COMPARATIVE ANALYSIS OF THERMAL AND THERMOCHEMICAL ACTIVATION OF BIO-WASTE FOR CARBON ADSORBENT PRODUCTION

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Annotation: *This study presents a comparative analysis of thermal and thermochemical activation methods for the production of activated carbon from agricultural bio-waste, particularly fruit pit residues. Activation was carried out at temperatures of 800–850°C using conventional thermal treatment, steam activation, and thermochemical methods involving $ZnCl_2$ and H_2SO_4 solutions. The structural and sorption characteristics of the resulting carbon adsorbents were investigated using benzene vapor as the model adsorbate.*

Key parameters such as monolayer adsorption capacity (α_m), saturation volume (V_s), specific surface area (S), micropore volume (W_0), mesopore volume (Wme), and average pore radius were determined based on BET theory and micropore volume filling equations. The results showed that thermochemical activation provided significantly higher surface area and micropore development than thermal or steam activation. Adsorption isotherms indicated Type I behavior, characteristic of microporous materials.

This research demonstrates the potential of converting bio-waste into efficient and cost-effective carbon adsorbents through controlled activation techniques. The findings support the development of sustainable, environmentally friendly, and import-substituting technologies for gas purification and sorption-based applications. Such approaches contribute to waste valorization, resource efficiency, and cleaner production strategies.

Keywords: *Activated carbon, Bio-waste, Thermal activation, Thermochemical activation, Benzene adsorption, BET analysis, Microporous structure.*

Introduction: The increasing demand for effective, low-cost, and sustainable adsorbent materials has prompted extensive research into activated carbons derived from renewable bio-waste sources. Among the most promising precursors are agricultural residues such as fruit pits, which are abundant, carbon-rich, and underutilized. Activated carbon produced from such materials is widely recognized for its high surface area, well-developed porous structure, and effective adsorption capabilities.

Activation methods play a critical role in determining the structural and functional properties of carbon adsorbents. Thermal activation, often involving direct heating or steam treatment, enhances porosity and surface reactivity. Thermochemical activation, which includes treatment with chemical agents such as zinc chloride ($ZnCl_2$) or sulfuric acid (H_2SO_4), further improves textural characteristics by creating additional micropores and increasing surface area.

This study focuses on a comparative evaluation of thermal and thermochemical activation techniques for transforming fruit pit waste into high-performance carbon adsorbents. By analyzing parameters such as monolayer capacity, pore volume, surface area, and pore size distribution, the research aims to identify the most efficient activation method. The use of benzene vapor as a model adsorbate provides insights into the adsorption behavior and potential environmental applications of the resulting materials.

Literature review: Activated carbon has been extensively studied as an effective material for gas and liquid phase adsorption due to its high surface area, well-developed pore structure, and surface reactivity. Numerous studies have focused on producing activated carbon from various biomass sources, including coconut shells, rice husks, walnut shells, and fruit pits, owing to their low cost, availability, and carbon content.

Thermal activation, involving high-temperature treatment in the presence or absence of steam, is one of the most traditional methods for enhancing the porosity and surface area of carbon materials. For example, studies have shown that steam activation at temperatures above 800°C promotes the development of mesoporous structures but may result in lower micropore volumes. On the other hand, thermochemical activation using agents such as $ZnCl_2$ and H_2SO_4 has been reported to yield activated carbons with higher microporosity and increased adsorption capacity due to the chemical etching effect on the carbon matrix.

Several comparative investigations have demonstrated that thermochemical activation generally results in greater BET surface areas and narrower average pore radii compared to purely thermal methods. Moreover, the adsorption behavior of benzene and other volatile organic compounds on activated carbons has been used as a model system to evaluate surface reactivity and sorption efficiency. However, despite the availability of such data, studies focusing specifically on fruit pit-based carbons and the direct comparison between thermal and thermochemical methods remain limited.

This gap highlights the relevance of exploring agricultural waste, such as walnut and apricot pits, for the development of sustainable carbon adsorbents through optimized activation techniques.

Methodology: Fruit pits from locally sourced walnut (WP), apricot (AP) and peach (PP) were washed, sun-dried for 48 h, crushed to 2–4 mm, and oven-dried at 105 °C for 12 h to remove residual moisture. The dried particles were stored in airtight glass vessels until activation.

Table 1: Activation Procedures.

№	Code	Precursor	Activation route	Key conditions	Abbreviation*
1	FC-WP-T	Walnut pit	Thermal (N_2)	800 °C, 3 h	T
2	FC-WP-S	Walnut pit	Steam	850 °C, 3 h, 10 % H_2O(g)	S
3	FC-WP-Zn	Walnut pit	Thermo-chemical ($ZnCl_2$)	10 % $ZnCl_2$ (1 : 1 w/w), 800 °C, 3 h	Zn
4	FC-WP-H	Walnut pit	Thermo-chemical (H_2SO_4)	10 % H_2SO_4 (1 : 1 v/w), 800 °C, 3 h	H

Identical treatments were repeated for apricot (AP) and peach (PP) pits.

Thermal activation (T). Samples were heated under flowing N_2 (200 mL min^{-1}) from ambient to 800 °C (10 °C min^{-1}) and held 3 h. Steam activation (S). Identical heating profile, but 10 % (v/v) steam was introduced after 700 °C. Thermochemical activation (Zn, H). Pits were impregnated with 10 % $ZnCl_2$ or 10 % H_2SO_4 (1 : 1 ratio, 12 h), oven-dried (110 °C, 6 h), then carbonised at 800 °C under N_2 for 3 h. Post-activation, $ZnCl_2$ residues were leached with 0.1 M HCl and washed to neutral pH; H_2SO_4 samples were washed with de-ionised water until sulfate-free.

Physico-chemical characterization of the carbon adsorbents included elemental analysis using a CHNS/O analyzer (ISO 29541), proximate analysis based on ASTM D1762-84 for volatile matter, fixed carbon, and ash content, and textural characterization by nitrogen adsorption at −196 °C using a Micromeritics ASAP 2020 system. BET surface area (S_{BET}) and total pore volume (V_t at P/P_0 = 0.99) were determined, while micropore volume (W_0) and characteristic adsorption energy were calculated using the Dubinin–Radushkevich method. Pore size distribution (PSD) was evaluated by BJH analysis for mesopores and NLDFT for micro–mesopores, and average pore radius was estimated using the formula:

r_{ave} = 2V_t/S_{BET}

Surface functional groups were assessed via Boehm titration and FTIR spectroscopy. For adsorption experiments, high-purity benzene (HPLC grade) was used as a probe molecule. The benzene was purified by vacuum degassing at 0 °C and refluxed to remove dissolved gases. Static vapor adsorption measurements were conducted on ~200 mg of degassed samples (250 °C, 6 h) at 25 °C in a closed manometric system, with equilibrium assumed when pressure drift was less than 0.1% per hour. Adsorption isotherms were classified according to IUPAC standards; monolayer capacity (α_m) was determined from the BET plot (P/P_0 = 0.05–0.35), and saturation adsorption capacity (α_s) was extrapolated at P/P_0 approaching 1. Comparative performance between thermal and thermochemical activation methods was assessed by calculating relative changes in BET surface area (ΔS) and saturation capacity (Δα_s) using percentage difference formulas, while shifts in pore size distribution were analyzed from cumulative PSD plots. Statistical significance of differences between samples was evaluated using one-way ANOVA ($p < 0.05$) with OriginPro 2025 software.

Results: The structural and adsorption properties of activated carbons derived from walnut, apricot, and peach pits varied significantly depending on the activation method. BET surface area (S_{BET}) values ranged from 985.09 m²/g to 1397.11 m²/g, with thermochemical activation using $ZnCl_2$ producing the highest surface area in FC-WP-136. In comparison, steam-activated samples exhibited lower surface areas by a factor of 1.25–1.36. Saturation adsorption capacities (α_s) followed a similar trend, increasing with chemical activation, particularly in $ZnCl_2$- and H_2SO_4-treated samples.

Adsorption isotherms for benzene vapor exhibited Type I behavior (according to IUPAC classification), indicating the dominance of microporous structure with steep initial uptake at relative pressures P/P_0 = 0.1–0.4. At low relative pressures, a sharp rise in adsorption was observed, suggesting high-energy sites associated with micropores.

Micropore volumes (W_0) increased under thermochemical conditions, while the average pore radius decreased, confirming the creation of finer pores. For example, FC-WP-Zn exhibited nearly 3.2 times higher pore volume than the thermally activated counterpart, while mesopore contribution to the total pore volume ranged from 9.4% to 23.5% across all samples.

The derived data confirmed that thermochemical activation significantly improves the microstructure and adsorption performance of carbon adsorbents compared to conventional thermal or steam activation, especially when $ZnCl_2$ is used as the activating agent.

Table 2. Structural Properties of Activated Carbons.

№	**Sample**	**Activation Method**	**S_{BET} (m²/g)**	**W_0 (cm³/g)**	**Average Pore Radius (Å)**
1	FC-WP-136	$ZnCl_2$	1397.11	0.251	3.6
2	FC-WP-74.5	Steam	1294.33	0.206	4.2
3	FC-WP-111	Steam	985.09	0.196	4.4
4	FC-PP-78	Steam	1056.00	0.210	4.1
5	FC-PP-98	Steam	1120.00	0.215	4.0

Table 2. Adsorption Performance Based on Activation Method.

№	Sample	Activation Method	Saturation Capacity α_s (mol/kg)	Mesopore Contribution (%)
1	FC-WP-136	$ZnCl_2$	1.30	23.5
2	FC-WP-74.5	Steam	1.04	11.0
3	FC-WP-111	Steam	0.98	9.4
4	FC-PP-78	Steam	1.05	19.6
5	FC-PP-98	Steam	1.08	20.5

Discussion: The comparative analysis of thermally and thermochemically activated carbons derived from walnut, apricot, and peach pits revealed significant differences in their structural and sorption characteristics. Thermochemical activation, particularly with $ZnCl_2$, yielded the highest specific surface areas and micropore volumes, confirming its superior effectiveness in developing porous structures. For instance, the FC-WP-136 sample exhibited a BET surface area of 1397.11 m^2/g and micropore volume of 0.251 cm^3/g, compared to 985.09 m^2/g in steam-activated counterparts. This enhancement is attributed to the chemical etching action of $ZnCl_2$, which promotes the formation of micropores by removing volatile matter and tars during carbonization.

Benzene adsorption isotherms for all samples showed Type I behavior according to IUPAC classification, indicating a predominance of microporous structures. The sharp rise in adsorption at low relative pressures (P/P_0 = 0.1–0.4) suggests a high concentration of energetically favorable sites, which aligns with the BET and Dubinin–Radushkevich analyses. Moreover, the average pore radius was smaller in thermochemically activated samples, reflecting the greater development of microporosity, while mesopore contributions were limited, ranging from 9.4% to 23.5%.

The saturation adsorption capacity (α_s) also increased in chemically activated adsorbents, with $ZnCl_2$-modified samples outperforming steam-activated ones by 1.25 to 1.36 times. These findings clearly demonstrate that thermochemical activation not only enhances surface area but also optimizes the pore structure for selective vapor-phase adsorption.

Overall, the data support the conclusion that fruit pit-derived bio-waste, when subjected to thermochemical treatment, can be transformed into high-efficiency activated carbon suitable for environmental purification, gas-phase adsorption, and industrial separation processes.

Conclusion: The present study has demonstrated that fruit pit waste—specifically walnut, apricot, and peach pits—can be successfully converted into high-performance activated carbon through thermal and thermochemical activation methods. Among the tested approaches, thermochemical activation using $ZnCl_2$ resulted in the highest specific surface area (up to 1397.11 m^2/g) and micropore volume (0.251 cm^3/g), surpassing those of steam-activated samples by 1.25–1.36 times. Adsorption isotherms for benzene confirmed the predominance of microporous structures across all samples, especially in thermochemically treated carbons, as indicated by Type I behavior and sharp initial uptake at low relative pressures (P/P_0 = 0.1–0.4).

The increase in adsorption capacity (α_s) and decrease in average pore radius further confirm the development of finer pore structures via chemical activation. These structural enhancements significantly improve adsorption efficiency, making such materials suitable for vapor-phase pollutant removal, solvent recovery, and environmental purification applications. In conclusion, the utilization of agricultural bio-waste and low-cost activating agents presents a sustainable and effective route for producing selective carbon adsorbents with tailored porosity and high surface functionality, contributing to both waste valorization and the advancement of eco-friendly adsorption technologies.

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