

Physicochemical, Morphological, Structural, Thermal and Elemental Characterization of Fe/Mn/N Tri-Doped Cassava Peel Nano biochar: An FTIR, SEM-EDS, XRD, DSC and XRF Study

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Abstract

Agro-waste-derived biochar is widely explored as a low-cost adsorbent for heavy metal remediation, but its performance depends critically on surface chemistry, morphology, crystallinity, thermal stability and elemental composition, properties that must be established before adsorption mechanisms can be meaningfully interpreted. This study reports the comprehensive physicochemical, morphological, structural, thermal and elemental characterization of Fe/Mn/N tri-doped cassava peel (*Manihotesculenta*) nanobiochar synthesized by sequential pyrolysis (500⁰C, 2 h), wet impregnation with FeCl₃.6H₂O, MnCl₂.6H₂O and urea (1:1:2 v/v) at 80⁰C, and secondary pyrolysis (600⁰C, 2 h). The synthesized material was characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS), X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) and X-ray Fluorescence (XRF). ATR-FTIR spectra showed a dominant hydroxyl stretch at 3300-3400 cm⁻¹ and C-O/C-O-C stretching at 1036-1088 cm⁻¹ in raw cassava peel, with pronounced attenuation after carbonisation and the emergence of new metal-oxygen and nitrogen-associated vibrations following Fe/Mn/N doping. SEM micrographs revealed a transformation from a loose, flaky undoped surface to a more compact, micropore-rich morphology decorated with aggregated metal-oxide nanoparticles after tri-doping. DSC thermograms of the undopedbiochar showed a dehydration onset at 52.40 ⁰C and a major decomposition peak at 210.05 ⁰C (enthalpy 175.6021 J/g), with the thermal transition window extending to 385.12⁰C. XRD patterns displayed a broad amorphous carbon hump between 2theta = 20-30 degrees superimposed with low-intensity crystalline reflections near 2theta = 35⁰C and 62⁰C, consistent with finely dispersed magnetite (Fe₃O₄)-type or Fe-Mn spinel nanophases. XRF confirmed the biogenic base composition (K, Ca, Si) of the precursor and verified successful incorporation of Fe and Mn dopants, alongside trace Rb,Sr and Zn. Collectively, these results confirm successful synthesis of a multifunctional, nanostructured Fe/Mn/N tri-doped biochar with enhanced surface reactivity, positioning it as a promising engineered adsorbent for heavy metal remediation of industrial wastewater.

Keywords: biochar characterization; cassava peel; Fe/Mn/N tri-doping; FTIR; SEM-EDS; XRD; DSC; XRF; nanoadsorbent

1. Introduction

Produced water is the largest-volume waste stream generated during oil and gas exploration and processing, and its complex matrix of dissolved salts, hydrocarbons, chemical additives

and heavy metals such as cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), copper (Cu), mercury (Hg) and zinc (Zn) poses severe ecological and human-health risks owing to the non-biodegradability, toxicity and bioaccumulative potential of these metals (Ogolo, Anih&Onyekonwu, 2022; Khalef, Hassan & Saleh, 2022). Conventional treatment options, including chemical precipitation, membrane filtration and ion exchange, are frequently constrained by high operating cost, sludge generation, membrane fouling and limited efficiency in multi-component systems (Shamshad&Rehman, 2025), which has stimulated interest in adsorption using low-cost, agriculturally derived materials (Raji, Karim, Karam&Khalloufi, 2023). Cassava peel is an abundant lignocellulosic agro-industrial by-product in many developing countries, rich in cellulose, hemicellulose and lignin-derived functional groups capable of binding metal ions (Rogoski, Pereira, Cesca, de Oliveira & de Andrade, 2023). However, raw cassava peel and conventional, unmodified biochar derived from it typically suffer from limited surface area, weak metal-binding affinity and poor selectivity. Doping biochar with transition metals and heteroatoms has been shown to overcome these limitations: iron (Fe) introduces magnetic character and enhances surface complexation, manganese (Mn) contributes redox activity capable of transforming toxic metal species into less harmful forms, and nitrogen (N) doping increases surface basicity and electron-rich active-site density. The simultaneous incorporation of Fe, Mn and N into cassava-peel biochar is therefore expected to produce synergistic, multifunctional adsorption behaviour combining electrostatic attraction, ion exchange, surface complexation and redox interactions. Before such a tri-doped adsorbent can be meaningfully evaluated for heavy metal removal, its physicochemical, morphological, structural, thermal and elemental properties must first be rigorously established. Surface functional groups govern the chemistry of metal binding and are best probed by Fourier Transform Infrared Spectroscopy (FTIR); surface morphology and pore architecture, which determine active-site accessibility, are visualised by Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS); crystalline phase composition and the degree of graphitisation are resolved by X-ray Diffraction (XRD); thermal stability and decomposition behaviour are quantified by Differential Scanning Calorimetry (DSC); and bulk elemental composition, including confirmation of dopant incorporation, is verified by X-ray Fluorescence (XRF). Despite growing interest in doped biochar adsorbents, comprehensive multi-technique characterization of Fe/Mn/N tri-doped cassava-peel biochar remains scarce in the literature.

This article addresses this gap by reporting, from a broader doctoral investigation into Fe/Mn/N tri-doped cassava peel nanobiochar for heavy metal remediation of simulated wastewater, the specific objective of characterizing the physicochemical, morphological, structural, thermal and elemental properties of the synthesized biochar using FTIR, SEM-EDS, XRD, DSC and XRF. The results establish the structural and chemical basis on which the material's adsorption behaviour, reported elsewhere, can be interpreted, and provide a reference characterization profile for future work on doped agro-waste biochars (Tang *et al.*, 2022; Xiao *et al.*, 2025). Framed within the wider doctoral study, characterization was guided by the following questions: what physicochemical and structural transformations accompany the conversion of raw cassava peel into undoped and subsequently Fe/Mn/N tri-doped biochar; how does tri-doping alter surface morphology and pore architecture relative to the undoped material; what is the thermal decomposition profile of the biochar across the pyrolysis-relevant temperature range; what crystalline and amorphous phases coexist within the doped carbon matrix; and does elemental analysis independently confirm successful incorporation of the intended Fe and Mn dopants alongside the biogenic mineral background of the precursor. Addressing these questions using FTIR, SEM-EDS, XRD, DSC and XRF in combination, rather than any single technique in isolation, provides a mutually corroborating characterization framework that strengthens confidence in the successful synthesis of the

engineered nanobiochar and establishes the structural basis for its subsequent evaluation as a heavy-metal adsorbent.

2. Materials and Methods

2.1 Feedstock and Reagents

Fresh cassava peels were sourced from cassava-processing outlets in Naze, Owerri West Local Government Area, Imo State, Nigeria, and transported in clean polyethylene bags to the Centre for Industrial Studies, Federal University of Technology, Owerri, for processing. All reagents, including ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), manganese chloride ($\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$), urea ($\text{CH}_4\text{N}_2\text{O}$), hydrochloric acid and sodium hydroxide, were of analytical grade and used without further purification; distilled water was used throughout.

2.2 Biochar Synthesis

Cassava peels were manually sorted, washed free of adhering soil and starch residues, air-dried for 9 days, and oven-dried at 105°C for 24 h. The dried peels were mechanically pulverized and sieved to a uniform particle size to maximise surface area for impregnation, then preserved in airtight desiccators. Primary carbonisation was carried out in a muffle furnace at 500°C for 2 h (heating rate $10^\circ\text{C}/\text{min}$) under oxygen-limited conditions to yield undopedbiochar, which was washed to neutral pH and oven-dried.

For doping, precursor solutions were prepared by dissolving 5g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 5g $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 g urea, each in 100 mL deionised water. Fifty grams of undopedbiochar were dispersed in 500 mL of the combined $\text{FeCl}_3 \cdot \text{MnCl}_2$ -urea solution (volumetric ratio 1:1:2) and agitated at 300 rpm and 80°C for 4 h to promote penetration of Fe_3^+ , Mn_2^+ and nitrogen species into the porous carbon matrix, followed by 24 h ageing at room temperature. The impregnated slurry was oven-dried at 105°C for 12 h and then subjected to secondary pyrolysis at 600°C for 2 h ($10^\circ\text{C}/\text{min}$, oxygen-limited) to produce Fe-Mn-N tri-doped cassava peel nanobiochar. The product was washed to neutral pH, oven-dried, pulverized and sieved through a 100 micrometre mesh, then stored in airtight desiccators. A pristine (undoped) biochar, prepared under identical pyrolysis conditions without dopant addition, served as the control/reference sample for all characterization comparisons.

Table 1: Summary of key synthesis conditions for Fe/Mn/N tri-doped cassava peel nanobiochar.

Stage	Key parameters
Feedstock pre-treatment	Manual sorting, washing, air-drying (9 days), oven-drying at 105°C for 24 h
Primary pyrolysis (undopedbiochar)	Muffle furnace, 500°C , 2 h, heating rate $10^\circ\text{C}/\text{min}$, oxygen-limited
Dopant precursor solutions	5 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 5 g $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$, 10 g urea, each in 100 mL deionised water
Impregnation	50 g biochar in 500 mL mixed precursor solution (Fe:Mn:urea = 1:1:2 v/v), 300 rpm, 80°C , 4 h, then 24 h ageing
Drying of impregnated biochar	105°C , 12 h
Secondary pyrolysis (tri-doped nanobiochar)	Muffle furnace, 600°C , 2 h, heating rate $10^\circ\text{C}/\text{min}$, oxygen-limited
Post-synthesis processing	Washing to neutral pH, oven-drying (105°C , 12 h), pulverization, sieving through 100 micrometre mesh

2.3 Characterization Techniques

FTIR analysis was performed on an ATR-FTIR spectrometer over the 4000–400 cm^{-1} range at 4 cm^{-1} resolution with 32 cumulative scans, on raw cassava peel, undoped biochar, and Fe/Mn/N tri-doped biochar before and after adsorption, to identify hydroxyl, carbonyl, carboxyl and nitrogen-containing surface functional groups. Surface morphology was examined by Scanning Electron Microscopy on gold-sputtered, carbon-tape-mounted samples, complemented by Energy Dispersive Spectroscopy (EDS) for point elemental analysis, comparing undoped and tri-doped biochar. Thermal behaviour was assessed by Differential Scanning Calorimetry using a PerkinElmer DSC 4000 system, heating 10 mg samples from 30 to 400 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ under nitrogen flow to resolve endothermic and exothermic transitions. Crystalline phase composition was determined by X-ray Diffraction over a 2 θ range of 10–80 $^{\circ}$ at a scan speed of 2 $^{\circ}\text{C}/\text{min}$. Bulk elemental composition was determined by X-ray Fluorescence spectroscopy on pressed powder pellets (10 g, hydraulic press, prolene-film-covered sample cups), measured in triplicate against certified reference materials, to confirm successful Fe/Mn incorporation and quantify base and trace elements.

3. Results

The results are organized to follow the logical progression of the characterization objective: production of the biochar precursor materials, followed by the five analytical techniques used to interrogate its surface chemistry (FTIR), morphology and elemental fingerprint (SEM-EDS), crystalline structure (XRD), thermal behaviour (DSC), and bulk elemental composition (XRF). Presenting the undoped biochar alongside the Fe/Mn/N tri-doped material throughout allows the specific structural and chemical consequences of tri-doping to be isolated from the more general effects of pyrolytic carbonisation common to both materials.

3.1 Biochar Production

The synthesis progressed through five visually distinct stages: (a) dried raw cassava peel, (b) pulverized and sieved biomass, (c) impregnation of the biochar with the mixed Fe-Mn-urea precursor solution, (d) sieving of the dried impregnated biochar, and (e) the final Fe/Mn/N tri-doped nanobiochar product recovered after secondary pyrolysis (Plate 1). Visual inspection showed a progressive darkening and textural refinement of the material from the fibrous raw peel to a fine, black, free-flowing nanobiochar powder after secondary calcination.

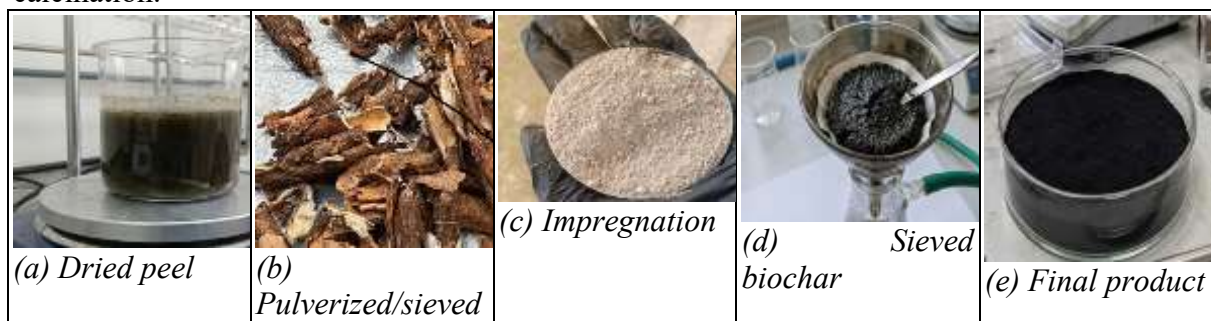


Plate 1: Production stages of Fe/Mn/N tri-doped cassava peel nanobiochar: (a) dried cassava peel, (b) after pulverization/sieving, (c) impregnation, (d) sieved impregnated biochar, and (e) final product after secondary calcination.

3.2 FTIR Analysis: Surface Functional Groups

Figure 1 presents the comparative ATR-FTIR spectra of raw cassava peel, undoped biochar, and Fe/Mn/N tri-doped biochar before and after heavy metal adsorption. Raw cassava peel exhibited a dominant broad absorption band at 3300–3400 cm^{-1} , assigned to O-H stretching

vibrations of cellulose and hemicellulose, together with a sharp peak at 1036-1088 cm^{-1} attributed to C-O/C-O-C stretching within the lignocellulosic framework. Carbonisation to undoped biochar produced a marked reduction in the intensity of the -OH band, reflecting loss of moisture and thermal degradation of oxygen-containing functionalities. Following Fe/Mn/N doping, new and shifted vibrations appeared in the fingerprint region, consistent with the formation of metal-oxygen (M-O) bonds and the introduction of nitrogen-containing functional groups that provide additional coordination sites for metal ions. After adsorption, shifts in the 1028-1051 cm^{-1} region and intensity changes in the -OH/C=O envelope (1600-1700 cm^{-1}) indicated active participation of oxygenated surface groups in metal-ion binding through surface complexation and electron-donor interactions.

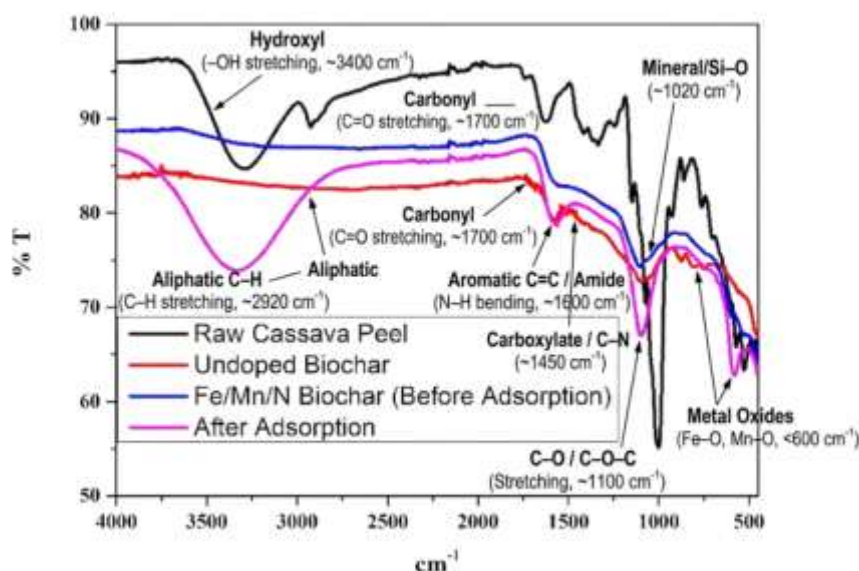


Figure 1: ATR-FTIR spectra of raw cassava peel, undoped biochar, and Fe/Mn/N tri-doped cassava peel biochar before and after heavy metal adsorption.

3.3 SEM Analysis: Surface Morphology

Figure 2 shows SEM micrographs of (a) undoped and (b) Fe/Mn/N tri-doped cassava peel biochar. The undoped biochar displayed a highly fragmented, irregular and flaky surface with heterogeneous pore distribution, typical of lignocellulosic biomass after pyrolytic removal of volatile matter. After tri-doping, the surface became noticeably more compact and smoother in places, interspersed with well-defined micropores and small aggregated particles attributable to deposition of Fe and Mn oxide nanoparticles onto and within the existing pore network. This transformation from a loose, flaky undoped structure to a filled, functionalized tri-doped surface is consistent with successful incorporation of metal-oxide phases and is expected to enhance specific surface area and active-site density.

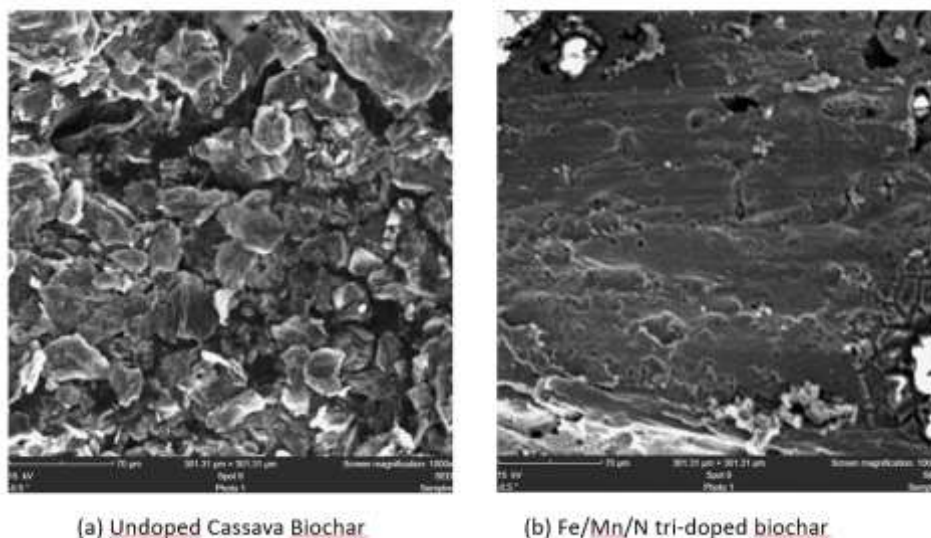


Figure 2: Scanning Electron Microscopy (SEM) micrographs of (a) undoped cassava peel biochar and (b) Fe/Mn/N tri-doped cassava peel biochar.

3.4 DSC Analysis: Thermal Behaviour

Figures 3 and 4 present DSC thermograms of undoped and Fe/Mn/N tri-doped cassava peel biochar, respectively, over the 30-400 °C range. The undoped biochar exhibited a primary endothermic event with an onset temperature of 52.40 °C, attributed to evaporation of surface-bound moisture and loss of light volatiles. A prominent thermal event was subsequently observed at 210.05 °C, with an associated enthalpy change of 175.6021 J/g, corresponding to decomposition of residual hemicellulose and early-stage cellulose breakdown. The transition continued to an end temperature of 385.12 °C, marking conversion of the remaining biomass into a stable carbonaceous char over a wide thermal window indicative of steady, controlled decomposition favourable for high-yield biochar formation with preserved porosity.

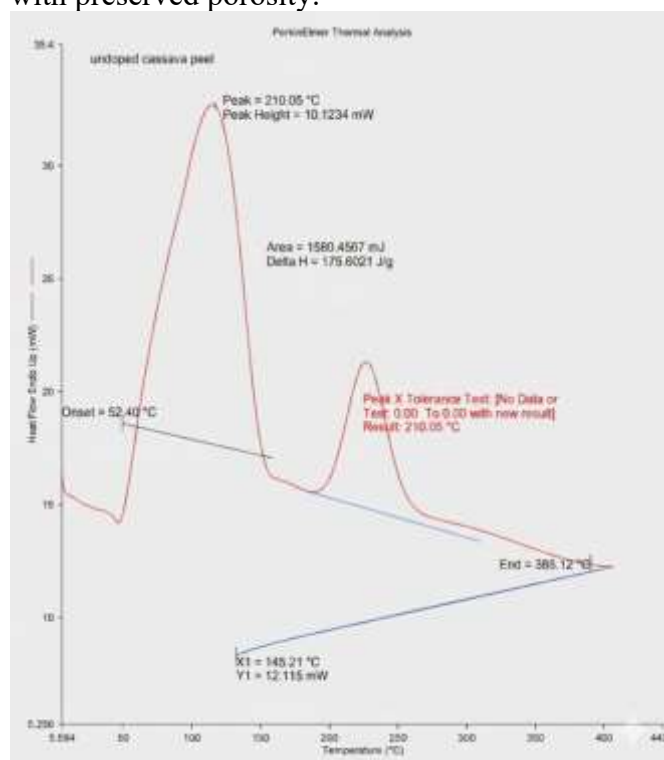


Figure 3: Differential Scanning Calorimetry (DSC) thermogram of undoped

cassava peel biochar.

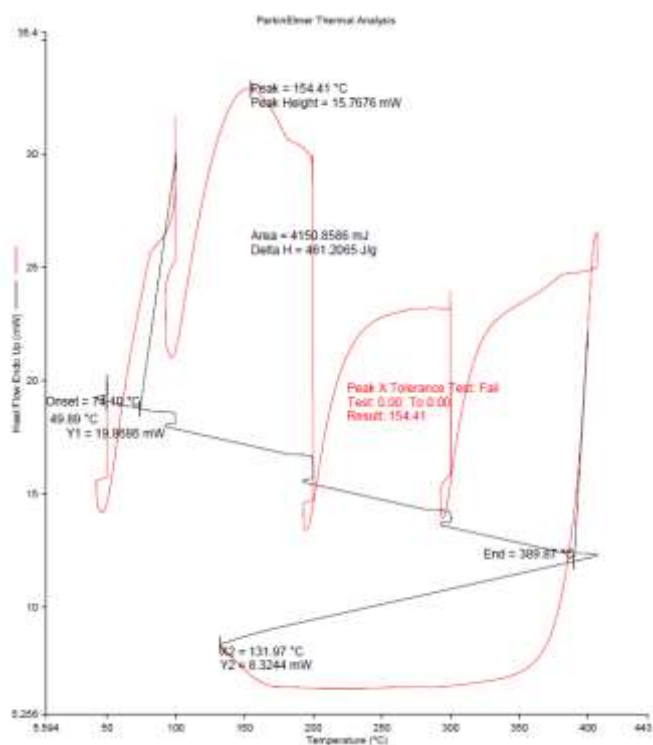


Figure 4: Differential Scanning Calorimetry (DSC) thermogram of Fe/Mn/N tri-doped cassava peel biochar over the temperature range 50-400 °C.

3.5 XRD Analysis: Crystalline Structure

Figure 5 presents the XRD pattern of Fe/Mn/N tri-doped cassava peel biochar over the scanned 2theta range of 10-80 °C. The diffractogram is dominated by a broad, hump-like feature between 2theta = 20 °C and 30 °C, characteristic of the amorphous carbon (002) plane typical of moderate-temperature biochars, superimposed with discrete, lower-intensity peaks. Table 2 summarises the expected and observed 2theta positions of the major reflections identified in the pattern.

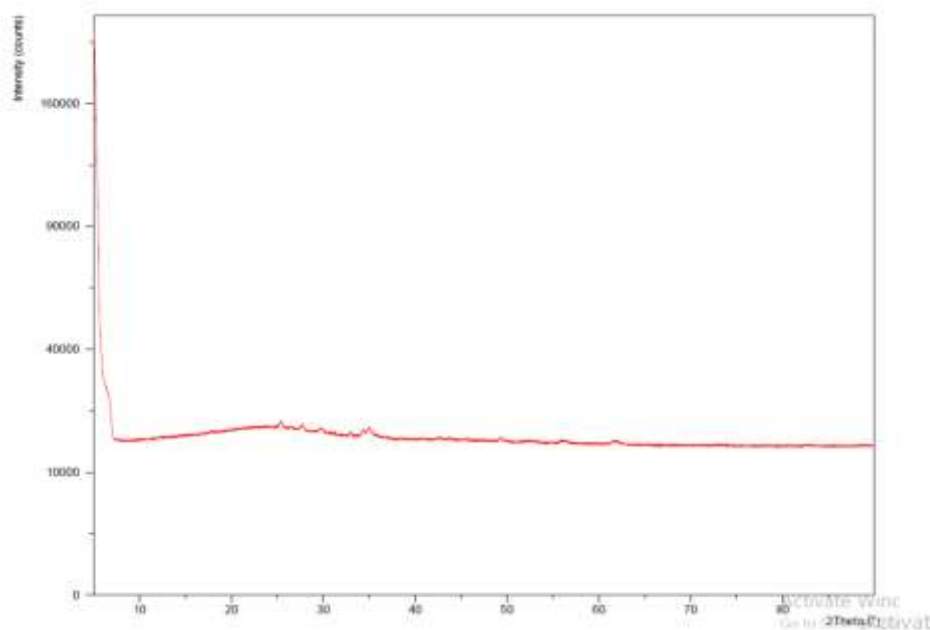


Figure 5: X-ray Diffraction (XRD) pattern of Fe/Mn/N tri-doped cassava peel biochar.

Table 2: Summary of expected and observed XRD diffraction angles for Fe/Mn/N tri-doped cassava peel biochar (band width 1.455 deg 2theta).

S/N	Expected 2theta (deg)	Actual 2theta (deg)	Difference (deg)
1	28.419	27.929	-0.490
2	47.277	47.384	0.107
3	56.096	56.502	0.406
4	69.103	70.068	0.965
5	76.348	76.197	-0.151
6	88.004	88.909	0.905

3.6 XRF Analysis: Elemental Composition

Figure 6 shows the XRF spectrum of Fe/Mn/N tri-doped cassava peel biochar, and Table 3 summarises the classes of elements detected. The spectrum confirmed the persistence of naturally occurring biogenic minerals (potassium, calcium and silicon) from the cassava peel precursor as residual ash content after pyrolysis, alongside clearly resolved Kalpha and Kbeta emission lines for iron and manganese, verifying successful impregnation and incorporation of the intended dopants. Minor trace peaks corresponding to rubidium, strontium and zinc were also detected.

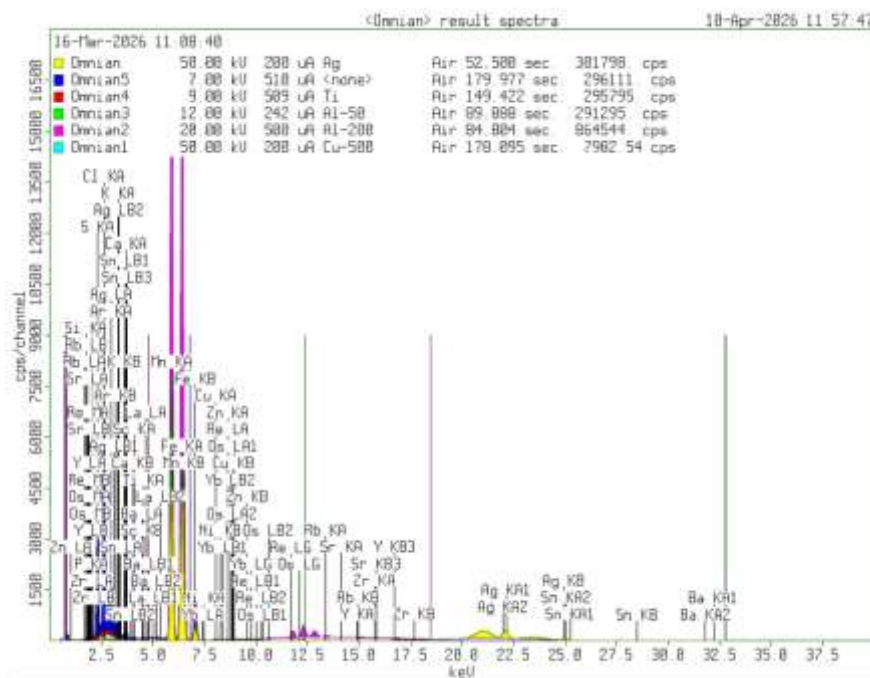


Figure 6: X-ray Fluorescence (XRF) spectrum of Fe/Mn/N tri-doped cassava peel biochar.

Table 3: Summary of elemental categories identified by X-ray Fluorescence (XRF) spectroscopy of Fe/Mn/N tri-doped cassava peel biochar.

Category	Elements identified	Likely source / significance
Biogenic base elements	K, Ca, Si	Natural ash-forming minerals retained from cassava peel precursor after pyrolysis

Category	Elements identified	Likely source / significance
Dopant elements	Fe, Mn	Confirmed incorporation of iron and manganese via characteristic K-alpha/K-beta lines
Trace elements	Rb, Sr, Zn	Minor biogenic/adventitious trace minerals contributing to ion-exchange capacity

4. Discussion

4.1 Functional Group Transformation and Adsorption-Relevant Chemistry

The FTIR results trace a coherent chemical transformation pathway from raw biomass to functional nano-adsorbent. The strong -OH and C-O/C-O-C bands in raw cassava peel reflect its native cellulose-hemicellulose-lignin composition (Kayiwa *et al.*, 2025), while their attenuation upon carbonisation is consistent with thermally driven dehydration and deoxygenation reactions typical of pyrolytic conversion (Xiao, 2022). The appearance of new metal-oxygen vibrations and nitrogen-associated features after Fe/Mn/N doping demonstrates that the impregnation-pyrolysis route successfully grafts inorganic and heteroatom functionalities onto the carbon backbone rather than merely depositing loosely bound precursor salts (Xiao *et al.*, 2025; Zaman *et al.*, 2023). The post-adsorption peak shifts around 1028-1051 cm⁻¹ and within the 1600-1700 cm⁻¹ envelope confirm that oxygenated surface groups act as electron donors that form stable complexes with cationic metal species (Zhao *et al.*, 2023; Odeyemi *et al.*, 2023), while the combination of Lewis acid sites from the Fe/Mn oxide phases and basic sites from nitrogen functionalities is expected to confer a diverse, synergistic set of metal-binding mechanisms (Zhao, Jiang, Chen, Wang & Nan, 2025).

It is also worth noting that the sequential nature of the synthesis route, primary pyrolysis followed by wet impregnation and secondary pyrolysis, appears to be reflected in the layered pattern of spectral change: the first pyrolysis step drives the bulk deoxygenation and aromatisation typical of biochar formation, while the second, lower-temperature-mediated impregnation and re-calcination step is responsible for the more targeted, localized changes associated with dopant incorporation. This staged spectral evidence supports the interpretation that Fe, Mn and N species are chemically anchored to residual oxygenated sites on the carbon surface rather than simply physically mixed with the biochar matrix, which has direct implications for the durability and reusability of the resulting adsorbent under repeated aqueous contact.

4.2 Morphological Evidence of Successful Doping

The SEM observations corroborate the FTIR findings at the microstructural scale. The irregular, flaky, heterogeneous morphology of undoped biochar is characteristic of lignocellulosic biochar produced by conventional pyrolysis, in which volatilisation of organic matter leaves a roughened, disordered carbon framework (Arshad, Qadir & Hussain, 2024). The more compact, micropore-decorated surface of the tri-doped material, interspersed with aggregated nanoparticles, mirrors observations reported for other metal-modified biochars in which impregnation followed by secondary pyrolysis promotes nucleation of nanoscale metal-oxide domains on the carbon matrix (Wang, Pei, Zhang, Li, Song, Guo & Shu, 2026). This morphological densification, coupled with partial pore filling by metal-oxide deposits, is consistent with an increase in functionalized surface area and active-site density that would be expected to enhance adsorption capacity through surface complexation and electrostatic interaction (Tang *et al.*, 2022).

4.3 Thermal Stability and Decomposition Behaviour

The DSC thermal profile is typical of starch-, cellulose- and lignin-rich cassava biomass, in which an initial low-temperature endothermic event corresponds to moisture and light volatile loss, followed by a more energetic exothermic-type decomposition regime associated with hemicellulose degradation and early cellulose breakdown (Egbosiuba, 2022). The relatively wide thermal transition window observed here, extending from approximately 52 degC to 385 degC, indicates a gradual, well-controlled decomposition pathway that is advantageous for biochar production, since it favours steady char yield and helps preserve the developed porosity needed for effective adsorption (Hamissou, Appiah, Sylvie, Ousmaila, Casimir & Kouassi Benjamin, 2023). Although a direct doped-versus-undoped enthalpy comparison would further clarify the influence of Fe/Mn/N incorporation on thermal stability, the sustained decomposition profile observed is consistent with a thermally robust carbon framework capable of withstanding the secondary pyrolysis step used in the tri-doping procedure.

4.4 Crystalline Phase Composition

The dominant broad hump between $2\theta = 20^\circ\text{C}$ and 30°C confirms that the tri-doped biochar retains a predominantly amorphous carbon matrix, consistent with the (002) graphitic reflection typical of biochars produced at moderate pyrolysis temperatures and with the largely amorphous character generally reported for cassava-peel-derived carbons (Arshad *et al.*, 2024). The low-intensity but discrete peaks near $2\theta = 35^\circ\text{C}$ and 62°C are attributable to crystalline transition-metal oxide phases, such as the (311) reflection of magnetite (Fe_3O_4) or related Fe-Mn spinel structures, providing direct structural evidence of successful metal-oxide phase formation within the carbon matrix during doping and secondary pyrolysis (Tang *et al.*, 2022). The comparatively low intensity of these crystalline reflections relative to the amorphous background suggests that the doped metal species are finely and predominantly dispersed as nanoparticles rather than large bulk crystallites, a configuration that maximises exposed surface reactivity while preserving the porous carbon architecture, both of which are beneficial for adsorption performance. From a materials-design perspective, the balance observed here between amorphous carbon and finely dispersed crystalline dopant phases is close to an optimal configuration for an adsorbent: a fully crystalline, bulk metal-oxide phase would offer limited accessible surface area, whereas an amorphous, poorly dispersed dopant distribution would compromise the redox and Lewis-acid functionalities that Fe and Mn are intended to contribute. The XRD evidence therefore indicates that the impregnation and secondary pyrolysis conditions used in this study, namely 80°C agitation during impregnation followed by 600°C secondary carbonisation, were appropriately calibrated to achieve nanoscale dopant dispersion without inducing excessive sintering or bulk crystallite growth.

4.5 Elemental Composition and Confirmation of Doping

The XRF results provide compositional confirmation that complements and corroborates the FTIR, SEM and XRD findings. Detection of potassium, calcium and silicon reflects the natural mineral (ash) content inherent to cassava peel biomass, which persists through pyrolytic carbonisation (Odeyemi *et al.*, 2023). More importantly, the clear identification of iron and manganese $K\alpha/K\beta$ emission lines provides direct, independent verification that the impregnation-pyrolysis protocol successfully incorporated the intended dopants into the biochar matrix, consistent with the metal-oxide signatures already inferred from XRD and the M-O vibrations observed by FTIR. The presence of trace rubidium, strontium and zinc indicates a diverse residual mineral profile that may further contribute auxiliary ion-exchange capacity in a complex, multi-metal wastewater system.

4.6 Integrated Interpretation

Taken together, the five characterization techniques present a mutually consistent and complementary picture: FTIR demonstrates the chemical transformation of surface functional groups and the introduction of new metal- and nitrogen-associated moieties; SEM visualises the accompanying morphological densification and nanoparticle deposition; DSC establishes that the base carbon framework is thermally robust across the pyrolysis-relevant temperature range; XRD confirms the coexistence of an amorphous carbon matrix with finely dispersed crystalline metal-oxide nanophases; and XRF independently verifies the elemental identity and successful incorporation of the Fe and Mn dopants. This convergent, multi-technique evidence base confirms that the impregnation-secondary pyrolysis route successfully produced a structurally sound, chemically functionalized, nanostructured Fe/Mn/N tri-doped cassava peel biochar, providing the material foundation on which subsequent heavy-metal adsorption performance can be reliably interpreted (Wang, Lan, Bo, Gong & Ou, 2023; Wang & Guo, 2023).

4.7 Comparison with Related Doped Biochar Systems

The characterization trends observed for Fe/Mn/N tri-doped cassava peel nanobiochar align broadly with patterns reported for other transition-metal- and heteroatom-modified biochars derived from agricultural residues. The attenuation of oxygen-containing FTIR bands upon carbonisation, followed by the appearance of new metal-oxygen vibrations after doping, mirrors observations for Fe-Mn oxide-modified biochars used for Pb(II) removal, in which similar spectral shifts were linked directly to enhanced metal-binding capacity (Tang *et al.*, 2022). The SEM-observed transition from a flaky, irregular undoped surface to a more compact, nanoparticle-decorated tri-doped surface is consistent with reports on transition-metal-modified activated carbons, where impregnation-pyrolysis routes are shown to generate dispersed metal-oxide domains that increase functional surface area without collapsing the underlying porous carbon framework (Wang *et al.*, 2026). Likewise, the coexistence of a dominant amorphous carbon hump with low-intensity crystalline reflections attributable to Fe-Mn oxide nanophases, as observed here by XRD, has been reported as a hallmark of successful, well-dispersed metal doping in biochar-based adsorbents rather than bulk-phase segregation, which would instead produce sharp, high-intensity diffraction peaks (Zhao, Jiang, Chen, Wang & Nan, 2025). The XRF-confirmed retention of biogenic K, Ca and Si alongside newly introduced Fe and Mn is similarly consistent with characterization profiles reported for other cassava-peel-derived biochars and biosorbents, where natural mineral content persists through pyrolysis and coexists with any subsequently introduced functional dopants (Odeyemi *et al.*, 2023; Schwantes *et al.*, 2022). This consistency across independent studies strengthens confidence that the multi-technique characterization reported here reliably captures genuine, reproducible material transformations associated with Fe/Mn/N tri-doping, rather than artefacts specific to a single measurement or instrument.

5. Conclusion and Recommendations

This study characterized the physicochemical, morphological, structural, thermal and elemental properties of Fe/Mn/N tri-doped cassava peel nanobiochar synthesized via sequential pyrolysis and wet impregnation. FTIR confirmed the progressive transformation of surface functional groups from the native hydroxyl- and C-O-rich raw biomass, through the deoxygenated undoped biochar, to a tri-doped material bearing new metal-oxygen and nitrogen-associated functionalities that actively participate in metal-ion binding upon adsorption. SEM revealed a clear morphological densification and development of micropores decorated with metal-oxide nanoparticles following doping, relative to the flaky, irregular undoped surface. DSC established a thermally stable decomposition profile

spanning approximately 52-385 °C, characteristic of cassava-derived lignocellulosic char. XRD confirmed a predominantly amorphous carbon matrix hosting finely dispersed crystalline Fe-Mn oxide nanophases, and XRF independently verified successful incorporation of iron and manganese dopants alongside the natural biogenic mineral background of the precursor. These convergent, multi-technique results confirm that the Fe/Mn/N tri-doped cassava peel nanobiochar was successfully synthesized as a structurally sound, nanostructured, multifunctional material with enhanced surface chemistry relative to undoped biochar, satisfying the specific objective of comprehensive material characterization within the broader study on heavy-metal remediation of simulated wastewater. The findings also contribute to the valorization of cassava peel, an abundant agro-industrial waste, into an engineered, high-value nanoadsorbent consistent with circular-economy and waste-to-resource principles. It is recommended that future work complement the present characterization suite with Brunauer-Emmett-Teller (BET) surface-area and pore-size analysis, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) to further resolve nanoparticle size distribution, pore architecture and surface oxidation states. Quantitative, doped-versus-undoped comparative DSC and thermogravimetric analysis would further clarify the specific contribution of Fe/Mn/N doping to thermal stability. Point-resolved SEM-EDS elemental mapping before and after adsorption is also recommended to directly visualise the spatial distribution of captured heavy metals on the characterized biochar surface, strengthening the mechanistic linkage between the material properties established here and the adsorbent's pollutant-removal performance.

More broadly, the characterization workflow demonstrated here, combining spectroscopic, microscopic, thermal, structural and elemental techniques within a single coherent evidence base, offers a replicable template for evaluating other engineered, agro-waste-derived adsorbents. As interest in doped and multi-functionalized biochars for water treatment continues to grow, rigorous, multi-technique material characterization of the type reported in this study will remain essential for distinguishing genuinely functionalized nanostructured adsorbents from superficially modified materials, and for building the mechanistic understanding needed to optimise synthesis conditions for target pollutant systems.

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