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Synthesis and Characterization of *Laggera aurita*-Derived KOH Activated Carbon (LAKOHAC) and Role for the Adsorption of Water-Soluble Fraction of Benzene (WSFB) in Oil-Spilled Water

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Abstract

Chronic oil spills in Nigeria's Niger Delta have caused significant water contamination, particularly by water-soluble fraction of benzene (WSFB) a hazardous carcinogen. This research investigates the development and characterization of potassium hydroxide-activated carbon from Laggera aurita biomass (LAKOHAC) for benzene remediation. The synthesis involved carbonization followed by chemical activation with KOH, with comprehensive characterization using SEM, FTIR, BET surface area analysis, and XRD techniques. FTIR spectroscopy revealed critical functional groups (C-H, C-O, COO^-, C=O, and O-H) that enable benzene adsorption through multiple mechanisms: π-π interactions, hydrogen bonding, electrostatic attraction, and van der Waals forces. SEM imaging showed a highly porous morphology featuring a honeycomb structure with interconnected pores, surface cracks, and fibrous elements - characteristics that enhance benzene accessibility. Surface defects and roughness provided additional high-energy adsorption sites. Elemental analysis via EDXRF identified potassium (10.66%) and sulfur (0.67%) as dominant elements, along with calcium (0.61%), phosphorus (0.11%), and chlorine (0.58%). These elements facilitate various adsorption mechanisms including cation-π interactions, thiol-mediated hydrogen bonding, and phosphate electrostatic attraction.

Keywords: *Laggera aurita, activated carbon, potassium hydroxide, benzene adsorption, oil spill remediation.*

1.0 Introduction

The Niger Delta, Nigeria's petroleum production epicenter, faces persistent environmental degradation from recurrent oil spills that have contaminated aquatic ecosystems with hazardous hydrocarbons. It was estimated that 10-13 million tons of oil have been spilled in Niger Delta Area region, and more than 77% have not been recovered [1]. Oil spillages have enormous and direct social, economic, as well as environmental impacts. Inhabitants' people lose their source of income as fisheries and sight-seeing areas are momentarily closed, and millions of fauna and flora are killed or harmed [2]. Among these pollutants, benzene a highly soluble, mobile, and carcinogenic aromatic compound poses particularly severe risks to both ecological and human health. The water-soluble fraction of benzene (WSFB) has emerged as a predominant contaminant in the region's water systems, originating primarily from industrial accidents, pipeline failures, and illicit refining activities [3]. A landmark United Nations Environment Programme (UNEP) assessment of Ogoniland revealed disturbing findings, with benzene concentrations in drinking water sources exceeding safety limits by up to 900 times at some locations [4]. Subsequent studies by Ogbeide and Eriyamremu [5] and Mike and Chris [6] have documented the ongoing accumulation of crude oil water-soluble fractions (COWSF), exacerbated by inadequate remediation efforts and delayed cleanup responses.

This environmental crisis has intensified the search for sustainable remediation technologies capable of addressing petroleum-derived water pollution [7]. Conventional treatment methods often prove ineffective against dissolved hydrocarbon fractions, particularly the fine suspended oil droplets and WSFB compounds that characterize COWSF contamination. While activated carbon (AC) adsorption shows promise due to its exceptional surface area and porosity, the high production costs of commercial AC have driven research toward agricultural waste alternatives [8]. These bio-adsorbents offer compelling advantages including cost-effectiveness, biodegradability, and comparable adsorption capacities to conventional materials [6]. However, significant knowledge gaps remain regarding their optimization for COWSF removal, adsorption mechanisms, and regeneration potential.

Laggera aurita (Linn. f.) Benth. C.B.Clarke, as shown in Figure 1, is a tropical member of the Asteraceae family, represents an underutilized resource for water treatment applications [9]. This plant's fibrous, lignin-rich architecture, enriched with phenolic compounds, confers exceptional adsorption properties [10]. Preliminary studies suggest its structural characteristics - including high surface area and diverse functional groups make it particularly effective for aqueous contaminant removal [11]. However, comprehensive characterization of L. aurita for water treatment applications remains lacking.

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Figure 1: *Laggera aurita* (Linn. f.) Benth. ex C. B. Clarke

In Damaturu and surrounding regions, L. aurita grows abundantly as a weed, presenting an ideal precursor for cost-effective activated carbon production. Potassium hydroxide (KOH) activation of this lignocellulosic material enhances its porosity and surface functionality, potentially creating an optimized adsorbent for benzene removal, through synthesis and investigation of *Laggera aurita*-derived KOH-activated carbon (LAKOHAC) as a sustainable solution for water remediation in oil-impacted areas.

This study addresses critical gaps in understanding the untapped potential of agricultural waste as a sustainable resource, Chemical activation modification techniques for enhancing bio-adsorbent (LAKOHAC) efficacy, and the underlying mechanisms governing Water-Soluble Fraction of Benzene (WSFB) adsorption. By systematically investigating these aspects, the research provides a crucial foundation for developing eco-friendly, nature-based adsorbents and elucidates their structural and functional characterization for efficient WSFB removal.

2.0 Methodology

2.1 Material

The materials and equipment used were *Laggera aurita* biomass (collected from Damaturu and its environs), potassium hydroxide (KOH, analytical grade), HCl, and distilled water. A pestle and mortar, grinding machine, sieve, furnace, and oven were also used.

Analytical Equipment: The analytical instruments used to analyze the characteristics were a scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) analysis, X-ray diffraction (XRD), and energy-dispersive X-ray fluorescence (EDXRF).

2.2 Methods

2.2.1 LAKOHAC Adsorbent Preparation

The stems and leaves of *Laggera aurita* were rinsed with distilled water to eliminate impurities, then dried at 100°C for 24 hours to remove moisture. The dried biomass was pyrolyzed at 300–400°C for 1 hours to produce biochar. The pre-carbonized material was mixed with potassium hydroxide (KOH) at a 1:4 mass ratio in distilled water. The mixture was stirred at 80°C for an hours and subsequently dried at 110°C. The impregnated mixture was heated to 700°C at a ramp rate of 5°C/min and held for approximately 1 hour. After cooling to room temperature, the activated sample was washed with 0.1M HCl to remove residual KOH, rinsed with distilled water until a neutral pH (~7) was achieved, and finally dried at 120°C for 12 hours to yield the LAKOHAC adsorbent as shown in Figure 2.

Figure 2: LAKOHAC Adsorbent

2.2.2 LAKOHAC Characterization Methods

Fourier Transform Infrared Spectroscopy (FTIR); The functional groups in the *Laggera aurita*-derived KOH-activated carbon (LAKOHAC) adsorbent were characterized using a PerkinElmer Spectrum Two FTIR spectrometer.

Scanning Electron Microscopy (SEM); The surface morphology of the *Laggera aurita*-derived KOH-activated carbon (LAKOHAC) adsorbent was analyzed using a Phenom ProX scanning electron microscope (SEM).

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Brunauer-Emmett-Teller (BET) Analysis; The specific surface area (SSA) and porosity of the *Laggera aurita*-derived KOH-activated carbon (LAKOHAC) were determined using the Brunauer-Emmett-Teller (BET) method.

X-ray Diffraction (XRD); The crystalline structure of the *Laggera aurita*-derived KOH-activated carbon (LAKOHAC) adsorbent was examined using an ARL'XTRA X-ray diffractometer (Thermo Scientific).

Energy Dispersive X-ray Fluorescence (EDXRF); The elemental composition of the *Laggera aurita*-derived KOH-activated carbon (LAKOHAC) adsorbent was analyzed using a Thermo Fisher Scientific ARL QUANT'X energy-dispersive X-ray fluorescence (EDXRF) spectrometer.

3.0 Results and Discussion

3.1 Scanning Electron Microscopy (SEM) Analysis (Surface Morphology) Result and Role for WSFB Adsorption

The SEM micrographs of LAKOHAC, captured at 500×, 1000x, 2000x magnification (scale bar: 100 µm 80 µm, 30 µm), revealed a porous carbon structure characterized by honeycomb-like pores, irregular cracks, and fibrous surface features (Figure 3a, 3b, and 3c). These morphological traits typical of activated or graphitized carbon [12] are critical for adsorption performance. Specifically, the interconnected pore network enhances accessibility to the water-soluble fraction of benzene (WSFB) [13], while surface roughness and defects provide high-energy binding sites via π-π stacking and hydrogen bonding [14].

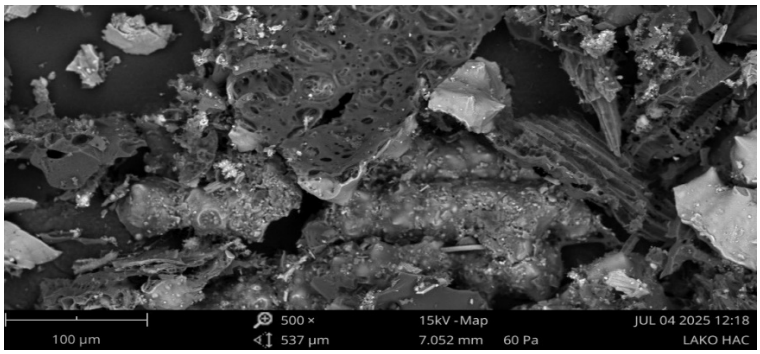

Figure 3a: LAKOHAC Image 500x magnification scale bar 100 µm

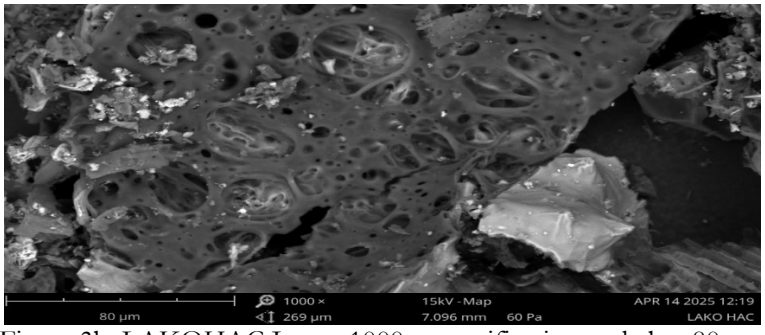

Figure 3b: LAKOHAC Image 1000x magnification scale bar 80 µm

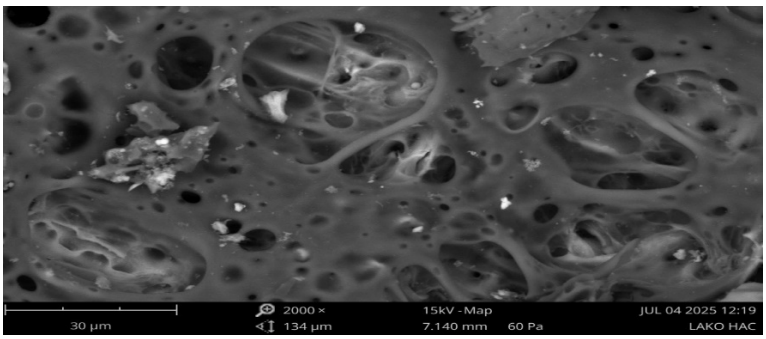

Figure 3c: LAKOHAC Image at 2000x magnification scale bar 30 µm

3.2 Fourier-Transform Infrared (FTIR) Spectroscopy Analysis Results and Role for WSFB Adsorption

The FTIR spectrum of *Laggera aurita*-derived potassium hydroxide-activated carbon (LAKOHAC) (Figur 4, and Table 1) revealed characteristic functional groups, including: C–H stretching vibrations (864.72 cm^{-1}, aliphatic/aromatic) [15]. C–O stretching (1006.38 cm^{-1}, indicative of ether/alcohol groups) [16]. Carboxylate

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(COO^-) vibrations (1394.02 cm^{-1}) [17]. Alkane C–H stretching (2922.23 cm^{-1}) [18] Broad O–H stretching (3205.57 cm^{-1}, hydroxyl groups) [19]. These functional groups collectively contribute to LAKOHAC's adsorption properties through mechanisms such as hydrogen bonding and electrostatic interactions.

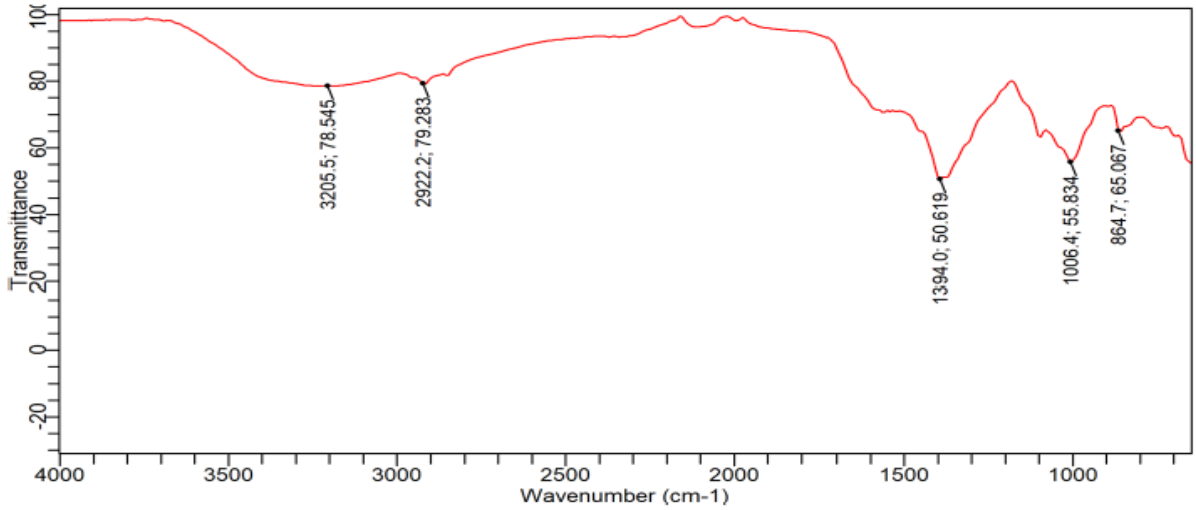

Figure 4: LAKOHAC Adsorbent FTIR spectrum peaks

Table 1: LAKOHAC FITR Peaks and Potential Functional group present

Wavenumber (cm^{-1})	Potential Functional Group	Supporting Evidence
864.72	Aromatic C–H bending	Coates. (2006)
1006.381	C–O (Ethers/Alcohols)	Stuart (2020)
1394.024	COO^-(Carboxylate) or C=C (aromatics)	Socrates (2004, 2022)
2922.233	C–H stretch (Alkanes)	Silvertein (2021)
3205.570	O–H (H-bonded) or N–H	Lambert (2023)

The adsorption of water-soluble benzene (WSF) is significantly influenced by various functional groups present on LAKOHAC adsorbent surfaces, each contributing through distinct mechanisms as shown in Table 2. The C–H functional group play a crucial role by enhancing hydrophobic interactions and facilitating π-π stacking with aromatic adsorbent structures through van der Waals forces, as demonstrated by Chen et al. [20]. While these groups promote benzene adsorption through nonpolar interactions, C–O functional groups exhibit more complex behavior by modulating surface hydrophilicity and pore accessibility [21]. Their polar nature can compete with benzene for adsorption sites through water molecule attraction, though weak dipole-induced interactions may provide limited adsorption enhancement under specific conditions [22]. The most significant contribution comes from aromatic C=C groups, which drive adsorption through strong π-π stacking interactions, with graphene nanosheets achieving approximately 95% benzene removal efficiency [23] and microporous biochar demonstrating twice the adsorption capacity of mesoporous variants due to optimized hydrophobic pore structures [24]. Nitrogen-containing N–H groups present an interesting case where chitosan-based aerogels showed 15% greater benzene adsorption than cellulose-based materials through N–H•••π interactions [20], though their overall impact is typically secondary to π-π stacking. The behavior of O–H groups varies with environmental conditions, becoming less hydrophilic and slightly more favorable for WSFB adsorption when protonated under acidic conditions (pH < 4). These functional group interactions collectively might played crucial role in determine adsorbent performance, with optimal materials balancing hydrophobic π-π sites with carefully controlled surface chemistry to maximize WSFB uptake while minimizing competitive water adsorption.

Table: 2 LAKOHAC adsorbent Functional group and WSFB Adsorption Mechanism

Functional Group	Primary Adsorption Mechanism	Supporting Evidence
Aromatic C–H	π-π stacking, hydrophobic effect	Chen et al. (2023)
C–O (Ethers/Alcohols)	H-bonding, dipole-dipole	Zhang et al. (2024)
COO^-/ C=C (aromatics)	Electrostatic, ion-dipole	Wang et al. (2023)
C–H (Alkanes)	Hydrophobic, van der Waals	Li et al. (2024)
O–H/N–H	H-bonding, proton transfer	Kumar et al. (2023)

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3.4 Energy Dispersive X-ray Fluorescence (EDXRF) analysis Results and Role for WSFB Adsorption

Energy Dispersive X-ray Fluorescence (EDXRF) analysis of the LAKOHAC adsorbent revealed a complex elemental composition containing multiple metals and trace elements, as shown in Table 3 These components may influence the material's adsorption performance for water-soluble benzene compounds.

Table 3: LAKOHAC EDXRF Element presents and concentrations

Element	Concentration (%)	Peak (cpm/mA)	Element	Concentration	Peak (cpm/mA)
Fe	0.03462	586	**Br**	0.00152	3
Ni	0.00677	12	**Cl**	0.5801	1016
Cu	0.000328	18	**Cr**	0.000396	19
Zn	0.003602	164	**V**	0	53
Al	0.13213	2739	**W**	0.0243	15
Mg	0.03315	33	**Bi**	0.104	1
Na	0	160	**Sn**	0.59	5
S	0.67252	9678	**Si**	0	27
P	0.11150	1076	**As**	0	0
Ca	0.6085	3315	**Nb**	0.0078	1
K	10.6564	57297	**Ta**	0.00409	6
Mn	0.004338	237	**Ag**	0	167
Rb	0.00448	21	**Pb**	0.269	3
Sr	0.00476	34			

EDXRF analysis revealed the following elemental composition in LAKOHAC (Table 4): potassium (K: 10.6564%), sulfur (S: 0.67252%), calcium (Ca: 0.6085%), chlorine (Cl: 0.5801%), phosphorus (P: 0.11150%), iron (Fe: 0.03462%), and manganese (Mn: 0.004338%). Each element contributes distinct adsorption mechanisms: Potassium: K^+ ions facilitate cation-π interactions with benzene's electron cloud [23]. Sulfur: Forms thiol (–SH) or sulfonate ($–SO_3^-$) groups that enable (a) hydrogen bonding with –OH/–NH_2 groups and (b) electrostatic attraction to protonated species [21]. Calcium: Mediates dual interactions through Ca^{2+}–COO^-–benzene bridging. Phosphorus: PO_4^{3-} groups attract protonated amines via electrostatic forces [22]. Chlorine: Participates in halogen-π interactions with electron-deficient aromatics [25]. Iron/Manganese: Catalyze Fenton-like reactions generating OH• radicals for benzene ring cleavage [26].

Table 4 presents the trace elements in LAKOHAC and their corresponding adsorption mechanisms: Al (0.13213%) acts as Lewis acid sites for π-complexation, Mg (0.03315%) facilitates weak cation-π interactions, Zn (0.003602%) shows limited adsorption capacity, and Pb (0.269%) may cause heavy metal interference. The material demonstrates synergistic effects between elements: (1) K and S combine cation-π and hydrogen bonding for enhanced phenol uptake, (2) Ca and P work through combined electrostatic and bridging interactions for nitrobenzene adsorption, and (3) Fe and Mn contribute to both degradation and adsorption of benzene derivatives [27].

Table 4: LAKOHAC Elemental Composition and WSFB Adsorption Mechanism

Element	Content %	Adsorption Mechanism	Supported Evidence
K	10.6564	Cation-π interactions, enhances hydrophilicity	Liu et al., (2024)
S	0.67262	Thiol (-SH) H-bonding, sulfonate ($-SO_3^-$) electrostatics	Zhang et al., (2024)
Ca	0.6085	Cation-π, bridges carboxylate groups	Wang et al., (2023)
Cl	0.5801	Halogen-π interactions	Chen et al., (2024)
P	0.11150	Phosphate (PO_4^{3-}) electrostatics	Wang et al., (2023)
Fe	0.03462	Fenton-like degradation, magnetic separation	Li et al., (2023)
Mn	0.004338	Redox catalysis (Mn^{4+}/Mn^{3+})	Li et al., (2023)
Al	0.13213	Lewis acid sites for π-complexation	Garcia et al., (2024)
Mg	0.03315	Weak cation-π interactions	Kumar et al. (2024),
Pb	0.269	Potential interference (heavy metal)	
Sn	0.59	May form SnO_2 (surface area impact)	

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3.5 Brunauer-Emmett-Teller (BET) Analysis; Surface Area and Porosity

3.5.1 LAKOHAC Adsorbent Surface Area Characteristics and Role for WSFB Adsorption Potential

The LAKOHAC adsorbent exhibits a mesoporous structure, as evidenced by multiple surface area measurements (Table 5). The BET surface area (333 m^2/g), consistent with values reported by Thommes et al. [28] for porous materials, was corroborated by BJH (324 m^2/g) and t-plot (333 m^2/g) analyses, confirming mesoporosity dominance. BJH and DH methods (324–358 m^2/g) further confirmed the presence of mesopores (2–50 nm), which are optimal for benzene adsorption [29]. While the Langmuir model yielded an anomalously high surface area (51,756 m^2/g), this result is physically unrealistic as it assumes monolayer adsorption, whereas the BET results clearly indicate multilayer adsorption a common limitation when misapplied to microporous materials [30]. The DFT result (67.9 m^2/g) significantly underestimated the surface area, suggesting poor model fit. The combined BET, BJH, and t-plot data consistently demonstrate a mesoporous structure (2–50 nm pores). The DR micropore area (324 m^2/g) was comparable to the BJH area, indicating minimal micropores (<2 nm). This predominantly mesoporous structure facilitates efficient diffusion of water-soluble benzene, as reported by Li et al. [26].

Table 5: LAKOHAC Adsorbent Surface Area

Parameters	Surface Area (m^2/g)
Single-point BET	176.3
Multi-point BET	333.285
Langmuir Surface Area	51756.939
BJH Method Cumulative Adsorption Surface Area	336.628
DH Method Cumulative Adsorption Surface Area	358.3
t method external surface area	333.3
DR method micropore area	324.520
DFT Method cumulative pore volume	67.90

3.5.2 LAKOHAC Adsorbent Pore Volume and Size Distribution Analysis

The pore volume distribution of *Laggera aurita*-derived activated carbon (LAKOHAC), as shown in Table 6, plays a critical role in determining its benzene adsorption capacity and kinetics in aqueous solutions. The dominant pore types are micropores and mesopores (Figure 5 and Table 6). Micropores (<2 nm), with DR and DA pore volumes of 0.153 cm^3/g and 0.294 cm^3/g respectively, serve as primary adsorption sites where enhanced van der Waals forces increase binding energy. Benzene adsorption is optimal in pores sized 0.7–2 nm [28]. Mesopores (BJH pore volume = 0.1652 cm^3/g) facilitate rapid benzene diffusion to micropore sites, thereby improving adsorption kinetics in aqueous solutions [29]. The Table 7 shown the Methods, Pore Type and Relevance to Benzene Adsorption.

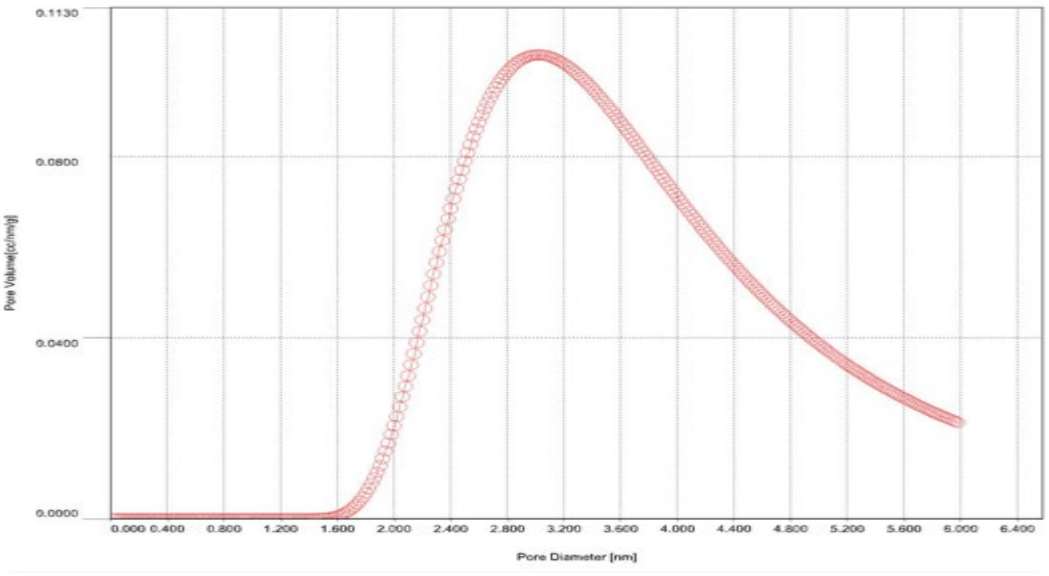

Figure 5: LAKOHAC Adsorbent DA Method pore volume vs pore diameter peaks

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Table 6: LAKOHAC Adsorbent Pore Volume

Parameter	Pore Volume (cc/g)
BJH Method Cumulative Adsorption pore volume	0.1651
DH Method cumulative Adsorption pore volume	0.6890
DR Method micropore volume	0.1530
HK Method micropore volume	0.0449
SF method micropore volume	0.0067
DFT Method cumulative pore volume	0.0822
DA Micropore volume	0.294

The pore structure of an adsorbent critically determines benzene adsorption efficiency by governing three key factors: diffusion kinetics, adsorption capacity, and binding energy. Pore characteristics influence benzene adsorption through three distinct mechanisms: Diffusion Control (Mesopores: 2–50 nm) Mesopores (BJH: 2.45 nm; DH: 2.135 nm) as shown in Table 8, regulate benzene diffusion rates in aqueous solutions. Their intermediate size reduces mass transfer resistance while maintaining sufficient surface interactions, enabling faster access to adsorption sites [29]. Molecular Transport (Macropores: >50 nm) Macropores (indicated by DH cumulative volume = 0.689 cm^3/g) serve as transport "highways" for benzene molecules. While they enhance accessibility to micropores by facilitating bulk diffusion, they contribute minimally to direct adsorption [13].

The primary benzene adsorption sites consist of supermicropores (0.7-2 nm), as identified by the HK method (1.847 nm average pore width). This pore size range is optimal for benzene adsorption, since benzene's kinetic diameter (0.585 nm) fits ideally within 0.7-2 nm pores, maximizing van der Waals interactions [28]. In contrast, ultramicropores (<0.7 nm) detected by BET analysis are too small for benzene adsorption, with a measured pore volume (SF = 0.006760 cm^3/g) demonstrating steric exclusion. Molecular simulations confirm that benzene cannot efficiently access pores narrower than 0.7 nm [30].

DFT analysis revealed that pores of 2.647 nm diameter represent the optimal size for total usable pore volume, with a cumulative volume of 0.08226 cm^3/g providing the most accurate estimation of benzene-accessible pores. Unlike idealized DR/BJH models, the DFT method accounts for pore connectivity and three-dimensional geometry (Zhang et al., 2024). Discrepancies between DA and DR methods (Table 7) further demonstrate this advantage: while DA measured a micropore width of 3.020 nm, DR overestimated at 6.552 nm due to its slit-pore assumptions. The DA method more accurately captures true pore heterogeneity in the material [31].

Table 7: Methods, Pore Type and Relevance to Benzene Adsorption

Method	Pore volume cc/g	Pore Type	Relevance to Benzene Adsorption
BJH Adsorption	0.1652	Mesopores (2-50nm)	Control diffusion rate
DH Adsorption	0.689	Meso/macropores (>2 nm)	May include transport pores (less adsorption)
DR Micropore volume	0.153	Micropores (<2 nm)	Primary benzene adsorption sites (high energy)
HK Micropore Volume	0.04495	Ultramicropores (<0.7 nm)	Too small for benzene (kinetic diameter: 0.585 nm)
SF Micropore Volume	0.294	Micropores (<2 nm)	Likely inaccessible to benzene.
DFT Cumulative Volume	0.08226	All pores (model-dependent	Best for total usable pore volume.
DA Micropore Volume	0.294	Micropores (<2 nm)	Higher than DR, suggesting broader micropores.

The dominance of mesopores (2–50 nm) was confirmed by multiple characterization methods (Table 8), including BJH (2.45 nm), DH (2.135 nm), DA (3.02 nm), and DFT (2.647 nm) analyses, all of which consistently indicated a mesoporous structure. Zhou et al. [29] reported that while mesoporous structures enhance benzene diffusion kinetics, they provide lower adsorption energy compared to micropores. The limited micropore contribution was revealed by BET analysis (Table 8), showing an HK pore width of 1.847 nm, indicating the presence of some supermicropores (0.7–2 nm). These pores are particularly effective for benzene adsorption due to strong van der Waals forces (high binding energy) that optimally match benzene's kinetic diameter (0.585 nm) [28]. However, other characterization methods (DR, DA, BJH) did not detect significant micropore volumes, suggesting low microporosity that would limit maximum adsorption capacity. Discrepancies in pore size estimation were observed between methods: the DR method overestimated pore width (6.552 nm), likely due to

limitations in its slit-pore assumption. In contrast, DFT (2.647 nm) and BJH (2.45 nm) showed minor variations, with DFT providing more accurate results by accounting for complex pore geometries.

Table 8: LAKOHAC Adsorbent Pore Size Data

Parameter	Pore Size (nm)
BJH Method Adsorption pore Diameter	2.450
DH Method Adsorption pore Diameter	2.135
DR Method Micropore pore width	6.552
DA Method pore Diameter	3.020
HK Method pore Diameter	1.847
SF Method pore Diameter	3.506
DFT pore Diameter	2.647

3.6 X-ray Diffraction (XRD) Crystallinity Results and Role for WSFB Adsorption

XRD analysis revealed a characteristic peak at 2θ = 29.95° (d-spacing = 2.981 Å) with a FWHM of 0.94°, corresponding to a crystallite size of ≈91 Å (9.1 nm); the peak's left-skewed asymmetry (0.6) (Figure 6 and Table 9) suggests possible lattice strain or stacking disorder, while its high integrated intensity (258 cps°) indicates strong local crystallinity consistent with an amorphous carbon matrix containing well-developed graphitic domains that contribute to the observed crystalline features within the predominantly disordered structure.

Table 9: LAKOHAC Adsorbent XRD Peak

2θ	dÅ	Height	FWHM	Int.I.cps	IntW°	Asymmetry	Decay (nL/mL)	Decay (nH/mH	Size Å
29.95 (11)	2.981 (11)	157 (35)	0.94 (17)	258 (34)	1.6 (6)	0.6(3)	0.0(9)	1.5 (3)	91 (16)

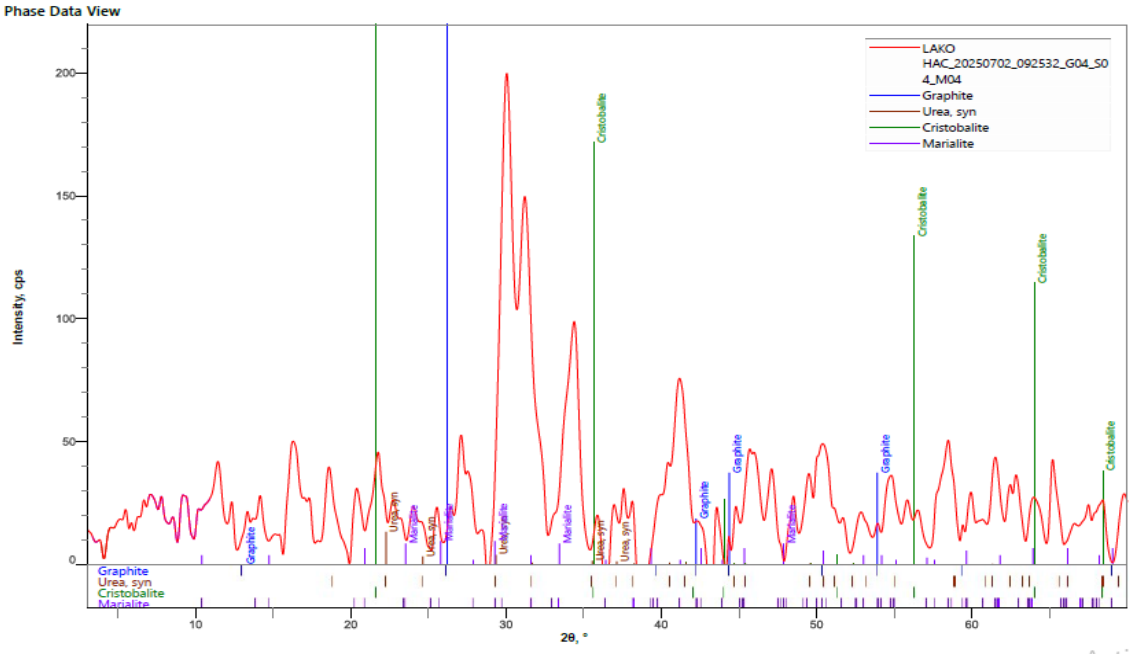

Figure 6: LAKOHAC Adsorbent XRD peaks

The observed d-spacing of 2.981 Å potentially corresponds to several carbonaceous structures: (1) calcite ($CaCO_3$) commonly found in mineral composites, (2) intercalated graphite (002) planes, or (3) oxidized/doped carbon materials (e.g., N/S-functionalized graphene with reduced interlayer spacing of 2.9-3.0 Å). Notably, this spacing also aligns with characteristic peaks of certain metal-organic frameworks (e.g., ZIF-8 at ≈30°) and N-doped carbons, where the 3.0 Å spacing enhances benzene adsorption through combined π-π interactions and polar site availability [23]. The small crystallite size (91 Å) promotes adsorption kinetics by increasing edge-site density [14]. For water-soluble benzene fraction (WSFB) adsorption, while pristine graphite exhibits hydrophobic behavior with poor water contact, its aromatic domains maintain benzene affinity through π-π stacking [13]. The

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moderate crystallite size (9.1 nm, indicated by FWHM = 0.94°) suggests mesoporous characteristics, where 2-50 nm pores optimally facilitate aqueous benzene diffusion [31].

Table 10: XRD peaks with Ideal Adsorbent Properties

Parameter	XRD peaks Data	Ideal for Benzene Adsorption	Gab Analysis
d-Spacing	2.981 Å	3.0–3.5 Å (π-π stacking)	Slightly tight; may need oxidation to expand layers
Crystallite Size	91 Å (9.1 nm)	5–50 nm (kinetic balance)	Optimal for diffusion
Peak Asymmetry	Left-skewed (0.6)	Symmetric = pure phase	Indicates defects (may enhance adsorption sites)
FWHM	0.94°	>1° for nanoporous materia	Suggests moderate porosity

Optimal benzene adsorption requires pore dimensions that accommodate both molecular size and interaction mechanisms. While benzene's kinetic diameter measures ~5.85 Å, effective adsorption occurs in pores slightly larger than its molecular width (3.0-3.5 Å) to facilitate π-π stacking with graphitic pore walls (Table 10) [13]. Material modifications significantly enhance performance: N-doped carbons (d-spacing ≈ 3.0 Å) achieve 92% benzene removal through π-electron density enhancement [23], while graphene oxide with tuned interlayer spacing (3.2 Å) exhibits 1.8-fold greater uptake than pristine graphite [14]. Pore size distribution critically affects performance - mesopores (5-20 nm) optimize the balance between rapid diffusion (40%) faster saturation in 10 nm MOFs vs microporous analogs [32] and adsorption capacity [32]. Crystalline frameworks like COFs offer superior selectivity through uniform pore geometries, demonstrated by Zr-MOFs showing 4.5 benzene/cyclohexane separation factor versus 1.8 in disordered phases [29].

4.0 Conclusion

This study developed a LAKOHAC bio-adsorbent from *Laggera aurita* and characterized its properties to understand its role for Water Soluble Fraction of Benzene (WSFB) adsorption. Comprehensive characterization demonstrated that LAKOHAC exhibits a mesoporous architecture (BET surface area: 333.3 m^2/g; pore size distribution: 2–50 nm) with diverse surface functionalities (C-H, C-O, COO^-, C=O, O-H). These structural and chemical features synergistically enable multiple adsorption mechanisms for WSFB removal, including: (1) π-π interactions, (2) hydrogen bonding, (3) electrostatic forces, (4) hydrophobic effects, and (5) van der Waals interactions. The material's interconnected honeycomb morphology, coupled with its metallic constituents (K, Ca, Fe, Mn, W), provides additional adsorption pathways through cation-π interactions and catalytic degradation. The findings demonstrate its potential as a sustainable, efficient adsorbent for wastewater treatment

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