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Biochar-loaded nano zero-valent iron from agricultural waste enhances copper immobilization during composting: Implications for safe soil amendment and crop production

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A R T I C L E I N F O

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A B S T R A C T

This study presents a novel approach for the valorization of agricultural waste by converting waste tea residues into a functional composite, biochar-loaded nano zero-valent iron (nZVI@BC), and applying it to produce a value-added and safe organic fertilizer via swine manure composting. The addition of nZVI@BC, particularly at 50 g/kg (T5), dramatically enhanced the immobilization of copper (Cu), reducing its bioavailable fraction by 43.14 % and effectively transforming it into stable forms. We identified that the release and consumption of available phosphorus (AP), mediated by the compost microbial community (e.g., Clostridia), was the dominant mechanism (89.3 % explanation), leading to the precipitation of stable copper-phosphate minerals. The resulting compost product not only exhibited significantly reduced environmental risks but also possessed optimal physicochemical properties (e.g., CEC, pH, EC) for agricultural application. This work demonstrates a sustainable strategy for the synergistic valorization of multiple agricultural wastes—tea residue and swine manure—into a high-value, safe soil amendment, contributing to the circular bio-economy in the agro-industrial sector.

1. Introduction

The sustainable management of livestock and agricultural waste is a critical challenge for the circular economy in the agro-industrial sector. In China, the livestock farming industry discharges billions of tons of manure annually, placing a heavy burden on the environment (Lu et al., 2014; Wang et al., 2016). Composting is a widely adopted biochemical process for converting these nutrient-rich wastes into stable organic amendments, facilitating resource recycling and organic waste treatment (Jeong et al., 2017). However, the land application of compost, particularly from swine manure (SM), is often limited due to the presence of heavy metals (HMs) such as copper (Cu).

Copper-containing additives (e.g., copper sulfate) are commonly used in livestock feeds to promote growth and prevent disease (Chen et al., 2019; Cui et al., 2021). It is worth noting that only a small proportion of HMs is absorbed by livestock, and most are excreted with manure (Li et al., 2015; Wei et al., 2018). The environmental risk and phytotoxicity of Cu depend more on its bioavailability and mobility than on its total concentration (Chen et al., 2022; Liang et al., 2017; Lu et al., 2018). Therefore, strategies to reduce the bioavailability of HMs during composting are essential to produce safe, marketable organic fertilizers for agricultural use.

The composting process is accompanied by the speciation transformation of HMs, where the bioavailable fractions (exchangeable and reducible) are converted into stable forms (oxidizable and residual), thereby reducing their toxicity (Guo et al., 2019; Jindo et al., 2016). This transformation can be attributed to chelation with organic matter, precipitation of metal phosphates, or adsorption by microorganisms (Chen et al., 2020). The precipitation pathway is highly dependent on the availability of phosphorus (AP) and is a well-documented

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passivation mechanism (Zheng et al., 2020; Wei et al., 2016). However, current strategies often focus on the external addition of phosphate materials, while the mobilization of the inherent and abundant phosphorus pool within the compost itself to achieve metal immobilization remains a less explored yet promising approach. The addition of passivators is considered a reliable method to enhance this process (Ren et al., 2018; Zheng et al., 2020). For instance, biochar (BC) amendment has been reported to reduce the bioavailability of Cu and other HMs in SM compost (Cui et al., 2020), while zero-valent iron (ZVI) can effectively promote the speciation transformation of Zn and Cu (Li et al., 2023). These findings highlight the potential of using cost-effective and functional amendments to improve compost quality and safety.

Recently, composites such as biochar-loaded nano zero-valent iron (nZVI@BC) have garnered attention for environmental remediation, leveraging the synergistic effects of both components (Dong et al., 2017; Wang et al., 2019; Xu et al., 2016). The biochar matrix enhances the dispersion and reactivity of nZVI while preventing oxidation, making it a promising material for HM immobilization. For example, nZVI@BC has shown excellent performance in stabilizing As and Cr in contaminated soils (Song et al., 2022; Su et al., 2016). However, its application as an additive during composting, particularly for Cu immobilization in SM composting, remains underexplored. Moreover, the potential of nZVI@BC derived from agricultural waste (e.g., tea residues) to produce value-added compost products for soil amendment has not been adequately addressed. Furthermore, a comprehensive understanding of the correlations and causal relationships between the microbial communities, key physicochemical factors (like AP), and the resulting Cu speciation transformation, which is critical for elucidating the underlying mechanisms, is still lacking.

To address this research gap, we hypothesize that the addition of nZVI@BC, synthesized from agricultural waste, will significantly promote the transformation of copper from bioavailable to stable fractions during swine manure composting by modulating the microbial-mediated release of inherent phosphorus and subsequent precipitation reactions, thereby producing a safer final product for land application. To test this hypothesis, the present study was designed with the following specific objectives: (1) To evaluate the influence of nZVI@BC amendment on key composting parameters (e.g., pH, AP, CEC) and the succession of the bacterial community throughout the process; (2) To monitor the speciation transformation of Cu and to characterize the changes in functional groups of the compost matrix using FTIR spectroscopy, aiming to identify potential immobilization mechanisms; (3) To elucidate the driving mechanisms behind Cu passivation by employing multivariate statistical analyses (e.g., RDA, VPA, and SEMs) to decipher the intricate relationships between bacterial communities, critical physicochemical factors (particularly available phosphorus), and Cu fractions.

We anticipate that this study will provide a mechanistic understanding of how nZVI@BC facilitates Cu immobilization. The findings are expected to offer a scientific basis for developing novel, value-added soil amendments from agricultural waste, contributing to sustainable organic waste management and safe crop production.

2. Materials and methods

2.1. Materials and chemicals

The raw materials used in the experiments were all agricultural by-products, with the aim of achieving resource recycling and reducing the agricultural environmental risks associated with composting. Swine manure (SM) was obtained from a local farm in Fuzhou City, Fujian Province, China, with a C:N ratio of 12.35. Natural wood chips were obtained from a local timber mill with a C:N ratio of 250.5. Waste tea leave, a common agricultural processing by-product, typically from pruning during the non-harvest season, were obtained from a tea plantation in Zhangzhou City, Fujian Province, China. The Cu standard solution was prepared according to the National Standard GB/T 23349–2009 of the People's Republic of China. All other reagents and chemicals used in the experiments were of analytical grade.

2.2. Synthesis of nZVI@BC

To prepare the BC, the SM was kept under an argon environment at a temperature of 600°C for 2 h. The synthesis of nZVI@BC was conducted by accurately weighing 30 g of waste tea leaves and adding 500 ml of distilled water and heating at 80°C for 1 h. After that, 1 g of biochar was added in an anaerobic environment with continuous stirring for 30 min, and a certain proportion of a 0.1 mol/L $FeSO_4 \cdot 7H_2O$ solution was added under nitrogen protection with stirring for 30 min. This was then washed three times with anhydrous ethanol and then vacuum dried at 60°C for 12 h. The detailed synthesis method and characterization information of nZVI@BC can be found in our previously published article (Yang et al., 2025).

2.3. Experiment design

After passing the SM through a 0.85 mm sieve, the C:N ratio was adjusted to 20 using wood chips, and the moisture content was adjusted to approximately 55 % using distilled water. The three experimental designs consisted of a blank test without the addition of nZVI@BC (T0), the addition of 20 g/kg of nZVI@BC (T2), and the addition of 50 g/kg of nZVI@BC (T5) (all addition rates of nZVI@BC were calculated based on the dry weight of the compost mixture. The determination of addition levels was primarily based on preliminary experimental validation, with reference to the study by Yang et al. 2025 regarding nZVI@BC dosage). The compost fermentation unit used for the experiment was a 2 L High-density polyethylene drum in a 55°C constant temperature incubator. Three blasts and three aerations were performed each day. The sampling times for the determination of the physicochemical properties and the continuous extraction of HMs were set at the 1st, 5th, 10th, 15th, and 20th days of composting, and the compost samples were obtained using the multi-point sampling method. The sampling time for the high-throughput sequencing was at 9:00 a.m. on the 1st, 10th, and 20th days after the blast aeration, and the samples were placed in a freezer at –80°C for storage.

2.4. Physicochemical property analysis

Fresh compost samples were added to sterilized ultrapure water at a ratio of 1:10 (w/v) and then shaken at 160 r/min for 2 h. The filtered suspension was used to determine the property (pH), oxidation–reduction potential (ORP), and electrical conductivity (EC). The amount of AP was found using the molybdenum antimony colorimetric method. The CEC was determined by weighing 3.5 g of a sample dried at 105°C for 24 h, and the method referred to the National Environmental Protection Standard of the People's Republic of China (HJ 889–2017). After weighing a certain amount of the sample dried at 105°C for 24 h, it was ground into a powder that weighed approximately 2.0 g, calcined in a muffle furnace at 550°C for 3 h, and the CEC was finally determined using the subtraction method of volatile solids (VS) (Koyama et al., 2020). Functional group changes were tested using FTIR (Thermo Fisher NICOLET IS10, USA) in the wavelength range of 4000–400 cm^{-1} at 1 and 20 d of composting.

2.5. Analysis of the Cu fractions

The CU speciation analysis was performed using a modified European Community Bureau of Reference (BCR) sequential extraction method, and the concentration was measured using an atomic absorption light spectrophotometer (WFX–130B, China). The extracted Cu was classified into four fractions that included exchangeable (Exc), reducible (Red), oxidizable (Oxi), and residual (Res), of which the Cu in the fraction of Exc and Red was the active fraction that can be easily utilized by organisms, while that in the fraction of Oxi and Res was the stable fraction that cannot be easily utilized by organisms.

2.6. DNA extraction and high-throughput sequencing

After sample collection, Genomic DNA was extracted from the collected samples using the E.Z.N.A.® Soil DNA Kit (Omega Bio tek, Norcross, GA, USA) following the manufacturer's instructions, and then subjected to high-throughput sequencing. Operational taxonomic unit (OTU) clustering was performed on the quality-controlled spliced sequences according to 97 % similarity, and chimeras were excluded.

2.7. Statistical analysis

Three replicate groups were used in all experiments. The values were presented as means, and the error lines were calculated for the standard deviations. Excel 2016 was used for the data statistics, and Origin 2021 was used for graphing. Venn, a principle component analysis (PCoA), and community bar charts were performed using R language (version 3.3.1). The VPA was conducted using R language (version 3.3.1) in the vegan package (version 2.4.3), the RDA analysis was conducted using Canoco Ver. 5.0, and the structural equation models were conducted using IBM SPSS Amos Ver. 26.

A structural equation model (SEM) was constructed to test the hypothesized causal relationships derived from the redundancy analysis (RDA) and variance partitioning analysis (VPA) results, as well as established mechanisms from literature. The model included the bacterial community, pH, available phosphorus (AP), and bioavailable Cu (sum of Exc-Cu and Red-Cu) as variables. The proposed paths (Bacteria→AP, AP→Bioavailable-Cu, etc.) were designed to test the specific hypothesis that the microbial community influences Cu speciation primarily through mediating AP release and subsequent precipitation, rather than through direct effects. The model was evaluated using maximum likelihood estimation, and its fit was assessed using standard indices (χ^2, RMSEA, CFI).

3. Results and discussion

3.1. Physicochemical characteristics of composting

The pH is one of the most critical physicochemical parameters in composting, as it influences microbial activity, enzyme function, and the speciation transformation of heavy metals. Generally, an increase in pH promotes the immobilization of cationic metals like Cu through mechanisms such as precipitation and adsorption (Abollino et al., 2003; Wei et al., 2018). The initial pH of the composting mixtures ranged from 7.73 to 7.84. As shown in Fig. 1(a), the pH values in all treatments increased throughout the 20-day process, with values in the nZVI@BC-amended groups (T2 and T5) being slightly lower than those in the control (T0). This observed increase in pH can be primarily attributed to two concomitant microbial processes: (i) the rapid microbial degradation of volatile organic acids produced during the initial acidic phase, and (ii) the extensive ammonification of nitrogenous organic compounds (e.g., proteins, amino acids), which releases ammonia (NH_3/NH_4^+) and consumes protons (H^+). The marginally lower pH in T2 and T5 could be related to the acidic nature of the nZVI@BC material itself or its influence on specific microbial metabolic pathways affecting acid production and consumption. Upon compost maturation, the pH stabilized within an optimal range (8.62–8.76) for agricultural application.

Concurrently, the available phosphorus (AP) content exhibited a decreasing trend across all treatments (Fig. 1(b)), with the most significant reduction observed in T5 (91.49 mg kg^{-1}). This decline in AP can be attributed to both microbial uptake for cellular growth and, more importantly, to precipitation reactions with metal cations (e.g., Al^{3+}, Fe^{3+}, Cu^{2+}) under the prevailing alkaline conditions (Wei et al., 2016). The greater decrease in AP in the nZVI@BC treatments, particularly T5, suggests enhanced precipitation, potentially forming stable metal-phosphorus complexes. This enhanced precipitation in nZVI@BC treatments can be mechanistically explained by the unique properties of

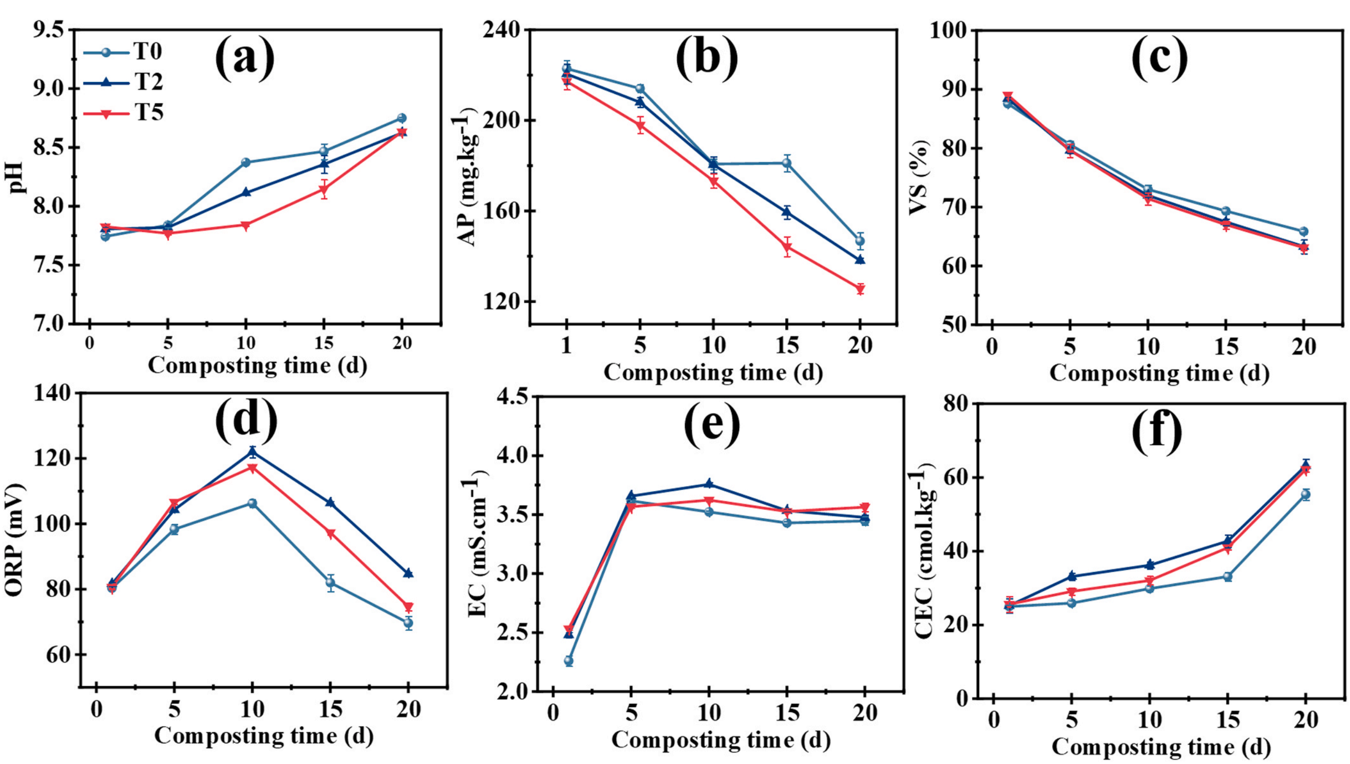

Fig. 1. ˆ#hemical parameters during composting. (a): pH; (b): available phosphorus (AP); (c): volatile solids (VS); (d): oxidation–reduction potential (ORP); (e): electrical conductivity (EC); and (f): the cation exchange capacity (CEC). Note: T0 (control); T2 (added 20 g/kg nZVI@BC); T5 (added 50 g/kg nZVI@BC).

the composite. Firstly, the nano zero-valent iron (nZVI) core undergoes gradual oxidation and corrosion during composting, releasing ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions (Wang et al., 2019). These ions can directly react with phosphate anions to form highly insoluble iron-phosphate precipitates (e.g., Vivianite, $Fe_3(PO_4)_2$), thereby consuming AP (Xu et al., 2016). Secondly, the released iron ions can act as additional nucleation sites or co-precipitants, facilitating the formation of copper-phosphate minerals (e.g., $Cu_3(PO_4)_2$) by coprecipitation (Xu et al., 2016). Thirdly, the biochar (BC) component, with its high surface area and porosity, likely adsorbed and concentrated metal cations (including Cu^{2+} and the released Fe ions) and phosphate anions on its surface, effectively increasing their local concentration and promoting precipitation reactions (Wang et al., 2019; Xu et al., 2016). This synergistic effect between the nZVI and BC components of the amendment provided more pathways and opportunities for AP to be immobilized through precipitation. This is a critical mechanism for Cu immobilization, as the formation of insoluble copper phosphate minerals (e.g., $Cu_3(PO_4)_2$) directly transfers Cu from bioavailable fractions to the stable residual fraction.

Volatile solids (VS) are considered the most straightforward judgment of compost maturity, and VS decomposition produces humus that can easily complex with HM ions that can convert HMs to a stable fraction (Robledo-Mahón et al., 2019; Wei et al., 2016). Fig. 1(c). During the entire composting process, VS was degraded continuously, and the highest VS degradation was 24.86 % in T5.

As shown in Fig. 1(d), The observed decrease in oxidation-reduction potential (ORP) during the maturation phase (days 10–20) is indicative of a shift towards micro-aerobic or anaerobic conditions within the compost matrix. This shift is likely driven by sustained microbial respiration consuming available oxygen faster than it can be replenished, a common phenomenon in the later stages of composting as porosity decreases (Capuani et al., 2013). Under these conditions, microbial communities increasingly utilize alternative electron acceptors (e.g., nitrate, Fe^{3+}), which drives the ORP down. The moderated ORP decrease in nZVI@BC treatments, particularly T2, may be attributed to the biochar component improving bulk porosity and oxygen diffusion, thereby mitigating severe anaerobiosis (Wei et al., 2018).

EC is a measure of the amount of soluble salts that can be extracted from the compost material, and crop growth will be affected when the EC value is greater than 4.0 $mS.cm^{-1}$ (Zhao et al., 2022; Zhou et al., 2018). Fig. 1(e) shows that all three experimental groups showed a rapid increase from days 1–5. All three groups showed more stable EC values after 5–20 days of composting when the EC values basically stabilized at 3.41–3.59 $mS.cm^{-1}$ without exceeding the EC limit of 4.0 $mS.cm^{-1}$.

CEC can reflect the maturity and nutrient retention capacity of compost, and it increases during the composting process. When the value reaches above 60.0 $cmol.kg^{-1}$, the compost can be considered mature (Gavilanes-Terán et al., 2016). As shown in Fig. 1(f), the CEC values of T2 and T5 increased more rapidly during composting than those of T0, and they reached 63.21 and 62.19 $cmol.kg^{-1}$ at 20 days of composting for T2 and T5, respectively.

3.2. FTIR spectroscopy

Fourier transform infrared (FTIR) spectroscopy was employed to track the changes in functional groups and identify potential mechanisms for Cu immobilization. The spectra for treatment T5 on day 1 and day 20 are presented in Fig. 2. The notable attenuation of peaks at 2930 cm^{-1} (C-H stretching of aliphatic groups), 1650 cm^{-1} (C═C stretching of aromatics), and 1040 cm^{-1} (C-O stretching of polysaccharides) indicates extensive degradation of organic matter by microorganisms during composting, which is consistent with the observed reduction in volatile solids (VS) (Li et al., 2020; Lv et al., 2013; Wang et al., 2017). Critically, the decreased intensity of the distinct peaks at approximately 870 cm^{-1} and 560 cm^{-1} , which are characteristic of P-O bending and O-P-O stretching vibrations within phosphate (PO_4^{3-}) groups, provides crucial spectroscopic evidence for the involvement of phosphorus in metal sequestration (Lonappan et al., 2018). This observation, coupled with the significant decrease in available phosphorus (AP) content measured in Section 3.1, strongly suggests the precipitation of metal-phosphate minerals under the alkaline conditions of the mature compost.

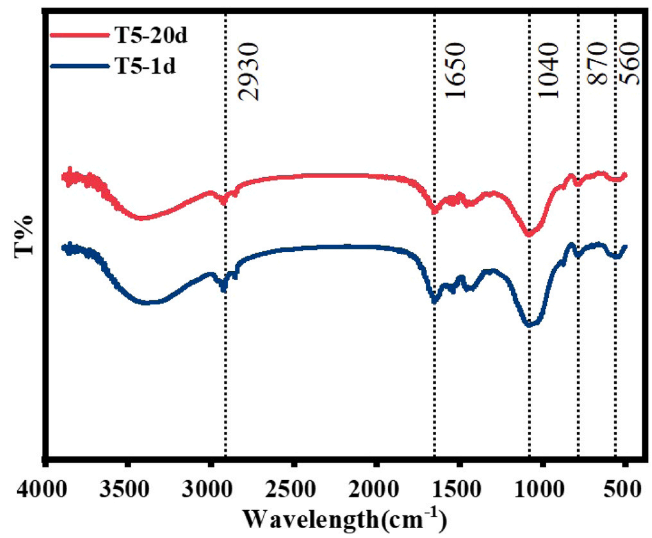

Fig. 2. Fourier transform infrared (FTIR) adsorption spectra derived from T5 on the day 1 and 20 compost samples.

We hypothesize that copper is immobilized through the formation of highly stable copper phosphate precipitates, such as $Cu_3(PO_4)_2$ (libethenite) or Cu-phosphate complexes. This mechanism is a well-documented pathway for heavy metal passivation in composting environments rich in phosphorus (Wei et al., 2016; Zheng et al., 2020). The precipitation reaction between released phosphate anions and Cu^{2+} ions effectively transfers copper from the bioavailable exchangeable and reducible fractions to the stable residual fraction, as confirmed by the sequential extraction results (Section 3.4). Therefore, the FTIR analysis not only reflects the humification process but also directly supports the proposed primary mechanism of Cu stabilization via phosphate precipitation facilitated by nZVI@BC addition.

3.3. Changes in the microbial community during composting

The Venn diagram of Fig. 3(a) shows that after 20 days of composting, the three experimental groups still shared a large number of operational taxonomic units (OTUs) that reached 94, and the number of individual OTUs for T0, T2, and T5 was only 15, 16, and 21, respectively. The addition of nZVI@BC exhibited more individual OTUs, but the difference was not obvious. This may have been because the three composts had the same initial feedstock and similar final microenvironments; thus, the community composition of the later composts tended to be the same.

The PCoA analysis shown in Fig. 3(b) indicates that the composting time was the key factor that changed the bacterial OTU variability. In addition, the addition of nZVI@BC during the late stage of composting, especially on day 20, was an important reason for the partial variability in the bacterial OTUs.

Fig. 3(C) presents the analysis of compost bacteria at the genus level. The results show that the abundance of typically anaerobic genera, such as *Clostridium*, *Terrisporobacter*, and *Caldicoprobacter*, was influenced by the addition of nZVI@BC. While the biochar component is known to improve overall porosity and oxygen diffusion, the complex heterogeneous nature of the compost matrix inevitably creates localized anaerobic micro-niches. Notably, the abundance of Clostridia (class level) increased during the thermophilic phase (day 10), reaching a maximum

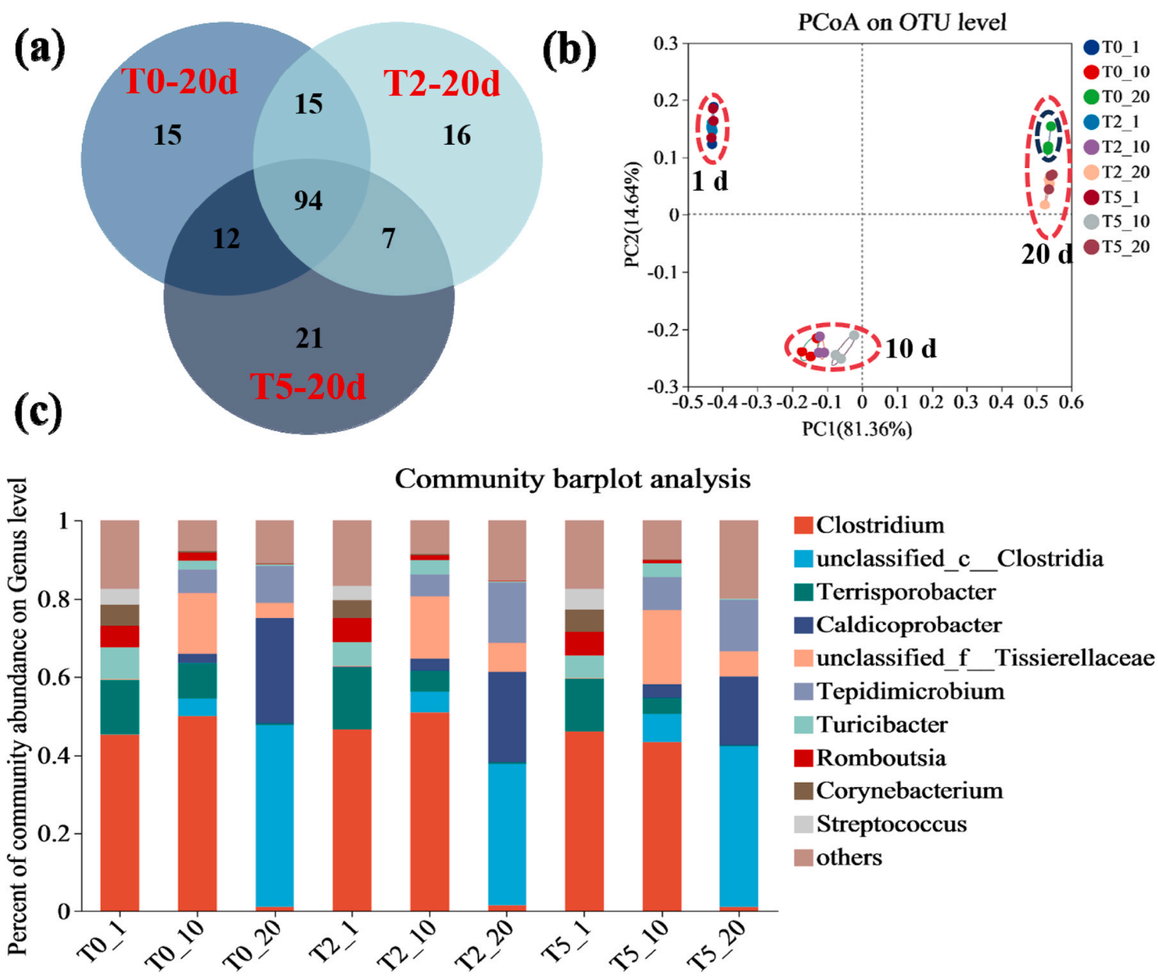

Fig. 3. Changes in the bacterial communities during composting. (a): Venn diagram analysis based on the OTUs during composting; (b): Principal coordinate analysis (PCoA) based on the OTUs during composting; (c): Percentage of redistribution of the microbial components during composting based on the genus level.

of 7.2 % in T5.

This observation is critical and can be explained by the unique physiology of certain Clostridia members. Many are known for their role in phosphorus metabolism. Under anaerobic conditions, they can solubilize inorganic phosphates to obtain energy, leading to the release of available phosphorus (AP) into the environment. Subsequently, under the prevailing aerobic conditions of the compost, these same organisms or others can excessively uptake phosphorus (Wei et al., 2016). This metabolic versatility makes them key players in phosphorus cycling. Therefore, the increased abundance of Clostridia in the nZVI@BC treatments, particularly T5, is not a contradiction but rather a functional indicator of enhanced microbial-mediated AP release. This process is essential for the subsequent precipitation of copper phosphate minerals, as supported by the decrease in AP content (Fig. 1b) and the FTIR analysis (Fig. 2). Similarly, the addition of nZVI@BC promoted the abundance of *Tissierellaceae* and *Tepidimicrobium* (peaking at 27.6 % in T5), which are associated with the degradation of complex polymers like cellulose and lignin, playing a critical role in humification and the formation of humic acids (HA) that can chelate Cu (Li et al., 2025).

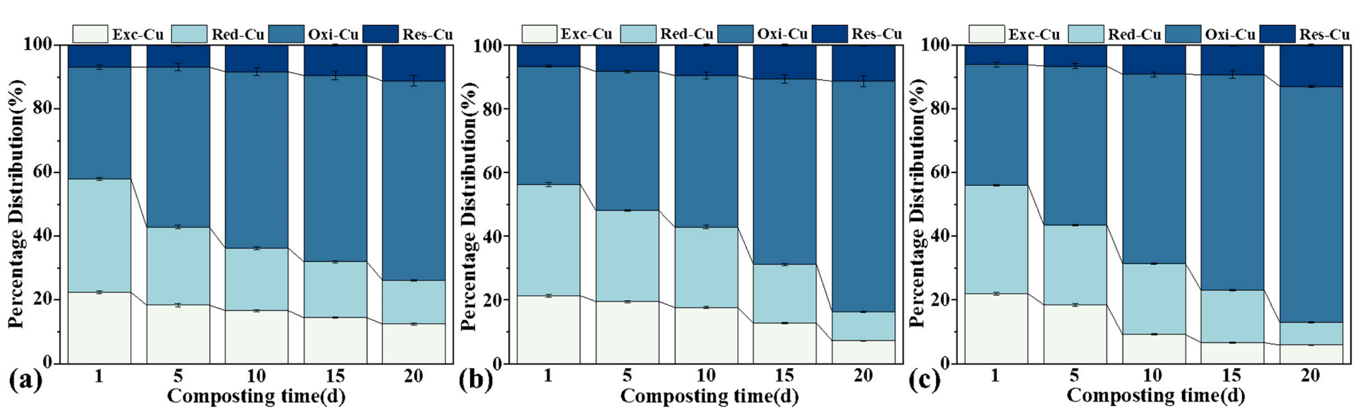

Fig. 4. Dynamic changes in the Cu fractions during the composting process. (a): T0; (b): T2; and (c): T5.

3.4. Cu distribution

The chemical fraction of HMs can intuitively reflect environmental hazards. According to the toxicity, mobility, and bioavailability of HMs found in this study, in terms of toxicity, mobility, and bioavailability, the Exc, Red, Oxi, and Res fractions showed decreasing activities and environmental hazards in that order. Fig. 4(a–c) shows that the Exc and Red fractions were transformed to the Oxi and Res fractions in all of the composting experimental groups throughout the composting process, indicating that Cu in all of the experimental groups was gradually transformed to the more stable fraction as the compost gradually matured. The addition of nZVI@BC significantly promoted the transformation of Cu from active to stable fractions, demonstrating a clear dose-dependent effect. After the 20-day composting period, the proportion of bioavailable Cu (Exc + Red) decreased from an initial value of 58.05–26.20 % in the control group (T0), representing a reduction of 31.85 %. The addition of nZVI@BC enhanced this immobilization process. In T2, the bioavailable fraction was corresponding to a decrease of 40.0 % ($p < 0.05$ vs. T0). Most notably, treatment T5 exhibited the most effective performance, with the bioavailable Cu fraction diminishing from 56.09 % to 12.95 %, which was significantly lower than both T0 and T2 ($p < 0.01$). This represents a total reduction of 43.14 % in the active pools of Cu, unequivocally confirming that a higher dosage of nZVI@BC leads to a more profound stabilization of Cu. The detailed concentration data for all Cu fractions, including three replicates, are provided in Table S1 (Supplementary Material).

3.5. Relationship between the Cu fractions and the physicochemical parameters

To investigate how the compost physicochemical properties affect the transformation of Cu speciation during composting, we analyzed the correlations between the four Cu fractions and the physicochemical properties, as well as the degree of explanation and contribution between the correlations, using an RDA. As demonstrated in Fig. 5 and Table 1, the primary controlling factor for the transformation of Cu speciation was AP, with a high degree of explanation of 89.3 %. AP was followed by VS (2.2 %), pH (1.1 %), ORP (1.5 %), EC (1 %), and CEC (0.4 %) (Fig. 1). The ordination biplot demonstrated a positive correlation between AP and Exc-Cu and Red-Cu, and a negative correlation between AP and Oxi-Cu and Res-Cu ($P < 0.05$).

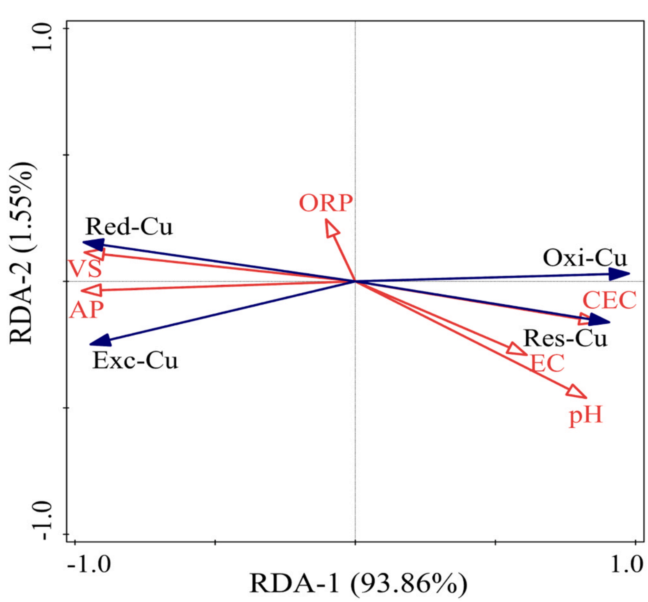

Fig. 5. RDA ordination biplot between the Cu fractions and the physicochemical parameters.

Table 1
The degree of explanation and contribution of each physicochemical property to the speciation transformation of Cu.

Name	Explains%	Contribution%	pseudo-F	P
AP	89.3	93.5	109	0.002
VS	2.2	2.3	3.2	0.102
pH	1.1	1.1	1.6	0.194
ORP	1.5	1.6	2.6	0.124
EC	1	1.1	1.9	0.16
CEC	0.4	0.4	0.7	0.462

This strong yet seemingly counter-intuitive positive correlation suggests that the consumption of AP, rather than its mere presence, is the critical driver for Cu immobilization. The significant decrease in AP content observed in Section 3.1, particularly in the nZVI@BC treatments, is posited to be directly linked to the formation of insoluble copper phosphate precipitates (e.g., $Cu_3(PO_4)_2$) under the alkaline composting conditions. This mechanism is strongly corroborated by the attenuation of phosphate-related peaks in the FTIR spectra (Fig. 2) and is a well-documented pathway for heavy metal passivation (Zheng et al., 2020; Wei et al., 2016).

3.6. AP and bacterial community controls on the Cu fractions

According to the RDA analysis, we know that AP was the most important physicochemical factor that controlled the Cu speciation changes. To further explore the link that existed between the bacterial genera and AP and how they jointly drove the changes in Cu speciation, we used a VPA to perform the analysis of the degree of contribution between AP and bacteria to the change in Cu speciation. We then established structural equation modeling (SEM) to validate the model of the interaction between the four components: Cu speciation, AP, pH, and bacterial communities. Fig. 6(a) shows that bacteria alone explained only 0.1 % of the Cu speciation changes, and AP explained 13.7 % of the Cu speciation changes. Critically, their interactive effect dominated, jointly explaining 74.8 % of the variance, with a residual explanation of 11.4 %. The minimal pure effect of bacteria contrasted with the dominant interactive effect indicates that the microbial community influences Cu speciation primarily through mediating the release and transformation of AP, rather than through direct actions such as biosorption. This finding aligns with the observed shifts in the bacterial community (Section 3.3), particularly the proliferation of Clostridia, which are known for their role in phosphorus solubilization and release under anaerobic micro-niches, thereby supplying phosphate ions for subsequent metal precipitation (Wei et al., 2016).

The SEM was constructed based on the hypotheses generated from our RDA/VPA and established microbial-metal interaction mechanisms (as detailed in Section 2.7). Fig. 6(b) shows the path relationship between AP and bacteria on the changes in the Exc-Cu and Red-Cu, and the results showed that there was a significant positive correlation between bacteria and AP and a significant positive correlation between AP and Exc-Cu and Red-Cu. The results (Fig. 6b) showed significant positive path coefficients from bacteria to AP ($\beta = 0.84$, $P < 0.001$), from AP to bioavailable Cu ($\beta = 0.89$, $P < 0.001$), and from bacteria directly to bioavailable Cu ($\beta = 0.66$, $P < 0.001$). The model fit indices ($\chi^2 = 2.385$, df = 2, P = 0.303; RMSEA < 0.001; CFI = 1.000) indicated a good fit to the data. The SEM thus provides robust statistical support for the hypothesized causal pathway: the bacterial community facilitated the release of AP, and the consumption of AP through precipitation reactions was the primary mechanism driving the reduction of bioavailable Cu. This model effectively integrates the physicochemical and microbial findings into a coherent mechanism for nZVI@BC-promoted Cu passivation.

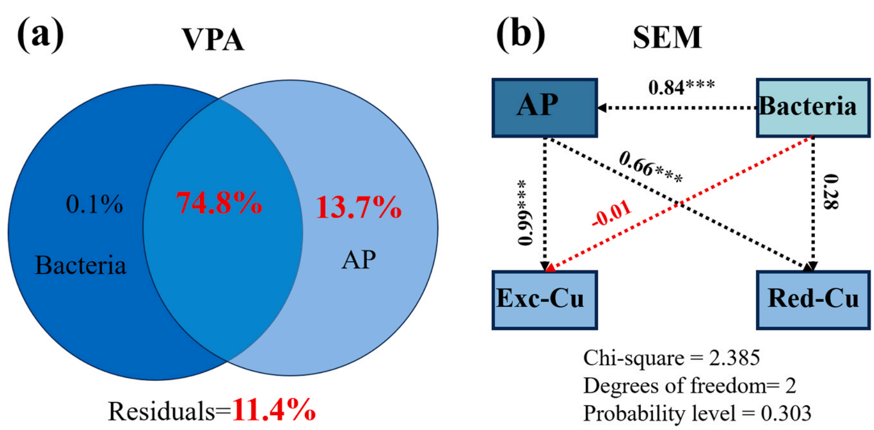

Fig. 6. VPA (a) and SEMs (b) representing hypothesized causal relationships among the Cu fractions, bacterial communities, and AP. Significance levels are the following: $*P < 0.05$, $**P < 0.01$, and $***P < 0.001$.

4. Conclusion

This study demonstrates that biochar-loaded nano zero-valent iron (nZVI@BC), synthesized from agricultural waste tea residues, serves as a highly effective amendment for promoting copper (Cu) immobilization during swine manure composting. The addition of 50 g/kg nZVI@BC (T5) most significantly enhanced the transformation of Cu from bioavailable fractions to stable residues, achieving a remarkable 43.14 % reduction in the active pools of Cu compared to the control. Multivariate analyses (RDA, VPA, and SEM) unequivocally identified available phosphorus (AP) as the paramount factor (89.3 % explanation) driving this process, with the microbial community (particularly Clostridia) acting primarily through mediating AP release rather than direct biosorption. Combined with FTIR evidence, we conclude that the primary mechanism underlying Cu passivation is the precipitation of insoluble copper-phosphate minerals (e.g., $Cu_3(PO_4)_2$), facilitated by the synergistic effect of nZVI corrosion (releasing Fe ions) and the biochar's superior adsorption capacity.

Critically, from an environmental risk perspective, the application of nZVI@BC not only enhances metal stabilization but also mitigates potential ecological hazards. The final compost product exhibited a significant decrease in the mobile and bioavailable Cu fractions, which are the primary concerns for soil health and crop safety. Furthermore, the physicochemical parameters of the matured compost (e.g., pH, EC, CEC) in all nZVI@BC treatments fell within optimal ranges for agricultural application, indicating that the amendment did not induce secondary salinity or phytotoxicity issues. The successful transformation of Cu into stable mineral phases significantly reduces its leaching potential and bioavailability, thereby minimizing the environmental risks associated with land application of swine manure compost.

Beyond the mechanistic insights, this work highlights a promising strategy for the value-added utilization of agricultural waste. By converting waste tea leaves into a functional composting amendment, this approach aligns perfectly with the principles of a circular bio-economy. The nZVI@BC-enhanced composting process transforms livestock manure, another abundant agricultural waste, into a safe and high-value organic fertilizer. This closed-loop strategy not only addresses the critical challenge of heavy metal contamination but also produces a marketable soil amendment that can contribute to sustainable agriculture by improving soil fertility and reducing reliance on chemical fertilizers. Future research should focus on the long-term field-scale evaluation of this compost product to validate its efficacy and safety in real-world agricultural settings.

CRediT authorship contribution statement

Daifeng Lin: Software, Investigation, Data curation. **Zeyang Lu:** Supervision, Software, Investigation. **Yuanping Zhong:** Software, Investigation, Data curation. **yang wenqing:** Writing – original draft, Visualization, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Zuliang Chen:** Writing – review & editing, Methodology. **Qinghua Chen:** Writing – review & editing, Supervision, Data curation. **Deming Yang:** Validation, Supervision, Investigation. **Haifang Zeng:** Methodology, Investigation. **Qian Zhuo:** Methodology, Investigation.

Declaration of Competing Interest

The authors declare that they have no know competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2025.122036.

Data availability

Data will be made available on request.

References

Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., Mentasti, E., 2003. Adsorption of heavy metals on na-montmorillonite. effect of ph and organic substances. Water Res. 37 (7), 1619–1627.
Capuani, A., Werner, S., Behr, J., Vogel, R.F., 2013. Effect of controlled extracellular oxidation–reduction potential on microbial metabolism and proteolysis in buckwheat sourdough. Eur. Food Res. Technol. 238 (3), 425–434.
Chen, X., Zhao, Y., Zeng, C., Li, Y., Zhu, L., Wu, J., Chen, J., Wei, Z., 2019. Assessment contributions of physicochemical properties and bacterial community to mitigate the bioavailability of heavy metals during composting based on structural equation models. Bioresour. Technol. 289, 121657.
Chen, X., Zhao, Y., Zhang, C., Zhang, D., Yao, C., Meng, Q., Zhao, R., Wei, Z., 2020. Speciation, toxicity mechanism and remediation ways of heavy metals during composting: a novel theoretical microbial remediation method is proposed. J. Environ. Manag. 272, 111109.
Chen, X., Du, Z., Guo, T., Wu, J., Wang, B., Wei, Z., Jia, L., Kang, K., 2022. Effects of heavy metals stress on chicken manures composting via the perspective of microbial community feedback. Environ. Pollut. 294, 118624.

Cui, H., Ou, Y., Wang, L., Yan, B., Li, Y., Ding, D., 2020. The passivation effect of heavy metals during biochar-amended composting: emphasize on bacterial communities. Waste Manag. 118, 360–368.
Cui, H., Ou, Y., Wang, L., Yan, B., Li, Y., Bao, M., 2021. Critical passivation mechanisms on heavy metals during aerobic composting with different grain-size zeolite. J. Hazard. Mater. 406, 124313.
Dong, H., Zhang, C., Hou, K., Cheng, Y., Deng, J., Jiang, Z., Tang, L., Zeng, G., 2017. Removal of trichloroethylene by biochar supported nanoscale zero-valent iron in aqueous solution. Sep. Purif. Technol. 188, 188–196.
Gavilanes-Terán, I., Jara-Samaniego, J., Idrovo-Novillo, J., Bustamante, M.A., Moral, R., Paredes, C., 2016. Windrow composting as horticultural waste management strategy – a case study in Ecuador. Waste Manag. 48, 127–134.
Guo, X.X., Liu, H.T., Wu, S.B., 2019. Humic substances developed during organic waste composting: formation mechanisms, structural properties, and agronomic functions. Sci. Total Environ. 662, 501–510.
Jeong, K.H., Kim, J.K., Ravindran, B., Lee, D.J., Wong, J.W., Selvam, A., Karthikeyan, O. P., Kwag, J.H., 2017. Evaluation of pilot-scale in-vessel composting for hanwoo manure management. Bioresour. Technol. 245 (Pt A), 201–206.
Jindo, K., Sonoki, T., Matsumoto, K., Canellas, L., Roig, A., Sanchez-Monedero, M.A., 2016. Influence of biochar addition on the humic substances of composting manures. Waste Manag. 49, 545–552.
Koyama, M., Nagao, N., Syukri, F., Rahim, A.A., Toda, T., Tran, Q.N.M., Nakasaki, K., 2020. Ammonia recovery and microbial community succession during thermophilic composting of shrimp pond sludge at different sludge properties. J. Clean. Prod. 251, 119718.
Li, H., Zhang, T., Tsang, D.C.W., Li, G., 2020. Effects of external additives: biochar, bentonite, phosphate, on co-composting for swine manure and corn straw. Chemosphere 248, 125927.
Li, K., Fu, M., Ma, L., Yang, H., Li, Q., 2023. Zero-valent iron drives the passivation of zn and cu during composting: fate of heavy metal resistant bacteria and genes. Chem. Eng. J. 452, 139136.
Li, W., Gao, X., Fan, R., Gai, J., Li, G., Luo, W., Qi, X., Xu, Z., 2025. Cornstalks regulate bacterial dynamics to benefit organic humification in food waste digestate composting. Environ. Technol. Innov. 37, 104044.
Li, Y., Liu, B., Zhang, X., Gao, M., Wang, J., 2015. Effects of cu exposure on enzyme activities and selection for microbial tolerances during swine-manure composting. J. Hazard. Mater. 283, 512–518.
Liang, J., Yang, Z., Tang, L., Zeng, G., Yu, M., Li, X., Wu, H., Qian, Y., Li, X., Luo, Y., 2017. Changes in heavy metal mobility and availability from contaminated wetland soil remediated with combined biochar-compost. Chemosphere 181, 281–288.
Lonappan, L., Rouissi, T., Kaur Brar, S., Verma, M., Surampalli, R.Y., 2018. An insight into the adsorption of diclofenac on different biochars: mechanisms, surface chemistry, and thermodynamics. Bioresour. Technol. 249, 386–394.
Lu, D., Wang, L., Yan, B., Ou, Y., Guan, J., Bian, Y., Zhang, Y., 2014. Speciation of cu and zn during composting of pig manure amended with rock phosphate. Waste Manag. 34 (8), 1529–1536.
Lu, J., Watson, J., Zeng, J., Li, H., Zhu, Z., Wang, M., Zhang, Y., Liu, Z., 2018. Biocrude production and heavy metal migration during hydrothermal liquefaction of swine manure. Process Saf. Environ. Prot. 115, 108–115.
Lv, B., Xing, M., Yang, J., Qi, W., Lu, Y., 2013. Chemical and spectroscopic characterization of water extractable organic matter during vermicomposting of cattle dung. Bioresour. Technol. 132, 320–326.
Ren, X., Awasthi, M.K., Wang, Q., Zhao, J., Li, R., Tu, Z., Chen, H., Awasthi, S.K., Zhang, Z., 2018. New insight of tertiary-amine modified bentonite amendment on the nitrogen transformation and volatile fatty acids during the chicken manure composting. Bioresour. Technol. 266, 524–531.
Robledo-Mahón, T., Martín, M.A., Gutiérrez, M.C., Toledo, M., González, I., Aranda, E., Chica, A.F., Calvo, C., 2019. Sewage sludge composting under semi-permeable film at full-scale: evaluation of odour emissions and relationships between microbiological activities and physico-chemical variables. Environ. Res. 177, 108624.
Song, P., Xu, H., Sun, S., Xiong, W., Yang, Z., 2022. Remediation of arsenic-spiked soil by biochar-loaded nanoscale zero-valent iron: performance, mechanism, and microbial response. J. Clean. Prod. 380, 134985.
Su, H., Fang, Z., Tsang, P.E., Zheng, L., Cheng, W., Fang, J., Zhao, D., 2016. Remediation of hexavalent chromium contaminated soil by biochar-supported zero-valent iron nanoparticles. J. Hazard. Mater. 318, 533–540.
Wang, H., Zhang, M., Li, H., 2019. Synthesis of nanoscale zerovalent iron (nZVI) supported on biochar for chromium remediation from aqueous solution and soil. Int. J. Environ. Res. Public Health 16 (22), 4430.
Wang, Q., Wang, Z., Awasthi, M.K., Jiang, Y., Li, R., Ren, X., Zhao, J., Shen, F., Wang, M., Zhang, Z., 2016. Evaluation of medical stone amendment for the reduction of nitrogen loss and bioavailability of heavy metals during pig manure composting. Bioresour. Technol. 220, 297–304.
Wang, Q., Awasthi, M.K., Zhao, J., Ren, X., Li, R., Wang, Z., Wang, M., Zhang, Z., 2017. Improvement of pig manure compost lignocellulose degradation, organic matter humification and compost quality with medical stone. Bioresour. Technol. 243, 771–777.
Wei, X., Liu, D., Li, W., Liao, L., Wang, Z., Huang, W., Huang, W., 2018. Biochar addition for accelerating bioleaching of heavy metals from swine manure and reserving the nutrients. Sci. Total Environ. 631-632, 1553–1559.
Wei, Y., Wei, Z., Cao, Z., Zhao, Y., Zhao, X., Lu, Q., Wang, X., Zhang, X., 2016. A regulating method for the distribution of phosphorus fractions based on environmental parameters related to the key phosphate-solubilizing bacteria during composting. Bioresour. Technol. 211, 610–617.
Xu, Y., Fang, Z., Tsang, E.P., 2016. In situ immobilization of cadmium in soil by stabilized biochar-supported iron phosphate nanoparticles. Environ. Sci. Pollut. Res. 23 (19), 19164–19172.
Yang, W., Zhong, Y., Lu, Z., Lin, D., Zhuo, Q., Zeng, H., Yang, D., Chen, Z., 2025. Synthesis of biochar-loaded Green synthetic iron nanocomposite and passivation mechanism of cadmium in pig manure aerobic composting. Environ. Technol. Innov. 40, 104377.
Zhao, B., Wang, Y., Ma, L., Li, Y., Deng, Y., Chen, X., Xu, Z., 2022. Adding an appropriate proportion of phosphogypsum ensured rice husk and urea composting to promote the compost as substrate utilization. Bioresour. Technol. 344.
Zheng, G., Wang, X., Chen, T., Yang, J., Yang, J., Liu, J., Shi, X., 2020. Passivation of lead and cadmium and increase of the nutrient content during sewage sludge composting by phosphate amendments. Environ. Res. 185, 109431.
Zhou, H., Meng, H., Zhao, L., Shen, Y., Hou, Y., Cheng, H., Song, L., 2018. Effect of biochar and humic acid on the copper, lead, and cadmium passivation during composting. Bioresour. Technol. 258, 279–286.