biochar particles, thereby impacting their surface area, reactivity, and performance in various applications. An increase in pyrolysis temperature from 300 °C to 500 °C has resulted in a marked reduction in both median and mean particle sizes for the non-activated and ZnCl₂-activated samples. For non-activated biochar, the median particle size is decreased from 11.489 μm (S300NZC) to 5.704 μm (S500NZC), and the mean particle size is reduced from 17.334 μm to 11.494 μm. A similar trend is observed for ZnCl₂-activated biochars, where the median size has been decreased from 8.444 μm (S300ZC) to 5.749 μm (S500ZC), and the mean size from 9.461 μm to 8.052 μm. These reductions in particle dimensions are primarily attributed to enhanced thermal degradation and devolatilization processes at higher temperatures. Elevated pyrolysis temperatures accelerate the breakdown of biomass polymers such as cellulose, hemicellulose, and lignin, resulting in fragmentation and pore collapse. This leads to the formation of smaller, denser, and more homogeneous carbon particles.

Table 1. Particle size distribution of biochar.

Parameter		S300NZC	S300ZC	S500NZC	S500ZC
Transmittance (Red) (%)		88.4	81.1	60.8	58.6
Transmittance (Blue) (%)		88.7	82.1	59.5	57.8
Median size (μm)		11.489	8.444	5.704	5.749
Mean size (μm)		17.334	9.461	11.494	8.052
Diameter on cumulative(μm)	10 (%)	4.387	4.393	1.616	2.208
	50 (%)	11.489	8.444	5.704	5.749
	90 (%)	33.330	15.299	25.913	14.589

The incorporation of ZnCl₂ as an activating agent has further intensified the size reduction at both temperature levels. At 300 °C, ZnCl₂ activation has caused the mean particle size to decrease significantly from 17.334 μm (S300NZC) to 9.461 μm (S300ZC). At 500 °C, a similar reduction is observed from 11.494 μm (S500NZC) to 8.052 μm (S500ZC). The chemical activation process promotes depolymerization and enhances porosity by facilitating the removal of volatile matter and inhibiting tar formation. ZnCl₂, a Lewis acid, exhibits a strong dehydrating effect that disrupts hydrogen bonding and weakens the cellulose-lignin matrix during pyrolysis, thereby promoting finer particle formation through structural disintegration.

Moreover, the cumulative size distribution (D₁₀, D₅₀, and D₉₀ values) confirms a general narrowing of particle size distribution with increasing temperature and activation. Notably, the D₉₀ value, a measure of the diameter below which 90% of the particles fall, decreased from 33.330 μm (S300NZC) to 25.913 μm (S500NZC) in non-activated samples, and from 15.299 μm (S300ZC) to 14.589 μm (S500ZC) in activated samples. This reduction in D₉₀ indicates a substantial decline in the fraction of large particles and reflects an improvement in particle size uniformity. The D₁₀ values also reduced (e.g., from 4.387 μm in S300NZC to 1.616 μm in S500NZC), suggesting that a larger proportion of ultra-fine particles formed under higher severity conditions. In addition to particle size, optical transmittance data also suggest morphological evolution. The red and blue channel transmittance values progressively declined with increasing temperature and activation, suggesting denser and optically darker biochar particles, likely due to increased graphitization and aromatic condensation.

3.2. Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy

The surface morphology and elemental composition of the synthesized biochars are systematically analyzed using SEM-EDS, as illustrated in Figure 1(a–h). The SEM micrographs clearly show that both the pyrolysis temperature and ZnCl₂ activation play pivotal roles in tailoring the surface architecture of the biochars. At 300 °C, the non-activated biochar (S300NZC) exhibits a

relatively dense, compact structure with minimal porosity, indicating partial thermal degradation of the biomass. In contrast, the ZnCl_2 -activated S300ZC shows a moderately developed porous texture, with evident surface etching and early-stage pore formation due to the dehydrating and foaming effect of ZnCl_2 during pyrolysis. However, these morphological changes become significantly more pronounced at 500 °C. The non-activated S500NZC displays an aligned, tubular structure, likely retaining partially intact vascular bundles of the precursor biomass. Remarkably, the activated S500ZC exhibits a well-developed, interconnected, and sponge-like microporous framework with thin walls and abundant voids, indicative of enhanced carbon skeleton reorganization and volatile carbon matter removal facilitated by ZnCl_2 activation at higher temperature [26].

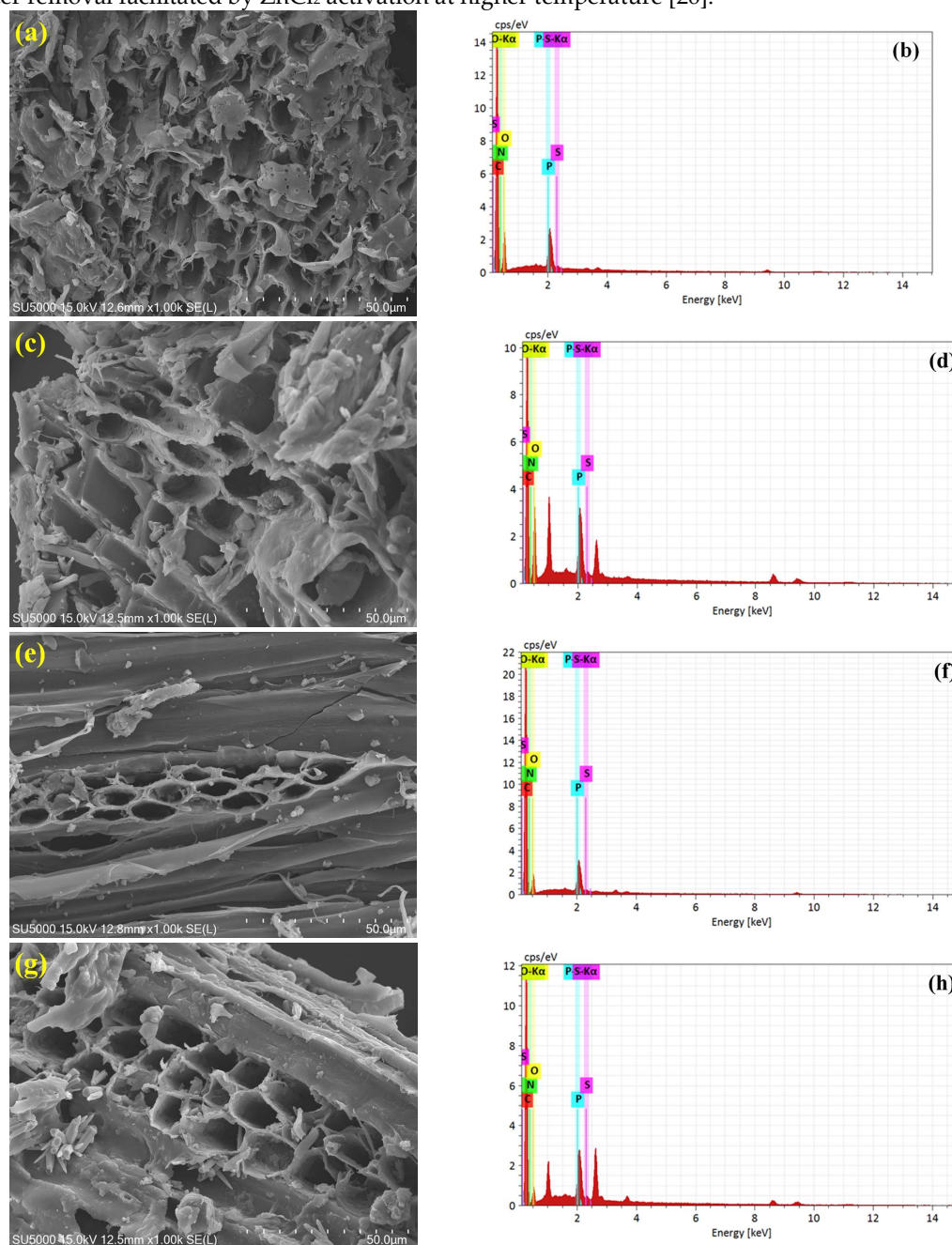


Figure 1. Surface Morphology by FE-SEM and respective EDS spectra of (a, b) S300NZC, (c, d) S300ZC, (e, f) S500NZC, and (g, h) S500ZC.

To complement the surface morphology, EDS spectra and elemental analysis (Table 2) provide vital information on the compositional evolution of the biochars under varying pyrolysis and activation conditions. Carbon, nitrogen, and oxygen dominate the elemental composition, with phosphorus and sulfur present as minor yet functional heteroatoms. A general trend of increasing carbon content with pyrolysis temperature is observed, rising from 60.1% in S300NZC to 66.7% in S500ZC, suggesting enhanced aromatization and graphitic structure formation at elevated temperatures. Concurrently, oxygen content decreases from 23.8% in S300NZC to 12.8% in S500ZC, reflecting substantial deoxygenation due to the loss of surface-bound oxygen functionalities. This is further supported by the calculated O/C molar ratios, which drop from 0.297 (S300NZC) and 0.425 (S300ZC) to 0.178 (S500NZC) and 0.144 (S500ZC), respectively. The decreasing O/C ratio signifies increasing carbonization, improved hydrophobicity, and structural stability of the high-temperature chars [27].

Table 2. EDS analysis of elemental distribution on biochar surfaces.

Biochar ID	Element	C	N	O	P	S
S300NZC	Mass (%)	60.1	12.7	23.8	3.2	0.2
S300ZC	Mass (%)	53.9	10.7	30.6	4.4	0.4
S500NZC	Mass (%)	65.7	15.8	15.6	2.8	0.1
S500ZC	Mass (%)	66.7	15.8	12.8	4.3	0.4

Interestingly, nitrogen content remains relatively high in the S500 samples (15.8% in both S500NZC and S500ZC), indicating the retention of thermally stable nitrogen species, such as pyridinic-N and graphitic-N, which contribute positively to electronic conductivity and active surface sites. ZnCl₂ activation also promotes phosphorus incorporation, as evident from the higher P content in S300ZC (4.4%) and S500ZC (4.3%) compared to their non-activated counterparts. Although sulfur is present in small amounts (0.1–0.4%), its retention, particularly in activated samples, may enhance surface reactivity and provide redox-active sites for CO₂ interaction or energy storage applications [28].

Elemental mapping from EDS confirms the uniform distribution of C, N, O, P, and S across the carbon matrix, suggesting homogenous presence rather than localized clustering. Such uniform heteroatom existence is essential for tailoring surface polarity, introducing defect sites, and enhancing adsorption, catalytic, or electrochemical behaviors. Collectively, these results emphasize that the synergistic effects of optimized pyrolysis temperature and ZnCl₂ activation result biochars with highly porous morphologies, high carbon content, reduced O/C ratio, and effective heteroatom doping, rendering them excellent candidates for advanced applications such as gas adsorption, energy storage, and catalysis [29].

3.3. FTIR Spectroscopy

The FTIR spectra of the biochar samples presented in Figure 2 (a-b) provide insightful information regarding the evolution of surface functional groups as influenced by pyrolysis temperature and ZnCl₂ activation. Across all samples, a broad absorption band centered around 3400 cm⁻¹ is observed, corresponding to the stretching vibrations of hydroxyl (–OH) and amine (–NH) groups [30,31], which are commonly derived from lignocellulosic biomass. This feature confirms the retention of polar functionalities that can influence hydrophilicity and surface reactivity. A weak but distinguishable peak at 2927 cm⁻¹, attributed to C–H stretching vibrations in aliphatic hydrocarbons, appears in both S300NZC and S300ZC [32,33]. However, this peak disappears in the 500 °C samples Figure 2(b), indicating the effective decomposition of thermally unstable aliphatic chains and volatile organic moieties under higher pyrolysis temperatures.

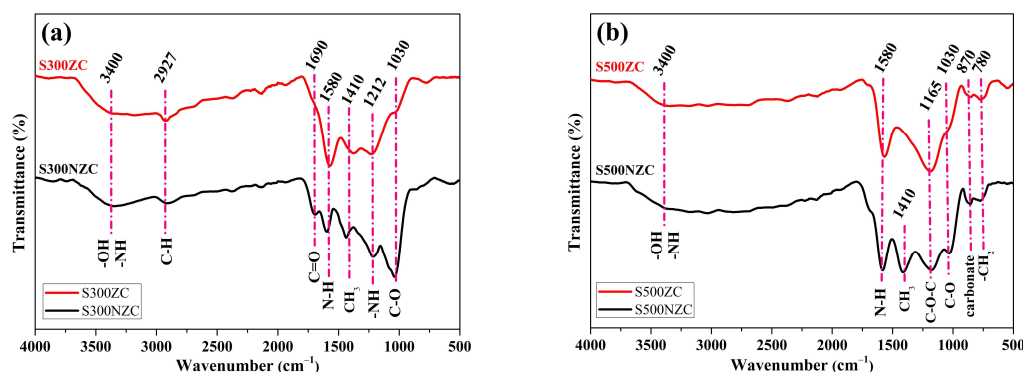


Figure 2. FTIR spectra of (a) S300N/ZC and S300ZC, (b) S500N/ZC and S500ZC.

The absorption band at 1690 cm^{-1} , associated with the stretching vibrations of carbonyl ($\text{C}=\text{O}$) groups in carboxylic acids or ketones [34,35], is clearly evident in S300N/ZC but diminishes in the ZnCl_2 -activated S300ZC and completely vanishes in both 500°C samples. This observation highlights the progressive loss of carboxyl functionalities with increasing temperature, consistent with enhanced decarboxylation and aromatization processes. A prominent and persistent peak around 1580 cm^{-1} , assigned to N-H bending and/or skeletal vibrations of aromatic rings [36,37], is present in all samples irrespective of treatment. This suggests the thermal stability of certain nitrogenous structures or aromatic domains, which are more resilient during pyrolysis and may play a crucial role in tuning adsorption and electrochemical properties.

Another noticeable feature is the band at 1410 cm^{-1} , attributed to $-\text{CH}_3$ bending vibrations [38]. This peak remains visible across all samples, although its relative intensity decreases at higher temperatures, indicating partial cleavage of methyl-substituted structures. In the 300°C samples, particularly S300ZC, a shoulder at 1212 cm^{-1} is observed, corresponding to N-H wagging modes typically found in primary or secondary amines [38]. This peak disappears entirely in both 500°C samples, pointing to the thermal degradation of labile nitrogen functionalities during high-temperature treatment.

The band at 1030 cm^{-1} , representative of C-O stretching vibrations from alcohols, ethers, or ester groups [39], appears across all samples but is significantly reduced in intensity for ZnCl_2 -activated specimens. This suppression of oxygenated functionalities suggests partial chemical etching and dehydration induced by the Lewis acidic nature of ZnCl_2 , which facilitates oxygen removal and promotes structural rearrangement. Importantly, at 500°C , especially in the S500ZC sample, several new features emerge: a distinct peak at 1165 cm^{-1} corresponding to asymmetric stretching of C-O-C linkages [40], a sharp peak at 870 cm^{-1} attributed to carbonate groups [36,41], and a smaller band at 780 cm^{-1} arising from CH_2 bending vibrations [42,43]. The presence of these bands indicates increased mineralization and formation of stable structural motifs during high-temperature pyrolysis, further promoted by the catalytic activation effects of ZnCl_2 .

The FTIR analysis reveals that elevated pyrolysis temperature facilitates the removal of labile organic and nitrogen-containing groups, while ZnCl_2 activation significantly alters the oxygenated functionalities, leading to structural reorganization and enhanced aromaticity. The persistence of nitrogen-associated peaks, especially the consistent 1580 cm^{-1} band in S500ZC, suggests that thermally stable nitrogen species remain embedded within the carbon framework. These moieties may contribute to improved CO_2 adsorption performance due to favorable acid-base interactions with the quadrupolar CO_2 molecules. The synergistic effect of temperature and chemical activation thus optimizes the surface chemistry of the biochar, enhancing its potential for environmental and energy applications.

3.4. Surface Area and Pore Structure

The nitrogen adsorption–desorption isotherms of the prepared biochar samples (S300NZC, S300ZC, S500NZC, and S500ZC) are presented in Figure 3(a–d), while the corresponding BJH pore size distribution plots are shown in Figure 4(a–d). These characterizations provide comprehensive insights into the surface area, porosity, and adsorption behavior of the biochars as influenced by pyrolysis temperature and ZnCl₂ activation. The quantitative BET surface area, micropore area, and BJH pore diameter values are summarized in Table 3.

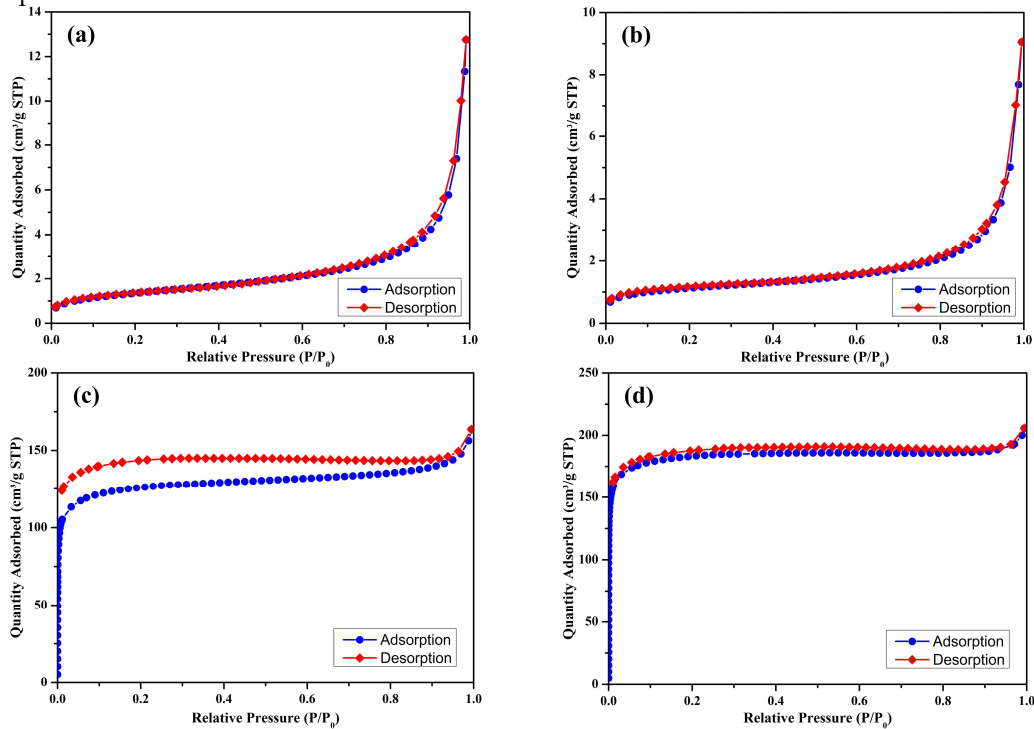


Figure 3. N₂ adsorption–desorption isotherms (at 77 K) of S300NZC (a), S300ZC (b), S500NZC (c), S500ZC (d).

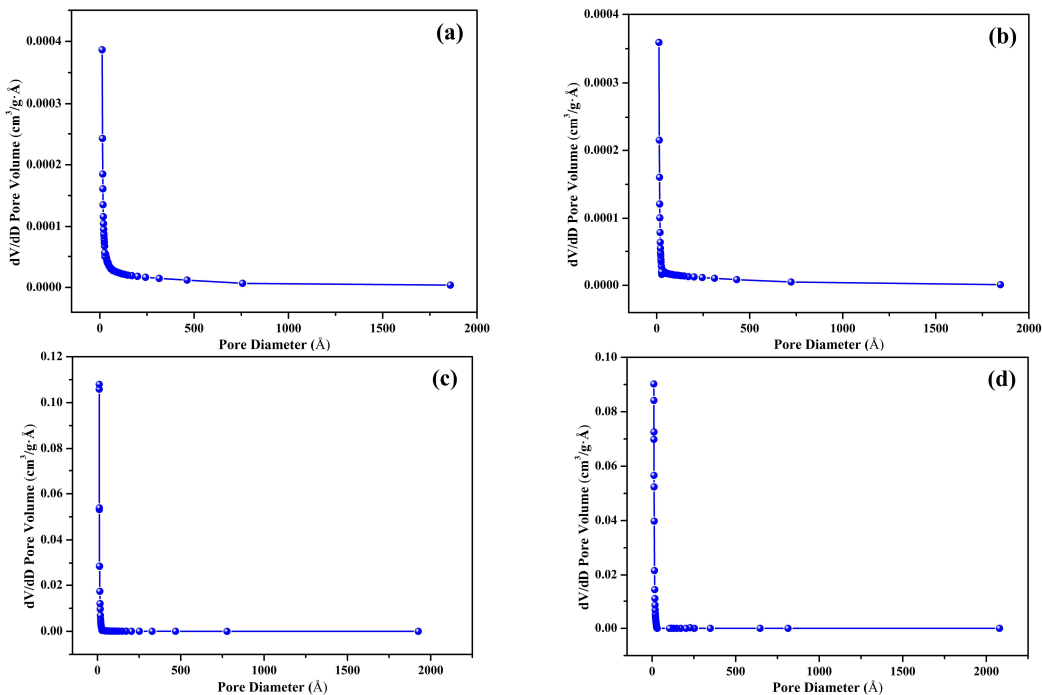


Figure 4. Pore size distribution by BJH method (a) S300NZC, (b) S300ZC, (c) S500NZC, and (d) S500ZC.

Table 3. N₂-BET results.

Biochar ID	BET Surface Area (m ² /g)	Micropore Area (m ² /g)	BJH Pore diameter (Å)
S300NZC	4.9574	0.2089	90.172
S300ZC	4.1229	1.3304	86.059
S500NZC	458.1404	365.0903	15.578
S500ZC	717.5997	616.6000	14.134

S300NZC and S300ZC (Figure 3a and 3b), pyrolyzed at 300 °C, exhibit Type III isotherms based on the IUPAC classification. These curves, characterized by gradual increases in nitrogen uptake with increasing relative pressure, suggest weak interactions between the adsorbate and adsorbent, typical of nonporous or macroporous materials. The isotherms lack sharp inflection points and display limited hysteresis, further confirming minimal micropore development. Correspondingly, the BET surface areas are very low, 4.96 m²/g for S300NZC and 4.12 m²/g for S300ZC. However, ZnCl₂ activation modestly improves the micropore area (from 0.21 m²/g to 1.33 m²/g), indicating some enhancement in pore formation due to partial chemical etching of the biomass matrix. The BJH pore diameters for both samples remain high, 90.17 Å for S300NZC and 86.06 Å for S300ZC, confirming the predominance of meso to macropores. These characteristics are further validated by the BJH plots in Figure 4(a–b), which show broad and poorly defined pore size distributions.

In contrast, the isotherms of S500NZC and S500ZC (Figure 3c and 3d), obtained at 500 °C, exhibit clear Type I(b) characteristics with a sharp increase in nitrogen uptake at low relative pressures ($P/P_0 < 0.1$), indicating the dominance of microporous structures. A pronounced plateau at higher pressures reflects the saturation of micropores, and the significant hysteresis suggests the presence of some mesopores. The BET surface areas increase drastically, reaching 458.14 m²/g for S500NZC and 717.60 m²/g for S500ZC. These increases are largely attributable to the elevated micropore areas, 365.09 m²/g and 616.60 m²/g, respectively, resulting from the combined effects of higher pyrolysis temperature and ZnCl₂ activation. The BJH pore diameters decrease substantially to 15.58 Å (S500NZC) and 14.13 Å (S500ZC), indicating enhanced pore confinement. The BJH plots in Figure 4(c–d) display narrower and more well-defined peaks, further affirming the development of a uniform microporous structure.

ZnCl₂ activation plays a minimal role at 300 °C, where limited devolatilization and structural rearrangement occur. However, at 500 °C, its effect is pronounced. Acting as a Lewis acid and dehydrating agent, ZnCl₂ facilitates extensive breakdown of lignocellulosic components and promotes the evolution of volatile matter, resulting in enhanced porosity and carbon content. The chemical activation thus substantially increases both surface area and micropore volume, as observed in S500ZC.

The data clearly show that temperature is a critical factor. Without sufficient thermal energy, the structural transformation necessary for micropore development remains incomplete, as seen in the low surface area of the 300 °C samples. Only when pyrolysis is performed at 500 °C does ZnCl₂ activation reach its full potential in producing biochars with ideal characteristics for gas-phase adsorption. The remarkable increase in surface area and microporosity, particularly in S500ZC, demonstrates the importance of synergistic thermal and chemical activation for developing efficient adsorbents. The high BET surface area (717.60 m²/g) and micropore dominance in S500ZC make it especially suitable for CO₂ adsorption, where the size and accessibility of adsorption sites are critical. The well-developed micro- and narrow mesopores shown in the BJH plots (Figure 4) further support this, as these pore structures are optimal for trapping CO₂ molecules via physisorption.

3.5. CO₂ Adsorption Characteristics

The CO₂ adsorption–desorption isotherms of the prepared biochar samples are illustrated in Figure 5(a–d). These isotherms, recorded at 25 °C, over a low relative pressure range (P/P_0 : 0.000–0.016), demonstrate the physisorption characteristics of CO₂ on the porous surfaces of the biochars. The CO₂ adsorption capacity data for each sample is summarized in Table 4.

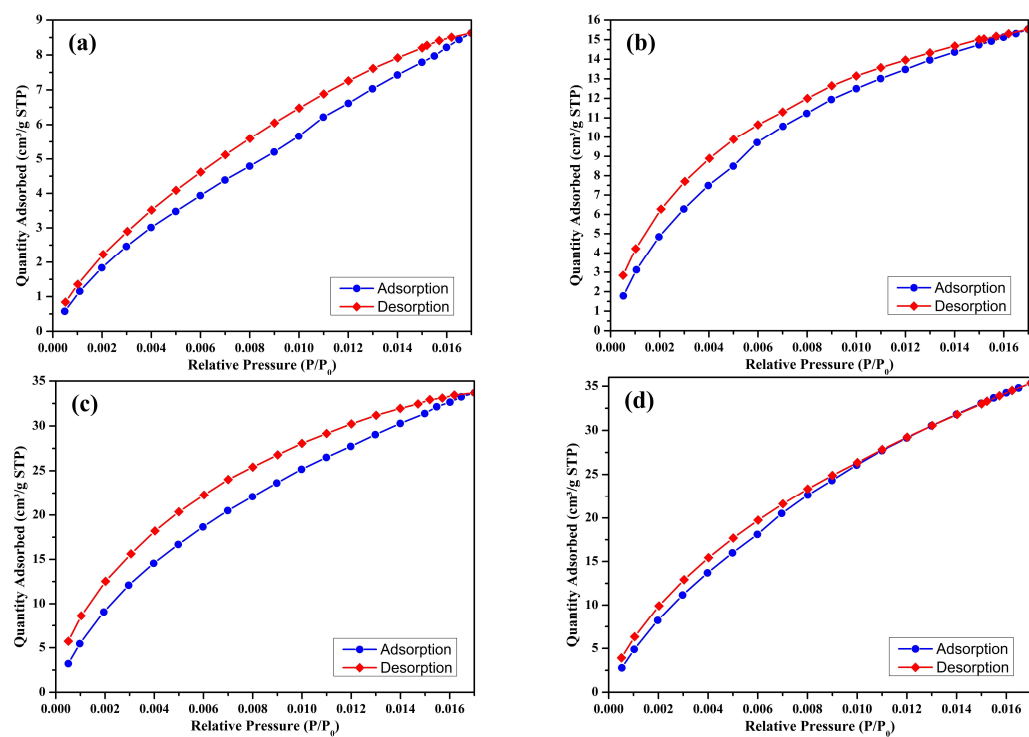


Figure 5. Carbon dioxide adsorption isotherm (at 298K) of S300NZC (a), S300ZC (b), S500NZC (c), S500ZC (d).

Table 4. CO₂ adsorption volume of biochar.

Biochar ID	CO ₂ adsorbed volume
S300NZC	8.691
S300ZC	15.5306
S500NZC	33.696
S500ZC	35.3396

At a pyrolysis temperature of 300 °C, the non-activated biochar (S300NZC) exhibits a CO₂ adsorption capacity of 8.691 cm³/g STP. When the same biochar is activated with ZnCl₂ (S300ZC), the CO₂ uptake increases substantially to 15.5306 cm³/g STP. This enhancement reflects the improved microporosity resulting from chemical activation, consistent with the corresponding increase in micropore area shown in the BET analysis. The isotherms for these two samples (Figure 5(a–b)) display a gradual increase in adsorption with rising pressure, indicative of a less developed microporous structure with limited high-energy adsorption sites.

In contrast, the biochars prepared at 500 °C show significantly higher CO₂ adsorption capacities. S500NZC adsorbs 33.696 cm³/g STP, while S500ZC achieves the highest capacity at 35.3396 cm³/g STP. The sharp rise in adsorption performance at this temperature can be directly attributed to the development of extensive microporosity, as confirmed by nitrogen adsorption data and the BET surface area analysis. Notably, S500ZC, which has the highest surface area (717.60 m²/g) and micropore area (616.60 m²/g), also possesses the smallest average pore diameter (14.13 Å), making it particularly suitable for CO₂ adsorption due to its proximity to the kinetic diameter of CO₂ molecules (~3.3 Å).

These results reveal the synergistic effects of ZnCl₂ activation and elevated pyrolysis temperature on enhancing CO₂ capture performance. At 300 °C, activation alone improves adsorption by creating additional micropores. However, the most significant impact is observed at 500 °C, where both thermal decomposition and chemical activation work together to generate a highly porous and adsorptive structure. The isotherms of the 500 °C samples (Figure 5(c–d)) show a steeper rise at low relative pressures, highlighting a strong interaction between CO₂ molecules and the narrow micropores, an essential characteristic for efficient adsorption at ambient conditions.

The CO₂ adsorption behavior observed follows the trend S300NZC < S300ZC < S500NZC < S500ZC, which aligns well with the progression in pore structure and surface area. The dominance of microporosity in CO₂ uptake is evident, as the increase in total surface area and micropore contribution leads to enhanced physisorption. While mesopores facilitate gas transport within the structure, micropores serve as the primary adsorption sites due to their favorable dimensions for gas molecule entrapment and interaction. This observation is further supported by the BET and BJH data, as well as the shape of the isotherms.

The CO₂ adsorption capacities of the biochars synthesized in this study are compared with other reported values in the literature and presented in Table 5. While some studies involving nitrogen-doped, amine-functionalized, or metal-oxide-supported biochars have achieved CO₂ uptake values exceeding 2.0 mmol/g, such modifications often involve complex synthesis procedures, costly reagents, or multiple processing steps that reduce scalability and sustainability. In contrast, the maximum adsorption capacity of 1.58 mmol/g (35.34 cm³/g STP) achieved by the ZnCl₂-activated sawdust biochar at 500 °C (S500ZC) in this study is highly promising, considering the simplicity, cost-effectiveness, and environmental friendliness of the activation route.

Table 5. Comparison of surface areas and CO₂ adsorption capacities of biochars made from different feedstocks.

No	Feedstock	Activation	Pyrolysis at (°C)	Post surface treatment	Surface area (m ² /g)	CO ₂ intake at 25 °C (mmol/g)	Surface features	Ref.
	Korean oak	-	400	-	-	0.597	-	[44]
	Soybean stover	-	700	-	-	0.707	-	[44]
	Japanese oak	-	500	-	-	0.379	-	[44]
	Rice husk	HF	830	N ₂ & ammonia at 600 °C	451.02	1.8	5.03 wt.% N	[45]
	Cotton stalk	KOH	600	N ₂ & ammonia at 700 °C	297	1.1	Amine groups	[46]
	Arundo donax	Chitosan/ZnCl ₂	500	-	1863	2.1	3.91 wt.% N	[47]
	Walnut shell	Mg(NO ₃) ₂ · 6H ₂ O	900	Heating in N ₂ at 500 °C	292	1.9	Amine groups	[48]
	Whitewood	Mg(NO ₃) ₂ · 6H ₂ O	500	Steam activation	615	1.1	5.41 wt.% N	[49]
	Africa palm shells	KOH	600	-	365	1.9	Ultra micropores	[50]
	Vine shoots	None	600	In CO ₂ for 3h at 800 °C	767	1.58	-	[51]
	Vine shoots	KOH: H ₂ O (5:1)	600	Heating at 700 °C for 1h	1439	1.98	Presence of N	[51]
	Whitewood	Steam	500	-	840	1.34	Presence of N	[52]
	Whitewood	CO ₂	500	-	820	1.43	Presence of N	[52]
	Whitewood	KOH	500	-	1400	1.77	Micro porosity	[52]
	Bamboo stem	None	500	-	9.72	1.01	Micro porosity	[13]
	Orange peel	None	500	-	51.63	0.63	Presence of amine	[13]

						functional groups	
Soybean	ZnCl ₂	600	CO ₂ Physical activation	811	0.93	Presence of N	[53]
Bagasse	ZnCl ₂	500	-	923	1.74	-	[54]
Rice husk	ZnCl ₂	500	-	927	1.29	-	[54]
Sawdust	None	300	-	4.95	0.39	Presence of N	Present study
Sawdust	None	500	-	4.12	0.69	Presence of N	Present study
Sawdust	ZnCl ₂	300	-	458.14	1.50	Presence of O- functional groups	Present study
Sawdust	ZnCl ₂	500	-	717.60	1.58	Presence of O- functional groups	Present study

For instance, certain nitrogen-doped biochars derived from urea or melamine modifications have demonstrated CO₂ uptakes around 1.8–2.3 mmol/g at 25 °C, but typically require high doping levels and post-pyrolysis treatments. Similarly, KOH or NaOH-activated carbon materials have shown high microporosity and adsorption performance; however, these activating agents are corrosive and generate hazardous by-products during synthesis. The ZnCl₂ activation employed here provides a balanced approach, offering competitive surface area development and microporosity without the need for additional surface functionalization.

Moreover, when comparing biochars derived from similar lignocellulosic biomass sources (e.g., wood chips, corn stover, bamboo), the CO₂ adsorption capacities usually range between 0.5–1.5 mmol/g, depending on pyrolysis temperature and activation method. The S500ZC sample in this work not only exceeds this range but does so with a relatively moderate activation protocol and using sawdust, a widely available and low-cost precursor.

Overall, the CO₂ adsorption study demonstrates that ZnCl₂-activated biochars, especially those prepared at higher pyrolysis temperatures, are highly effective for CO₂ capture. The significant difference in adsorption capacity between low- and high-temperature biochars highlights the importance of thermal treatment in tuning pore architecture. The BJH plots of the respective biochars, presented in Figure 5(a–d), further substantiate the textural differences influencing the adsorption behavior. Among all, S500ZC emerges as the most promising adsorbent, offering a high surface area, narrow pore size distribution, and superior CO₂ uptake, confirming the viability of ZnCl₂-activated sawdust-derived biochar as a sustainable CO₂ sorbent.

4. Conclusions

This study has systematically investigated the effects of ZnCl₂ chemical activation and pyrolysis temperature on the physicochemical and CO₂ adsorption properties of sawdust-derived biochars. Through comprehensive characterization, including particle size analysis, BET surface area, pore structure, and CO₂ adsorption isotherms, the role of activation and thermal treatment in tailoring the adsorption performance is clearly elucidated. The following key conclusions summarize the major findings of this work:

1. ZnCl₂ activation significantly enhances microporosity and surface area of sawdust-derived biochars, especially at elevated pyrolysis temperatures, making them more effective for gas adsorption applications.

2. Pyrolysis temperature plays a critical role in pore development. Samples prepared at 500 °C exhibit higher surface areas and more developed microporous structures than those produced at 300 °C.
3. The BET surface area increased from 4.12 m²/g (S500NZC) to 717.60 m²/g (S500ZC) after ZnCl₂ activation at 500 °C, demonstrating the powerful effect of chemical activation on pore architecture.
4. Average pore diameter reduced significantly upon activation, with S500ZC achieving a narrow average pore size of 14.13 Å, ideal for CO₂ adsorption due to its compatibility with the kinetic diameter of CO₂ molecules (~3.3 Å).
5. CO₂ adsorption capacity followed the trend S300NZC < S300ZC < S500NZC < S500ZC, correlating well with micropore area and BET surface area, emphasizing the dominant role of microporosity in CO₂ physisorption.
6. Maximum CO₂ adsorption capacity of 1.58 mmol/g (35.34 cm³/g STP) was achieved by the S500ZC sample, demonstrating the synergy between high pyrolysis temperature and ZnCl₂ activation.
7. Overall, ZnCl₂-activated sawdust biochar at 500 °C emerges as a sustainable, scalable, and efficient material for CO₂ capture, offering an excellent balance of high surface area, narrow pore distribution, and eco-friendly synthesis.

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