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Performance Comparison of Agricultural Waste-Derived Carbonized Sorbents for Phenol Adsorption

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Abstract

Carbonized sorbents were prepared from walnut and pistachio shells and comprehensively characterized using optical microscopy, SEM, FTIR spectroscopy, BET surface area analysis, and EDAX. The sorbents were evaluated for phenol removal from aqueous solutions under varying conditions, including particle size, pH, carbonization temperature (500–900 °C), and contact time. SEM analysis revealed the formation of porous structures, with needle-like particles observed on pistachio carbon surfaces at high magnification. FTIR confirmed the decomposition of cellulose, hemicellulose, and lignin after carbonization, with a simultaneous increase in aromatic C=C bonds. EDAX analysis demonstrated significant enrichment of carbon and persistence of mineral inclusions (K, Si, Ca), potentially influencing surface activity. Adsorption experiments showed that walnut shell sorbents exhibited higher phenol removal efficiency (R%) than pistachio shell sorbents. Maximum removal was observed at acidic pH (3–5), smaller particle sizes, and carbonization temperature at 800 °C. The results confirm that walnut and pistachio shells can serve as effective precursors for carbon sorbents, with walnut shell carbon showing superior performance for phenol removal.

Keywords: Walnut shell, Pistachio shell, Activated carbon, Phenol removal, Wastewater treatment.
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1. Introduction

Phenolic compounds are widely used in chemical, petrochemical, pharmaceutical, and textile industries and are frequently discharged into industrial effluents. Due to their toxicity, mutagenicity, and resistance to biodegradation, phenols are classified as priority pollutants by the U.S. Environmental Protection Agency (EPA) and the European Union. For example, the EPA's Toxicological Review of Phenol outlines multiple adverse health effects and environmental persistence of phenol, noting that it is among the first compounds listed as a priority pollutant because of its wide industrial use and toxic potential.[1] Even at low concentrations, phenol causes severe environmental problems, including acute toxicity to aquatic organisms (such as fish and invertebrates) and potential health risks to humans, affecting liver, kidney, and neurological functions.[2-4] Therefore, the removal of phenol from wastewater remains a critical environmental challenge.

This problem is part of a broader context of water pollution by organic and inorganic contaminants, where multiple classes of pollutants, such as microplastics and nitrate, pose serious risks to ecosystems and human health. Recent studies emphasize that microplastics represent an emerging category of global pollutants that require standardized analytical methods for accurate detection and mitigation strategies.[5] Likewise, high nitrate levels in groundwater and drinking water have been associated with increased health risks, particularly for infants and children, highlighting the urgency of developing effective, low-cost water treatment technologies.[6] These examples reinforce the need for sustainable and affordable approaches for water purification, including the adsorption of phenolic compounds from industrial effluents.

Several conventional methods have been applied for phenol removal, such as chemical oxidation, coagulation–flocculation, biological degradation, and membrane separation. However, these techniques often face limitations, including high operational costs, incomplete degradation, and secondary pollution. Adsorption has emerged as one of the most effective and environmentally friendly approaches due to its simplicity, regenerability, and high efficiency. For example, low-cost adsorbents have been extensively reviewed,[7] and it was noted that commercial activated carbon, although effective, is often too expensive for large-

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scale applications. Similarly, it has been demonstrated[8] that adsorbents derived from agricultural wastes provide high phenol removal rates with lower cost and simpler operation compared to membrane and advanced oxidation methods. Emphasize the advantages of adsorption as design flexibility and lack of harmful by-products but also caution regarding adsorbent cost and regeneration challenges.[9] Activated carbon remains the most widely used adsorbent due to its high specific surface area and porosity. Nonetheless, commercial activated carbon is costly, which restricts its large-scale application.

To overcome this barrier, research has increasingly focused on producing low-cost sorbents from agricultural residues and biomass waste. Various lignocellulosic by-products, such as rice husks,[10] coconut shells,[11] apricot stones,[12] almond shells,[13] and walnut shells,[14] have been successfully converted into carbonaceous sorbents with promising adsorption properties. Previous studies demonstrated that carbonaceous composites prepared from agricultural wastes can efficiently adsorb hydrocarbons from water and the sorption capacity of rice husks significantly increases after thermal treatment.[15] Furthermore, scanning electron microscopy studies of carbonized rice husks and apricot stones confirmed the development of porous structures upon pyrolysis.[16] These works support the feasibility of converting agricultural wastes into effective sorbents for organic contaminants.

Recent investigations have highlighted walnut and pistachio shells as particularly attractive precursors for carbon materials. Scientists[17] reported that pistachio shell-derived activated porous carbons exhibit high BET surface areas and excellent sorption performance. Chen *et al*.[18] enhanced phenol removal using chemically modified almond shell biochar, emphasizing the role of functional groups and pore development. Shi *et al*.[19] showed that walnut shell nanocarbon sorbents follow Freundlich isotherm behavior, indicating heterogeneous adsorption sites. Sun *et al*.[14] demonstrated that walnut shell biochar exhibits strong adsorption efficiency influenced by dosage, pore structure, and experimental conditions and investigated its adsorption mechanism for chloramphenicol, confirming π–π interactions, hydrogen bonding, and Langmuir-type adsorption.

Beyond experimental studies, broader perspectives on carbon sorbents from biomass have been provided. Kunarbekova *et al*.[20] reviewed innovative approaches for tailoring surface chemistry and structure of activated carbons to maximize pollutant removal while addressing sustainability challenges such as CO_2 emissions during production. These insights highlight the importance of balancing performance with environmental impact in designing next-generation carbon sorbents.

At the same time, it is crucial to highlight the novelty of the present work. Although numerous previous studies have investigated sorbents derived from agricultural residues, to the best of our knowledge, this is the first comparative study of walnut- and pistachio-shell-derived carbons prepared via carbonization under a controlled CO_2 atmosphere. The use of CO_2 during thermal treatment is particularly significant, as it not only provides an inert medium that prevents excessive oxidation but also promotes partial activation of the carbon matrix, thereby enhancing porosity and surface functionality. This novel preparation route distinguishes our work from earlier studies on agricultural waste sorbents, which predominantly relied on pyrolysis in nitrogen or air. As a result, the present study offers new mechanistic insights into how the CO_2-assisted carbonization pathway influences the morphology, surface chemistry, and adsorption performance of bio-derived carbons.

Taken together, previous works demonstrate that agricultural residues, particularly walnut and pistachio shells, represent sustainable and cost-effective feedstocks for carbonized sorbents. However, comparative studies of their physicochemical characteristics and adsorption behavior toward phenol under different conditions (pH, particle size, carbonization temperature, and contact time) remain limited. The aim of the present study is to prepare carbonized sorbents from walnut and pistachio shells, characterize their morphology, functional groups, elemental composition, and surface area, and evaluate their phenol removal efficiency under varying experimental parameters.

2. Materials and methods

2.1 Materials and sample preparation

Walnut and pistachio shells were first washed thoroughly with distilled water to remove dust and adhering impurities, and then oven-dried at 105–110 °C for 24 h. The dried shells were ground and sieved to obtain a uniform particle size fraction (typically <1 mm). The prepared biomass samples were placed in a steel reactor and subjected to carbonization in a muffle furnace under a continuous CO_2 flow (200 ml/min). The thermal treatment was carried out at different temperatures (500, 600, 700, 800, and 900 °C) for 1 h. The resulting carbonized sorbents were designated as W500, W600, W700, W800, W900 for walnut shells, and P500, P600, P700, P800, P900 for pistachio shells, respectively.

2.2 Experimental setup

IR spectra of the samples (tablets pressed with KBr) were recorded with an IR spectrometer (Nicolet-5700) in the wave number range from 4000 to 400 cm^{-1} with Fourier transformation.

The specific surface of the samples was determined by the BET method using a SORBTOMETR-M apparatus.

The microstructures of adsorbents were investigated with an SEM (Quanta 3D 200i, USA) at an accelerated voltage of 20 kV and a pressure of 0.003 Pa (performed by National Nanotechnological Laboratory of Open Type of Kazakh National University). Scanning electron microscopy with energy-dispersive X-ray spectroscopy (EDS/EDAX): Applied to to determine the elemental composition of raw and carbonized sorbents. Optical microscopy used to evaluate the macroscopic morphology of carbonized sorbents.

For the adsorption experiments, 50 mg of each carbonized sorbents derived from walnut shell and pistachio shell were placed in separate 100 mL conical flasks and mixed with 50 mL of aqueous phenol solution. Initial phenol concentrations were adjusted to 100, 200, and 300 mg/dm^3. The sealed flasks were agitated in a thermostated water bath at 298 K for 3 h to ensure that pseudo-equilibrium was reached. After equilibration, the suspensions were filtered to remove the carbonized sorbents, and the residual phenol concentration in the filtrates was determined using a UV–vis spectrophotometer at a wavelength of 270 nm.[21]

The percentage removal of phenol (R%) was determined as Eq. (1):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

The influence of particle size (0.2-5 mm), pH (range 3–11), contact time (0–300 min), and carbonization temperature (500–900 °C) on phenol adsorption was systematically investigated. Each experiment was repeated three times, and the mean values are reported.

3. Results and discussion

3.1 Phenol sorption of sorbents carbonized at different temperatures

The effect of carbonization temperature on the phenol removal efficiency (R%) of walnut and pistachio shell-derived sorbents was found to be significant. As the carbonization temperature increased from 500 to 800 °C, the removal efficiency markedly improved: for walnut shell sorbents, from 60 to 90%, and for pistachio shell sorbents, from 48 to 75% (Fig. 1). This enhancement is associated with the intensified thermal decomposition of the lignocellulosic matrix, leading to the formation of a more developed porous structure and an increase in specific surface area. In addition, at temperatures above 600 °C, partial aromatization and ordering of the carbon matrix occur, which promote the development of active adsorption sites capable of interacting with the aromatic ring of phenol through π–π interactions.

The maximum R% values for both sorbents were observed at 800 °C, indicating an optimal balance between pore structure development and the preservation of active surface functional groups. At higher carbonization temperatures (900 °C), the efficiency slightly decreased (86% for walnut shell and 72% for pistachio shell). This decline is most likely due to partial graphitization of the carbon matrix and collapse of micropores, reducing the number of available active sites. Similar observations have been reported in the literature, where excessively high carbonization temperatures were shown to decrease adsorption properties by diminishing surface area and functional groups.[22-26]

A comparison of the two sorbents revealed that walnut shell-based sorbents exhibited higher phenol adsorption capacity at all carbonization temperatures. This can be attributed to their more developed system of macro- and mesopores, as confirmed by microscopy, as well as a higher degree of carbonization, which facilitates effective interaction with phenol.

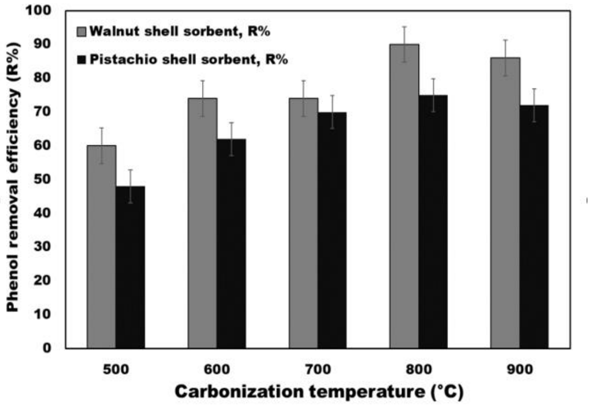

Fig. 1: Effect of carbonization temperature on the phenol removal efficiency (R%) of walnut and pistachio shell-derived sorbents.

Thus, the optimal carbonization temperature for achieving maximum sorption capacity toward phenol is approximately 800 °C. Lower temperatures lead to incomplete pore structure formation, while higher temperatures cause partial graphitization and a decrease in the accessibility of active sites.

Adsorption Kinetics of Phenol. The experiments show a typical adsorption behavior of phenol on the carbonized sorbents W800 and P800: a fast initial stage followed by a slower process that gradually reaches equilibrium (Fig. 2). Within the first 10–30 minutes, a significant amount of phenol is already adsorbed — about 57–77% removal for the walnut shell sorbent and about 42–64% for the pistachio shell sorbent. Pseudo-equilibrium in our experiments was reached within approximately 120–180 minutes.

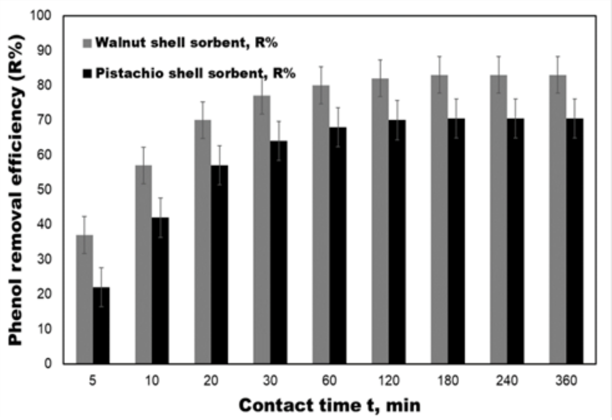

Fig. 2: Adsorption kinetics of phenol on walnut (W800) and pistachio (P800) shell sorbents.

The differences in kinetics and adsorption capacity can be explained by morphological and chemical properties. The walnut shell sorbent has a more developed system of macro- and mesopores and a higher degree of carbonization, which allows faster transport of phenol molecules into the pore network and provides a greater number of active sites. The pistachio shell sorbent has a denser structure and contains more residual oxygen-containing functional groups. While these groups contribute to adsorption, the lower pore development results in slower adsorption kinetics and lower overall capacity compared to walnut shell sorbents.

Similar kinetic patterns have been reported in the literature.[27] Studies on banana leaves and coffee husk biochars also showed a rapid initial uptake followed by slower equilibrium stages, consistent with diffusion into pores.[28]

3.2 Impact of particle size on the phenol removal efficiency for W800 and P800

The particle size of the carbonized sorbents derived from walnut and pistachio shells had a strong effect on phenol removal efficiency (R%). According to our results (Fig. 3 and 4), smaller particles significantly increased the adsorption capacity of both materials. This is due to the larger surface area, a higher number of accessible active sites, and reduced diffusion resistance inside the particles.

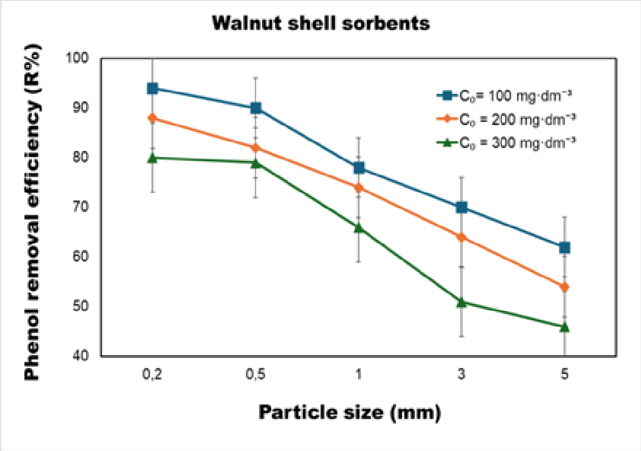

Fig. 3: Impact of particle size on the phenol removal efficiency (R%) for walnut shell-derived sorbent (W800).

For walnut shell sorbents, which have a more developed pore structure, phenol removal reached about 94% at an initial concentration of 100 mg/L and a particle size of 0.2 mm. Even at a higher initial concentration (300 mg/L) and larger particle size (3–5 mm), relatively high adsorption was still observed (about 46–51%). These results suggest that walnut shells are a more promising raw material for carbon sorbents because their system of macro- and mesopores allows faster diffusion of phenol molecules.

Pistachio shell sorbents showed lower performance compared to walnut shells under the same conditions. The maximum removal was about 82% at 100 mg/L and 0.2 mm particle size. When both phenol concentration and particle size increased, the efficiency dropped to about 34% (300 mg/L, 5 mm). This can be explained by the denser structure and less developed porosity of carbonized pistachio shells, which limits access of phenol molecules to active sites. However, the presence of residual oxygen-containing functional groups (confirmed by FTIR analysis) may explain why some adsorption activity remains even with larger particles.

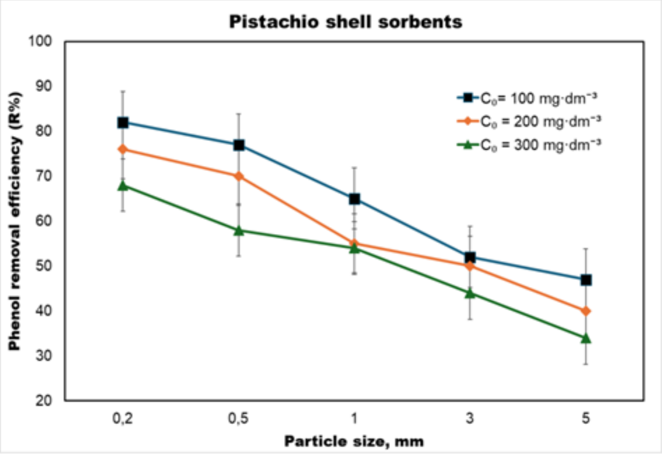

Fig. 4: Impact of particle size on the phenol removal efficiency (R%) for walnut shell-derived sorbent (P800).

The general trend for both materials is clear: reducing particle size significantly increases phenol removal. This is consistent with literature reports for other biosorbents and activated carbons, where adsorption efficiency increases with smaller particles due to higher surface area and reduced diffusion limitations.[29,30]

Comparative data from literature further support our findings and provide useful benchmarks. For instance, in a study of commercial activated carbons, maximum phenol adsorption capacities of 169.9, 176.6, and 212.96 mg/g were achieved for different carbon types (granular, powdered, coconut-shell-derived) under optimized conditions.[31]

In a comparative study between activated carbon (AC) and biochar (BC) for phenol removal, AC achieved ~95 % removal, while BC reached only ~55 %, highlighting the performance gap while also demonstrating the potential of biomass-derived sorbents.[32]

Overall, our results confirm that particle size optimization is an important factor in the design and practical use of carbonized sorbents from agricultural biomass. In particular, walnut shell sorbents with small particle sizes show the highest phenol adsorption capacity. Although commercial activated carbons still often outperform biomass-derived carbons in maximal capacity, our results are promising considering the low-cost CO_2-assisted carbonization route used. Including a direct comparison with commercial activated carbon (in future studies) would further strengthen the practical relevance of our approach.

3.3 Effect of pH on phenol removal efficiency for w800 and p800

The efficiency of phenol adsorption on carbonized walnut and pistachio shell sorbents depends strongly on the pH of the solution, which is consistent with well-known trends for biosorbents and activated carbons (Table 1).

Table 1: Effect of pH on the phenol removal efficiency (R%) of carbonized walnut and pistachio shell sorbents (C_0 = 100 mg/L, particle size = 0.2 mm, T = 298 K, t = 3 h).

pH	Walnut shell sorbent R%	Pistachio shell sorbent R%
3	92	80
5	90	76
7	82	68
9	70	56

At acidic pH values (3-5), phenol exists mainly in its non-dissociated form ($pK_a \approx 9.9$). In this state, phenol molecules are more easily adsorbed onto carbon surfaces through hydrophobic interactions and π-π stacking with the aromatic structure of the carbonized material. In our experiments, the highest removal efficiencies were obtained in this range (R = 90-92% for walnut shell and 76-80% for pistachio shell), with walnut shell sorbents showing better performance.

As pH increased to neutral and slightly alkaline values (6-9), adsorption efficiency gradually decreased. This was due to partial dissociation of phenol into phenolate ions ($C_6H_5O^-$) combined with the negative surface charge of the carbonized sorbents, caused by ionization of oxygen-containing groups (–OH, –COOH). Electrostatic repulsion reduced the binding of phenol.

At strongly alkaline conditions (pH > 10), a sharp drop in R% was observed. This can be explained by full dissociation of phenol and strong repulsion of phenolate ions from the negatively charged sorbent surface. In this range, the differences between the two sorbents became clearer: walnut shell retained higher removal values due to its well-developed porosity, while pistachio shell sorbents showed a stronger decrease in efficiency.

These findings are consistent with previous reports, which also showed that phenol removal by activated carbons and biosorbents is most effective in acidic media, while efficiency decreases with increasing pH.[33,34]

In summary, the optimal pH range for phenol adsorption on carbonized walnut and pistachio shell sorbents is mildly acidic (pH 3-5). Walnut shell sorbents are more resistant to pH changes and demonstrate higher adsorption capacity, making them more suitable for practical applications in wastewater treatment.

3.4 Mechanism of phenol adsorption

Phenol adsorption onto the carbonized walnut and pistachio shell sorbents occurs mainly through π-π stacking, hydrogen bonding, and electrostatic interactions, whose contributions depend on solution pH. At acidic pH (3-5), phenol ($pK_a \approx 9.9$) remains in its neutral form, enabling π-π donor-acceptor interactions with aromatic carbon domains and hydrogen bonding with surface -OH/-COOH groups, which explains the high removal efficiency (almost 90% for walnut).

With increasing pH, phenol ionizes to phenolate ($C_6H_5O^-$), and the surface becomes more negatively charged, leading to electrostatic repulsion and lower adsorption; at pH > 10, OH^- ions compete for sites, further reducing uptake. Such pH-dependent behavior agrees with previous findings for biochars and bentonite-based adsorbents, where π-π and hydrophobic interactions dominate under acidic conditions, while repulsive forces control adsorption at high pH.[35,36]

3.5 Influence of carbonization temperature on the BET surface area of sorbents from walnut and pistachio shells

The analysis of specific surface area (S_BET) for carbonized sorbents from walnut and pistachio shells showed that carbonization temperature plays a key role in shaping their textural properties. As the temperature increased from 500 to 800 °C, S_BET rose significantly: from 80 to 580 m²/g for walnut shell sorbents and from 50 to 350 m²/g for pistachio shell sorbents (Fig. 5). This increase is mainly due to the removal of volatile components, the development of micro- and mesoporous structures, and the formation of condensed aromatic fragments in the carbon matrix.

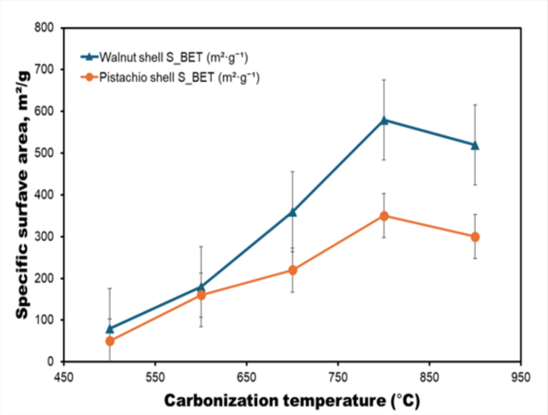

Fig. 5: Effect of carbonization temperature on the specific surface area (S_BET) of walnut- and pistachio-shell-derived sorbents.

The maximum surface area was recorded at 800 °C, which also coincided with the highest phenol removal efficiency (R%). This correlation confirms a direct relationship between adsorption capacity and textural characteristics: the larger the surface area and pore volume, the higher the probability of phenol adsorption.

When the temperature was further increased to 900 °C, the specific surface area decreased slightly (to 520 m²/g for walnut and 300 m²/g for pistachio). This reduction is explained by partial graphitization of the carbon matrix and collapse of the finest pores, which reduces the number of accessible active sites. Similar findings have been reported in the literature,

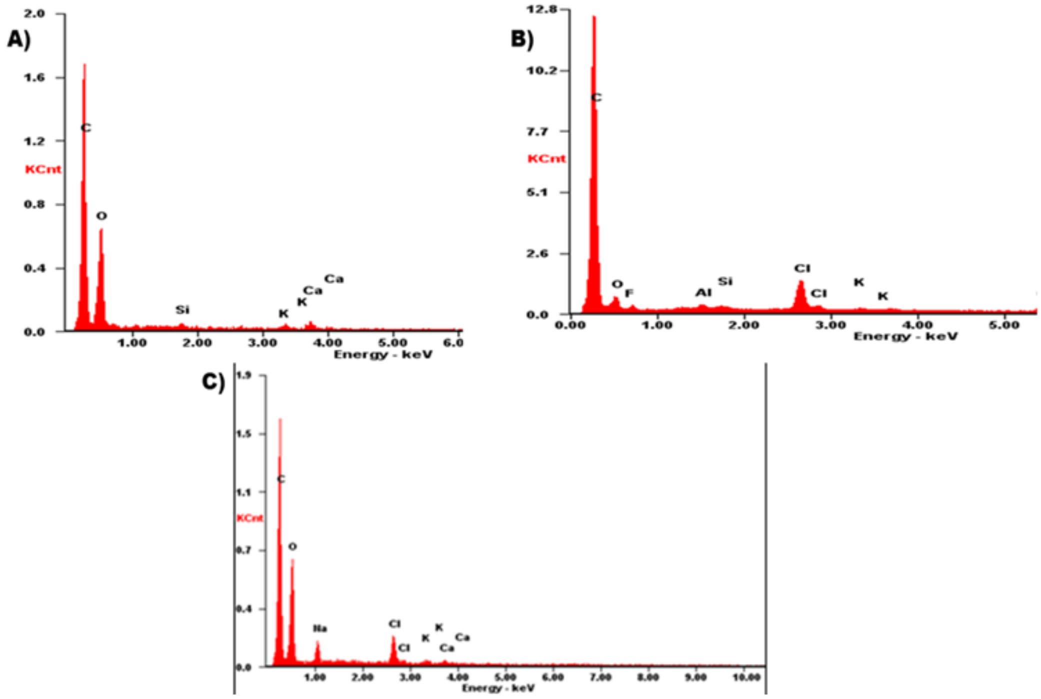

Fig. 6: EDAX spectra of raw walnut shell (A), carbonized walnut shell (B), and carbonized pistachio shell (C).

where the temperature range of 700–850 °C is considered optimal for producing activated carbon sorbents with the best adsorption capacity.[37,38]

A comparison of the two raw materials showed that walnut shell sorbents had higher surface areas and thus greater adsorption capacities than pistachio shell sorbents. This can be attributed to the natural structure of walnut shells, which upon thermal treatment develops a more extensive system of macro- and mesopores, increasing accessible surface area and promoting effective phenol adsorption.

In conclusion, the optimal carbonization temperature for obtaining sorbents with maximum surface area and high phenol adsorption efficiency is around 800 °C.

3.6 EDAX analysis of walnut and pistachio shell sorbents

The EDAX analysis of raw and carbonized walnut and pistachio shell sorbents revealed significant changes in elemental composition after thermal treatment. In the raw walnut shell samples, organic components dominated, consisting mainly of carbon and oxygen, along with mineral impurities such as Ca, K, and Si (Fig. 6A). After carbonization, the relative content of carbon increased due to the removal of volatile compounds such as water, CO_2, and organic fragments (Fig. 6B). At the same time, the oxygen content decreased, which can be explained by the decomposition of hemicellulose, cellulose, and lignin, as well as dehydration of the structure. Mineral components (K, Si) remained present and became more prominent in relative composition as the organic fraction decreased.

Similar mineral inclusions have also been reported for bamboo biochar and walnut shell-derived biochars. For example, it has been shown[39–41] that Ca, K, and Si do not disappear during carbonization but instead increase in relative content.

A comparison between walnut and pistachio shells shows that walnut shell sorbents after carbonization had a higher relative carbon content, which is consistent with their higher specific surface area and greater phenol adsorption capacity (Fig. 6C). Pistachio shells, on the other hand, retained more residual mineral impurities, which may influence their adsorption activity and selectivity toward different pollutants.

Overall, the EDAX analysis confirms the successful conversion of raw biomass into carbonized sorbents enriched in carbon while retaining mineral elements. These mineral inclusions can further modify the adsorption properties of the material, potentially contributing to its interaction with contaminants.

3.7 FTIR spectra of raw and carbonized walnut and pistachio shells

The FTIR spectra of raw walnut (Fig. 7A) and pistachio (Fig. 7B) shells exhibit characteristic absorption bands corresponding to the main functional groups of biopolymers (cellulose, hemicellulose, and lignin). A broad band at ~3400 cm^{-1} is attributed to the stretching vibrations of –OH groups associated with hydroxyl fragments of cellulose and phenolic hydroxyls of lignin. The bands in the region of ~2926–2855 cm^{-1} are assigned to the stretching vibrations of aliphatic –CH and $–CH_2$ groups.

A strong band at ~1742 cm^{-1} corresponds to carbonyl (C=O) groups in ester linkages of hemicellulose and lignin, whereas the signals at 1623–1634 cm^{-1} originate from aromatic C=C stretching vibrations. The bands in the range of 1500–1457 cm^{-1} are associated with bending vibrations of –

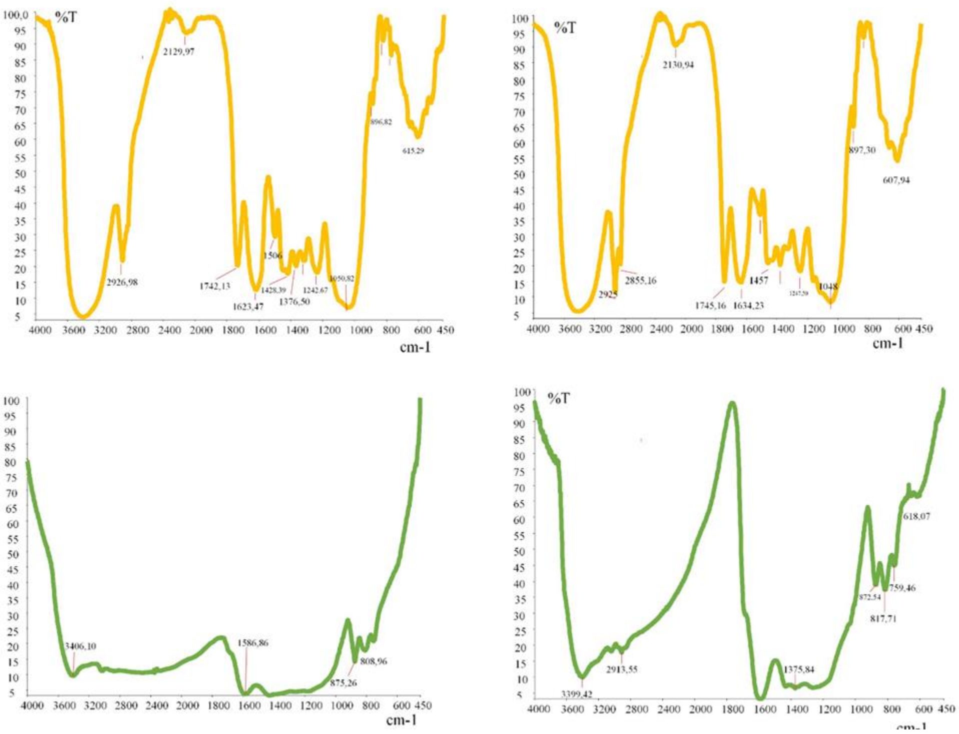

Fig. 7: FTIR spectra of walnut shell (A), pistachio shell (B), and carbonized sorbents derived from walnut shell (C) and pistachio shell (D).

CH_2 and $-CH_3$ groups, while the absorptions at 1050–900 cm^{-1} are attributed to C–O–C stretching in polysaccharides.

After carbonization (Fig. 7 C and D), the spectra undergo substantial changes. The intensity of the aliphatic bands at 2926–2855 cm^{-1} is significantly reduced, and the band at ~1742 cm^{-1} disappears, indicating decomposition of aliphatic fragments and carbonyl-containing structures. The broad –OH band at ~3400 cm^{-1} also decreases markedly, which can be ascribed to dehydration and thermal degradation of cellulose and hemicellulose.

These residual oxygenated groups (such as –OH and –COOH) may enhance the interaction of pistachio-based sorbents with polar molecules, whereas the more aromatic nature of walnut-based sorbents favors π–π interactions with aromatic contaminants like phenol. This spectral evidence helps explain the higher phenol removal efficiency (R%) of walnut shell sorbents compared to pistachio shell sorbents.[23,42]

Nevertheless, the bands in the region of 1600–1500 cm^{-1}, assigned to aromatic ring structures, remain clearly visible, demonstrating the enrichment of the material with aromatic frameworks. Additional low-frequency absorptions in the 800–600 cm^{-1} region further indicate the formation of more ordered carbonaceous structures.

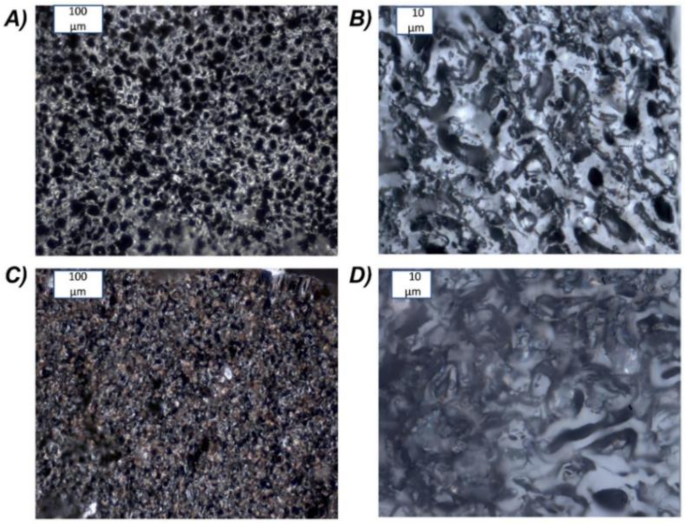

Fig. 8: Optical micrographs of carbonized sorbents derived from walnut shell (A, B) and pistachio shell (C, D) at different magnifications.

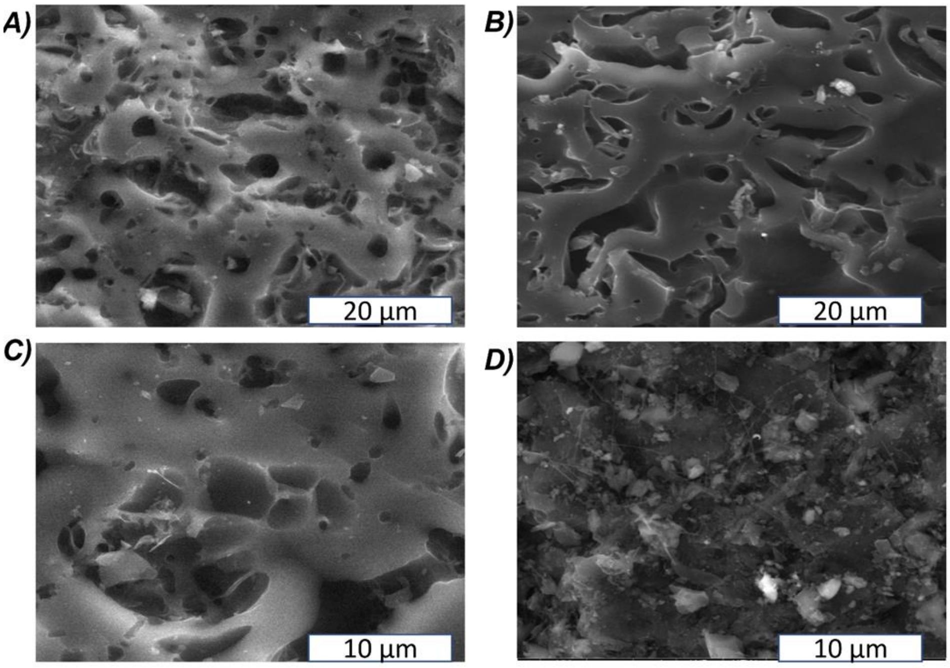

Fig. 9: SEM micrographs of carbonized sorbents derived from walnut shell (A, B) and pistachio shell (C, D) at different magnifications.

In summary, FTIR analysis confirms that carbonization is accompanied by the degradation of aliphatic and oxygen-containing functional groups and the enrichment of the material with aromatic structures. This transformation leads to the formation of a carbon framework that contributes to the improved adsorption properties of the resulting sorbents.

3.8 Optical and SEM characterization of carbonized walnut and pistachio shells

The carbonized sorbents derived from walnut and pistachio shells demonstrated clear morphological differences, as revealed by optical and scanning electron microscopy (Fig. 8 and 9).

Optical microscopy showed that both sorbents retained the porous features of the original biomass after carbonization. However, their surface uniformity differed. Walnut shell sorbents (Fig. 8 A and B) exhibited a more developed porous structure with visible channels, which can enhance adsorbate diffusion. In contrast, pistachio shell sorbents (Fig. 8 C and D) presented a less homogeneous pore distribution, with localized dense regions that may restrict transport through the surface.

SEM analysis (Fig. 9) provided more detailed insights into surface architecture. Walnut shell sorbents (Fig. 9 A and B) displayed a well-developed system of macro- and mesopores formed during thermal degradation of the lignocellulosic matrix. Such morphology contributes to high specific surface area and improved adsorption capacity. Pistachio shell sorbents (Fig. 9 C and D), however, had a denser surface with fewer large pores, which may limit accessibility to active sites. This structure, on the other hand, could provide greater mechanical stability. At higher magnification (Fig. 9D), needle-like particles were clearly observed on the surface of carbonized pistachio shells. These features are likely crystalline inclusions of inorganic origin (e.g., calcium- or silicon-containing residues), which increase micro-roughness and may affect adsorption mechanisms.

Overall, the observed morphological differences are directly linked to the raw material composition and the carbonization process. Walnut shell sorbents, with higher porosity and a more open structure, are better suited for applications where large surface area and diffusion pathways are essential, such as water and gas purification. Pistachio shell sorbents, with denser morphology and residual inorganic inclusions, may be advantageous in applications where mechanical strength and durability are required.

These findings are consistent with recent studies, which showed that walnut shell-derived carbons generally develop more accessible porous networks during carbonization, enhancing their adsorption properties.[43-44] Pistachio shell carbons, while less porous, can still serve as efficient sorbents after suitable activation or modification, as demonstrated in recent work.[17]

4. Conclusion

This study demonstrated an efficient and environmentally friendly CO_2 -assisted carbonization route for converting walnut and pistachio shells into effective carbon sorbents for phenol removal. The CO_2 atmosphere promoted in-situ activation, resulting in enhanced porosity and surface functionality without chemical additives.

Comprehensive characterization confirmed that walnut shell carbons possess a more developed macro/mesoporous network and higher surface area (580 m^2/g) compared to pistachio carbons (350 m^2/g). As a result, walnut sorbents achieved superior adsorption efficiency (~94% at pH 3-5) and faster kinetics following pseudo-second-order behavior.

The adsorption process was governed by π-π interactions and hydrogen bonding under acidic conditions and by electrostatic repulsion at higher pH, consistent with the observed mechanism. These findings demonstrate that agricultural residues can be transformed into low-cost, sustainable sorbents with performance comparable to commercial activated carbon. The proposed CO_2 -assisted approach provides new insight into waste valorization and offers a scalable pathway for producing carbon materials for water purification and other environmental applications.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

CRediT Statement

Altynov Yerkebulan: Conceptualization, Investigation, Writing - Original draft, **Tlektesova Dil'naz:** Investigation, Validation, Writing - Review & editing, **Inabat Sapargali:** Resources, Validation, Writing - Review & editing. **Seitkhan Azat:** Writing - Review & editing. **Zhexenbek Toktarbay:** Writing - Review & editing, **Kudaibergenov Kenes:** Supervision, Funding acquisition, Project administration.

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