

Review

Exolaccase-boosted humification for agricultural applications

Hailing Chu,^{1,5} Shunyao Li,^{2,5} Kai Sun,^{1,3,*} Youbin Si,¹ and Yanzheng Gao⁴

SUMMARY

Globally, phenolic contaminants have posed a considerable threat to agro-ecosystems. Exolaccase-boosted humification may be an admirable strategy for phenolic detoxification by creating multifunctional humic-like products (H-LPs). Nonetheless, the potential applicability of the formed H-LPs in agricultural production is still overlooked. This review describes immobilized exolaccase-enabled humification in eliminating phenolic pollutants and producing artificial H-LPs. The similarities and differences between artificial H-LPs and natural humic substances (HSs) in chemical properties are compared. In particular, the agronomic effects of these reproducible artificial H-LPs are highlighted. On the basis of the above summary, the granulation process is employed to prepare granular humic-like organic fertilizers, which can be applied to field crops by mechanical side-deep fertilization. Finally, the challenges and perspectives of exolaccase-boosted humification for practical applications are also discussed. This review is a first step toward a more profound understanding of phenolic detoxification, soil improvement, and agricultural production by exolaccase-boosted humification.

INTRODUCTION

Soil plays a vital role in the global carbon cycle because it is the largest terrestrial carbon pool (Van Oost et al., 2007). In the agro-ecosystems, natural humic substances (HSs) are considered to be one of the fundamental factors sustaining soil fertility, productivity, and health (Dehsheikh et al., 2020; Yang et al., 2021). Alarmingly, the humus level of arable soils after prolonged use is diminishing because of the depletion of organic carbon. For instance, annual loss of HSs reaches 600–700 kg ha⁻¹ in Ukraine (Petrychenko et al., 2018). So it is extremely important to augment the content of HSs in the agro-ecosystems for guaranteeing soil fertility and crop yield. However, renewing the humus balance is a long-term process and is very expensive (Guillaume et al., 2021). Artificial humic-like products (H-LPs) are a kind of heterogeneous polymers, which have the biochemical properties similar to those of natural HSs (Li et al., 2022a). Thus, researchers have devoted attention to create H-LPs by artificial humification to support the sustainable development of agricultural production (Li et al., 2022b).

A substantial amount of phenolic compounds are present in environmental matrices (Ferrera et al., 2004; Sun et al., 2022). They are waste products and potential contaminants that can be converted into useful artificial H-LPs (Catherine et al., 2016; Liu et al., 2021a). With the rapid development of the global economy, phenolic pollution has become a tremendously serious environmental issue that causes a broad-scale threat to water-soil-crop agro-ecosystems and humanity (Othmani et al., 2022; Zhong et al., 2018). Phenolic contaminants such as phenols, bisphenols, alkylphenols, aminophenols, and halophenols from sewage treatment plants are released into the agro-ecosystems by overland runoff and wastewater irrigation (Glover et al., 2021). They are able to trigger a series of genotoxicity events and mortality risks at a relatively low level (nM–mM) owing to these pollutants present high toxicity and biologically degradation-resistant (Chae et al., 2020; Li et al., 2022a; Singh et al., 2021). For instance, phenol-containing wastewater is capable of disturbing the reproduction and inheritance of *Sarotherodon melanotheron*, leading to the feminization of male fish (Adeogun et al., 2019). Furthermore, it is also can damage soil health, reduce crop productivity, and destroy agro-ecological balance (Liu et al., 2021b; Mei et al., 2019). Consequently, how to effectively evade environmental risks of phenolic contaminants has drawn increasing attention.

In the past 30 years, many physiochemical and biological treatment strategies such as biochar adsorption, electrochemical detoxification, advanced oxidation, microbial metabolism, and plant uptake

¹Anhui Province Key Laboratory of Farmland Ecological Conservation and Pollution Prevention, College of Resources and Environment, Anhui Agricultural University, Hefei, 230036 Anhui, China

²Laboratory of Wetland Protection and Ecological Restoration, Anhui University, Hefei, 230601 Anhui, China

³CAS Key Laboratory of Urban Pollutant Conversion, Department of Environmental Science and Engineering, University of Science and Technology of China, Hefei, 230026 Anhui, China

⁴College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing, 210095 Jiangsu, China

⁵These authors contributed equally

*Correspondence: sunkai@ahau.edu.cn
<https://doi.org/10.1016/j.isci.2022.104885>



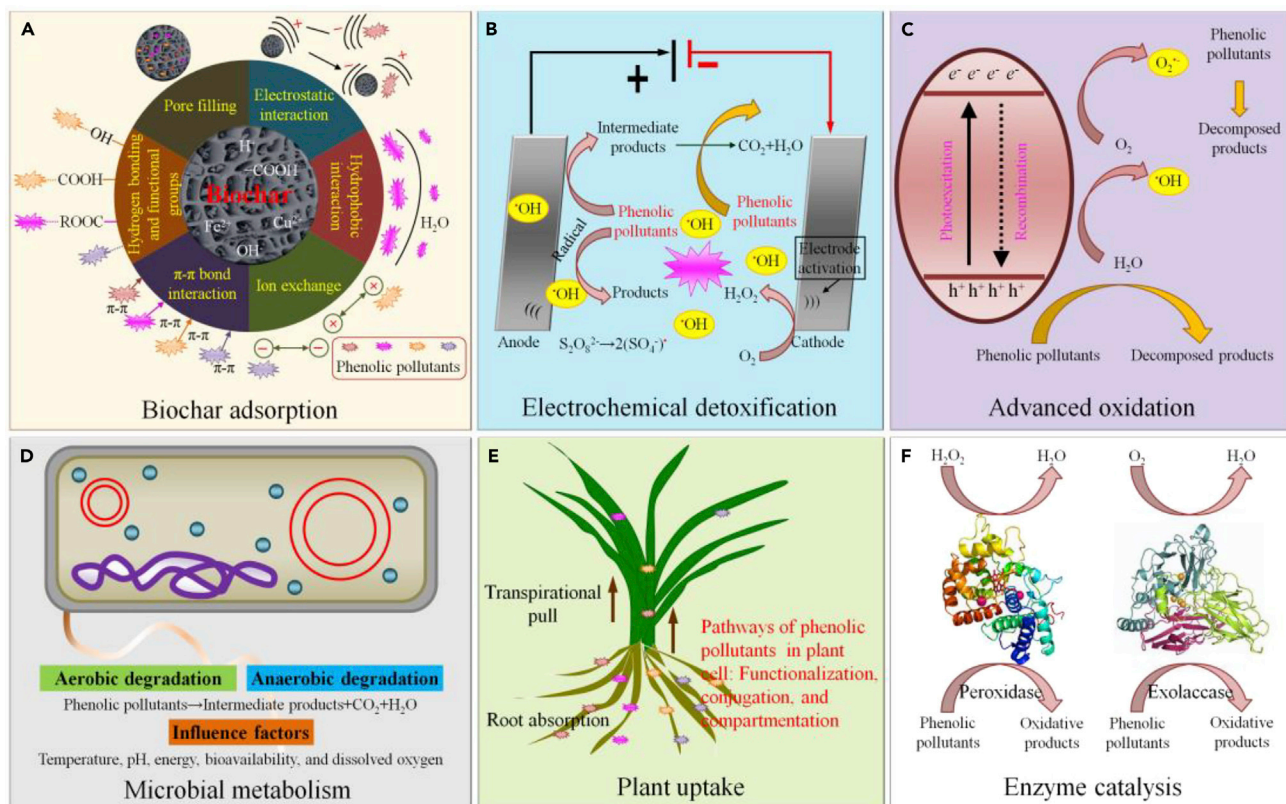


Figure 1. The existing physicochemical and biological technologies for treating phenolic pollutants in water

- (A) Biochar adsorption;
 (B) Electrochemical detoxification;
 (C) Advanced oxidation;
 (D) Microbial metabolism;
 (E) Plant uptake;
 (F) Enzyme catalysis.

(Figures 1A–1E), etc., have been used to decontaminate phenol-polluted water (Cheng et al., 2021; Hodges et al., 2018; Patidar and Srivastava, 2022; Saleem et al., 2018; Viggor et al., 2020). However, these technologies are actually expensive, inefficient, time-consuming, or prone to secondary pollution (Martinez-Huitle et al., 2015; Paul et al., 2005; Wang et al., 2022). Fortunately, exolaccase-boosted humification and copolymerization have proved effective in dealing with the ecological risks of phenolic pollutants (Liu et al., 2021a; Li et al., 2022b; Sun et al., 2021a). Such an enzyme initiates the single-electron oxidation of phenolics, amino acids, and other small humic molecules with O_2 as the terminal electron acceptor (without H_2O_2 , also listed in Figure 1F), producing multiple unstable reactive radical intermediates for subsequent complicated copolymerization (Chen et al., 2019; Su et al., 2019). The processes are similar to natural humification reactions, which not only antagonize the mineralization of organic carbon/nitrogen but also contribute to the formation of H-LPs (Cha et al., 2017; Lee et al., 2019; Sun et al., 2022). Particularly, the produced artificial H-LPs may play a significant role in maintaining soil ecosystem services (Li et al., 2022b). However, their potential multifunctional applications for agricultural production have been rarely reported.

The aim of this review is to emphasize exolaccase-boosted humification of phenolic pollutants and its practical application values in soil fertility and crop productivity. First, immobilization of exolaccase is introduced to enlarge the humification of substrates and expand the yield of artificial H-LPs, through maintaining enzymatic activity, stability, and reusability. Second, copolymerization and detoxification mechanisms of phenolics by exolaccase-initiated humification are explained. Subsequently, the similarities and differences between artificial H-LPs and natural H-Ss in chemical properties are also uncovered. In particular,

the agronomic performances of artificial H-LPs are systematically summarized. It is proposed that the fertilizer granulation and mechanical side-deep fertilization of H-LPs are utilized to promote crop growth in sustainable agriculture. Our review provides new insights into the applications of exolaccase-boosted humification and copolymerization in phenolic detoxification, soil amelioration, and agricultural production for the first time.

EXOLACCASE-INITIATED ARTIFICIAL HUMIFICATION

Exolaccase-initiated humification and copolymerization have been tentatively used for environmental remediation and humic-like formation (Li et al., 2022b; Sun et al., 2021b, 2022). The stability and reusability of immobilized exolaccase make it more advantageous in phenolic humification, in comparison with free enzymes (Fernandez-Fernandez et al., 2013). Our previous study revealed that immobilized exolaccase was capable of copolymerizing various phenolic contaminants and small humic precursors to create highly cross-linked supramolecular H-LPs (Sun et al., 2021a). Nevertheless, it is necessary to exploit a well-designed method to immobilize exolaccase, and then enable the practical applications of catalyst in enzymatic humification. More particularly, the treatment processes intend to lessen greenhouse gas emission (i.e., CO₂ and NH₃) and yield artificial H-LPs by radical-based copolymerization, which may realize the reutilization of humified products in agricultural production (Li et al., 2022b; Wang et al., 2022).

Immobilization of exolaccase

Versatile exolaccase from white-rot fungi such as *Trametes versicolor*, *Trametes hirsuta*, *Coriolus versicolor*, and *Pleurotus ostreatus* is a multicopper oxidase that widely exists in nature (Wesenberg et al., 2003). Currently, ultrafiltration, two-phase extraction, three-phase partitioning, and foam fractionation have been used for purifying fungus-secreted exolaccase (Kanaujiya et al., 2019). Researchers consider exolaccase as a promising “green catalyst” for polymerizing phenolic contaminants and cleaning water bodies because it has the characteristics of high redox potential (450–790 mV), energy saving, and environmental protection (Chen et al., 2019; Morsi et al., 2020). In exolaccase-started humification and copolymerization processes, the enzyme acts like a transit station, taking electrons from substrates and using those electrons to reduce one O₂ into two H₂O (Sun et al., 2016). Subsequently, the produced multiple radical intermediates are spontaneously coupled outside the reactive site of enzyme to form C–C, C–O–C, and/or C–N–C binding H-LPs (Liu et al., 2021a). Despite this, environmental conditions such as temperature, pH, metal ions, indigenous microbes, and the fact that exolaccase is easily soluble in water pose significant challenges to large-scale applications of exolaccase-boosted humification in phenolic copolymerization (Al-Ansari et al., 2022; Chen et al., 2019). Of interest, immobilization of enzyme using an inexpensive and readily available carrier solves the problem. It not only improves the stability and activity of the enzyme but also makes the enzyme reusable (Cao et al., 2021; Daronch et al., 2020).

It is well known that encapsulation and covalent binding are the most conventional methods of exolaccase immobilization (Fernandez-Fernandez et al., 2013). For instance, exolaccase is encapsulated in alginate (a low-cost and nontoxic raw material) to protect the enzyme from the threat of external environments and prevent enzyme leakage, which shows superior storage stability and reusability (Kucharzyk et al., 2018). The disadvantage is the existence of a large mass transfer resistance between substrates and immobilized exolaccase (Daronch et al., 2020). For covalent binding, the active functional groups of carriers chemically react with the nucleophilic groups of exolaccase, forming tight covalent bonds (Zhou et al., 2021). This method makes exolaccase less susceptible to inactivation and more reusable while significantly reducing enzyme leakage, but it may alter the spatial conformation of enzyme and thus inactivate it. Notably, our early results disclosed that combining encapsulation and covalent binding (cross-linked-entrapped exolaccase in Ca-alginate beads) was a very effective way to maintain the activity and stability of enzyme, and boost exolaccase-started humification (Sun et al., 2021a). Such pattern was beneficial to sustainability eliminate phenolic pollutants and generate multifarious artificial H-LPs in the range of pH 3–6 and 20–60°C.

Formation mechanism of humic-like polymers

Small humic precursors, such as phenols, phenolic acids, amino acids, and their derivatives, are abundant in nature and difficult to recycle, gaining worldwide interest in research (Qi et al., 2012; Zhu et al., 2021; Zhou et al., 2022). Exolaccase-activated humification promotes the formation of multiple copolymeric products with phenolic contaminants and small humic precursors as parents (Liu et al., 2021a; Li et al., 2022a). Moreover, protein and carbohydrate are decomposed in the initial stage by microbes to increase the abundance

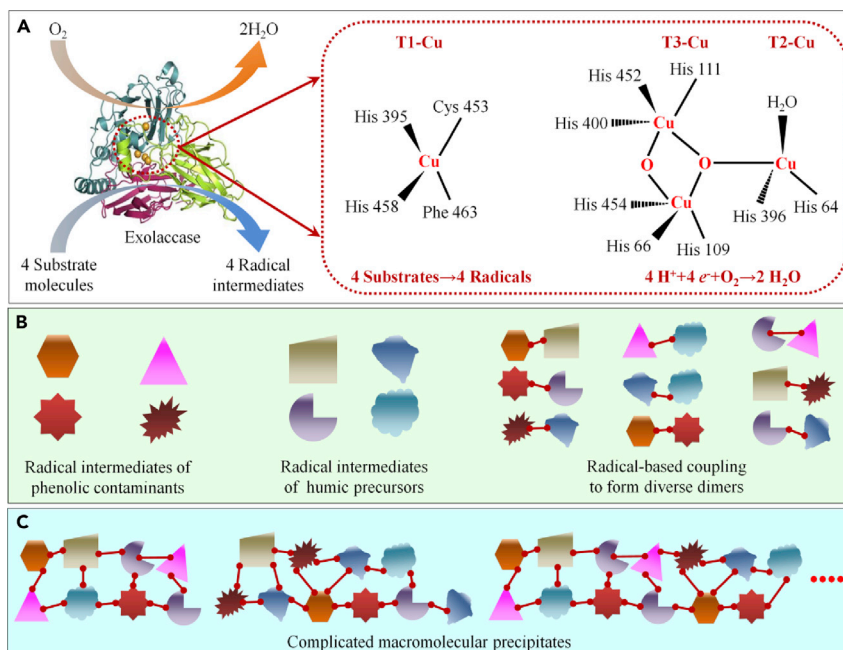


Figure 2. Humification mechanism of exolaccase-boosted phenolic pollutants and small humic precursors

(A) In the first step, small phenolics and humic precursors are oxidized at T1-Cu site of exolaccase to create unstable radical intermediates;
 (B) In the second step, the formed radical intermediates are randomly coupled via C–C, C–O–C, and/or C–N–C binding to produce dimers;
 (C) In the third step, these dimers can still be coupled by continuous polymerization to generate more complicated macromolecular precipitates.

of humic precursors, thereby accelerating the generation of H-LPs in exolaccase-boosted humification (Li et al., 2022b; Wang et al., 2022; Zhang et al., 2019). Phenolic compounds are considered as the main “building blocks” of artificial H-LPs. The oxidation efficiency of exolaccase depends on redox potential of T1-Cu site (Farran et al., 2021). As shown in Figure 2, the mechanism of humification boosted by exolaccase is that T1-Cu into enzyme molecules oxidizes low-molecular-weight phenolics and humic precursors to obtain multitudinous reactive radical intermediates, accompanied by dissolved O₂ consumption at T2/T3-Cu sites (Sun et al., 2021b). Subsequently, these unstable active intermediates can be randomly coupled by C–C, C–O–C, and/or C–N–C covalent binding to form dimeric products (Meng et al., 2021; Niu et al., 2021). These isomers of dimers are further oxidized and copolymerized via repeated radical coupling to generate more complicated macromolecular precipitates (Chen et al., 2019). It is well documented that only a very few phenolic contaminants are re-released from the loosely bound copolymers, revealing that these formed humic-like structures have great environmental stability (Sun et al., 2022). Even so, the safety of H-LPs generated by phenolic pollutants and other small molecular structures still needs to be prudently evaluated in complex environmental matrices.

The macromolecular H-LPs formed by radical-caused heterogeneous polymerization of small substrates are remarkably similar to natural humification processes, which are beneficially used in phenolic detoxification, organic carbon sequestration, and soil improvement in sustainable agriculture (Li et al., 2022b; Yoon et al., 2020). Liu et al. (2021a) revealed that exolaccase boosted radical coupling of 17β-estradiol (E2) and humic precursors, resulting in a large number of highly and intricately copolymerized products by radical-based covalent binding mechanism. The removal rate of E2 in the biochemical process was as high as > 99%. More importantly, the formed copolymers contained a large amount of aromatic, hydroxyl, and carboxyl functional groups, similar to natural HSs. They are expected to be regarded as humic-like organic fertilizers, which can be used to crop and/or rhizosphere, stimulate physiological and molecular mechanisms that promote crop growth and development (Cha et al., 2017; Lee et al., 2019; Li et al., 2022b). According to the analysis above, a fluidized-bed bioreactor containing immobilized exolaccase is established to treat phenolic pollutants and produce artificial H-LPs (Figure 3A). As described in

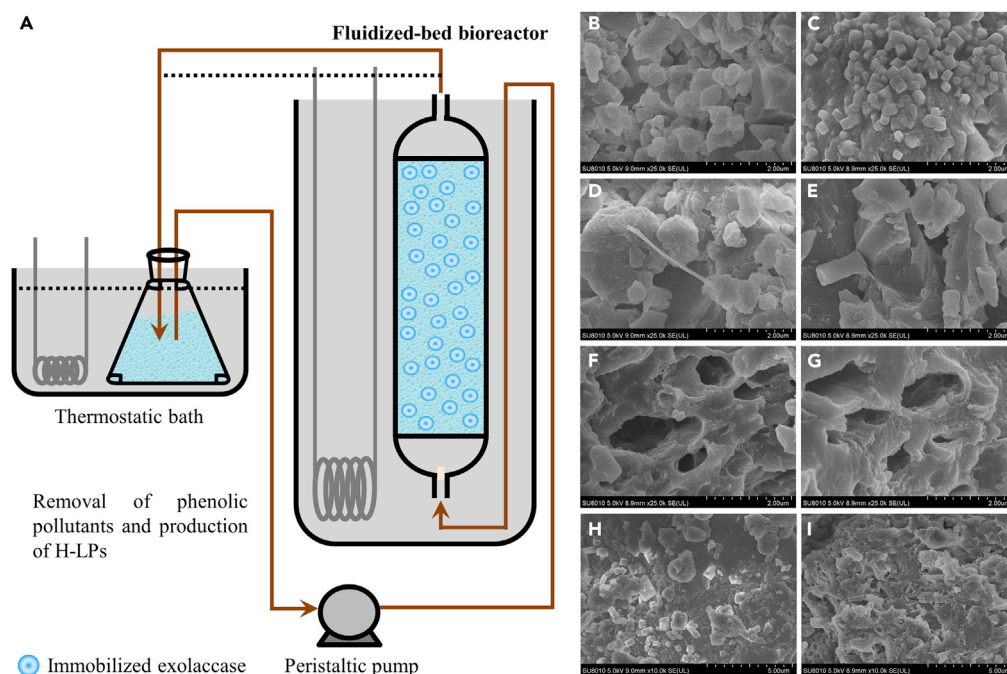


Figure 3. Immobilized exolaccase-boosted humification in fluidized-bed bioreactor to detoxify phenolic pollutants and obtain artificial H-LPs

(A) Fluidized-bed bioreactor;

(B–E) Copolymerization products of bisphenol A (BPA) and small phenolics (unpublished data);

(F–I) Copolymerization products of BPA, amino acids, and glucose (unpublished data). Small phenolics, amino acids, and glucose are usually used in humic precursors.

Figures 3B–3I, the bioreactor not only detoxicates phenolic contaminants during water treatment but also aids in the formation and acquisition of artificial H-LPs. These H-LPs act as “living” organic carbon that can participate in the regulation of the biogeochemical cycles in agricultural production (Li et al., 2022b). This shows exolaccase-boosted humification opens a new avenue for eliminating phenolic pollutants and synthesizing artificial H-LPs under controllable conditions.

SIMILARITIES AND DIFFERENCES BETWEEN ARTIFICIAL AND NATURAL HUMUS

As is generally known, in nature the formation of natural HSs is extremely sluggish and complicated (Baveye and Wander, 2019; Jeong et al., 2018). Simultaneously, over-cultivation leads to increasing humus loss in the agro-ecosystems. The mode and mechanism of exolaccase-started artificial humification and copolymerization are similar to natural humification (Lee et al., 2019; Li et al., 2022b). It conforms to the concepts of green, environmental protection, low carbon, energy-saving, and sustainable development (Chen et al., 2019). Moreover, the created useful H-LPs by immobilized exolaccase are stable and comparably inexpensive. Especially, the chemical characteristics of the produced H-LPs can be manipulated through altering reactor conditions (Wang et al., 2020). Hence, clarifying the similarities and differences between artificial H-LPs and natural humus in chemical properties is expected to enrich the practical applications of humified products in soil improvement and agricultural production.

Elemental composition and functional groups

Natural and artificial humified products have analogical elemental composition and functional groups (Min et al., 2019). For example, Yang et al. (2019) revealed that both H-LPs and natural humus contained C, H, O, N, S, and P elements. Notably, the N content in the natural HSs ranged from 0.7% to 5.1% (Nardi et al., 2021), which was more than 3.56 times that of artificial H-LPs. Although Ca, Mg, Fe, and Si occur at relatively low level in the natural HSs, it is important to replenish these elements for synthesis of artificial H-LPs. In addition, the phenolic hydroxyl, carboxyl, quinonyl, and aromatic components are also detected in both natural and artificial humified products (Cha et al., 2017; da Silva et al., 2020; Liu et al., 2021a), manifesting

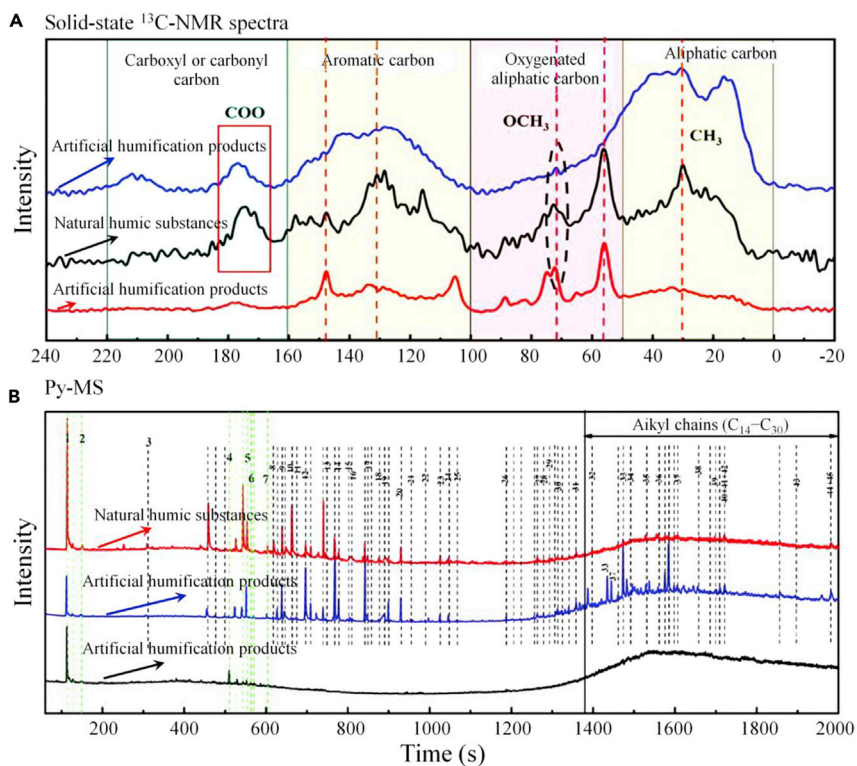


Figure 4. Differences in composition and structure between natural and artificial humified products (Yang et al., 2019)

(A) ^{13}C -NMR spectra from artificial H-LPs and natural HSs;
(B) Py-MS obtained by artificial H-LPs and natural HSs.

that artificial H-LPs in water have acidic and colloidal performances. Like natural HSs, artificial H-LPs also can play vital roles in the removal and transformation of toxic micropollutants (Li et al., 2022b). The contents of phenolic hydroxyl and carboxyl groups commonly range from 1.0 to 2.2mmol g^{-1} and from 3.8 to 6.7mmol g^{-1} in the natural HSs, respectively (Nardi et al., 2021). Compared with artificial H-LPs, natural HSs present more aromatic structures but less oxygenated functional groups (Yang et al., 2019). This shows that artificial H-LPs can act as biostimulators in promoting plant growth, improving microbial activity, and ameliorating soil quality (Li et al., 2022b; Sun et al., 2022).

Chemical structure

Solid-state ^{13}C -nuclear magnetic resonance (^{13}C -NMR), pyrolysis-mass spectrometry (Py-MS), and confocal Raman microscopy have been generally used to reveal the chemical structures of humified products (Yang and Antonietti, 2020a; Zou et al., 2021). As disclosed in Figure 4A, ^{13}C -NMR spectra of artificial H-LPs and natural HSs contain 4 chemical regions: Aliphatic carbon, oxygenated aliphatic carbon, aromatic carbon, and carboxyl/carbonyl carbon (Sannigrahi et al., 2006). Differences in aromatic carbon regions combined with major methoxy signals suggest that the lignin-derived phenolic components are the key aromatic backbone for the generation of natural and artificial humified products (Yang et al., 2019; Yoon et al., 2020). Differences in carboxyl/carbonyl carbon regions demonstrate that the carboxyl content of natural HSs is higher than that of artificial H-LPs. The “fingerprint plots” of Py-MS imply that artificial H-LPs and natural HSs have a high degree of similarity. The typical spectral peaks are divided into 4 parts: Protein peaks, polysaccharide peaks, lignin peaks, and lipid-based peaks (Figure 4B). In addition, a few representative fragments of pyrrole, pyridine, and other N-containing compounds are also found and recognized in their molecular structures. Compared with artificial H-LPs, more N-containing compounds are released in the natural HSs. These results indicate that some similarities and differences exist both in artificial H-LPs and natural HSs. Even so, it remains extremely difficult to confirm the precise structures of artificial H-LPs at the molecular level (Su et al., 2019).



Figure 5. The practical applications of artificial H-LPs in sustainable agriculture

- (A) Soil amelioration;
- (B) Organic carbon storage;
- (C) Microbial diversity;
- (D) Soil remediation;
- (E) Crop growth promoter;
- (F) Disease resistance.

AGRONOMIC EFFECTS OF HUMIC-LIKE POLYMERS

Agricultural soil quality provides a basic guarantee for crop growth and food security production (Lu et al., 2015; Li et al., 2021). Excessive agricultural investments, such as the large-scale applications of chemical fertilizers and over-cultivation have led to significant declines in soil quality and fertility (Liu and Diamond, 2005). So it is urgent to seek eco-friendly strategies to ameliorate soil quality and enhance crop productivity. Natural humus as a highly functional copolymer maintains the stability of agricultural eco-environments and diminishes soil pollution, but its time-consuming formation restricts its practical applications in sustainable agriculture (Lee et al., 2019; Olaetxea et al., 2018). Fortunately, exolaccase-boosted artificial humification and copolymerization have been recently highlighted (Li et al., 2022b). The characteristics of the formed H-LPs by exolaccase are perfectly similar to natural HSs in both structures and functions. Consequently, applying artificial H-LPs in sustainable agriculture has great potential to bring economic and ecological benefits. Figure 5 exhibits the practical values of artificial H-LPs in sustainable agriculture, mainly to elucidate their great potential.

Soil amelioration

Soil water-holding capacity is one of the main factors affecting soil nutrients and self-purification ability. Artificial H-LPs are capable of effectively maintaining soil water-holding capacity because their porous structures enhance the permeability and capillarity of soil (Lan et al., 2021). Moreover, the hydrophilic carboxyl and hydroxyl groups in artificial H-LPs also help to form the hydrogen bonds between H₂O and

H-LPs (Yang and Antonietti, 2020b). It is confirmed that various functional groups in artificial H-LPs play a crucial role in soil amelioration (Li et al., 2022b; Yang et al., 2021). For instance, lots of acidic groups in artificial H-LPs resist soil alkalization. The carboxyl and phenolic hydroxyl groups in H-LPs produce anions which attract more exchangeable cations such as K^+ , Ca^{2+} , Na^+ , and Mg^{2+} , consequently enhancing soil cation exchange capacity and making for crop uptake (Wu et al., 2021). The carboxyl groups in artificial H-LPs react with phosphate minerals to increase the content of dissolved phosphorus in soil and supply the essential phosphorus element for crop growth (Yang et al., 2021). In addition, artificial H-LPs also can reduce Fe^{3+} into Fe^{2+} in soils for expediting Fe uptake by crop. These results imply that the application of artificial H-LPs significantly improves the physicochemical properties of soil and thus increases its fertility.

Organic carbon storage

Organic carbon storage in the pedosphere is considerably higher than that in the biosphere and atmosphere (Lal et al., 2015). Enhancing soil carbon sequestration in cropland by 0.4 wt% every year is beneficial to diminishing CO_2 productivity and thus solving climate crisis (Lan et al., 2021). The chemical characteristics of artificial H-LPs regulate the metabolism of microbes and plants to affect the soil carbon reservoir (Wei et al., 2021; Yang et al., 2021). A study by Tang et al. (2021) revealed that artificial H-LPs promoted carbon sequestration in black soil by stimulating microbial activities for binding CO_2 , thereby increasing nutrient availability for crop growth. In addition, artificial H-LPs can also enhance photosynthesis to transform more CO_2 into organic matter (Tang et al., 2022). Given that artificial H-LPs are complex carbonaceous copolymers, they are more difficult to degrade by soil microbes compared with natural organic matters (Wei et al., 2021). Thus, artificial H-LPs are retained in the soil as inert carbon components.

Microbial diversity

Cell membrane as a special biological sieve has high or low permeability for various substances, affecting the absorption of nutrients by microbial cells (Wu et al., 2022). Of interest, artificial H-LPs improve the permeability of microbial cell membranes to accelerate the absorption of mineral nutrients (Villain-Gambier et al., 2019). This is because H-LPs containing a quinone and/or hydroquinone group receive electrons or provide electrons as an intermediate to provide energy for microbial respiration (Yang et al., 2021). Moreover, the pressure of nutritional competition between microbes can be alleviated by the application of artificial H-LPs as supplementary carbon sources (Zhang et al., 2021), thus increasing the communities of specific soil microbes such as *Acidobacteria*, *Actinobacteria*, and *Bacteroidetes* (Pukalchik et al., 2019). Indirect impacts of artificial H-LPs on the basic activities of microbes are also recognized. There are complex interactions between crop rhizosphere and microbes. Under the induction of artificial H-LPs, root cells secrete a large number of biochemical compounds, such as succinic acid and malic acid, which improve the activities of microbes near plant roots and change the structures of microbial communities (Figure 6). The normal growth of microbes and a healthy soil environment are inseparable; Artificial H-LPs coordinate the balance between microbial communities by improving the physicochemical properties of soil (Lee et al., 2019).

Agricultural soil remediation

Heavy metals and organic contaminants in agricultural soil at a certain concentration cause direct crop mortality and can pose a major health risk to humans through the food chain (Alengebawy et al., 2021; Li et al., 2022b). This provides a background for artificial H-LPs to play a valuable role. As indicated in Figure 7, artificial H-LPs in soil are able to lower the genotoxicity of heavy metals and eliminate organic pollutants by adsorption, complexation, ion exchange, and redox processes. As negatively charged colloids, artificial H-LPs gather pollutant molecules into lots of large masses by electrostatic adsorption, making it difficult for these macromolecular products to cross the cell membrane and then accumulate in crops (Philippe and Schaumann, 2014; Yang and Hodson, 2018). This is because the highly active oxygen- and nitrogen-containing groups in artificial H-LPs, such as phenolic hydroxyl, carboxyl, and amino groups, are complexed with heavy metals to reduce their mobility and uptake/bioavailability (Wang et al., 2020). Furthermore, the natural realization of reduction reactions between heavy metals and artificial H-LPs also contributes to the conversion of heavy metals into a less toxic state and even eliminating their toxicity (Yang et al., 2021). For organic contaminants, artificial H-LPs bind organic molecules by hydrogen bonding, van der Waals, charge transfer, and hydrophobic interactions, and thus reduce their toxicity and bioavailability (Lipczynska-Kochany, 2018). In addition, artificial H-LPs also act as electron acceptors and redox mediators in microbial processes. They can obtain electrons from microbes, which are subsequently delivered

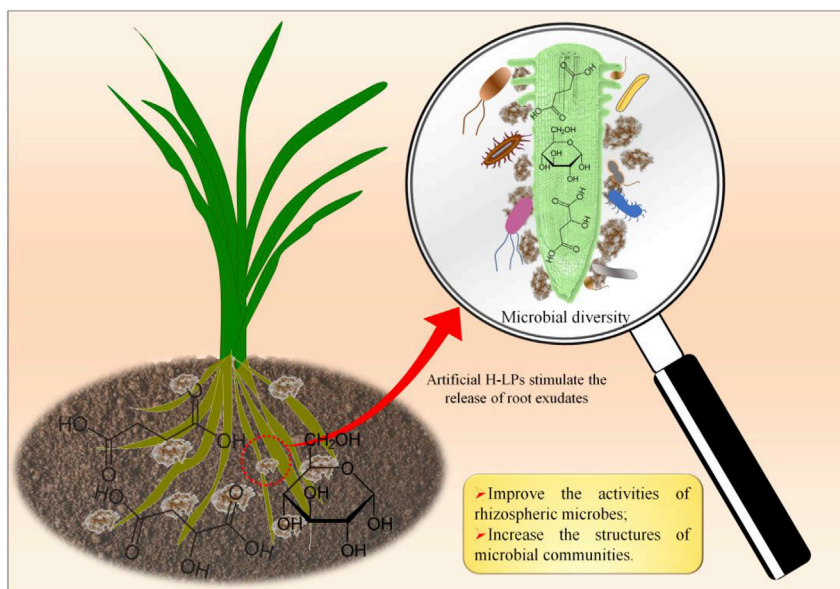


Figure 6. Effect of artificial H-LPs on the communities of rhizospheric microbes

Artificial H-LPs can stimulate the release of root exudates, consequently improving the activities of rhizospheric microbes and increasing the structures of microbial communities.

to organic pollutants and/or related radical intermediates, greatly increasing the degradation rate of organic contaminants.

Crop growth promoter

The complex supramolecular structures of artificial H-LPs and their related bioactivity in crops have been infrequently described (Cha et al., 2017; Li et al., 2022b). One of the most important issues is the interaction mechanisms of artificial H-LPs and crop-soil-microbe in the rhizosphere. Based on the existing literature, the positive effects of artificial H-LPs on plant growth and crop productivity are reflected in the following 4 aspects (Shah et al., 2018; Sun et al., 2022; Yang et al., 2021; Yakimenko et al., 2021).

- (1) Artificial H-LPs profitably promote the absorption and metabolism of nutrients in crops (Figure 8). The negative charges of artificial H-LPs facilitate the ability of membrane proteins to transport NO_3^- by ion channels, which avoids the alkalization of root cells (Yoon et al., 2020). In addition, artificial H-LPs are also able to regulate the expression of plasma membrane $\text{K}^+/\text{Ca}^{2+}$ transporters, H^+ -ATPase, and other related genes/proteins/enzymes involved in nitrogen assimilation, cell division, and development, consequently accelerating the absorption rate of nutrients by root cells (DeHita et al., 2020; Garcia et al., 2019; Yang et al., 2021).
- (2) The recalcitrant and labile carbon of artificial H-LPs can trigger the division and growth of root cells by molecular processes and signaling pathways (Sun et al., 2022; Soria et al., 2022). Recalcitrant carbon binds to the external cell receptors and contributes to root elongation and biomass production whereas labile carbon enters the root cells via the epidermis, surface clustering, or physicochemical interactions and promotes the occurrence of new roots (García et al., 2019; Nardi et al., 2021), so that crop absorbs more H_2O and nutrients. In addition, the released small fragments from artificial H-LPs also can exert hormone-like effects in crops.
- (3) Artificial H-LPs affect the synthesis of some specific compounds in a crop and thus interfere with the secondary metabolism of the crop (Bernstein et al., 2019). For example, the increase in the concentrations of indoleacetic acid and NO in crop roots caused by artificial H-LPs facilitate the growth of above-ground plant parts (Nardi et al., 2016). Besides, artificial H-LPs are also expected to modulate reactive oxygen species (ROS) and enzyme-responsive genes in crops (Cha et al., 2017; Dou et al., 2015).
- (4) Different from the abovementioned, artificial H-LPs also act as soil conditioners that can improve soil quality to provide a positive rhizospheric environment for crop growth and development (Guo et al.,

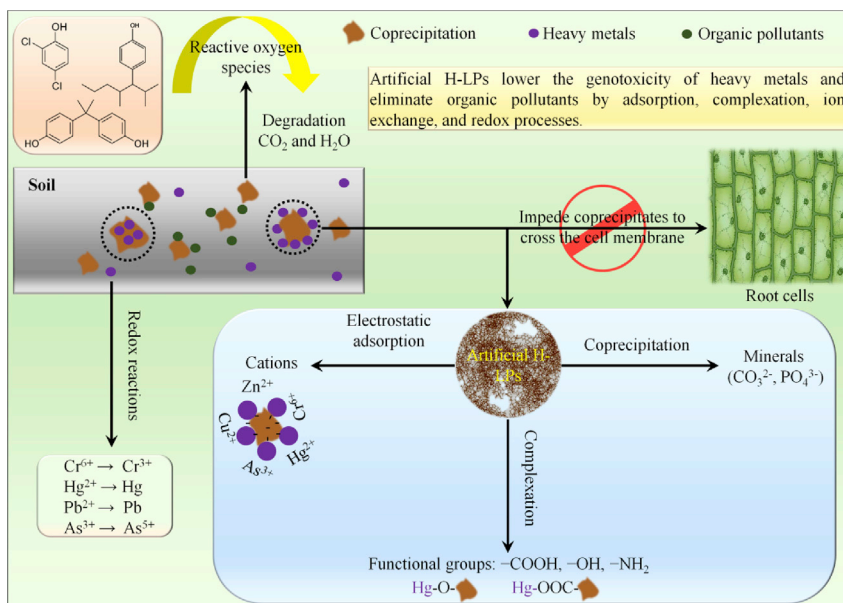


Figure 7. Action mechanisms of artificial H-LPs in soil remediation

Artificial H-LPs are helpful in lowering the genotoxicity of heavy metals and eliminating organic pollutants through adsorption, complexation, ion exchange, and redox processes.

2019). For instance, the formation of soluble H-LPs with a complex pattern of micro-nutrient is generally reported as a strategy to increase crop nutrition of microelements (Canellas et al., 2015). In summary, artificial H-LPs as a biological biostimulants enhance crop growth and nutrient uptake.

Crop disease resistance

Soil-borne diseases caused by multiple pathogens pose a huge threat to crop growth and eco-environmental health (Delgado-Baquerizo et al., 2020). Oxygen-containing groups in the molecular structures of artificial H-LPs can enhance the antioxidant properties of crops. For example, the phenolic group is capable of scavenging radicals to terminate the radical chain reactions, which resists the degradation caused by the free radicals (Yang et al., 2021). Carboxyl provides antioxidant and anti-inflammatory properties because of its available deprotonation (Guo et al., 2019). Quinone is liable for the generation of ROS with appropriate level, which is beneficial for the healing of crop wounds (Ahmad et al., 2021). In addition, artificial H-LPs induce the synthesis of resistant proteins in crops, such as chitinase and peroxidase, and may also increase the content of certain vitamins, and these antioxidants play a significant role in the plant's defense mechanism against pathogens (Renuka et al., 2018). A previous report by Yoon et al. (2020) disclosed that the specific aromatic structures of O/C and H/C ratios ranging from 0.2 to 0.4 and 0.5 to 1.0 in artificial H-LPs, stimulated the plant to make stress resistance responses against pathogens, which could be indicated from the controlled stability of resistant protein PR-1 in *Arabidopsis thaliana*.

ENVIRONMENTAL AND AGRICULTURAL BENEFITS

HSs are mainly extracted from nature by chemical processes, easily leading to resource shortage. Exolaccase can boost humification of various phenolic pollutants and thus contribute to generating useful copolymeric precipitates with C–C, C–O–C, and/or C–N–C covalent binding (Chen et al., 2019; Liu et al., 2021a; Sun et al., 2022). These artificial H-LPs have stable chemical structures and various biological functions (Yang et al., 2021). In terms of eco-environmental remediation, exolaccase-initiated radical coupling reactions effectively avoid the ecological risks of the parent compounds (Li et al., 2022b). In the direction of agricultural production, the generated artificial H-LPs are highly similar to natural HSs, they play an important role in maintaining the structure and function in the pedospheric and biospheric zones and regulating the material and energy cycles of the agro-ecosystems (Yang et al., 2021). These conform to the requirements of developing green agriculture with both quantity and quality.

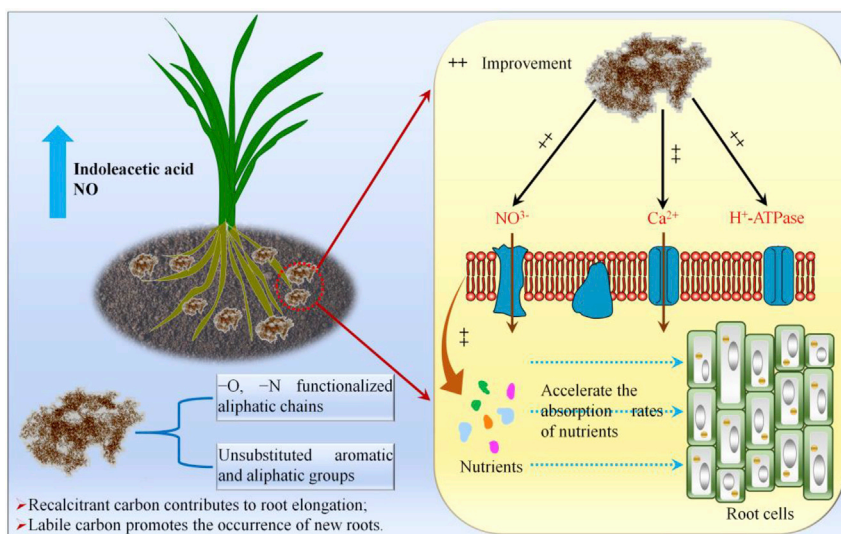


Figure 8. The roles of artificial H-LPs in crop growth

Artificial H-LPs are able to promote plant growth and improve crop productivity by several different mechanisms.

Converting incompact artificial H-LPs into granular fertilizers for storage and utilization can alleviate the pressure on agricultural production because of its advantages of convenient loading, transportation, and fertilization (Vejan et al., 2021). One of the most important benefits of granulation is that makes granular fertilizers drier and prolongs their effective period (Agyin-Birikorang et al., 2018). In agriculture, mechanical side-deep fertilization is an important part of the growth process of farmland crops. As exhibited in Figure 9, it breaks plough pan and thus increases nutrient availability. In addition, mechanical side-deep fertilizing technology also can improve agricultural yield, save labor input, promote sustainable agricultural development, and further create conditions for the liberation of agricultural productivity (Zhong et al., 2021). For example, Min et al. (2021) found that mechanical side-deep fertilization increased the utilization efficiency of agronomic nitrogen by 30% and saved 26% of fertilizer input while ensuring that rice yield is unchanged. Compared with time-consuming and energy-consuming artificial fertilization, the mechanical side-deep fertilization of humic-like granular fertilizers is undoubtedly a better pathway to apply for crop rhizosphere. It follows that exolaccase-boosted humification has great benefits for environmental remediation and agricultural production.

CHALLENGES AND PERSPECTIVES

Natural HSs play a crucial role in sustaining soil health and crop productivity but their supply is insufficient (Yang et al., 2021). Marked interests in eco-friendly soil fertilization have caused great concern in agriculture. Exolaccase is honored as “green catalyst” in the biosphere for phenolic copolymerization and humic-like formation (Li et al., 2022b; Sun et al., 2022). Although exolaccase-boosted humification exhibits a great potential in environmental remediation and agricultural production, there still remain several challenges:

- (1) The stability of exolaccase in the complicated environments is one of the critical issues. To maintain the stability of exolaccase, a well-designed immobilization strategy needs to be established (Ren et al., 2019). The entrapment and crosslinking-immobilized exolaccase is endowed with excellent stability and catalytic activity, which enhances exolaccase-started humification (Sun et al., 2021a). In addition, it is also necessary to modulate the abundances of laccase-producing microbes for the generation of exolaccase *in situ* (Li et al., 2022b).
- (2) In exolaccase-boosted humification, processing conditions impact the chemical structures of artificial H-LPs. Artificial H-LPs with different chemical structures can be formed depending on the reactor conditions such as specific agitation and pressure (Mogharabi and Faramarzi, 2014; Su et al., 2019). Hence, efforts are required for the optimization of processing conditions to improve the productivity and quality of artificial H-LPs.

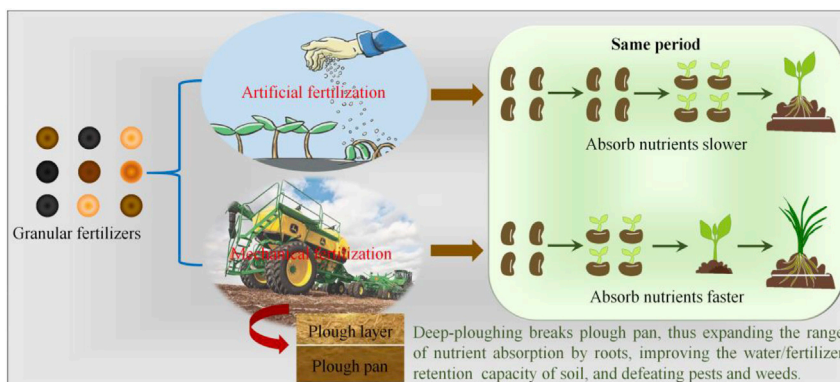


Figure 9. Mechanical side-deep fertilization of artificial H-LPs to break plough pan, increase nutrient availability, and enhance crop productivity

Mechanical side-deep fertilization is beneficial to improve agricultural yield, save labor input, promote sustainable agricultural development, and further create conditions for the liberation of agricultural productivity.

- (3) The interaction mechanisms of artificial H-LPs and crop-soil-microbe should be further clarified. Rhizosphere is considered as a hotspot for the interactions between artificial H-LPs and crop-soil-microbe (Puglisi et al., 2013). In this regard, uncovering the biochemical functions of artificial H-LPs that can provide a more detailed theoretical basis to develop their new application values in sustainable agricultural contest.

Conclusions

In this review, we present a new insight into exolaccase-boosted humification for agricultural applications. Immobilization technology enhances the stability and reusability of exolaccase, which is conducive to the formation and copolymerization of phenolic radicals through C–C, C–O–C, and/or C–N–C covalent binding mechanism. Such processes not only alleviate the genotoxicity of phenolic pollutants but also boost the generation of humified products. It is noted that these macromolecular products have a large number of phenolic hydroxyl, carboxyl, quinonyl, and aromatic groups, with high similarity to natural HSs. Consequently, they may be exploited as artificial H-LPs in the rhizosphere to ameliorate soil quality, promote crop growth, increase microbial diversity, and regulate the global carbon cycle. Even so, the current application of exolaccase-boosted humification and copolymerization in agriculture still needs to be cautious. In addition, it is also urgent for investigators to enhance the productivity and quality of artificial H-LPs by exolaccase-started humification and to illustrate in detail the interaction mechanisms of H-LPs and crop-soil-microbe. In summary, our review concisely delineates exolaccase-boosted humification and its potential applications in sustainable agriculture that will be a milestone for further study in this field.

LIMITATIONS OF THE STUDY

Authors did not notice any limitation of the study because no experiment was conducted.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (41907314) and the Natural Science Research Project of Education Department of Anhui Province (KJ2021A0136 and KJ2021A0083). We are grateful to Dr. Abdul Latif for polishing the English expressions in this paper.

AUTHOR CONTRIBUTIONS

H.C.: Original draft preparation, figure and table conceptualization. S.L.: Original draft preparation, figure and table conceptualization, funding acquisition. K.S.: Conceptualization, original draft preparation, figure and table conceptualization, review and editing, funding acquisition, supervision. Y.S.: Review. Y.G.: Review. All authors contributed to critically revising the manuscript and gave final approval for publication.

DECLARATION OF INTERESTS

The authors declare no competing financial interest.

REFERENCES

- Adeogun, A.O., Ibor, O.R., Chukwuka, A.V., Regoli, F., and Arukwe, A. (2019). The intersex phenomenon in *Sarotherodon melanotheron* from Lagos lagoon (Nigeria): occurrence and severity in relation to contaminants burden in sediment. *Environ. Pollut.* 244, 747–756.
- Agyin-Birikorang, S., Winings, J.H., Yin, X., Singh, U., and Sanabria, J. (2018). Field evaluation of agronomic effectiveness of multi-nutrient fertilizer briquettes for upland crop production. *Nutr. Cycl. Agroecosys.* 110, 395–406.
- Ahmad, U.M., Ji, N., Li, H., Wu, Q., Song, C., Liu, Q., Ma, D., and Lu, X. (2021). Can lignin be transformed into agrochemicals? Recent advances in the agricultural applications of lignin. *Ind. Crops Prod.* 170, 113646.
- Al-Ansari, M.M., Li, Z., Masood, A., and Rajaselvam, J. (2022). Decolourization of azo dye using a batch bioreactor by an indigenous bacterium *Enterobacter aerogenes* ES014 from the waste water dye effluent and toxicity analysis. *Environ. Res.* 205, 112189.
- Alengebawy, A., Abdelkhalik, S.T., Qureshi, S.R., and Wang, M.Q. (2021). Heavy metals and pesticides toxicity in agricultural soil and plants: ecological risks and human health implications. *Toxics* 9, 42.
- Baveye, P.C., and Wander, M. (2019). The (bio) chemistry of soil humus and humic substances: why is the “new view” still considered novel after more than 80 years? *Front. Environ. Sci.* 7, 27.
- Bernstein, N., Gorelick, J., Zerahia, R., and Koch, S. (2019). Impact of N, P, K, and humic acid supplementation on the chemical profile of medical cannabis (*Cannabis sativa* L.). *Front. Plant Sci.* 10, 736.
- Canellas, L.P., Olivares, F.L., Aguiar, N.O., Jones, D.L., Nebbioso, A., Mazzei, P., and Piccolo, A. (2015). Humic and fulvic acids as biostimulants in horticulture. *Sci. Hortic.* 196, 15–27.
- Cao, P., Liu, H., Wu, D., and Wang, X. (2021). Immobilization of laccase on phase-change microcapsules as self-thermoregulatory enzyme carrier for biocatalytic enhancement. *Chem. Eng. J.* 405, 126695.
- Catherine, H., Penninckx, M., and Frédéric, D. (2016). Product formation from phenolic compounds removal by laccases: a review. *Environ. Technol. Innov.* 5, 250–266.
- Cha, J.Y., Kim, T.W., Choi, J.H., Jang, K.S., Khaleda, L., Kim, W.Y., and Jeon, J.R. (2017). Fungal laccase-catalyzed oxidation of naturally occurring phenols for enhanced germination and salt tolerance of *Arabidopsis thaliana*: a green route for synthesizing humic-like fertilizers. *J. Agric. Food Chem.* 65, 1167–1177.
- Chae, Y., Kim, L., Kim, D., Cui, R., Lee, J., and An, Y.J. (2020). Deriving hazardous concentrations of phenol in soil ecosystems using a species sensitivity distribution approach. *J. Hazard Mater.* 399, 123036.
- Chen, M., Waigi, M.G., Li, S., Sun, K., and Si, Y. (2019). Fungal laccase-mediated humification of estrogens in aquatic ecosystems. *Water Res.* 166, 115040.
- Cheng, N., Wang, B., Wu, P., Lee, X., Xing, Y., Chen, M., and Gao, B. (2021). Adsorption of emerging contaminants from water and wastewater by modified biochar: a review. *Environ. Pollut.* 273, 116448.
- da Silva, L.S., Constantino, I.C., Bento, L.R., Tadini, A.M., Bisinoti, M.C., Boscolo, M., Ferreira, O.P., Mounier, S., Piccolo, A., Spaccini, R., et al. (2020). Humic extracts from hydrochar and Amazonian Anthrosol: molecular features and metal binding properties using EEM-PARAFAC and 2D FTIR correlation analyses. *Chemosphere* 256, 127110.
- Daronch, N.A., Kelbert, M., Pereira, C.S., de Araújo, P.H.H., and de Oliveira, D. (2020). Elucidating the choice for a precise matrix for laccase immobilization: a review. *Chem. Eng. J.* 397, 125506.
- De Hita, D., Fuentes, M., Fernández, V., Zamarreño, A.M., Olaetxea, M., and García-Mina, J.M. (2020). Discriminating the short-term action of root and foliar application of humic acids on plant growth: emerging role of jasmonic acid. *Front. Plant Sci.* 11, 493.
- Dehsheikh, A.B., Mahmoodi Sourestani, M., Zolfaghari, M., and Enayatzamir, N. (2020). Changes in soil microbial activity, essential oil quantity, and quality of Thai basil as response to biofertilizers and humic acid. *J. Clean. Prod.* 256, 120439.
- Delgado-Baquerizo, M., Guerra, C.A., Cano-Díaz, C., Egidi, E., Wang, J.T., Eisenhauer, N., Singh, B.K., and Maestre, F.T. (2020). The proportion of soil-borne pathogens increases with warming at the global scale. *Nat. Clim. Chang.* 10, 550–554.
- Dou, J., Lin, P., Kuang, B.Y., and Yu, J.Z. (2015). Reactive oxygen species production mediated by humic-like substances in atmospheric aerosols: enhancement effects by pyridine, imidazole, and their derivatives. *Environ. Sci. Technol.* 49, 6457–6465.
- Farran, R., Mekmouche, Y., Vo, N.T., Herrero, C., Quaranta, A., Sircoglou, M., Banse, F., Rousselot-Pailley, P., Simaan, A.J., Aukaloo, A., et al. (2021). Tracking light-induced electron transfer toward O₂ in a hybrid photoredox-laccase system. *iScience* 24, 102378.
- Fernandez-Fernandez, M., Sanromán, M.Á., and Moldes, D. (2013). Recent developments and applications of immobilized laccase. *Biotechnol. Adv.* 31, 1808–1825.
- Ferrera, Z.S., Sanz, C.P., Santana, C.M., and Rodriguez, J.J.S. (2004). The use of micellar systems in the extraction and pre-concentration of organic pollutants in environmental samples. *TrAC, Trends Anal. Chem.* 23, 469–479.
- García, A.C., van Tol de Castro, T.A., Santos, L.A., Tavares, O.C.H., Castro, R.N., Barbara, R.L.L., and García-Mina, J.M. (2019). Structure-property-function relationship of humic substances in modulating the root growth of plants: a review. *J. Environ. Qual.* 48, 1622–1632.
- Glover, C.M., Liu, Y., and Liu, J. (2021). Assessing the risk from trace organic contaminants released via greywater irrigation to the aquatic environment. *Water Res.* 205, 117664.
- Guillaume, T., Bragazza, L., Levasseur, C., Libohova, Z., and Sinaj, S. (2021). Long-term soil organic carbon dynamics in temperate cropland-grassland systems. *Agric. Ecosyst. Environ.* 305, 107184.
- Guo, X., Liu, H.T., and Wu, S.B. (2019). Humic substances developed during organic waste composting: formation mechanisms, structural properties, and agronomic functions. *Sci. Total Environ.* 662, 501–510.
- Hodges, B.C., Cates, E.L., and Kim, J.H. (2018). Challenges and prospects of advanced oxidation water treatment processes using catalytic nanomaterials. *Nat. Nanotechnol.* 13, 642–650.
- Jeong, H.J., Cha, J.Y., Choi, J.H., Jang, K.S., Lim, J., Kim, W.Y., Seo, D.C., and Jeon, J.R. (2018). One-pot transformation of technical lignins into humic-like plant stimulants through fenton-based advanced oxidation: accelerating natural fungus-driven humification. *ACS Omega* 3, 7441–7453.
- Kanaujiya, D.K., Paul, T., Sinharoy, A., and Pakshirajan, K. (2019). Biological treatment processes for the removal of organic micropollutants from wastewater: a review. *Curr. Pollut. Rep.* 5, 112–128.
- Kucharzyk, K.H., Benotti, M., Darlington, R., and Lalgudi, R. (2018). Enhanced biodegradation of sediment-bound heavily weathered crude oil with ligninolytic enzymes encapsulated in calcium-alginate beads. *J. Hazard Mater.* 357, 498–505.
- Lal, R., Negassa, W., and Lorenz, K. (2015). Carbon sequestration in soil. *Curr. Opin. Environ. Sustain.* 15, 79–86.
- Lan, Y., Du, Q., Tang, C., Cheng, K., and Yang, F. (2021). Application of typical artificial carbon materials from biomass in environmental remediation and improvement: a review. *J. Environ. Manage.* 296, 113340.
- Lee, J.G., Yoon, H.Y., Cha, J.Y., Kim, W.Y., Kim, P.J., and Jeon, J.R. (2019). Artificial humification of lignin architecture: top-down and bottom-up approaches. *Biotechnol. Adv.* 37, 107416.
- Li, H., Santos, F., Butler, K., and Herndon, E. (2021). A critical review on the multiple roles of manganese in stabilizing and destabilizing soil organic matter. *Environ. Sci. Technol.* 55, 12136–12152.
- Li, S., Hong, D., Chen, W., Wang, J., and Sun, K. (2022a). Extracellular laccase-activated humification of phenolic pollutants and its application in plant growth. *Sci. Total Environ.* 802, 150005.
- Li, S., Sun, K., Latif, A., Si, Y., Gao, Y., and Huang, Q. (2022b). Insights into the applications of extracellular laccase-aided humification in livestock manure composting. *Environ. Sci. Technol.* 56, 7412–7425.
- Lipczynska-Kochany, E. (2018). Humic substances, their microbial interactions and effects on biological transformations of organic pollutants in water and soil: a review. *Chemosphere* 202, 420–437.

- Liu, J., and Diamond, J. (2005). China's environment in a globalizing world. *Nature* 435, 1179–1186.
- Liu, Q., Liu, J., Hong, D., Sun, K., Li, S., Latif, A., Si, X., and Si, Y. (2021a). Fungal laccase-triggered 17 β -estradiol humification kinetics and mechanisms in the presence of humic precursors. *J. Hazard Mater.* 412, 125197.
- Liu, Y., Wu, T., White, J.C., and Lin, D. (2021b). A new strategy using nanoscale zero-valent iron to simultaneously promote remediation and safe crop production in contaminated soil. *Nat. Nanotechnol.* 16, 197–205.
- Lu, Y., Jenkins, A., Ferrier, R.C., Bailey, M., Gordon, I.J., Song, S., Huang, J., Jia, S., Zhang, F., Liu, X., et al. (2015). Addressing China's grand challenge of achieving food security while ensuring environmental sustainability. *Sci. Adv.* 1, e1400039.
- Martínez-Huitle, C.A., Rodrigo, M.A., Sirés, I., and Scialdone, O. (2015). Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review. *Chem. Rev.* 115, 13362–13407.
- Mei, Q., Sun, J., Han, D., Wei, B., An, Z., Wang, X., Xie, J., Zhan, J., and He, M. (2019). Sulfate and hydroxyl radicals-initiated degradation reaction on phenolic contaminants in the aqueous phase: mechanisms, kinetics and toxicity assessment. *Chem. Eng. J.* 373, 668–676.
- Meng, Q., Wang, S., Niu, Q., Yan, H., Li, G., Zhu, Q., and Li, Q. (2021). Illite/smectite clay regulating laccase encoded genes to boost lignin decomposition and humus formation in composting habitats revealed by metagenomics analysis. *Bioresour. Technol.* 338, 125546.
- Min, D.W., Kim, K., Lui, K.H., Kim, B., Kim, S., Cho, J., and Choi, W. (2019). Abiotic formation of humic-like substances through freezing-accelerated reaction of phenolic compounds and nitrite. *Environ. Sci. Technol.* 53, 7410–7418.
- Min, J., Sun, H., Wang, Y., Pan, Y., Kronzucker, H.J., Zhao, D., and Shi, W. (2021). Mechanical side-deep fertilization mitigates ammonia volatilization and nitrogen runoff and increases profitability in rice production independent of fertilizer type and split ratio. *J. Clean. Prod.* 316, 128370.
- Mogharabi, M., and Faramarzi, M.A. (2014). Laccase and laccase-mediated systems in the synthesis of organic compounds. *Adv. Synth. Catal.* 356, 897–927.
- Morsi, R., Bilal, M., Iqbal, H.M.N., and Ashraf, S.S. (2020). Laccases and peroxidases: the smart, greener and futuristic biocatalytic tools to mitigate recalcitrant emerging pollutants. *Sci. Total Environ.* 714, 136572.
- Nardi, S., Pizzeghello, D., Schiavon, M., and Ertani, A. (2016). Plant biostimulants: physiological responses induced by protein hydrolyzed-based products and humic substances in plant metabolism. *Sci. Agric.* 73, 18–23.
- Nardi, S., Schiavon, M., and Francioso, O. (2021). Chemical structure and biological activity of humic substances define their role as plant growth promoters. *Molecules* 26, 2256.
- Niu, Q., Meng, Q., Yang, H., Wang, Y., Li, X., Li, G., and Li, Q. (2021). Humification process and mechanisms investigated by Fenton-like reaction and laccase functional expression during composting. *Bioresour. Technol.* 341, 125906.
- Olaetxea, M., De Hita, D., Garcia, C.A., Fuentes, M., Baigorri, R., Mora, V., Garnica, M., Urrutia, O., Erro, J., Zamarreño, A.M., et al. (2018). Hypothetical framework integrating the main mechanisms involved in the promoting action of rhizospheric humic substances on plant root- and shoot-growth. *Appl. Soil Ecol.* 123, 521–537.
- Othmani, A., Magdoui, S., Senthil Kumar, P., Kapoor, A., Chellam, P.V., and Gökkuş, Ö. (2022). Agricultural waste materials for adsorptive removal of phenols, chromium (VI) and cadmium (II) from wastewater: a review. *Environ. Res.* 204, 111916.
- Patidar, R., and Srivastava, V.C. (2022). Ultrasound-assisted electrochemical treatment of cosmetic industry wastewater: mechanistic and detoxification analysis. *J. Hazard Mater.* 422, 126842.
- Paul, D., Pandey, G., Pandey, J., and Jain, R.K. (2005). Accessing microbial diversity for bioremediation and environmental restoration. *Trends Biotechnol.* 23, 135–142.
- Petrychenko, V., Korniychuk, O., and Voronetska, I. (2018). Biological farming in conditions of transformational changes in the agrarian production of Ukraine. *Agric. Sci. Pract.* 5, 3–12.
- Philippe, A., and Schaumann, G.E. (2014). Interactions of dissolved organic matter with natural and engineered inorganic colloids: a review. *Environ. Sci. Technol.* 48, 8946–8962.
- Puglisi, E., Pascazio, S., Suci, N., Cattani, I., Fait, G., Spaccini, R., Crecchio, C., Piccolo, A., and Trevisan, M. (2013). Rhizosphere microbial diversity as influenced by humic substance amendments and chemical composition of rhizodeposits. *J. Geochem. Explor.* 129, 82–94.
- Pukalchik, M., Kydraliev, K., Yakimenko, O., Fedoseeva, E., and Terekhova, V. (2019). Outlining the potential role of humic products in modifying biological properties of the soil-A review. *Front. Environ. Sci.* 7, 80.
- Qi, G., Yue, D., Fukushima, M., Fukuchi, S., and Nie, Y. (2012). Enhanced humification by carbonated basic oxygen furnace steel slag-I. Characterization of humic-like acids produced from humic precursors. *Bioresour. Technol.* 104, 497–502.
- Ren, S., Li, C., Jiao, X., Jia, S., Jiang, Y., Bilal, M., and Cui, J. (2019). Recent progress in multienzymes co-immobilization and multienzyme system applications. *Chem. Eng. J.* 373, 1254–1278.
- Renuka, N., Guldhe, A., Prasanna, R., Singh, P., and Bux, F. (2018). Microalgae as multi-functional options in modern agriculture: current trends, prospects and challenges. *Biotechnol. Adv.* 36, 1255–1273.
- Saleem, H., Rehman, K., Arslan, M., and Afzal, M. (2018). Enhanced degradation of phenol in floating treatment wetlands by plant-bacterial synergism. *Int. J. Phytoremediation* 20, 692–698.
- Sannigrahi, P., Sullivan, A.P., Weber, R.J., and Ingall, E.D. (2006). Characterization of water-soluble organic carbon in urban atmospheric aerosols using solid-state ¹³C NMR spectroscopy. *Environ. Sci. Technol.* 40, 666–672.
- Shah, Z.H., Rehman, H.M., Akhtar, T., Alsamadany, H., Hamooh, B.T., Mujtaba, T., Daur, I., Al Zahrani, Y., Alzaharani, H.A.S., Ali, S., et al. (2018). Humic substances: Determining potential molecular regulatory processes in plants. *Front. Plant Sci.* 9, 263.
- Singh, A.K., Bilal, M., Iqbal, H.M.N., and Raj, A. (2021). Trends in predictive biodegradation for sustainable mitigation of environmental pollutants: recent progress and future outlook. *Sci. Total Environ.* 770, 144561.
- Soria, R., González-Pérez, J.A., de la Rosa, J.M., San Emeterio, L.M., Domene, M.A., Ortega, R., and Miralles, I. (2022). Effects of technosols based on organic amendments addition for the recovery of the functionality of degraded quarry soils under semiarid Mediterranean climate: a field study. *Sci. Total Environ.* 816, 151572.
- Su, J., Fu, J., Silva, C., and Cavaco-Paulo, A. (2019). Can laccase-assisted processing conditions influence the structure of the reaction products? *Trends Biotechnol.* 37, 683–686.
- Sun, K., Hong, D., Liu, J., Latif, A., Li, S., Chu, G., Qin, W., and Si, Y. (2021a). *Trametes versicolor* laccase-assisted oxidative coupling of estrogens: conversion kinetics, linking mechanisms, and practical applications in water purification. *Sci. Total Environ.* 782, 146917.
- Sun, K., Li, S., Si, Y., and Huang, Q. (2021b). Advances in laccase-triggered anabolism for biotechnology applications. *Crit. Rev. Biotechnol.* 41, 969–993.
- Sun, K., Liu, Q., Liu, J., Li, S., Qi, X., Chen, M., Si, Y., and Gao, Y. (2022). New insights into humic acid-boosted conversion of bisphenol A by laccase-activated co-polyreaction: kinetics, products, and phytotoxicity. *J. Hazard Mater.* 436, 129269.
- Sun, K., Luo, Q., Gao, Y., and Huang, Q. (2016). Laccase-catalyzed reactions of 17 β -estradiol in the presence of humic acid: resolved by high-resolution mass spectrometry in combination with ¹³C labeling. *Chemosphere* 145, 394–401.
- Tang, C., Li, Y., Song, J., Antonietti, M., and Yang, F. (2021). Artificial humic substances improve microbial activity for binding CO₂. *iScience* 24, 102647.
- Tang, C., Yang, F., and Antonietti, M. (2022). Carbon materials advancing microorganisms in driving soil organic carbon regulation. *Research* 2022, 9857374.
- Van Oost, K., Quine, T.A., Govers, G., De Gryze, S., Six, J., Harden, J.W., Ritchie, J.C., McCarty, G.W., Heckrath, G., Kosmas, C., et al. (2007). The impact of agricultural soil erosion on the global carbon cycle. *Science* 318, 626–629.
- Vejan, P., Khadiran, T., Abdullah, R., and Ahmad, N. (2021). Controlled release fertilizer: a review on developments, applications and potential in agriculture. *J. Control Release.* 339, 321–334.

- Viggor, S., Jöesaar, M., Soares-Castro, P., Ilmjärv, T., Santos, P.M., Kapley, A., and Kivisaar, M. (2020). Microbial metabolic potential of phenol degradation in wastewater treatment plant of crude oil refinery: analysis of metagenomes and characterization of isolates. *Microorganisms* 8, 652.
- Villain-Gambier, M., Bourven, I., Guibaud, G., and Marrot, B. (2019). Influence of proteins and humic-like substances from soluble microbial products on membrane bioreactor fouling under normal and stress conditions. *Process Biochem.* 78, 140–147.
- Wang, S., Wang, Y., He, X., and Lu, Q. (2022). Degradation or humification: rethinking strategies to attenuate organic pollutants. *Trends Biotechnol.* <https://doi.org/10.1016/j.tibtech.2022.02.007>.
- Wang, X., Muhmood, A., Dong, R., and Wu, S. (2020). Synthesis of humic-like acid from biomass pretreatment liquor: quantitative appraisal of electron transferring capacity and metal-binding potential. *J. Clean. Prod.* 255, 120243.
- Wei, Z., Ahmed Mohamed, T., Zhao, L., Zhu, Z., Zhao, Y., and Wu, J. (2021). Microhabitat drive microbial anabolism to promote carbon sequestration during composting. *Bioresour. Technol.* 346, 126577.
- Wesenberg, D., Kyriakides, I., and Agathos, S.N. (2003). White-rot fungi and their enzymes for the treatment of industrial dye effluents. *Biotechnol. Adv.* 22, 161–187.
- Wu, J., Wang, T., Wang, J., Zhang, Y., and Pan, W.P. (2021). A novel modified method for the efficient removal of Pb and Cd from wastewater by biochar: enhanced the ion exchange and precipitation capacity. *Sci. Total Environ.* 754, 142150.
- Wu, X., Liu, J., Liu, Z., Gong, G., and Zha, J. (2022). Microbial cell surface engineering for high-level synthesis of bio-products. *Biotechnol. Adv.* 55, 107912.
- Yakimenko, O., Stepanov, A., Patsaeva, S., Khundzhua, D., Osipova, O., and Gladkov, O. (2021). Formation of humic-like substances during the technological process of lignohumate® synthesis as a function of time. *Separations* 8, 96.
- Yang, F., and Antonietti, M. (2020a). Artificial humic acids: sustainable materials against climate change. *Adv. Sci.* 7, 1902992.
- Yang, F., and Antonietti, M. (2020b). The sleeping giant: a polymer view on humic matter in synthesis and applications. *Prog. Polym. Sci.* 100, 101182.
- Yang, F., Tang, C., and Antonietti, M. (2021). Natural and artificial humic substances to manage minerals, ions, water, and soil microorganisms. *Chem. Soc. Rev.* 50, 6221–6239.
- Yang, F., Zhang, S., Cheng, K., and Antonietti, M. (2019). A hydrothermal process to turn waste biomass into artificial fulvic and humic acids for soil remediation. *Sci. Total Environ.* 686, 1140–1151.
- Yang, T., and Hodson, M.E. (2018). Investigating the potential of synthetic humic-like acid to remove metal ions from contaminated water. *Sci. Total Environ.* 635, 1036–1046.
- Yoon, H.Y., Jeong, H.J., Cha, J.Y., Choi, M., Jang, K.S., Kim, W.Y., Kim, M.G., and Jeon, J.R. (2020). Structural variation of humic-like substances and its impact on plant stimulation: implication for structure-function relationship of soil organic matters. *Sci. Total Environ.* 725, 138409.
- Zhang, T., Wu, X., Shaheen, S.M., Rinklebe, J., Bolan, N.S., Ali, E.F., Li, G., and Tsang, D.C.W. (2021). Effects of microorganism-mediated inoculants on humification processes and phosphorus dynamics during the aerobic composting of swine manure. *J. Hazard Mater.* 416, 125738.
- Zhang, Z., Zhao, Y., Yang, T., Wei, Z., Li, Y., Wei, Y., Chen, X., and Wang, L. (2019). Effects of exogenous protein-like precursors on humification process during lignocellulose-like biomass composting: amino acids as the key linker to promote humification process. *Bioresour. Technol.* 291, 121882.
- Zhong, W., Wang, D., and Wang, Z. (2018). Distribution and potential ecological risk of 50 phenolic compounds in three rivers in Tianjin, China. *Environ. Pollut.* 235, 121–128.
- Zhong, X., Peng, J., Kang, X., Wu, Y., Luo, G., Hu, W., and Zhou, X. (2021). Optimizing agronomic traits and increasing economic returns of machine-transplanted rice with side-deep fertilization of double-cropping rice system in southern China. *Field Crops Res.* 270, 108191.
- Zhou, W., Zhang, W., and Cai, Y. (2021). Laccase immobilization for water purification: a comprehensive review. *Chem. Eng. J.* 403, 126272.
- Zhou, X., Li, J., Zhang, J., Deng, F., Chen, Y., Zhou, P., and Li, D. (2022). Bioaugmentation mechanism on humic acid formation during composting of food waste. *Sci. Total Environ.* 830, 154783.
- Zhu, N., Zhu, Y., Liang, D., Li, B., Jin, H., and Dong, Y. (2021). Enhanced turnover of phenolic precursors by *Gloeophyllum trabeum* pretreatment promotes humic substance formation during co-composting of pig manure and wheat straw. *J. Clean. Prod.* 315, 128211.
- Zou, J., Huang, J., Zhang, H., and Yue, D. (2021). Evolution of humic substances in polymerization of polyphenol and amino acid based on non-destructive characterization. *Front. Environ. Sci. Eng.* 15, 5.