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Biochar

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Enhanced carbon retention in *Litchi* biochar via in-situ limewater coating and self-limited oxygen pyrolysis regulated by water-fire interaction

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Abstract

Biochar, a carbon-rich material with a porous structure, holds significant potential for mitigating climate change through carbon sequestration. However, its widespread adoption has been hindered by high production costs, primarily associated with oxygen-restricted systems and energy-intensive production processes. This study introduced a cost-effective, field-adapted strategy to enhance carbon retention in biochar derived from *Litchi* branches through limewater coating and synergistic water-fire interaction. *Litchi* branches were pretreated with limewater to create a surface coating, then underwent in-situ carbonization via self-oxygen-limited pyrolysis to form a dark-red char which was then quenched with limewater to produce biochar. Calcium (Ca)-mediated carbon retention during pyrolysis was investigated through Fourier-transform infrared spectroscopy (FTIR) coupled with scanning electron microscopy and energy-dispersive spectroscopy (SEM–EDS). The limewater-treated biochar achieved a significantly improved carbon conversion rate (86%) compared to CK (52%), the untreated biochar sample, with an enhanced specific surface area of 280 $m^2\ g^{-1}$. FTIR and SEM–EDS analyses revealed that the limewater treatment formed a calcium-enriched protective barrier that effectively suppressed the formation of CO_x during combustion. Additionally, mineral Ca-carbon composites formed during pyrolysis further improved carbon stabilization and retention. This study offers a practical and scalable solution for producing biochar under field conditions by addressing challenges related to cost-effectiveness and process efficiency, thereby promoting the application of biochar for carbon sequestration.

Highlights

- A field-adapted strategy for biochar production with potential cost advantages was developed.
- Limewater coating and self-oxygen-limited pyrolysis increased the biochar carbon conversion rate from 52% to 86%.
- A Ca-enriched protective barrier suppressed CO_x formation and enhanced carbon sequestration.

Keywords Carbon conversion rate, Limewater, Immersion, Coating, *Litchi* branches

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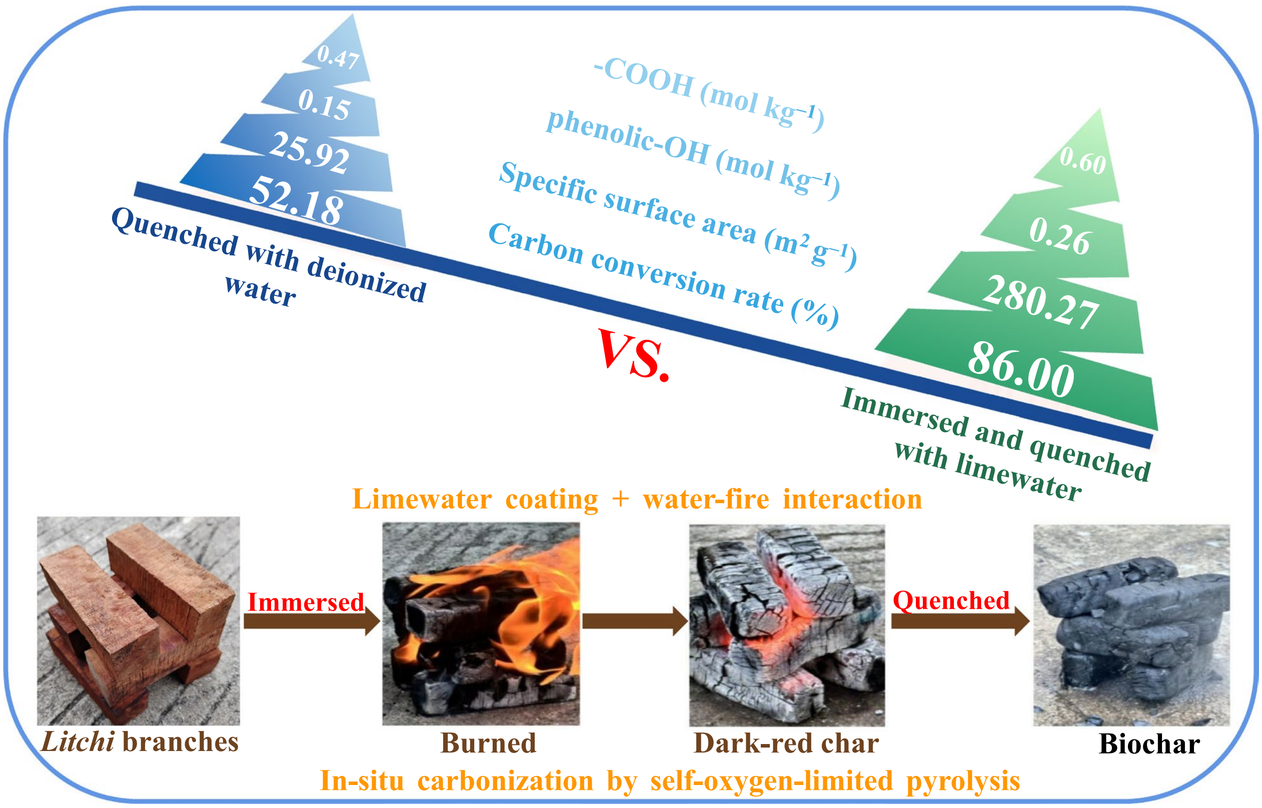
Graphical Abstract



1 Introduction

Biochar, a carbon-rich material with a porous structure, is conventionally produced through the pyrolysis of bio-waste under oxygen-limited conditions (Khater et al. 2024; Supraja et al. 2023; Shoudho et al. 2024; Tan and Yu 2024). With its high nutrient content, extensive specific surface area, and abundant functional groups, biochar has found widespread applications in enhancing soil fertility, increasing crop productivity, and supporting environmental remediation (Li et al. 2023; Manikandan et al. 2023; Pandian et al. 2024; Świechowski et al. 2024). More importantly, the carbon-rich composition and long-term stability of biochar have positioned it as a promising carbon-negative technology (Lehmann et al. 2021; Vickram et al. 2023; Woolf et al. 2010). Global estimates suggest that biochar has the potential to sequester 0.30–2.00 Gt of CO_2 annually (Fawzy et al. 2021), representing a significant contribution to global climate change mitigation efforts (Wang et al. 2023). The 2023 Annual Report of China highlights biochar as a critical technology for achieving carbon neutrality (Deng et al. 2024), with projections indicating an annual carbon sequestration capacity of 0.20 Gt CO_2 by 2030.

Despite being widely regarded as one of the most promising carbon negative technologies (Ayaz et al. 2025), the large-scale use of biochar remains constrained, primarily due to the substantial production and application costs associated with oxygen-limited pyrolysis (Campion et al. 2023; Zhu et al. 2023; Zhao et al. 2024). This approach necessitates specialized infrastructure and equipment to ensure oxygen-restricted conditions and energy supply (Hadiya et al. 2022). Additionally, the logistics of transporting bio-waste to production facilities and distributing the resultant biochar to application sites further elevate costs, which are estimated at approximately $350 per ton, yielding a limited profit margin of around $100 per ton (Campbell et al. 2018). These economic and logistical constraints also restrict the scalability of biochar production. Current global output is estimated at roughly 1 million tons per year (Batista et al. 2021), which, assuming a carbon content of 60%, corresponds to approximately 2.4×10^6 tons of CO_2 equivalent—sufficient to offset only 0.002 Gt of CO_2. This output falls two orders of magnitude short of the target sequestration level of 0.20 Gt CO_2. These challenges underscore the critical need for innovative strategies to develop more economically viable biochar production technologies.

The in-situ carbonization and sequestration of bio-waste present a promising strategy for reducing the production and application costs associated with biochar. Inspired by the formation of *Terra Preta* in the Amazon Basin and char derived from forest fires (Harder 2006; Wardle et al. 2008), Xiao et al. (2020) proposed a field-adapted method based on synergistic water-fire interaction. In this approach, biomass is ignited in open air, and the outer surface quickly combusts to form a thin ash or char layer that passively restricts oxygen diffusion into the core. This creates a low-oxygen environment inside the material—termed self-limited oxygen pyrolysis—which is fundamentally different from conventional oxygen-limited pyrolysis conducted in sealed or inert environments. The process is terminated after brief exposure (≤ 30 s) by rapid water quenching, thereby preserving the carbonized core and producing biochar (Xiao et al. 2023). This approach holds potential for lowering production costs and addressing logistical constraints, making it suitable for field-scale applications. However, the rudimentary nature of the production method often leads to biochar with sub-optimal carbon content, frequently failing to meet the international Class 1 standard for carbon content ($C\geq60\%$) in biochar (Klasson 2017; Lin et al. 2025). Furthermore, the mechanisms governing carbon retention during the pyrolysis and quenching stages is poorly understood, which limits the theoretical foundation necessary for optimizing this technique. Addressing these gaps is critical for advancing the practical application of the water-fire coupled method in biochar production.

In oxygen-limited pyrolysis, researchers often employ mineral modification to enhance the properties of biochar (Chon et al. 2024; Yan et al. 2020), including carbon content, specific surface area, and functional groups. For instance, calcium modification involves the introduction of calcium salts (e.g., $CaCO_3$ or $CaCl_2$) during pyrolysis, where calcium reacts with carbon precursors to form stable carbonate complexes (Campbell et al. 2018; Ren et al. 2018). This process promotes the condensation of aromatic carbon structures and suppresses the release of volatile organic compounds, thereby improving carbon retention. Similarly, iron modification utilizes iron compounds (e.g., $FeCl_3$ or Fe_2O_3) as catalysts to accelerate carbonization reactions and form Fe–C complexes, enhancing the stability of biochar (Nan et al. 2021; Weber and Quicker 2018). These findings provide valuable insights into improving biochar quality through mineral modification. Building on this, we propose exploring whether the mineral modification used in oxygen-limited pyrolysis can be adapted to the water-fire coupled carbonization. By introducing minerals—such as through pre-soaking bio-waste in mineral solutions or applying mineral coatings to the bio-waste surface—it may be possible to improve the carbon content of biochar (Iamsaard et al. 2022; Jiang et al. 2019). However, unlike the slow carbonization process of oxygen-limited pyrolysis, the combustion carbonization and water quenching in the water-fire coupled process are extremely rapid. It remains unclear whether minerals can effectively interact with carbon precursors within such a short time frame to achieve similar carbon retention effects (Campion et al. 2023; Owsianiak et al. 2021). Furthermore, the underlying mechanisms—such as how minerals influence carbon retention during rapid thermal transitions—are poorly understood.

To address the limitations of traditional pyrolysis and improve the effectiveness of the water-fire coupled method, this study explored the use of limewater pretreatment to enhance carbon retention during the in-situ carbonization of *Litchi* branches. Specifically, we investigated whether limewater immersion and coating could form a mineral barrier that reduces COx emissions and whether Ca^{2+} ions could interact with carbon precursors to promote the formation of stable carbon–mineral complexes. *Litchi* branches, a common type of orchard waste in southern China, were selected as the carbon precursor. The proposed approach was evaluated through a combination of chemical (elemental analysis, FTIR), structural (SEM–EDS), and physical (carbon conversion rate, specific surface area) analyses to assess biochar quality. This work aims to develop a low-cost, scalable strategy for biochar production using locally available materials and simple techniques.

2 Materials and methods

2.1 Source and preparation of biowaste from *Litchi* branches

The *Litchi* branches used in this study were collected from an orchard in Guangdong. The branches were cut into 10 cm × 4 cm × 5 cm pieces and each piece had an average mass of 113.6 ± 10.2 g. Subsequently, they were washed with deionized water to remove surface dust and oven-dried at 85 °C.

The branches were divided into three groups. One group was stored in sample boxes for later use. The other two groups were subjected to immersion treatments: one in deionized water and the other in limewater. These groups were oscillated at 150 r min^{-1} for 48 h at 25 °C on a constant temperature oscillator. The limewater immersion aimed to investigate the infiltration effect of $Ca(OH)_2$ within the branches and its influence on biochar properties. The deionized water immersion aimed to determine whether it was the water retained within the branches or the $Ca(OH)_2$ that affected the biochar properties during limewater immersion. After the immersion treatments, the branches were dried at 85 °C for 48 h and then individually transferred to sample boxes for subsequent carbonization.

2.2 Preparation of saturated limewater

Limewater was prepared by dissolving 1.74 g of calcium hydroxide in 1 dm^3 of deionized water. The solution was refrigerated at 4 °C and stored in sealed glass bottles for subsequent use in saturated limewater immersion and coating treatments.

2.3 Experimental design

The experiment included six treatments, as detailed in Table 1. Each treatment had four replicates. The branches were ignited using liquefied natural gas (LNG) and carbonized through open field burning to form dark-red char. Within 0–30 s exposure time (the interval between the formation of a burning char and its extinction by deionized water or saturated limewater spray, the exposure time was selected because it has been shown that the resultant biochar has higher carbon content, specific surface area, and functional groups compared

Table 1 Different treatments of *Litchi* branches

Treatment	Detailed information
CK	The branches were burned to dark-red char and quenched with deionized water to form biochar.
T1	The branches were burned to dark-red char and quenched with limewater to form biochar.
T2	The branches were immersed in deionized water, burned to char, and quenched to form biochar.
T3	The branches were immersed in deionized water, burned, and quenched with limewater to form biochar.
T4	The branches were immersed in limewater, burned, and quenched with deionized water to form biochar.
T5	The branches were immersed in limewater, burned, and quenched with limewater to form biochar.

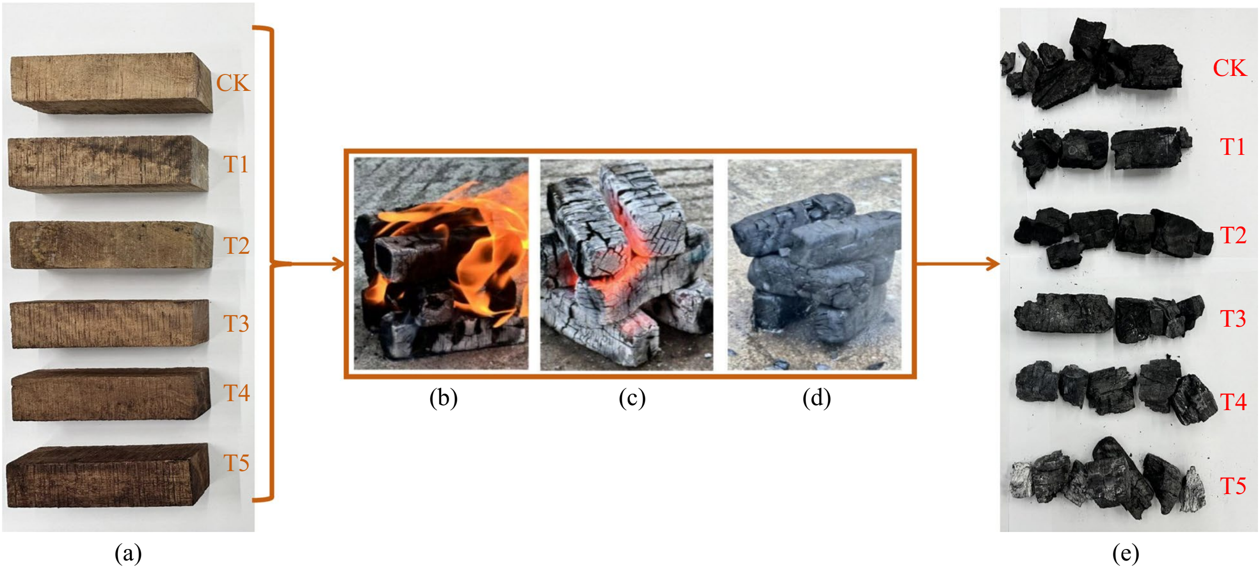


Fig. 1 Schematic representation of biochar production: (**a**) *Litchi* branches as the raw material; (**b**) Pyrolysis of the inner core under oxygen-limited conditions; (**c**) Formation of dark-red char; (**d**) Quenching process; (**e**) Final *Litchi* biochar product. CK refers to biochar produced by burning branches to dark-red char and quenching with deionized water. T1 involves quenching with limewater instead. T2 and T3 include pre-immersion in deionized water, followed by burning and quenching with deionized water (T2) or limewater (T3). T4 and T5 involve pre-immersion in limewater, followed by burning and quenching with deionized water (T4) or limewater (T5)

to other exposure times) (Xiao et al. 2023), the char was quenched with deionized water or limewater to form biochar.

2.4 Aerobic carbonization via water-fire coupled process

The *Litchi* biochar was prepared at the Ecological Experiment Station (23°09′09″ N, 112°41′52″ E) of the Guangdong Provincial Key Laboratory of Eco-environmental Studies and Low-carbon Agriculture in Peri-urban Areas. The carbonization process is shown in Fig. 1. *Litchi* branches were randomly stacked, and liquefied natural gas was used to ignite the branches evenly around the perimeter of the pile, allowing them to burn openly in air to ensure consistent combustion. Once the branches developed a dark-red char, they were quickly transferred into sample containers containing 280 cm^3 of deionized water or limewater for quenching. This quenching process was completed within 0 to 30 s to form biochar (Xiao et al. 2023). Prior to quenching, the carbonization temperature at different locations within the same batch of biochar (with four replicate measurements) was measured using a non-contact infrared thermometer (DT-8833, Shanghai, China), with a working range of −50 to 800 °C and a resolution of 0.1 °C. The temperature was maintained at 597.8 ± 14.9 °C. Afterward, all biochar samples were dried at 85 °C for 12 h, then weighed, ground, and passed through a 100-mesh sieve for subsequent analysis.

2.5 Sample collection and analysis

The biochar samples were mixed with CO_2-free deionized water at a 1:10 ratio ($w\ v^{-1}$) and shaken at 160 $r\ min^{-1}$ for 30 min, and then analyzed for pH using a pH meter (Five Easy Plus, METTLER TOLEDO, Shanghai, China). Ash content was determined by the loss-on-ignition method, heating samples at 800 °C for 4 h in a muffle furnace (SX-G18123, Tianjin, China). Total C, H, and N were measured using an elemental analyzer (Vario Micro cube, Elementar, Germany). The –COOH and phenolic–OH contents were determined using the acid-base titration method from the International Humic Substances Society (IHSS 2025). Surface area was measured with an automated surface area and pore size analyzer (Autosorb-iQ, Quantachrome Boynton Beach, FL, USA). Functional groups were qualitatively analyzed using Fourier-transform infrared spectroscopy (FTIR) spectroscopy (Thermo Fisher Nicolet iS5, Waltham, MA, USA) within the spectral range of 500–4000 cm^{-1} at a resolution of 2.0 cm^{-1} (Gao et al. 2023). High-resolution scanning electron microscopy (SEM, Hitachi S-4800, Japan) combined with energy-dispersive X-ray spectroscopy (EDS, HORIBA EX-350, Japan) was used to assess the surface microstructure and elemental composition (Shi et al. 2023).

2.6 Data processing

The carbon conversion rate (CCR), an essential metric that quantifies the proportion of carbon retained in biochar relative to the carbon in the *Litchi* branches feedstock. The CCR was calculated using the following formula:

$$CCR = m_1 \times C_1 / m \times C_0 \tag{1}$$

where, m is the mass of the biowaste of *Litchi* (g) after undergoing pretreatment. m_1 is the mass of *Litchi* biochar (g). C_0 is the C contents of *Litchi* feedstock (%), while C_1 is the C contents of *Litchi* biochar (%).

Statistical analysis was performed using IBM SPSS Statistics 21. One-way ANOVA (Duncan's test, $p < 0.05$) evaluated significant differences in carbon conversion rate, elemental contents, ash content, pH, specific surface area, and oxygen functional groups (–COOH, phenolic–OH) of *Litchi* biochar among the treatments. Pearson correlation analysis identified relationships among these variables ($p < 0.05$, $p < 0.01$). The findings were visually represented using Origin 2024.

3 Results

3.1 Limewater immersion and coating boosts carbon retention of *Litchi* biochar

Biochar produced without immersion or coating (CK) exhibited the lowest carbon content at 70%, whereas biochar treated with both limewater immersion and coating (T5) achieved the highest carbon content, reaching approximately 81.73% (Fig. 2), with the difference being statistically significant ($p < 0.05$). Biochar subjected to limewater immersion alone (T4) showed a significant increase in carbon content by 3.24% and 7.28% compared to biochar immersed in deionized water (T2) and the untreated control (CK), respectively. These findings highlight the effectiveness of limewater immersion in enhancing carbon retention during carbonization. Coating without immersion (T1) increased the carbon content by 6.23% compared to CK, though the difference was not statistically significant. In contrast, biochar derived from *Litchi* feedstock with coating and soaked in deionized water (T3) exhibited a significant 10.15% increase in carbon content compared to CK, and a 6.62% increase compared to T2. When limewater immersion was combined with coating (T5), the carbon content significantly increased from 69.58% to 81.73% compared to CK, and from 76.85% to 81.73% compared to T4, highlighting the synergistic effect of both treatments (Fig. 2). Biochar with coating exhibited higher H content than those without, regardless of immersion. The lowest H content was found in CK, while the highest (3.92%) occurred in biochar treated with both limewater immersion and coating (T5),

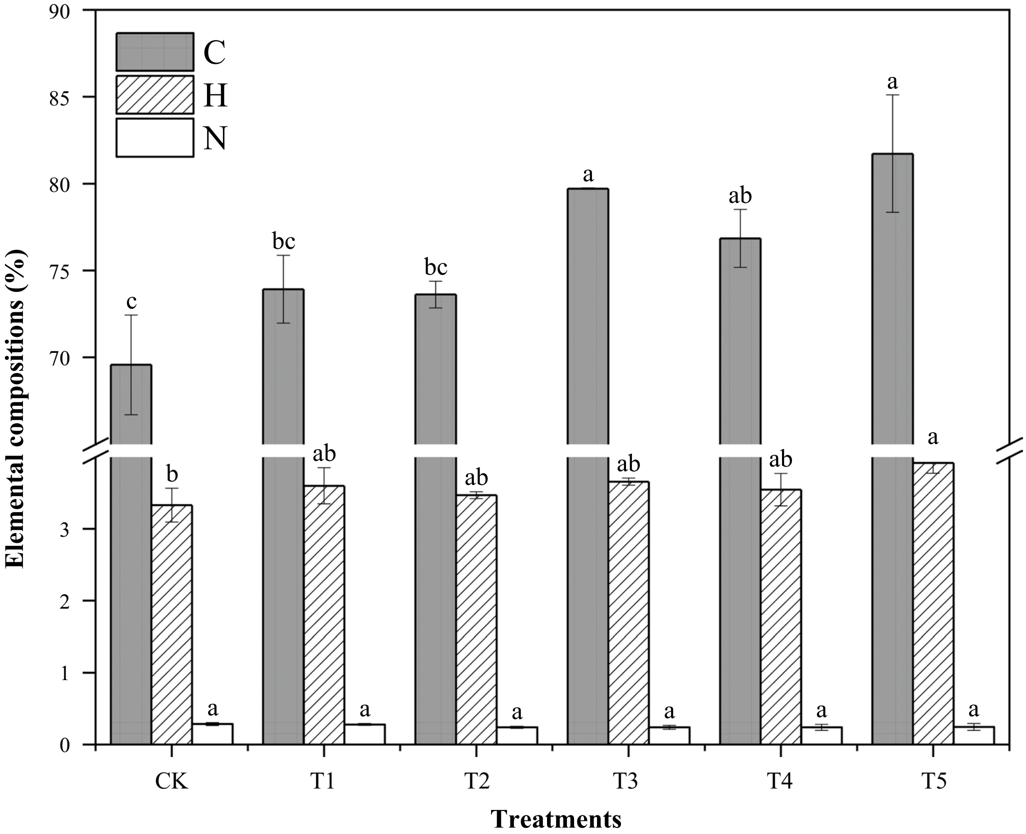


Fig. 2 Elemental compositions (C, H, N) of *Litchi* biochar under different treatments. The lowercase letters (a–c) indicate significant differences among the different treatments for the same parameter, while the treatments sharing the same letter indicate non-significant difference ($p < 0.05$, Duncan's test)

increasing from 3.31%. No significant differences were observed in nitrogen (N) contents among the treatments (Fig. 2).

The carbon conversion rate (CCR) of biochar progressively increased with immersion and coating treatments (Fig. 3). Biochar with coating showed significantly higher CCR compared to those without coating. Specifically, biochar immersed in deionized water without coating (T2) and with coating (T3) exhibited CCR increases of 18.69% and 17.88%, respectively, compared to the untreated control (CK). Furthermore, limewater-immersed biochar, both without coating (T4) and with coating (T5), demonstrated significantly higher CCR compared to their deionized water-immersed counterparts. Limewater immersion increased CCR by 5.48% (T4 vs. T2) and 8.12% (T5 vs. T3) ($p < 0.05$), highlighting the synergistic effect of limewater immersion and coating in enhancing carbon conversion efficiency.

3.2 Effects of limewater immersion and coating on ash content and surface area of *Litchi* biochar

A decreasing trend in ash content was observed from CK to T5 (Fig. 4a), with reductions of 1.08%, 2.93%, 1.33%, 4.01%, and 5.46%, respectively, compared to the control. Conversely, the specific surface area increased progressively in the same order of treatments (Fig. 4b), with values of 34.69, 45.57, 200.42, 215.02, and 254.35 m^2 g^{-1} for CK, T1, T2, T3, T4, and T5, respectively. Substantial increases were observed in T3, T4, and T5. These results indicate that limewater immersion and mineral coating effectively mitigate the adverse effects of O_2 during carbonization by reducing oxidation and preventing the combustion of carbon into ash.

3.3 Effect of limewater immersion and coating on the pH and functional groups of *Litchi* biochar

The pH of the biochar samples ranged from 7.98 to 8.53, indicating their alkaline nature (Table 2). The highest pH (8.53) was observed in biochar treated with both limewater immersion and coating (T5), significantly higher than all other treatments. Limewater immersion alone

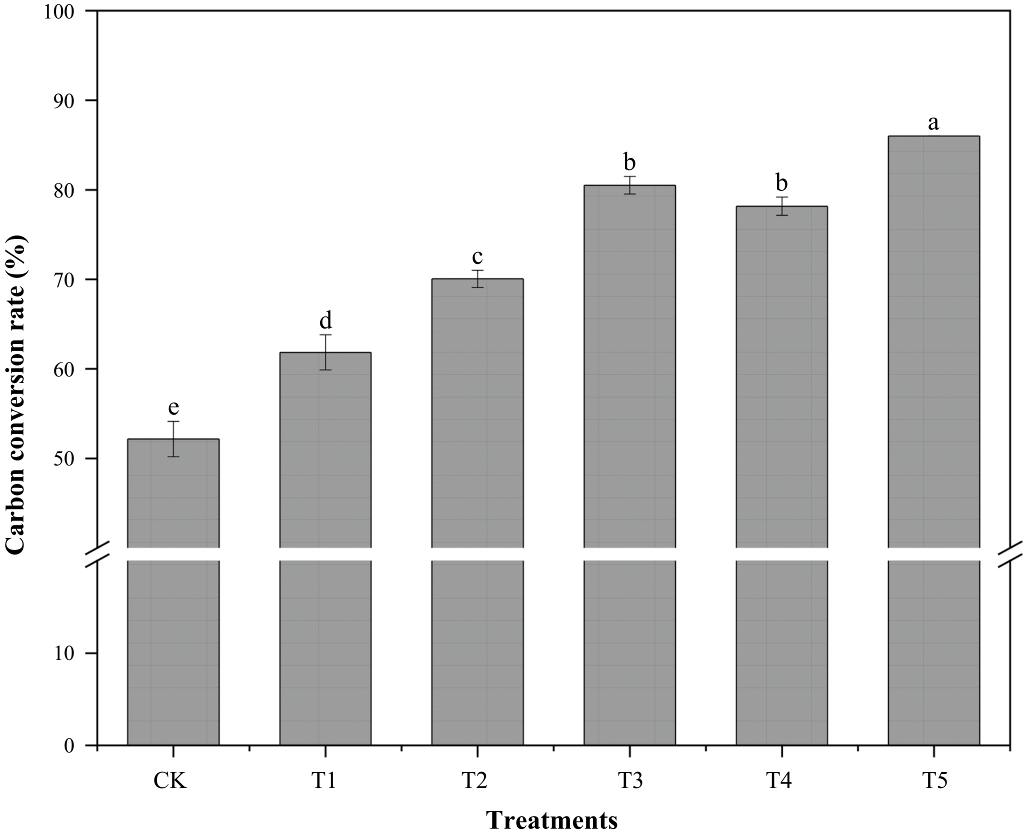


Fig. 3 The effects of immersion and coating with or without saturated limewater on the carbon conversion rate of *Litchi* biochar. The lowercase letters (a–e) indicate significant differences between different treatments for the same parameter, while the same letter indicates no significant difference ($p < 0.05$, Duncan's test)

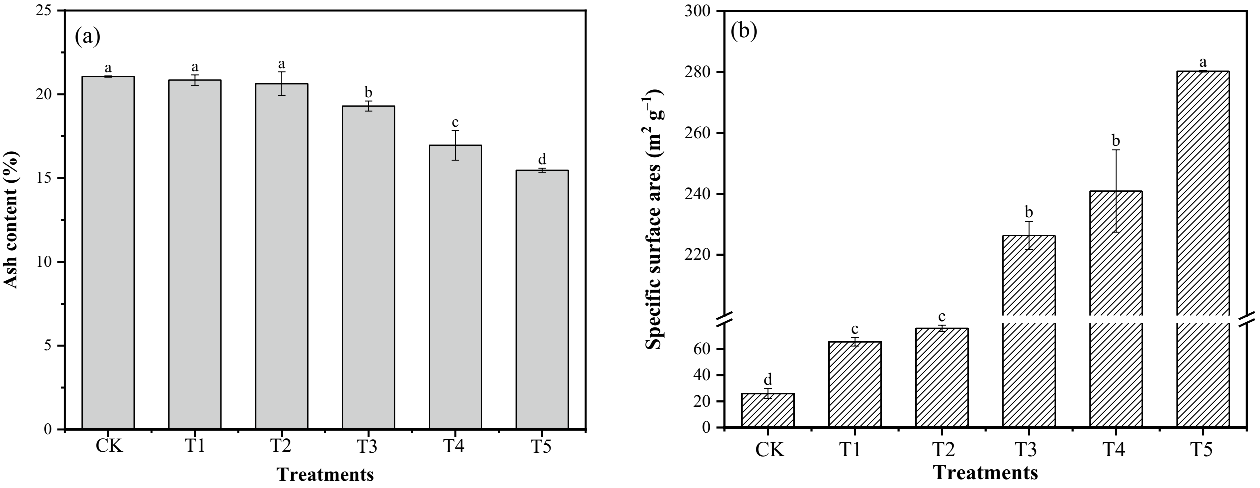


Fig. 4 Ash content (**a**) and specific surface area (**b**) as affected by with or without saturated limewater immersion and coating. The lowercase letters (a–d) indicate significant differences between different treatments for the same parameter, while the same letter indicates no significant difference ($p < 0.05$, Duncan's test)

Table 2 pH and pyrolysis as affected by with or without limewater immersion and coating

Index	Treatment					
	CK	T1	T2	T3	T4	T5
pH	7.98 ± 0.04 e	8.22 ± 0.03 c	8.14 ± 0.01 d	8.34 ± 0.02 b	8.23 ± 0.01 c	8.53 ± 0.04 a
Pyrolysis temperature (℃)	568.9 ± 27.8 a	569.4 ± 15.9 a	583.3 ± 22.7 a	611.6 ± 19.1 a	573.8 ± 22.5 a	603.5 ± 13.7 a

* Average value ± standard deviation. The lowercase letters (a–e) indicate significant differences between different experimental treatments for the same parameter, while the same letter demonstrates no significant difference ($p < 0.05$, Duncan's test)

(T4) increased the pH by 0.17 compared to the untreated control (CK), while deionized water immersion (T2) increased pH by 0.25. Coating further enhanced the alkalinity of the biochar regardless of the immersion method. For example, biochar treated with coating but no immersion (T1) showed a 0.25 pH increase relative to CK, and biochar treated with deionized water immersion and coating (T3) exhibited a 0.20 increase compared to T2. Notably, T5 demonstrated a higher pH (8.53) than T4 (8.23), highlighting the combined effect of limewater's inherent alkalinity and coating treatment in enhancing the pH of biochar.

The contents of –COOH and phenolic–OH in biochar increased across all treatments compared to the untreated control (CK) (Fig. 5). The highest levels of phenolic–OH (0.26 mol kg^{-1}) and –COOH (0.60 mol kg^{-1}) were observed in biochar treated with both limewater immersion and coating (T5), while the lowest levels were found in the control (CK). Immersion, whether in deionized water or limewater, increased the –COOH and phenolic–OH content, with limewater immersion showing higher levels compared to deionized water. Coating further enhanced these functional groups, particularly when combined with limewater immersion. These findings demonstrate that immersion and coating, especially when combined, effectively enhance the –COOH and phenolic–OH content in biochar.

3.4 FTIR, SEM–EDS, and correlation analysis reveal calcium-induced enhancement of biochar properties

FTIR analysis (Fig. 6) revealed the presence of key oxygen-containing functional groups such as –COOH and phenolic–OH in all treatments. Compared with the untreated control (CK), limewater immersion and coating treatments (T3–T5) showed stronger peaks in the range of 1514–1533 cm^{-1}, associated with C=C and C=O bonds, as well as red-shifts in the –COOH band, indicating potential interactions with Ca^{2+}. The –COOH peak shifted from 1674–1695 cm^{-1} in CK to 1686 cm^{-1} in T3 and T5. In addition, the COO– peak diminished in Ca-treated samples, suggesting complexation with calcium ions.

SEM images (Fig. 7a, c, e, g, i, and k) showed that biochar from T1, T3, and T5 exhibited smoother, more

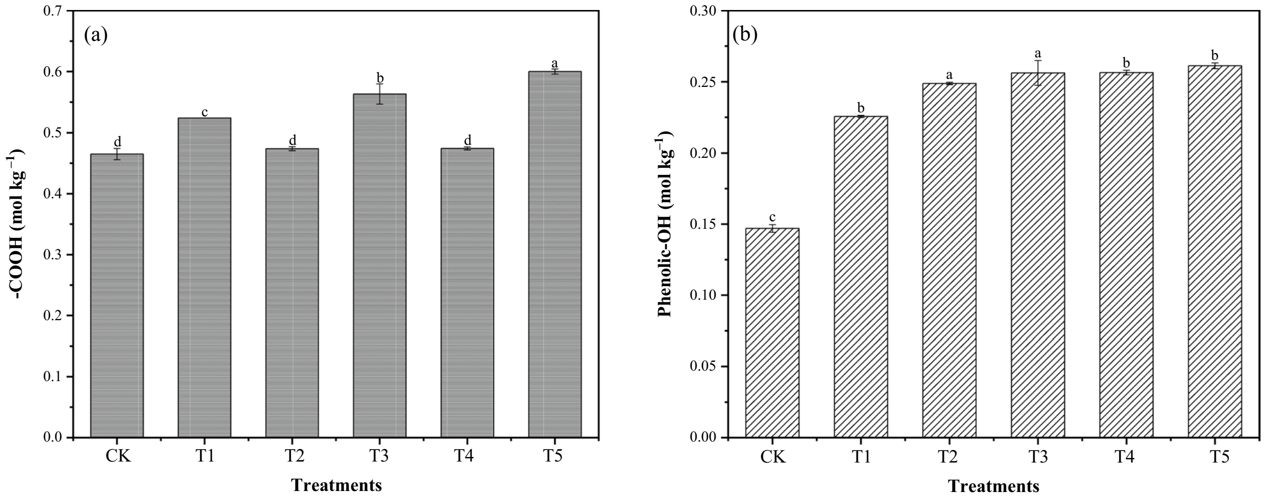


Fig. 5 Functional groups in biochar as affected by with or without saturated limewater immersion and coating. The lowercase letters (a–d) indicate significant differences between different treatments for the same parameter, while the same letter indicates no significant difference ($p < 0.05$, Duncan's test)

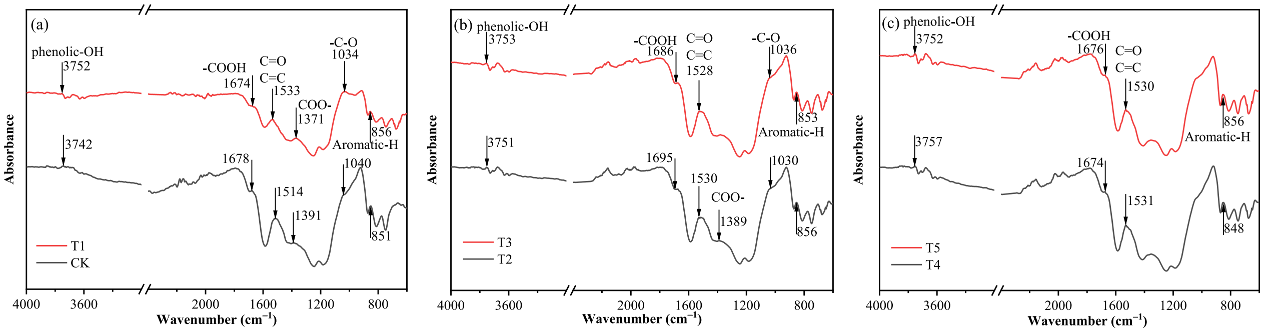


Fig. 6 Fourier-transform infrared spectroscopy (FTIR) spectra in biochar as affected by with or without saturated limewater immersion and mineral coating (**a**: CK and T1; **b**: T2 and T3; **c**: T4 and T5)

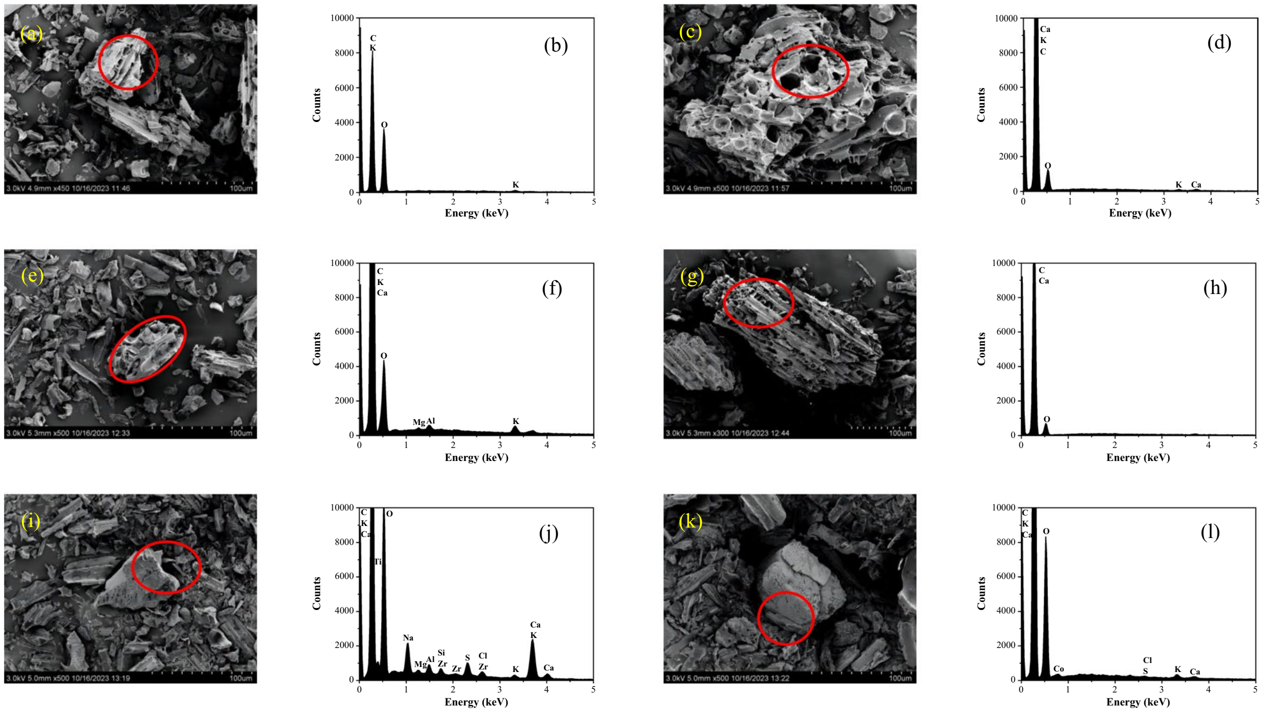


Fig. 7 Scanning electron microscopy (SEM) images and energy-dispersive spectroscopy (EDS) spectra of biochars from different immersion and coating treatments. SEM and EDS of CK (**a**–**b**); T1 (**c**–**d**); T2 (**e**–**f**); T3 (**g**–**h**); T4 (**i**–**j**); T5 (**k**–**l**)

compact surface morphologies compared to CK, T2, and T4, which displayed rough, porous, and ash-covered surfaces. EDS analysis (Fig. 7b, d, f, h, j, and l) confirmed the presence of C and O in all samples, while Ca was specifically detected in T1, T3–T5, supporting the incorporation of calcium via limewater immersion or coating. A trace Ca signal in T2 (deionized water only) may reflect minor background levels in the biomass or contamination during open-field carbonization.

CCR was positively correlated with pH, functional groups, and specific surface area, but negatively correlated with ash content (Fig. 8). Limewater immersion created oxygen-limited conditions during carbonization, reducing the impact of O_2 and promoting the formation of oxygen-containing functional groups. Without limewater or coating, biochar exposed to air lost functional groups, resulting in reduced specific surface area and CCR, along with increased ash content. Thus, limewater immersion and coating significantly enhance biochar quality and carbon sequestration.

4 Discussion

4.1 Limewater immersion and coating enhanced the functions of *Litchi* biochar

In this study, biochar produced without immersion or coating (CK) and biochar treated with deionized water immersion alone (T2) lacked a protective Ca^{2+} barrier, resulting in exposure to air during carbonization. This exposure caused significant losses of functional groups (Fig. 5), lower CCR (Fig. 3), reduced specific surface area (Fig. 4b), and increased ash content (Fig. 4a), highlighting the detrimental impact of air exposure during carbonization on biochar quality. In contrast, limewater immersion (T4) and deionized water immersion combined with coating (T3) effectively mitigated these effects by reducing losses of carbon (C), hydrogen (H), nitrogen (N) (Fig. 2), and functional groups, while improving CCR and specific surface area. Notably, limewater immersion with coating (T5) produced biochar with the highest CCR (Fig. 3), specific surface area (Fig. 4b), and functional group content (Fig. 5), indicating superior structural integrity and carbon retention.

These findings are consistent with previous reports demonstrating the benefits of oxygen-limited conditions and Ca^{2+} involvement during pyrolysis. Shanmugam et al. (2022) and Weber and Quicker (2018) reported that restricting oxygen exposure during biomass carbonization significantly enhances carbon retention and biochar quality. Nan et al. (2021) highlighted the catalytic role of Ca^{2+} in stabilizing C=O bonds and suppressing CO_x emissions, which aligns with our observation of improved functional group preservation and higher CCR in lime-treated samples. Conversely, Dai et al. (2021) found limited improvement when Ca was introduced after carbonization, underscoring the importance of Ca integration during the thermal decomposition process. Furthermore, our findings support the conceptual model proposed by Xiao et al. (2023), which describes limewater-treated branches as functioning like miniature oxygen-limited reactors during carbonization.

The enhanced performance of lime-treated samples, particularly T5, can be attributed to a combination of physical and chemical mechanisms. The carbonization of *Litchi* branches using limewater immersion and coating proceeds through four stages: (1) immersion of branches in limewater to form a protective mineral coating; (2) aerobic combustion of outer layers; (3) oxygen-limited pyrolysis of the inner core; and (4) final quenching with limewater to terminate combustion and promote char formation. The lime-derived $CaCO_3$ coating acts as a physical oxygen barrier, analogous to the walls of a closed reactor, thereby limiting oxygen infiltration and reducing oxidative degradation. This mechanism facilitates the conversion of biomass into stable biochar and suppresses ash formation and CO_x emissions (Shanmugam et al. 2022).

Simultaneously, Ca^{2+} ions infiltrated into the biomass during immersion play a catalytic role in stabilizing organic structures. These cations promote intra- and inter-molecular complexation, particularly with C=O and –COOH functional groups, and enhance aromatic condensation (Nan et al. 2020; Yang et al. 2018). This not only protects labile functional groups during pyrolysis but also promotes the development of a more ordered carbon matrix with higher thermal stability. Furthermore, the post-combustion coating step reinforces the oxygen-limited environment during quenching, minimizing structural disruption. Together, these effects demonstrate a synergistic enhancement of biochar properties through limewater immersion and coating.

4.2 Limewater immersion and coating exert positive impacts on properties of biochar

FTIR and SEM–EDS analyses (Figs. 6, 7) demonstrated that limewater and coating-treated biochar samples, particularly T5, exhibited stronger signals of –COOH and phenolic–OH groups, more consolidated carbon matrices, and clear incorporation of Ca^{2+} in T1, T3, and T5. These structural and chemical features were accompanied by higher CCR and lower ash content. Together, these results indicate that limewater immersion and coating enhance biochar quality by promoting both chemical stabilization and physical protection during pyrolysis.

The beneficial effects of limewater immersion and coating observed in this study are consistent with previous research demonstrating the role of Ca^{2+} in enhancing biochar properties. Keiluweit et al. (2010) and Dai et al. (2021) reported that Ca^{2+}-mediated cation bridging can reduce bond cleavage energy, while Jiang et al. (2019) linked greater retention of phenolic–OH groups to improved carbon yields. In addition, Nan et al. (2021) found that the incorporation of Ca during carbonization suppressed CO_x formation, and Weber and Quicker (2018) demonstrated that mineral coatings could effectively reduce ash accumulation and increase porosity. These findings align well with the improved chemical structure and surface characteristics observed in the T5 treatment.

The underlying mechanisms responsible for these enhancements likely involve a synergistic effect between physical oxygen shielding and chemical stabilization. Specifically, the $CaCO_3$ coating formed during limewater immersion acts as an external barrier, limiting oxygen diffusion during pyrolysis and thereby minimizing oxidative degradation. Meanwhile, Ca^{2+} ions infiltrate the biomass matrix, promoting intra-/inter-molecular complexation

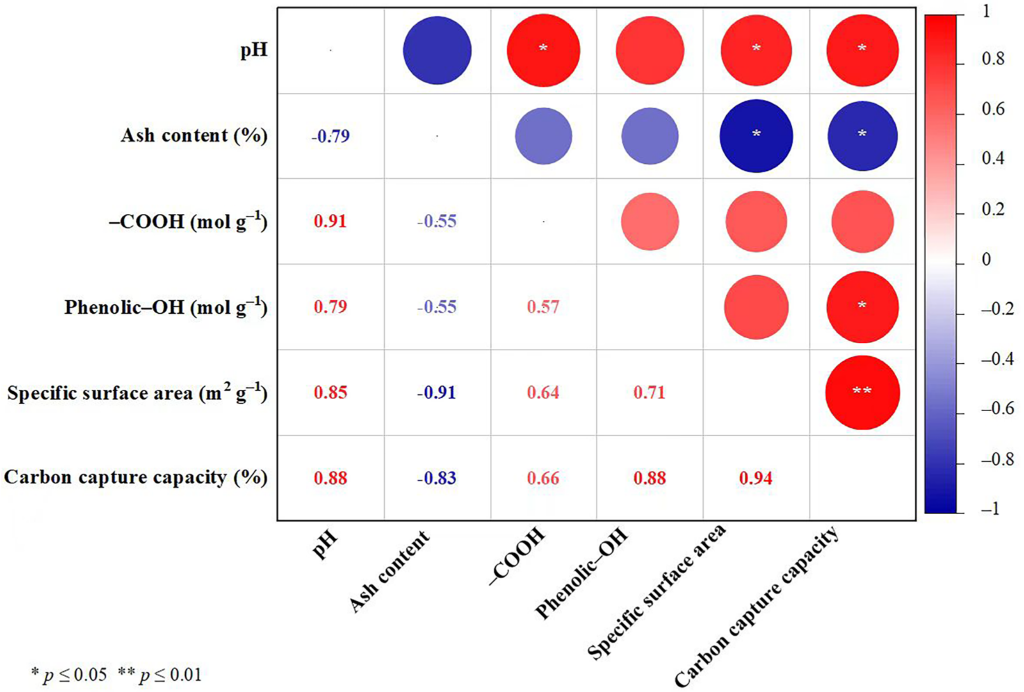


Fig. 8 Correlations between properties of *Litchi* biochars from different immersion and coating treatments. * significant at 0.05 level. ** significant at 0.01 level

with carboxyl and phenolic groups, enhancing hydrogen bonding, and facilitating π–π stacking among aromatics. These processes contribute to greater carbon retention, higher specific surface area, and improved structural stability of the resulting biochar (Guo et al. 2023; Iamsaard et al. 2022; Nan et al. 2020).

4.3 Enhancing biochar carbon conversion rates through innovative technologies

In this study, the integration of the water-fire method with limewater immersion and surface coating consistently produced biochar with a carbon content exceeding 60%. This treatment also led to notable improvements in CCR, specific surface area, and the retention of oxygen-containing functional groups, indicating the effectiveness of the method in enhancing both carbon yield and biochar quality under open combustion conditions. The process's minimal equipment requirements and ease of operation highlight its potential for broader adoption in low-cost biochar production. The enhanced CCR and carbon quality can be attributed to the synergistic effects of Ca^{2+} incorporation through limewater immersion and the protective function of the external coating (Li et al. 2018). During pyrolysis, Ca^{2+} ions promote the stabilization of surface functional groups and support the formation of more condensed carbon structures, while the coating serves to restrict oxygen ingress, thereby reducing oxidative degradation and ash formation. Together, these mechanisms contribute to a more efficient carbonization process and improved biochar characteristics.

4.4 The potential of achieving carbon neutrality in *Litchi* orchards through local production for local use

Based on the estimates from this study, converting pruned *Litchi* biomass into biochar using limewater immersion and mineral coating can sequester approximately 6000 kg of carbon per hectare, equivalent to around 22,000 kg CO_2-equivalent (CO_{2eq}), even after accounting for emissions generated during the carbonization process. This finding is particularly relevant in the context of large-scale *Litchi* cultivation. In China, *Litchi* orchards cover approximately 526,073 hectares (Cloud Fruit Network 2025), with an average yield of 13,500 kg of fruit and an estimated 22,500 kg of dry biomass waste produced per hectare annually (Hou et al. 2020). The life cycle carbon emissions of *Litchi* under cold chain logistics are estimated at 0.699 kg CO_{2eq} per kilogram of fruit, with 31.62% (0.221 kg CO_{2eq}) attributed to the cultivation stage (Ma 2022). This corresponds to approximately 3000 kg CO_{2eq} emissions from cultivation and about 9000 kg CO_{2eq} in total life cycle emissions per hectare. By adopting a local production–local utilization model, in which orchard waste is converted into biochar and directly returned to the soil, this approach not only avoids carbon emissions associated with open burning or decomposition but also promotes circular resource use and low-emission orchard management. Therefore, this method holds strong potential for offsetting the carbon footprint of *Litchi* cultivation and achieving carbon neutrality at the orchard scale.

5 Conclusions

The carbonization of *Litchi* branches, incorporating limewater immersion, coating, and quenching, was conducted through pyrolysis under oxygen-limited conditions, which were maintained by the protective coating. This process significantly improved the carbon conversion rate (CCR) of *Litchi* biochar, achieving up to 86%. The limewater coating physically retained carbon, preventing its oxidation to CO_x during combustion. Furthermore, calcium from the limewater was deposited onto or within the biochar during pyrolysis, optimizing the carbon structure and forming a mineral-carbon composite that enhanced carbon sequestration. Considering that the full life cycle carbon emissions for *Litchi* cultivation under cold chain logistics total approximately 9000 kg CO_{2eq} per hectare, this method can sequester an estimated 22,000 kg CO_{2eq} per hectare (equivalent to 6000 kg of carbon) when applied to *Litchi* orchards. While this sequestration contributes significantly to offsetting the carbon footprint of *Litchi* cultivation, it represents long-term carbon storage potential and supports efforts toward carbon neutrality, rather than immediate offsetting of the entire life cycle emissions.

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Author contributions

Conceptualization, Data curation, Formal analysis, Investigation, Methodology, and Writing—original draft: Liang Xiao & Wenhan Li; Formal analysis, Investigation, and Methodology: Jinghua Wu; Investigation and Methodology: Yueshi Li; Conceptualization, Validation, Writing—review and editing: Guodong Yuan; Investigation and Methodology: Yingya Wang & Qing Xu & Lirong Feng; Review and editing: Xiangying Hao & Fengxiang X. Han. The author(s) read and approved the final manuscript.

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Data availability

The data that support the fndings of this study are available from the corresponding author upon request.

Declarations

Ethics approval and consent to participate

This article does not contain any studies with human participants or animals performed by any of the authors. The manuscript is approved by all authors for publication. The authors declare that the work described is original research that has not been published previously, and not under consideration for publication elsewhere.

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

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