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Review

# Biotic and abiotic catalysts for enhanced humification in composting: A comprehensive review

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ABSTRACT

Humification is an environmentally important process that converts organic matter and/or pollutants into structurally refractory substances through various catalytic mechanisms. Humification is a major carbon sequestration strategy that can be enhanced using many biotic and abiotic catalysts. With the application of catalysts during composting, the content of humic substances can increase by more than 100% compared to control samples. Despite growing interest, there is a lack of comprehensive reviews of the different humification pathways driven by adding various types of catalysts. In this review, we consulted recent literature to compare catalysts with respect to their humification potentials, pathways, products, and operating conditions. We critically evaluated the advantages and limitations of individual catalysts to elucidate gaps in current knowledge and future research directions. In general, biotic catalysts show higher performance compared to metal oxides, whereas abiotic catalysts can be produced at a lower cost. Among the biotic catalysts, laccase is particularly attractive due to its eco-friendliness and high performance. Among abiotic catalysts, $MnO_2$ had the highest humification activity compared to other metal oxides, such as $Fe_2O_3$ or $Al_2O_3$, whereas clays with a 2:1-layered structure demonstrated higher potential than did those with a 1:1 structure. More research is recommended using advanced techniques to provide a more comprehensive comparison of catalyst performance. Finally, we have discussed the potential of novel catalysts to enhance humification.

## 1. Introduction

Many advanced techniques have been applied for the recycling of biomass, including anaerobic digestion, composting, pyrolysis, and hydrothermal technologies (Li et al., 2022a). Among these, composting is an inexpensive, practical, and safe strategy for recycling organic wastes, transforming biomass into stable forms, and eliminating the pathogens and micropollutants contained in waste (Li et al., 2022c). The major active ingredient in the composting process is organic matter (OM) (Li et al., 2022a). The fate of OM under composting conditions is determined by the interplay of the opposing but related processes of degradation and humification. The small molecules produced by degradation are the building blocks of humic substances (HS) generated via humification (Wang et al., 2022a). Humification can prevent carbon loss and greenhouse gas (GHG) emissions by converting the intermediate products of degradation into HS through various mechanisms. In addition, humification can stabilize potentially toxic elements (PTEs) and other pollutants (e.g., phenolic compounds and antibiotics) in HS (Chen et al., 2021). Therefore, humification, the final step of the composting process, is considered one of the most effective carbon sequestration strategies that enables simultaneous environmental remediation. However, composting and humification are slow and inefficient processes in the absence of suitable catalysts or additives (Guo et al., 2020), which promotes the complete degradation of OM, resulting in carbon and nitrogen losses and GHG emissions. The excessive emission of ammonia ($NH_3$) and GHGs (e.g., $CO_2$, $CH_4$, and $N_2O$) hampers the agronomic benefits of composting and creates secondary environmental problems (e.g., climate warming and ozone depletion) (Awasthi et al., 2016; Wang et al., 2018b). Therefore, the efficiency of humification requires further improvement.

Various types of biotic and abiotic catalysts have been proposed to

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**Abbreviations**

| | |
|---|---|
| HS | Humic Substances |
| OM | Organic Matter |
| GHG | Greenhouse Gas |
| HA | Humic Acid |
| FA | Fulvic Acid |
| AA | Amino Acid |

accelerate and enhance humification (Fig. 1). Several reviews have reported the characteristics and mechanisms of HS formation during the composting and artificial humification; however, a comprehensive understanding of the roles of different catalysts and their relative performance remains lacking (Table S1) (Lee et al., 2019; Li et al., 2022c; Wang et al., 2022a; Yang et al., 2021). Additionally, no previous review has compared the performance of biotically and abiotically catalyzed humification reactions. This review collates the recent scientific advances in catalyzed humification to provide a comprehensive characterization of the roles of catalysts in the enhancement of humification in composing and *in vitro* humification reactions. Specifically, we investigated the humification pathways and general roles of different catalysts and critically compared catalysts applied in the enhancement of humification reactions. Catalysts, classified into biotic (enzymes) and abiotic catalysts (metal oxides and clay minerals), were compared in terms of humification pathways, products, and operating conditions. Additionally, we investigated the potential applications of advanced catalysts for humification. Consequently, we provide insights into the future directions of this field of research.

## 2. Humification pathways and general roles of catalysts

### *2.1. Humification pathways in composting*

Humification occurs primarily during the cooling and maturation phases of composting (Zhang et al., 2019b). Biotic and abiotic catalysts, as external and artificial factors, can promote the humification process. HS are generated via a variety of pathways, including the Maillard, polyphenol, and integrated polyphenol-Maillard pathways (Fig. 2) (Wang et al., 2022a). These pathways participate in the formation of new chemical bonds and polymerization between HS precursors and may occur simultaneously and interact with each other (Wu et al., 2017b). Microbial chain elongation was recently identified as a new polymerization strategy (Joshi et al., 2021; Robles et al., 2021). In this route, short-chain and simple carboxylates, such as acetate and ethanol, are converted into long-chain carboxylates, such as hexanoate and octanoate. This process contributes to the formation of high molecular-weight HS and is considered an important step in the overall humification process (Joshi et al., 2021; Robles et al., 2021). Humification pathways are determined by the composition and structure of HS precursors, the production of which is closely related to bacterial activity (Gao et al., 2019; Wu et al., 2017b) as well as physical environmental parameters, such as temperature and moisture (Larionova et al., 2017; Li et al., 2021; Wang et al., 2022a). Conventional composting typically requires a long time to mature (up to 90–365 d) and high amount of energy to produce HS (Qi et al., 2012b). These combinations of factors contribute to the complexity of the humification process.

### *2.2. In vitro humification reactions and general roles of catalysts*

Unlike conventional composting, *in vitro* humification, where humification occurs without the participation of living organisms, offers many benefits, including fast turnaround times, minimal or no demand for controlled environmental conditions, and non-selectivity for source OM (Qi et al., 2012b). Several *in vitro* humification studies have demonstrated the independent roles of catalysts in composting. Among humification pathways (Fig. 2), the integrated polyphenol-Maillard reaction is the most comparable to those in natural systems (Zhang et al., 2021a). The precursors of *in vitro* humification are polyphenols, proteins, sugars, and amino acids (AAs) (Zhang et al., 2021b). Carbonyl-amine reactions that produce HS are one of the most commonly observed humification pathways (Hidalgo and Zamora, 2000). The kinetic rates and products of the humification reaction and the integrated polyphenol-Maillard pathway depend on the characteristics of the polyphenols (Liu and Huang, 2002). Polyphenols with *ortho*-OH or *para*-OH groups (e.g., pyrogallol) exhibit a greater propensity for direct electron transfer processes compared to polyphenols containing meta-OH groups (e.g., resorcinol). The latter are subject to more oxidative polymerization and ring cleavage reactions, which lead to the development of strongly aliphatic polymers (Bittner, 2006; Hardie et al., 2007). Additionally, depending on the functional groups of the phenolic compounds, dehalogenation, decarboxylation, or demethylation reactions can occur (Dec et al., 2003). For polyphenols and polyphenol-amine reactions, quinones, which are created by the oxidation of polyphenols and are highly unstable and reactive in an aqueous environment, quickly combine with the phenol, indole,

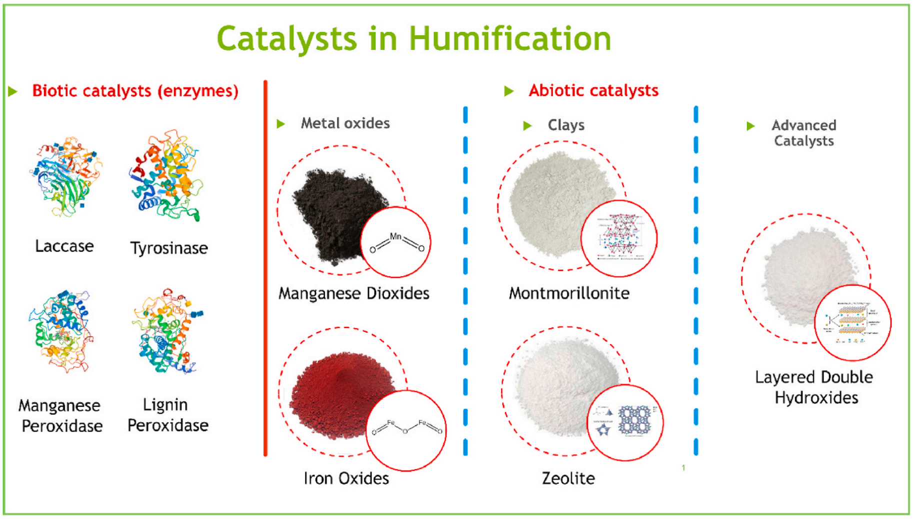


**Fig. 1.** Catalysts applied in humification.

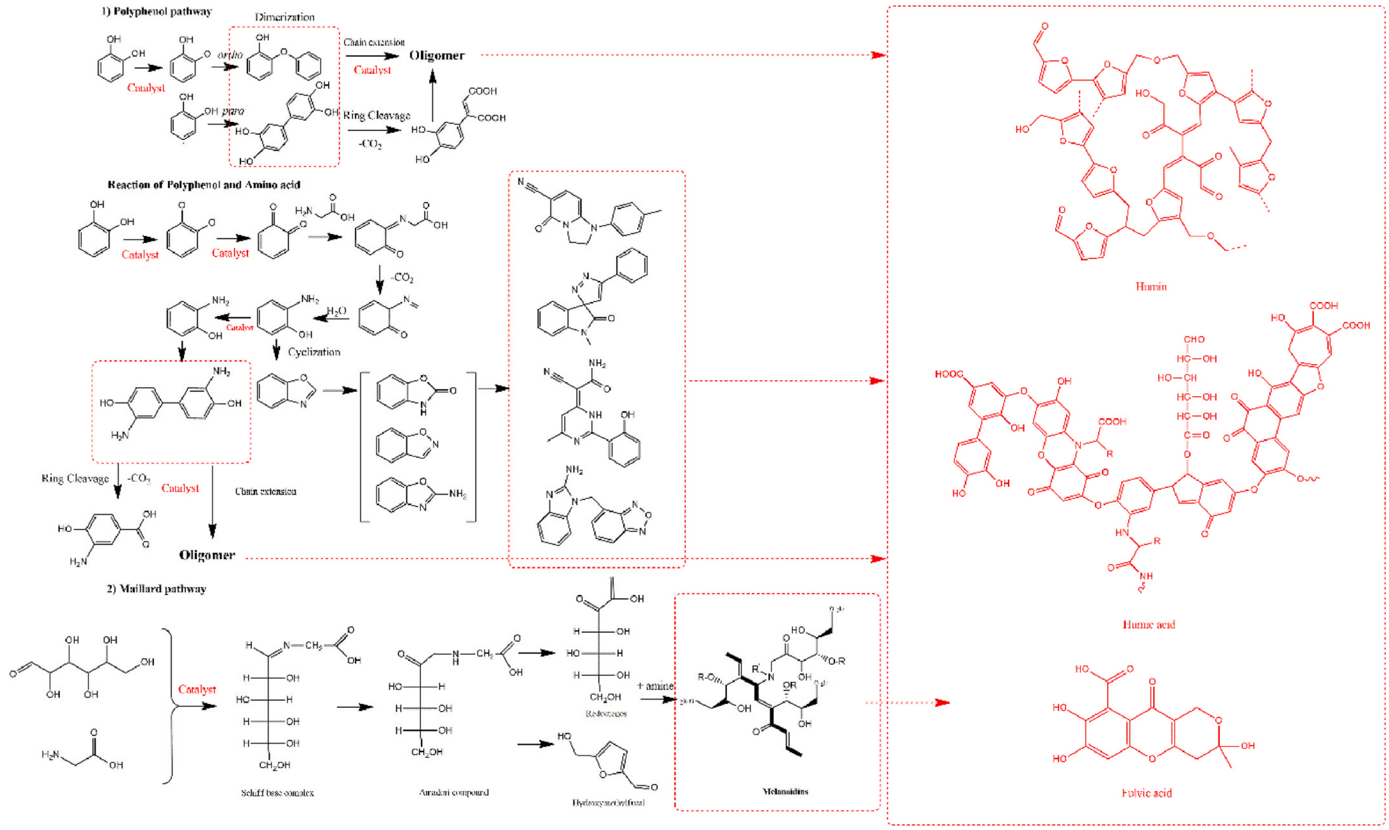


**Fig. 2.** Integrated polyphenol-Maillard humification reaction. Adapted from Zhang et al. (2021a).

sulfhydryl, amine, and/or imidazole of proteins, peptides, and AAs to generate brightly colored products (Bittner, 2006). To form HS, these colored products undergo a series of chain extension and ring cleavage reactions, which are partially illustrated in Fig. 2. The formation of quinone and condensation reactions are effectively enhanced with the addition of catalysts (Fig. 2). By serving as electron acceptors, the polyvalent metals, including Cu, Mn, and Fe, from diverse biotic and abiotic catalysts can accelerate the transformation of phenolic compounds (Hardie, 2008). The humification reaction is comparatively slow without catalysts. The Maillard reaction involves a condensation reaction between reducing sugars and amino acids (Fig. 2). Briefly, the reaction between the amine group of amino acids and carbonyl group of sugars forms Schiff's base compounds, which are continuously rearranged into Amadori compounds. Amadori compounds undergo retro-aldolization to form reductones under alkaline conditions or hydromethylfurfural under acidic conditions. In the presence of amino compounds, reductones and hydromethylfurfural are both highly reactive and readily polymerize to produce brown-colored melanoidins. The Maillard reaction is naturally slow at room temperature and can be enhanced with the assistance of catalysts, such as birnessite (Jokic et al., 2001b). In the presence of catalysts, sugars can be auto-oxidized and to generate dicarbonyl compounds, which are key components in the formation of melanoidins. Different analytical techniques (e.g., Fourier transform infrared, solid-state nuclear magnetic resonance [NMR], pyrolysis-gas chromatography/mass spectrometry, and elemental composition analysis) have revealed that artificial HS are similar to natural HS in terms of their structures and compositions (Yang et al., 2021). Techniques to produce artificial HS present a new opportunity for carbon sequestration of bio-labile OM and the controlled removal of organic contaminants, the effectiveness of which is largely reliant on the development of novel chemical linkages (Wang et al., 2022a).

## 3. Biotic catalysts (enzymes)

Several enzymes, including tyrosinase, peroxidase, and laccase, function as catalysts in humification (Kumar and Chandra, 2020; Su et al., 2018; Yoon et al., 2020). These enzymes are produced by a variety of bacteria, including *Citrobacter* sp., *Bacillus* sp., *Pseudomonas* sp., *Serratia marcescens*, and *Klebsiella pneumonia*, or fungi, including *Trametes versicolor*, *Ganoderma lucidum*, *Aspergillus nidulans*, and *Penicillium brefeldanum* (Kumar and Chandra, 2020). Enzymes facilitate the humification reaction by removing an electron from phenolic compounds to create a phenoxy free radical and reducing oxygen to water (Su et al., 2018). At their active sites, these enzymes have polyvalent metals, such as Cu, Fe, and Mn, which play key roles in accelerating the humification reaction.

### 3.1. Laccase

As part of the blue multi-copper oxidase family, laccase (EC 1.10.3.2) is found in a variety of fungi, including Ascomycetes, Basidiomycetes, and Deuteromycetes (Janusz et al., 2020). Besides the presence of polyvalent metals, the arrangement of active sites, where electrons are efficiently transferred, determine the activity of enzymes. One type-1 copper atom ($Cu_1$), one type-2 copper atom ($Cu_2$), and two type-3 copper atoms ($Cu_3$) are present in laccase (Fig. 3) (Su et al., 2018). The primary electron acceptor $Cu_1$ is abundant on the enzyme surface, where target substrates can be accommodated. After subtracting electrons from the substrate, the electrons are transferred to the remaining active sites ($Cu_2$ and $Cu_3$) via the His-Cys-His tripeptide, where $O_2$ is reduced to $H_2O$ (Su et al., 2018). The arrangement of active sites facilitates dioxygen binding, leading to the reduction of molecular oxygen (Giardina et al., 2009; Jeon et al., 2012). In addition to the decomposition of high-molecular-weight lignin, laccase can catalyze different HS precursors to polymerize stable HS, thereby increasing the humification

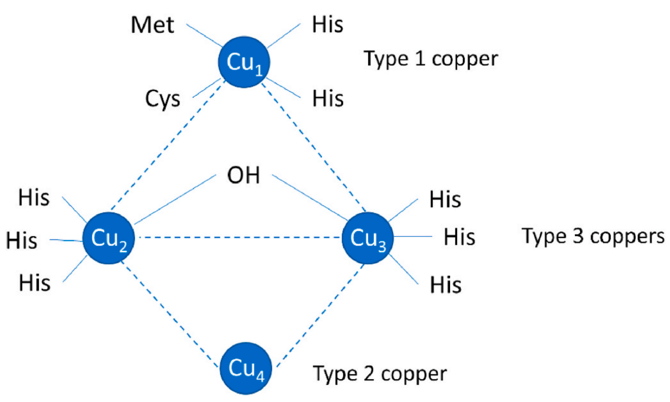


**Fig. 3.** Arrangement of active sites in laccase. Adapted from Su et al. (2018).

degree (Munk et al., 2015; Sun et al., 2020). Laccase activity was enhanced by the addition of $H_2O_2$, which can catalyze and break down lignocellulosic materials as a co-substrate of composting enzymes (e.g., manganese peroxidase, versatile peroxidase, lignin peroxidase, and lytic polysaccharide monooxygenases) (Bissaro et al., 2018; Levasseur et al., 2013). A previous study found that the amount of $H_2O_2$ initially increased and then decreased, implying the production of $H_2O_2$ and its consumption during the composition process (Niu et al., 2021). HS content and compost quality were higher in the presence of a Fenton-like reaction than that in the control. For example, amidic, aliphatic, quinonic, and aromatic compounds were more abundant with the addition of laccase and $H_2O_2$ (Niu et al., 2021).

Laccase participates in humification during composting via both direct and indirect pathways (Li et al., 2022c). In the direct route, fungal laccase can create unstable radical/quinone intermediates by promoting the one-electron transfer of a range of phenolic compounds at the T1-Cu site. These intermediates are automatically linked via different self-/co-polymerization pathways to produce a variety of hybrid polymers with limited bioavailability, biotoxicity, and solubility (Catherine et al., 2016). In the indirect pathway, enzymes convert appropriate mediators into unstable mediators that attack micropollutants (Li et al., 2022c). The enzymatic action of laccases relies on the properties of the micropollutants and environmental conditions (Li et al., 2022c). Fungal laccases have a higher redox potential ($E^o = 0.3–0.8$ V) than bacterial laccases (Dashtban et al., 2010; Dwivedi et al., 2011; Sun et al., 2021). Other exoenzymes (e.g., manganese peroxidase and lignin peroxidase) are less environmentally friendly than laccase because they depend on enzyme-destabilizing $H_2O_2$ for their catalytic activity (Li et al., 2022c). However, the application of laccase is limited by its high production cost, low stability, and poor recyclability (Lv et al., 2022). Additionally, laccase cannot directly transform some refractory organics, either because they have an extremely high $E^o$ or because they are too large to fit into the enzyme core for activation (Costa et al., 2019; Sun et al., 2021). This can be overcome by supplying natural or synthetic mediators, including syringaldehyde (SA), methyl syringate (MeS), acetosyringone (AS), 1-hydrobenzotriazole (HBT), 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), and 3,3′,5,5′-tetramethylbenzidine (TMB) (Couto and Herrera, 2006; Jeon and Chang, 2013). These compounds serve as intermediate substrates for laccase, whose oxidized forms can interact with target compounds that are bulky or have a high $E^o$ (Li et al., 2022c). The optimal conditions for laccase-aided composting were found to be a C/N ratio ranging from 20 to 30, ≥50% water-filled pore space, and aerobic conditions (Li et al., 2022c). GHG and $NH_3$ production can also be reduced by enriching laccase (Li et al., 2022c).

In an *in vitro* investigation, Li et al. (2022b) found that laccase-assisted humification converted phenolic compounds (17-*β*-estradiol [E2]) into HS within 2 h. However, the presence of HS-like substances, such as vanillic, ferulic, and humic acid (HA), reduced E2 elimination, which can be explained by 1) phenolic compounds are bound to HS via physiochemical mechanisms and 2) the oxidation and conversion of phenolic compounds are quenched by the humification of HS activated by laccase. HS contain abundant phenolic hydroxyl groups, which can easily react with the T1-Cu site of laccase to produce unstable reactive quinone intermediates that return the E2 radical to its initial state (Li et al., 2022b). Fungal laccase, which is cosmopolitan in nature, converts E2 and HS into closely self- and cross-linked species by adding water (Lee et al., 2019; Zhao et al., 2019). Humified products are then formed by radical self- or crosslinking driven by laccase activation (Sun et al., 2021), leading to the production of a wide range of macromolecular polymers and enhancing global carbon sequestration (Li et al., 2022b). Solid-state $^{13}C$ NMR revealed that E2-ferulic and E2-vanillic acid clusters exhibited more alkoxy-C and phenolic-C but lesser alkyl-C and aromatic-C bonds than did E2-HA. After laccase-driven humification, the abundance of aromatic-C and phenolic-C bonds decreased, whereas alkyl-C and alkoxy-C bonds became more dominant. Therefore, these humified aggregates were self- or co-polymerized by covalent C–C and/or C–O–C routes. Further, laccase promoted radical-induced polymerization when E2 and HS were converted into humus. Interestingly, after continual humification by the polymerization mechanisms induced by phenolic radicals, three closely knit self-/cross-linked precipitates, dark gray (E2-HA), dark brown (E2-vanillic acid), and deep yellow (E2-ferulic acid), were produced (Li et al., 2022b). Liu et al. (2021) found that fungal laccases converted more than 99% of the E2 (Liu et al., 2021). However, the presence of phenolic acids (PAs), such as gallic and caffeic acid, retarded the humification of E2 because their *o*-dihydroxy moieties can easily undergo oxidation to produce unstable *o*-quinone species, preventing the production of phenoxy radicals of E2 (Fig. 4) (Konar et al., 2017). Humification can be further retarded by increasing *O*-dihydroxy levels (Liu et al., 2021). The inhibitory effects of gallic acid were more pronounced than those of caffeic acid; therefore, the inhibitory effect depends on the quantity of phenolic-OH molecules and their locations in the humic precursors (Liu et al., 2021). Meanwhile, PAs have faster oxidation and self-polymerization potentials than E2 in laccase-triggered humification, thus competing with E2 for the T1-Cu site of fungal laccase (Dou et al., 2018). As secondary substrates, the polymerization byproducts of PAs can interfere with the E2 humification process (Rangelov and Nicell, 2019). Due to laccase-evoked sequential oxidative coupling, oligomer- and polymer-containing carbon-carbon/carbon-oxygen connections were inferred to be the major humified species in the E2 state. The presence of PAs not only prevented the degradation of E2 but also affected the humification products via cross-linking to E2, oxy-dehydrogenation, and self-polymerization. Interestingly, one study showed that the -COOH and -$OCH_3$ groups of PAs (e.g., vanillic and syringic acids) were eliminated in radical-causing self-copolymerization.

### 3.2. Other enzymes

Other enzymes, such as tyrosinase and peroxidase, can also be used to improve humification, though with less efficacy. Tyrosinase has a coupled binuclear copper active site that can accelerate the oxidation of *o*-biphenols to *o*-quinones. As previously mentioned, *O*-quinones can participate in polymerization reactions to form HS (Burton, 2005; Claus and Decker, 2006; Durán and Esposito, 2000). The activities of tyrosinase in polyphenol reactions is higher than that of birnessite in the same conditions (Dec et al., 2003). Peroxidase is also a candidate enzyme for humification, but requires $H_2O_2$ for activation (Dubey et al., 1998) Most peroxidases contain Fe in their structures. Soybean peroxidase is thought to be more active in polyphenol reactions than soybean peroxidase. The poly(catechol) produced by these enzymes appears to be thermally stable (Dubey et al., 1998). In contrast to tyrosinase, the catalytic activities of peroxidase seem to be lower than those of birnessite (Dec et al., 2003). Compared with laccase, peroxidase can

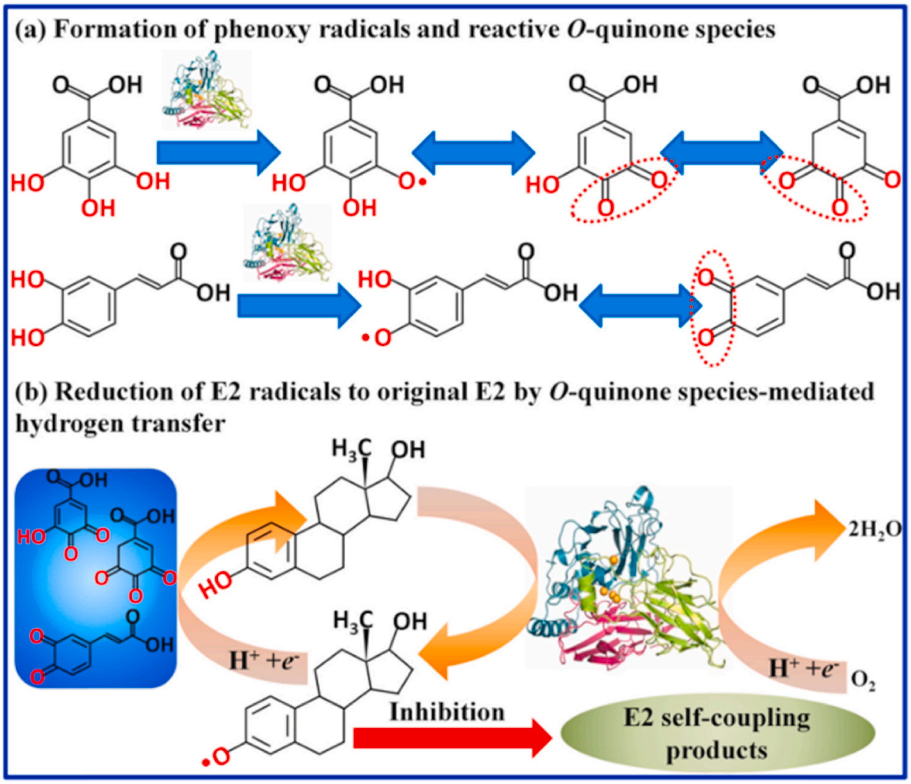


**Fig. 4.** *O*-dihydroxy moiety inhibits E2 removal and transformation in phenolic acids during L-THPs. Reprinted with permission from Liu et al. (2021). Copyright 2021, Elsevier.

effectively oxidize HS precursors, such as lignin, whereas the effect of tyrosinase negligible (Grönqvist et al., 2005). In contrast to laccases, peroxidase uses $H_2O_2$ as the final electron acceptor during polymerization instead of $O_2$ (Antúnez-Argüelles et al., 2020). With water as its only by-product, laccase is environmentally friendly, which is beneficial for its *in situ* applications and associated developments (Jeon and Chang, 2013; Li et al., 2020).

Despite the several benefits of enzymes, their high manufacturing cost and poor stability hamper their widespread use in composting (Lv et al., 2022). Inorganic minerals, chelators, detergents, and other substances may also interfere with enzymatic processes. Laccase can also be inactive owing to its attachment to particles or organic debris (Singh et al., 2017) and has a limited pH range (Li et al., 2020). For peroxidase, the use of $H_2O_2$ and the challenges of mass production are the two major limitations to its application (Li et al., 2020). These limitations can be overcome by enzyme immobilization on various media via adsorption, encapsulation/entrapment, covalent binding, and cross-linking (Daronch et al., 2020; Sheldon and van Pelt, 2013; Sun et al., 2021). Compared to free enzymes, immobilized laccase has superior thermal and acid–base stability while maintaining enzymatic acidity (Lau et al., 2003). Besides, the combination of multiple different enzymes in humification reactions should also be considered. Nanozymes—artificial enzymes generated from nanomaterials—are considered to be next-generation enzyme mimics, which have the advantages of low cost, long lifespans, and straightforward construction (Wu et al., 2019). Instead of using enzymes directly, microorganisms that excrete appropriate enzymes can be introduced into compost to increase humification performance (Li et al., 2022a; Qu et al., 2022; Wang et al., 2022b; Wu et al., 2022). The inoculation of microorganisms extended the thermophilic stage and increased the germination index, pH, and temperature during the composting of chicken manure with maize straw; thus, the transition of nitrogen, level of humification, and level of composting maturity were all increased (Wan et al., 2020). The activities of enzymes can be enhanced not only by adding supporting microorganisms but also by pretreatment with Fenton-like reaction reagents ($H_2O_2$) (Niu et al., 2021).

## 4. Abiotic catalysts

Abiotic catalysts, such as metal oxides ($MnO_2$, $Al_2O_3$, and $Fe_2O_3$), promote the conversion of HS precursors into polymers (Zhang et al., 2021a). As mentioned above, polyvalent metals (e.g., Cu, Fe, and Mn) in abiotic catalysts play a critical role in enhancing the humification reaction. These metals can function as Lewis acids and oxides to promote nucleophilic addition and polycondensation by obtaining electrons from micromolecular precursors (Miura et al., 2009). Humification can also be accelerated by the addition of various clay minerals (e.g., kaolin, allophane, zeolite, nontronite, and montmorillonite). The humification mechanism of clay is shown in Fig. 5 (Liu and Huang, 2002). Phenolic compounds, such as catechol, act as hard Lewis bases, whereas metal ions (e.g., Al, Fe, Mn, and Ti) and nonmetal elements (e.g., Si) are considered hard Lewis acids. Clays can complex with phenolic compounds via bond formation (e.g., metal-O and Si–O). The generation of semiquinone free radicals and their combination to create polyphenols appear to be accelerated when metal ions or Si replace H in catechol. This is because the electron cloud from phenolic oxygen delocalizes around the metal-O and Si–O connections and forms π-orbital bonds with the overlapped 2p orbitals of the C atoms in the aromatic ring. The semiquinone free radicals may undergo partial ring cleavage to form aliphatic fragments, leading to the production of carboxyl groups, followed by decarboxylation and $CO_2$ release (Liu and Huang, 2002).

### 4.1. Metal oxides

Metal oxide content plays an important role in the retention of OM (Zech et al., 1997; Zhang et al., 2019a). Metal oxides and organic molecules can exchange electrons during humification (Nishimoto et al., 2013; Zhang et al., 2019a). As mentioned above, polyvalent metals

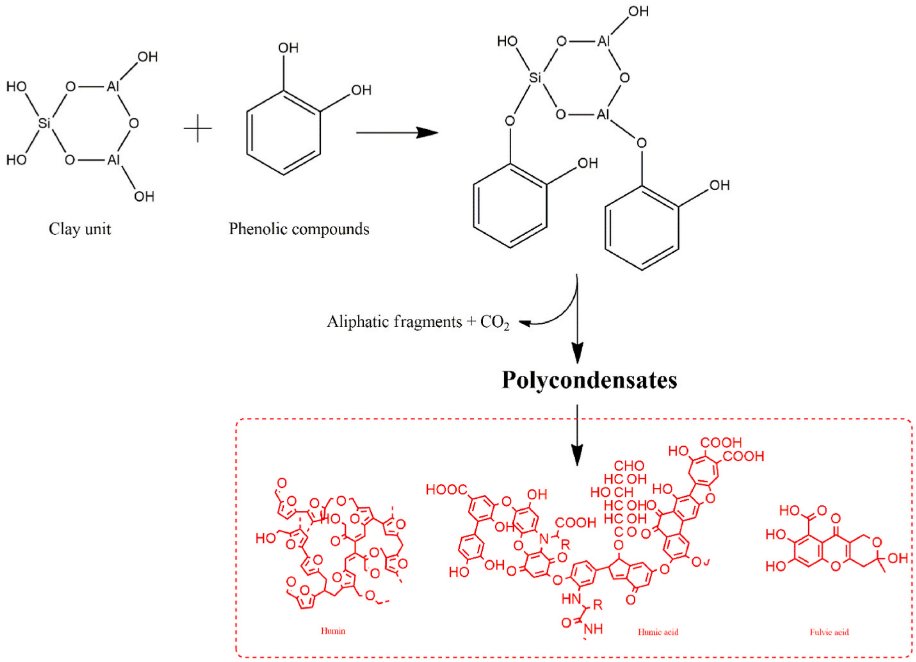


**Fig. 5.** Humification with clays as catalysts. Adapted from Liu and Huang (2002).

found in abiotic catalysts, such as Cu, Fe, and Mn, are essential for accelerating humification. By acquiring electrons from micromolecular precursors, these metals can act as Lewis acids in minerals and oxides to encourage nucleophilic addition and polycondensation (Miura et al., 2009). Metal oxides such as $MnO_2$ are commonly used to facilitate OM degradation and humification during composting in different ways (Qi et al., 2021a, 2021b): 1) the production of HS is increased by controlling microbial metabolism and accelerating the condensation of low-molecular-weight compounds through chemical catalysis (Qi et al., 2020, 2021a); 2) the levels of FA increase during composting through stimulated carbonyl-amine reactions between the simple components (Qi et al., 2019; Zhang et al., 2021b); 3) the bioavailability of HS is enhanced (Qi et al., 2021b); whereas 4) the formation of $NH_4^+$ and $NO_3^-$ is decreased, because nitrogen-containing compounds may participate in abiotic HS production accelerated by $MnO_2$ (Cáceres et al., 2018; Wu et al., 2018). However, the source of agricultural organic waste can affect the roles of metal oxides. For example, Wu et al. (2018) reported that $MnO_2$ may assist the condensation of HS precursors during the composting of corn straw, whereas it only stimulated the processing of HS by bacterial communities in the composting of chicken manure (Wu et al., 2018). Qi et al. (2019) observed that the addition of $MnO_2$ promoted the levels of both FA and HA condensation during corn straw composting but only increased the condensation level of FA during chicken manure composting (Qi et al., 2019). The feedstock-dependent role of $MnO_2$ on composting requires further investigation, based on the few studies that have reported conflicting results.

The unique roles of metal oxides during decomposition can be clarified and confirmed by observing the *in vitro* humification of HS precursors, such as catechol, glucose, and glycine, in the presence of minerals (Hardie et al., 2009; Qi et al., 2021b). Owing to their high specific area and oxidation potential, metal oxides such as $MnO_2$ tend to increase the oxidation of HS precursors (Li et al., 2012). FA is primarily produced by $MnO_2$ reduction, whereas the successive reduction products, MnO(OH) and Mn(II), produce HA. A previous study found that an increase in $MnO_2$ concentration led to an increase in FA formation, which corresponded to an increase in $CO_2$ (Zhang et al., 2019a). The ratio between OM and $MnO_2$ should be optimized to enhance the conversion of unstable FA into HA and minimize $CO_2$ emissions. The combined effects of $MnO_2$ and $O_2$ increase the production of HA. Additionally, $MnO_2$ enhanced the role of nitrogen in the generation of HA (Zhang et al., 2021c). Zhang et al. (2022) recently reported that the presence of $MnO_2$ and oxygen together could effectively promote HA formation. $MnO_2$ contributed more to the conversion of OM to FA, whereas $O_2$ contributed more to the transformation of FA to HA (Zhang et al., 2021c). The unique properties of metal oxides have also been observed via *in vitro* humification. For example, the Maillard reaction can occur at room temperature, although the reaction rate is still higher at 45 °C (Jokic et al., 2001b). The humification rate of birnessite in the Maillard system was more pronounced under light conditions than under dark conditions (Jokic et al., 2001a), light condition being another factor affecting humification. Jokic et al. (2001a) found that light irradiation enhanced the release of Mn(II) into the supernatant and reductive dissolution of birnessite (Jokic et al., 2001a). Additionally, the polyphenol polymerization of birnessite seems to be more pronounced than that of enzymes such as laccase and horseradish peroxidase, although it is lower than that of tyrosinase (Dec et al., 2003).

Similar to $MnO_2$, $Fe_2O_3$ and $Fe_3O_4$ nanoparticles (NPs) can assist microorganisms in degrading OM and proceeding with humification. In this process, an essential stabilizing mechanism is the interaction of OM with Fe (Zhao et al., 2019). The quantity of thermophilic bacteria for OM breakdown and AA metabolism can be enhanced by the addition of iron oxide NPs (Zhang et al., 2022). AA metabolism promotes HS production in the mature stage of composting (Wu et al., 2017a). Using a Fenton-like process combined with *Phanerochaete chrysosporium* and oxalic acid, $Fe_xO_y$ NPs promoted the generation of HA. Additionally, more functional groups, including carbonyl, hydroxyl, alkoxyl, amino, and carboxyl groups, were incorporated in the structures of HS compared to those in control samples without any additives (Chen et al., 2021).

Steel slag, the major by-product of steel production, can increase the polymerization of humic precursors owing to its high metal oxide content (Qi et al., 2012a, 2012b); the primary crystalline minerals in the slag were $MnO_2$, $CaCO_3$, $Fe_2O_3$, $Fe_3O_4$, and trace quantities of $FeCO_3$, $Ca_5(SiO_4)_2CO_3$, and $CaFeSiO_4$ (Qi et al., 2012b). The darkening rate in humification with steel slag is still lower than that with birnessite ($\delta$-$MnO_2$) but much higher than that with zeolite. Additionally, the Mw of steel slag-produced HA was much lower than that produced by birnessite (Qi et al., 2012b), which can be attributed to the weaker oxidation power of steel slag minerals versus birnessite (Qi et al., 2012a). Compared with birnessite-HA and zeolite-HA, steel slag-HA exhibited the lowest carbonyl-C content; this suggests that the majority of its oxygen-containing groups were attached to aromatic rings or aliphatic chains in the form of ethers or esters. The macromolecular structure of HA was dominated by phenolic acids and methylphenol derivatives (Qi et al., 2012a). Similar to $MnO_2$, Fe(III) ions from hematite ($Fe_2O_3$) and magnetite ($Fe_3O_4$) can complex with catechol and be reduced to Fe(II), which then converts catechol to oxidized species (e.g., quinone and semiquinone radicals) (Nishimoto et al., 2013). Meanwhile, oxidation–reduction processes involving $Fe_xO_y$ and $MnO_2$ can occur continuously in the presence of oxygen (Bulosan-Atendido et al., 2010). This is also favorable for environmentally sound recycling because the adsorption and complexation of HS on the surface of metal oxides can partially prevent metal ion leakage into the reaction solution (Qi et al., 2012b).

Several studies have attempted to compare the potential of metal oxides via *in vitro* humification reactions. In general, $MnO_2$ and $Fe_2O_3$ showed a higher humification capability than $Al_2O_3$ (Chen et al., 2010; Hardie et al., 2010). Chen et al. (2010) indicated that poorly crystalline $Fe_2O_3$ enhanced the humification of the polyphenol reaction of catechin to a greater extent than that by $MnO_2$ and $Al_2O_3$ (Chen et al., 2010). In contrast, Hardie et al. (2010) claimed that the activity of poorly crystalline $MnO_2$ was higher than that of $Fe_2O_3$ in the Maillard reaction of glycine and glucose as well as in the polyphenol-Maillard humification of catechol, glucose, and glycine (Hardie et al., 2010). This difference was attributed to a decrease in the electronegativity of Mn (1.55) compared to that of Fe (1.83) or Al (1.61) (Hardie, 2008). Owing to the lower electronegativity of Mn in the $MnO_2$-phenolic complex, the cloud of electrons surrounding the Mn–O bond can be delocalized to a greater extent than in the $Al_2O_3$- and $Fe_2O_3$-phenolic complex (Hardie, 2008). The higher humification potential of $MnO_2$ can also be explained by the redox potentials of different metal oxides: The $E^o$ values of the entire redox reaction of the $Fe_2O_3$- and $MnO_2$-catechol systems were +0.071 V and +0.509 V, respectively, whereas $Al_2O_3$ is not susceptible to redox reactions (Hardie, 2008).

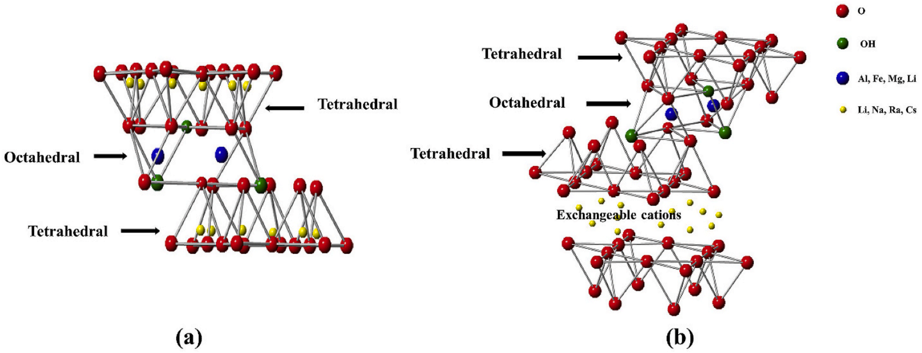
### 4.2. Clays

Clays are another favored additive for accelerating OM humification during composting. Clays consist of stacked layers of tetrahedral/octahedral sheets and are classified based on sheet arrangement as kaolinite, hectorite, halloysite, and montmorillonite (Khatoon et al., 2020). Octahedral sheets comprise of aluminum or magnesium in six-fold coordination with oxygen from a tetrahedral sheet with hydroxyl. Tetrahedral sheets contain silicon-oxygen tetrahedra coupled to neighboring tetrahedra, which share three corners. In contrast, the fourth corner of each tetrahedral sheet is linked to an adjacent octahedron via a covalent bond (Fig. 6) (Guo et al., 2018). Based on sheet arrangements, clays are classified into 1:1, 2:1, and 2:1:1 structures (Table S2). Awasthi et al. (2018a) found that the HA/FA ratio in a mixture of wheat straw and sewage sludge increased with the addition of Ca-bentonite (Awasthi et al., 2018b). Ren et al. (2019) demonstrated that the presence of tertiary amine bentonite could accelerate humification and decrease GHG emissions (Ren et al., 2019). Ren et al. (2020) reported that compost with 10% clay content promoted OM degradation and HA synthesis, but decreased FA content. Clay accelerates the production of aromatic carbon structures and the breakdown of aliphatic carbon. For example, after 10% clay addition, the compost exhibited the highest HA and FA and humification index (HIX) values, with 14.44% and 1.96% increases, respectively, compared to the control (Ren et al., 2020).

Montmorillonite can effectively enhance the degree of humification of manure compost (He et al., 2014; Song et al., 2021). Thermally treated montmorillonite and illite were recently observed to exert greater effects on microbial diversity and compost quality during the composting process than their non-treated counterparts: Untreated montmorillonite and illite were found to catalyze the formation of HA via abiotic pathways, whereas thermally treated minerals promoted the decomposition of HS precursors and the formation of HA in both direct (as catalysts) and indirect (by increasing the growth of humification-related microorganisms) manners (Pan et al., 2021).

Zeolite can be used to produce high-quality compost (Soudejani et al., 2019). Hydrated aluminosilicate minerals are composed of three-dimensional $SiO_4$ and $AlO_4$ tetrahedra and have a porous structure with a relatively high surface area and cation exchange capacity (Cui et al., 2021; Ozdemir et al., 2020; Villaseñor et al., 2011). Zhang and Sun (2015) reported that the combined use of zeolite and earthworms promoted humification and accelerated the degradation of cellulose and hemicellulose (Zhang and Sun, 2015). Awasthi et al. (2018a) demonstrated the effects of an amendment mixture (zeolite + lime) on enzymatic activities, OM degradation, and humification during composting. In the bio-oxidative phase of composting, lime considerably reduced the maturity period, enhanced the final product quality, and neutralized the pH (6.0–8.0) (Fang and Wong, 1999; Wong et al., 2009). The addition of a mixture of zeolite and lime resulted in high enzymatic activity levels and rapid humification of organic substances (Awasthi et al., 2018a). Compared to zeolite alone, biochar and zeolite can be combined to improve the breakdown of OM, quality of compost, and loss of nitrogen. Their combined use led to a remarkable increase in HA production and HA/FA ratios (Wang et al., 2017).

Similar to metal oxides, *in vitro* studies can elucidate the specific roles of clays in humification. Nitrogen addition from amines to aromatic carbons are promoted by the solid and/or Lewis acid catalysts found in clay minerals (Varma, 2002). Clays typically contain metal oxides in their structure. Different natural clays, such as allophanic soil, hydroxy-aluminosilicate (precursors to noncrystallite aluminosilicates), bentonite, and zeolite, can catalyze *in vitro* humification (Fukushima et al., 2009; Liu and Huang, 2002; Miura et al., 2009). The results of these studies, as well as the experimental conditions, are briefly described in Table S3. In general, clays with higher surface areas tended



(a) (b)

**Fig. 6.** Crystal structures of clay minerals: a) 1:1 type; b) 2:1 type. Reprinted with permission from Guo et al. (2018). Copyright 2018, MDPI.

to exhibit a greater humification potential. Allophanic soil, which has a surface area of 36.30 ± 0.05 $m^2/g$, showed a higher humification potential than clays with lower surface areas (e.g., bentonite [34.73 ± 0.07 $m^2/g$], zeolite [26.82 ± 0.04 $m^2/g$], and kaolin [3.30 ± 0.39 $m^2/g$]) (Miura et al., 2009). The structure of the clay is another factor that determines its humification potential. Owing to the lattice defects and large specific surface area of 2:1-layer silicates, which favor the adsorption of radicals or $O_2$ molecules, the effect of these materials on humification is typically greater than that of 1:1-layer silicates (Hardie, 2008). Miura et al. (2009) demonstrated that Fe and Ti in clays contributed more to humification than other elements (e.g., Al or Si) (Miura et al., 2009). Owing to the presence of Fe(III) as its primary structural cation in the octahedral sheet, nontronite exhibits a higher humification potential than montmorillonite and hectorite containing Al and Mg, respectively (Wang and Huang, 1986). $Ca^{2+}$ has also been found to correlate with the rate of the humification reaction (Miura et al., 2009).

Different abiotic catalysts can be used to enhance humification both directly and indirectly. These catalysts have the potential to mimic and replace biological ones. However, caution should be exercised in their application. The catalyst-to-OM ratio should be optimized to achieve efficient conversion of FA into HA and minimize the release of $CO_2$. Excessive oxidation may cause the rapid degradation of early HAs, resulting in unstable FAs that are easily transformed into low-molecular-weight organic substrates and mineralized to $CO_2$ (Qi et al., 2012b).

### *4.3. Advanced catalysts*

In addition to the common biotic and abiotic catalysts, *in vitro* humification can also be catalytically activated by advanced materials, such as artificial clays (Li et al., 2019; X. Zhang et al., 2021a). Layered double hydroxides (LDHs) are based on the $Mg(OH)_2$-brucite structure, with divalent cations replaced by trivalent cations, which renders a positive layer charge (Erickson et al., 2005). This positively charged layer can be neutralized by the inclusion of anions. Divalent and trivalent cations can be combined with various interlayer anions to generate various types of LDHs. The anions may be monovalent (e.g., chloride or nitrate) or divalent (e.g., carbonate, sulfate, and phosphate), though divalent anions are favored (Erickson et al., 2005). With their large surface area and volume, target molecules can be easily diffuse and reacted with the active sites of LDHs (Cao et al., 2020). In addition, LDHs could be designed to form a closed electron cycle, which permits the efficient flow of electrons between active sites (Fig. 7) (Wang et al., 2018a, 2020). Due to these unique characteristics, CuCoFe LDH has been used to mimic laccase for the detection of pheochromocytoma biomarkers by colorimetry (Huang et al., 2022). Recently, Zhang et al. (2021b) manufactured Mg/Fe-LDH to enhance the polyphenol- Maillard humification process. A complex of Fe(III) and catechol was produced by the reaction of iron released from Mg/Fe-LDH with catechol, similar to the abovementioned $Fe_xO_y$. Light illumination induced the production of environmentally persistent free radicals (EPFRs) from the Fe (III)-catechol complex. Mg/Fe-LDH particles stabilized the EPFRs, making catechol less likely to be oxidized and humified. The Fe (II)-catechol complex was partially converted back to catechol (Fig. 8) (Truong et al., 2010). Consequently, in contrast to reactions with $MnO_2$, the Mg/Fe-LDH-catalyzed humification process was more effective under dark conditions. The molecular weight and number of oxygen functional groups were higher in humification products under dark conditions in the absence of EPFRs. *Ortho*-aminophenol is one of the main byproducts of humification, and commonly self-couples with catechol radicals. The higher abundance of CHO molecules in the presence of Mg/Fe-LDH showed that Fe effectively improved the synthesis of C–C bonds (X. Zhang et al., 2021a). Another LDH, Zn/Al LDH, was embedded with $Fe_3O_4$ for the *in vitro* humification of phenolic compounds (Li et al., 2019). With this new material, the conversion rate of humification reached 65%, and HS characteristics were not affected by either substrate concentration or pH (Li et al., 2019).

## 5. Comparison of biotic and abiotic catalysts

Because composting is a complex process, humification efficiency could be affected by several factors, such as raw materials, pile volume, temperature, pH, moisture content, and aeration rate. Unfortunately, this complicates the comparison of catalyst activities. Therefore, in this section, we only compared the performance of catalysts under the same conditions as the *in vitro* humification reaction. Although biotic and abiotic catalysts shared the same humification mechanisms, there are still several differences between them regarding recycling abilities, humification mechanisms, humification products, and operating conditions. Tyrosinase and laccase (i.e., biotic catalysts) tend to continue oxidizing catechol after its initial addition, whereas abiotic catalysts (e.g., birnessite) lose their ability to oxidize catechol (Pal et al., 1994). For birnessite, Mn is changed or consumed as a terminal electron acceptor during the oxidative coupling reaction. Birnessite oxidizes polyphenols (e.g., catechol) and polymerizes them through the production of semiquinone radicals (McBride, 1987), whereas oxidation continues without the generation of semiquinone radicals in the presence of tyrosinase because the binuclear copper active site regulates electron transfer

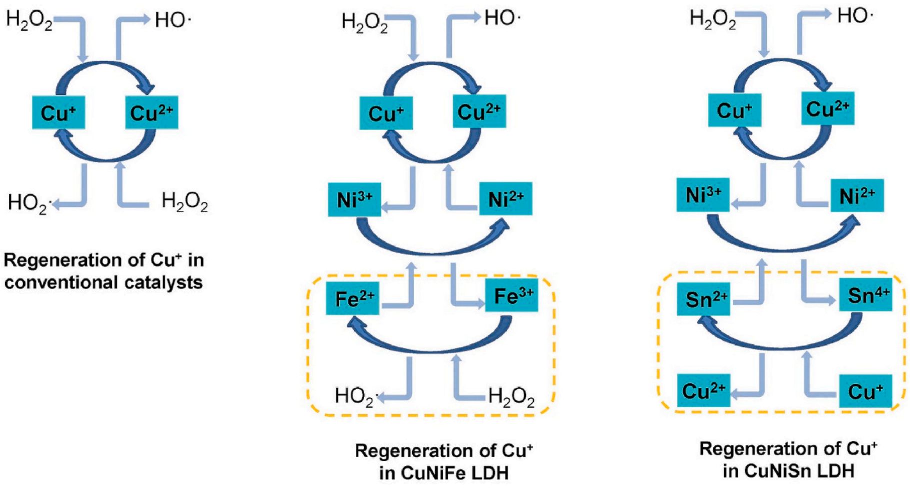


**Fig. 7.** Regeneration pathways of $Cu^+$-active species in conventional Fenton catalysts, CuNiFe LDH, and CuNiSn LDH, respectively. Reprinted with permission from Wang et al. (2020). Copyright 2020, Elsevier.

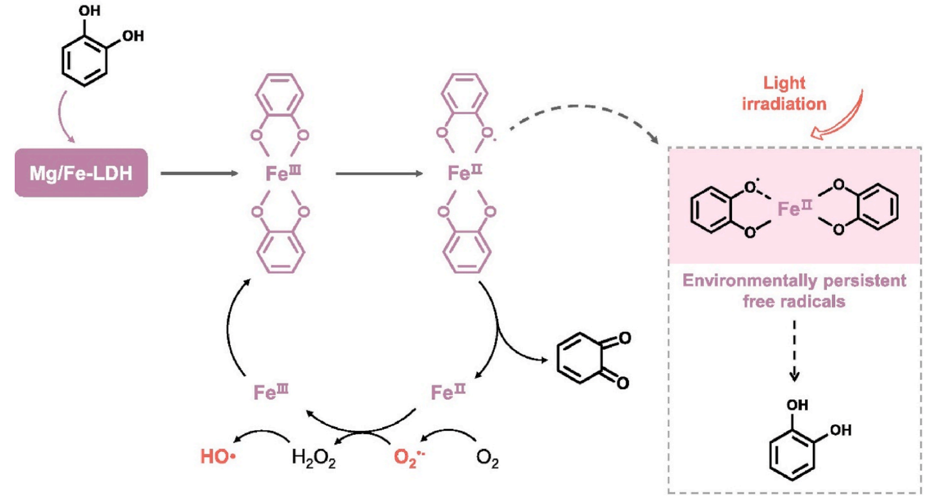


**Fig. 8.** Photochemical behavior of the Fe(III)–catechol complex in the existence of Mg/Fe-LDH. Reprinted with permission from Zhang et al. (2021a). Copyright 2021, Elsevier.

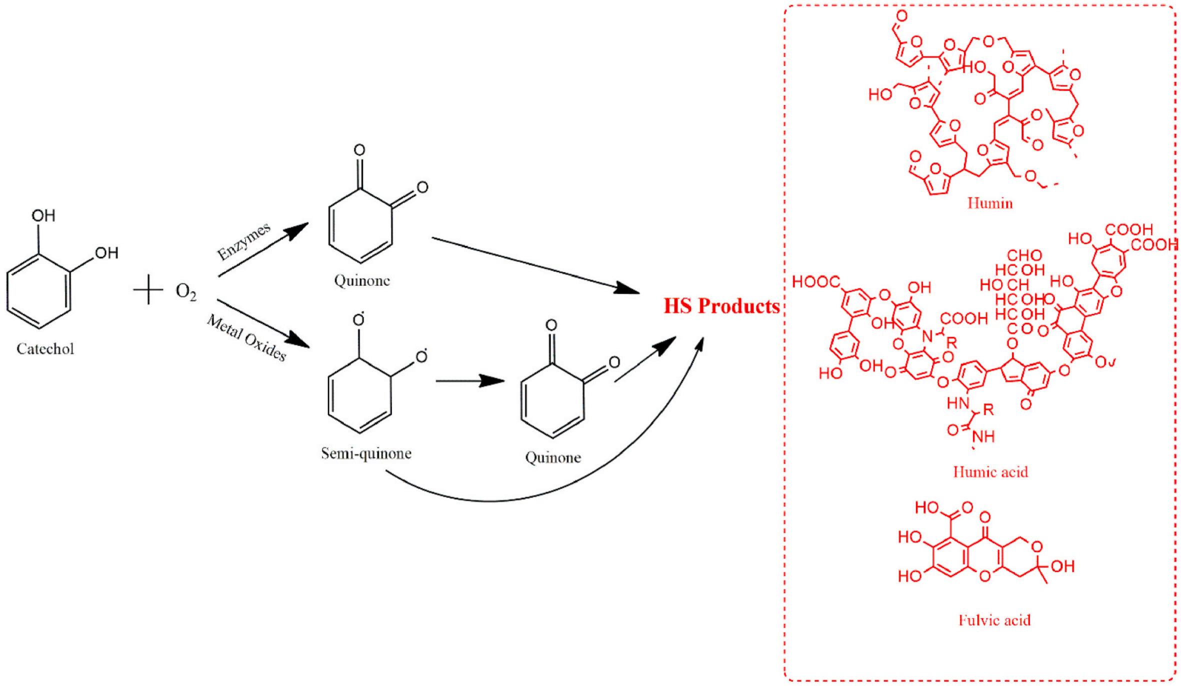


**Fig. 9.** Differences in oxidative polymerization between biotic and abiotic catalysts. Adapted from Naidja et al. (1999).

(Fig. 9) (Himmelwright et al., 1980). Depending on the redox potential of the surrounding substrate, $Mn^{2+}$ or $Fe^{2+}$ released during phenolic oxidation may be re-oxidized to higher-valence oxides, which would hinder their catalytic capability (McBride, 1987). In contrast, enzymes transfer electrons from an electron donor to an electron acceptor ($O_2$). Enzymes, such as tyrosinase, have slightly lower activation energies than metal oxides, such as birnessite (Naidja et al., 1999). The unique arrangement of active sites in enzymes could explain their higher humification potential compared to that of minerals or metal oxides; however, the humification potentials of these catalysts still depend on the target organic compounds. Therefore, a more comprehensive evaluation is needed. For example, $MnO_2$ exhibited a higher degree of darkening with hydroquinone and resorcinol than with tyrosinase, whereas this effect was reversed with catechol (Shindo and Huang, 1992). Additionally, the decarboxylation of *p*-hydroxybenzoic, vanillic, *p*-coumaric, and ferulic acid was higher with birnessite as the catalyst than with enzymes (Dec et al., 2001). Temperature plays an important role in determining the differences between biotic and abiotic catalysts. For example, denaturation of protein molecules causes the inactivation or inhibition of some enzymes at temperatures greater than 30 °C, whereas metal oxide oxidation activity increases at higher temperatures (Naidja et al., 1999). Differences between the abiotic and biotic catalysts were also observed in the final humification products. For example, the polymers produced by tyrosinase-catechol exhibited a higher level of aromatic ring condensation, whereas the products of birnessite catalysis had a higher proportion of aliphatic and smaller molecular weight components (Hardie, 2008). Finally, the production of enzymes is complicated and very expensive, whereas most of the abiotic catalysts mentioned in this review are common in nature or affordably synthesized. The main differences between the biotic and abiotic catalysts are summarized in Table 1.

**Table 1**
Major differences between biotic and abiotic catalysts of humification.

| | Biotic catalysts | Abiotic catalysts |
|---|---|---|
| Production cost | High | Low |
| Reusability | Recyclable | Loss of activity in following cycles |
| Humification activities | Comparatively higher activity rates | Comparatively lower activity rates |
| Operating condition | Some enzymes are inactivated at temperatures above 30 °C | Abiotic catalysts can operate at elevated temperatures (>30 °C) |
| Humification products | HS have higher aromatic ring condensation | HS have higher percentages of aliphatic and lower-molecular-weight components |
| Application in composting process | The use of biocatalysts is often limited by their high cost. Alternatively, adding related microorganisms can increase the concentration of HS by approximately 20% or the humification index by up to 1.75 times (Qu et al., 2022; Niu et al., 2021) | The addition of abiotic catalysts during composting can cause HS concentration surge by more than 100%. More commonly, the increase is around 10% |

## 6. Environmental implications and future studies

In addition to HS formed by conventional composting, HS from biotically or abiotically catalyzed humification reactions can be used as soil fertilizer. The characteristics of these artificial HS are similar to those of natural HS. The addition of various biotic and abiotic catalysts can enhance the degree of humification and stimulate degradation and sequestration during composting. By increasing the humification rate, catalysts can reduce the loss of OM and generation of GHG. Consequently, the HS generated from composting or *in vitro* humification can prevent the loss of OM when applied to the soil (Spaccini and Piccolo, 2020). For example, soil supplemented with HS solution showed a 12–30% preventive effect on the degradation of 2-decanol compared to control-treated soil samples (Piccolo et al., 1999). Soil amended with mature compost has a higher tendency for OM accumulation than soils treated with more conventional practices (e.g., reduced tillage and green manure) (Spaccini and Piccolo, 2020). A study demonstrated that the amount of organic carbon that can be sequestered by soil is inversely proportional to the hydrophobicity of the soil HS (Spaccini et al., 2002).

Although several studies have reported the positive functions of biotic and abiotic catalysts in accelerating the humification reaction, there are still some challenges in the characterization of catalysts because 1) composting is a complex process of degradation and humification, with the simultaneous occurrence of both biotic and abiotic degradation/humification pathways, and (2) the mechanisms of biotic/abiotic-catalyzed humification are not fully understood. In particular, it is critical that we elucidate the indirect roles of catalysts in regulating the growth of microbes involved in humification as well as their direct involvement in *in vitro* humification reactions (Table S3 and Table S4).

Although HS precursors can be rapidly converted into HS in the presence of catalysts, caution should be exercised when applying catalysts. First, despite effective carbon sequestration, humification still releases considerable amounts of chloride, $CO_2$, and methanol via oxidative coupling. The generation of these byproducts depends on the molecular structures of the organic pollutants and participating catalysts (Dec et al., 2003). For example, the humification of organic pollutants containing -Cl (e.g., 2,4-dichlorophenols), -COOH (e.g., *p*-hydroxybenzoic acid), and $-OCH_3$ (e.g., syringic acid or vanillic acid) can produce $Cl_2$, $CO_2$, and methanol, respectively, when attached to the aromatic carbons involved in coupling with unpaired electrons (Dec and Bollag, 1994). On the other hand, catalysts can influence the amount of by-product released during humification. For example, the polymerization of *p*-hydroxybenzoic and vanillic acid with tyrosinase produced less $CO_2$ than that with horseradish and laccase as catalysts (Dec et al., 2001). At the same time, the catalyst-to-OM ratio should be optimized to efficiently convert FA into HA while simultaneously minimizing the release of $CO_2$. Although strong oxidants result in a strong humification reaction, it could accelerate the initial formation of HA and additional formation of unstable FA, which could lead to the production of small-molecule organic substrates and mineralization into $CO_2$.

There is still room for the development and improvement of catalysts for humification reactions. For efficient composting, the addition of suitable microorganisms, thermal pretreatment (85–90 °C), and Fenton pretreatment should be considered to increase the rate of humification and synthesis of HS by ample supplementation of HS precursors, such as polysaccharides, simple sugars, AAs, and phenolic compounds (Chen et al., 2021; Wang et al., 2022a). For *in vitro* enzymatic oxidation reactions, further in-depth investigations should be conducted to extend their application to more useful enzymes from microorganisms, as the effects of only a few enzymes (e.g., laccase) have been explored. For abiotic-catalyzed humification reactions, current catalysts are mostly generated from conventional natural materials, and advanced catalysts or synthesized materials can be applied to enhance the humification process. Additionally, most previous studies have not explored the effects of catalyst properties, such as size, shape, and crystallinity, on composting or the *in vitro* humification process, which warrants further investigation. Although there have been many studies comparing humification catalysts, the field has not been updated with recent advancements in OM characterization. The similarities and differences between biotic and abiotic catalysts requires more comprehensive evaluation using advanced techniques, including fluorescence excitation emission matrix (EEM) spectroscopy, high-performance size exclusion chromatography, Fourier transform ion cyclotron resonance mass spectrometry, and NMR. Also, because biotic and abiotic catalysts coexist in nature, their interactions and manners in which they affect the humification process should be explored in future studies. Although HS can passivate heavy metals (Song et al., 2021) and the majority of abiotic catalysts primarily contain eco-friendly naturally occurring elements (such as Mn, Mg, Cu, and Fe), the environmental effects of these catalysts require further elucidation, as the dissolution of metal ions from catalysts has been recognized in some studies (Zhang et al., 2021a).

Approaches based on advanced materials or nanozymes to mimic and replace natural enzymes merit further consideration. Considering that only a few advanced catalysts have been applied in humification, there is still much room for developing specialized catalysts. For example, although different nanozymes have exhibited comparable or even higher activity rates than laccase with respect to environmental remediation (e.g., removal of phenolic compounds), they have not been tested for their humification potential (Hu et al., 2021; Huang et al., 2022; Le et al., 2022; Liang et al., 2022; Xu et al., 2021). Given the advances and limitations of conventional catalysts, future research should focus on the following aspects: low-cost synthesis, recyclability with constant rates of activity, higher performance than conventional catalysts, and a wide range of operational conditions in terms of temperature (25–45 °C), pH, and light availability. Moreover, the direct experimental comparison of mimic materials and natural enzymes for both composting and *in vitro* humification could provide insight into the development of effective and eco-friendly humification methods.

The terms “humic substances” and “humification” have been subject to controversy due to current gaps in knowledge. For instance, Lehmann and Kleber (2015) rejected the presence of humification, concluding that soil organic matter is a continuum of progressively decomposing organic compounds that does not accommodate large-molecule “persistent humic substances.” In contrast, Gerke (2018) proposed that the polymerization of polyphenol molecules could lead to the formation of HS. Given the divergent opinions in the literature, it is imperative that the humification pathways and characteristics of HS are clarified using more advanced techniques.

## 7. Conclusions

In this review, different biotic and abiotic catalysts with high humification potential were systematically compared with respect to their recycling abilities, humification mechanisms, humification products, and operating conditions. The presence of catalysts can increase HS content during composting from approximately 10% to >100% compared to control group samples, depending on the type of catalyst, dosage, starting materials, and experimental conditions. The unique roles of these catalysts in nature have been elucidated through individual composting experiments, especially focusing on biotic-/abiotic-catalyzed humification reactions. While humification pathways remain poorly understood, biotic and abiotic catalysts are considered to share similar pathways. However, differences exist between these catalysts in terms of humification steps, humification products, and operating conditions. Biotic catalysts seem to have a higher humification potential and greater reusability than abiotic catalysts, although the high cost of production and strict operating conditions prevent their widespread application. Given its high performance and eco-friendliness, laccase is the most appealing enzyme among biotic catalysts. Regarding abiotic catalysts, $MnO_2$ has shown the highest humification activity compared to other metal oxides, such as $Fe_2O_3$ or $Al_2O_3$, and clays with a 2:1-layered structure have a higher potential for humification than clays with a 1:1-layered structure.

Discovery and enhancement of catalysts for humification reactions has much potential remains. Current abiotic/biotic catalysts are restricted to conventional naturally occurring catalysts. Because many abiotic and biotic catalysts coexist in nature, further studies on their interactions and way in which they affect humification could help in resolving the challenges associated with enhanced humification. Although recent studies have demonstrated the humification potential of some advanced materials, the disadvantages of conventional catalysts provide ample motivation for the development of novel catalysts. Although humification is considered one of the most effective strategies for carbon sequestration, the process still results in the release of considerable and unavoidable amounts of chloride ions, $CO_2$, and methanol. Future studies should consider how this challenge can be addressed, while maintaining enhanced rates of humification.

## Author contributions

V.K.H.B.: conceptualization, investigation, writing—review and editing, resources, visualization, and writing—original draft; H.B.T.: resources, investigation, and writing—review and editing; S.H.: resources, investigation, and writing—review and editing; X.L.: resources, investigation, and writing—review and editing; J.H.: conceptualization, writing—original draft, writing—review and editing, supervision, project administration, and funding acquisition. All the authors have read and agreed to the published version of the manuscript.

## Declaration of competing interest

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

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2023.136832.

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# Supporting information:

# Biotic and abiotic catalysts for enhanced humification in composting: A comprehensive review

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# TABLE

**Table S1.** Recent review articles on humification

| Authors | Title | Highlights | Ref. |
|---|---|---|---|
| Lee et al. (2019) | Artificial humification of lignin: top-down and bottom-up approaches | • Introduction to HS and their natural roles, characterizations, and applications<br>• Introduction of artificial humification of lignin-related materials using top-down and bottom-up approaches | (Lee et al., 2019) |
| Yang et al. (2021) | Natural and artificial humic substances to manage minerals, ions, water, and soil microorganisms | • Summary of HS application in agriculture and environmental ecology<br>• Introduction of artificial HS synthesis technology: hydrothermal humification technology, hydrothermal carbonization technology, and hydrogen peroxide oxidation technology | (Yang et al., 2021) |
| Wang et al. (2022) | Degradation or humification: rethinking strategies to attenuate organic pollutants | • Decomposition and humification of OM as the main topics of this review<br>• Humification pathways and role of microorganisms in providing HS precursors<br>• Introduction of artificial HS synthesis technology: hydrothermal humification technology, hydrothermal carbonization technology, and hydrogen peroxide oxidation technology | (Wang et al., 2022) |
| Li et al. (2022) | Insights into the application of extracellular laccase-aided humification in livestock manure composting | • Highlight the role of laccase in humification during composting | (Li et al., 2022b) |

**Table S2.** Clay mineral classification. Reprinted with permission from (Guo et al., 2018). Copyright 2018, MDPI

| **Clay Layer Type** | **Clay Group** | **Clay Species** |
|---|---|---|
| 1:1 | Rectorite, Kaolinite, Halloysite, Chrysotile | Lizardite, Berthierine, Cronstedtite, Kellyite, Fraipontite, Brindleyite, Dickite, Nacrite |
| 2:1 | Smectite, Vermiculite, Pyrophylite talc, Mica, Brittle Mica | Montmorillonite, Laponite, Sepiolite, Hectorite, Bentonite, Vermiculite, Pyrophyllite, Talc, Muscovite, Paragonite, Clintonite, Bityite |
| 2:1:1 | Chlorite | Amesite, Cookeite |

**Table S3.** Catalysts in the *in vitro* humification reactions

| **Catalysts** | **Dose** | **Type of reaction** | **Precursors** | **Remarks/Impact** | **Ref.** |
|---|---|---|---|---|---|
| • Horseradish peroxidase (HRP)<br>• Soybean peroxidase | 1mg/mL | Polyphenol reaction | Catechol | • The amount of polymer produced by HRP-catalyzed reactions was significantly less than that produced by SBP-catalyzed reactions<br>• The polymer's yield was pH-dependent<br>• Poly(catechol) produced by enzyme has a comparatively good thermal stability | (Dubey et al., 1998) |
| • Horseradish peroxidase<br>• Tyrosinase<br>• Laccase | Horseradish peroxidase: 4 units/mL<br>Laccase: 40 units/mL<br>Tyrosinase: 1200 units/mL<br>Birnessite: 0.01 g/mL | Polyphenol reaction | Phenolic compounds | • The polyphenol polymerization of birnessite seems to be higher than those of laccase and horseradish peroxidase, but lower than tyrosinase<br>• During an oxidative coupling reaction, dehalogenation, decarboxylation, and demethylation happen depending on the phenolic compounds and catalysts that are used | (Dec et al., 2003) |
| Laccase | 1.0 U/mL | Polyphenol reaction | 17-β-estradiol (E2) + HS | • Laccase can convert E2 into HC within 2 hours<br>• The presence of HS, such as HA, vanillic acid, and ferrullic acid, reduced E2 elimination<br>• Hybrid E2-HA, E2-vanillic acid, and E2-ferrullic acid precipitates function as humic-like organic fertilizers, promoting radish root elongation, seed germination, and NaCl tolerance | (Li et al., 2022a) |
| Laccase | 1.0 U/mL | Polyphenol reaction | 17-β-estradiol (E2) + phenolic acids (PAs) | • Laccase can convert 99% of E2<br>• The presence of Pas, such as gallic acid (Gaa) and caffeic acid (Caa), retards the elimination of E2<br>• Organic pollutants in the environment are stabilized and detoxicated by the creation of self-co-polymerization species between E2 and PAs in the presence of laccase | (Liu et al., 2021) |

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| $MnO_2$ | 10 mg/mL | Integrated Polyphenol-Maillard reaction | Catechol + glucose + glycine | • The production of FA was mostly influenced by the reduction of $MnO_2$<br>• The catalysts MnOOH and Mn(II) aided in the production of HA.<br>• Lower $MnO_2$ concentration reduced FA production | (Zhang et al., 2019) |
| Birnessite (δ-$MnO_2$) | 25 mg/mL | Maillard reaction | Glucose + glycine | • The Maillard reaction between glucose and glycine can occur at 25 °C although the reaction rate remains higher when it is conducted at 45 °C | (Jokic et al., 2001b) |
| Birnessite (δ-$MnO_2$) | 25 mg/mL | Maillard reaction | Glucose + glycine | • The humification rate of birnessite in the Maillard system is higher under light condition than under dark condition | (Jokic et al., 2001a) |
| Birnessite (δ-$MnO_2$) | 25 mg/mL | Maillard reaction | Glucose + glycine | • Birnessite produced a substantial amount of amide N in addition to heterocyclic N | (Jokic et al., 2004) |
| Metal oxides from steel slag | 2 g/180 mL | Integrated Polyphenol-Maillard reaction | Catechol + glucose + glycine | • $Fe_2O_3$ and $Fe_3O_4$ on the steel slag's surface played as catalysts for the generation of HS from humic precursors<br>• In comparison to untreated slag, HS production was reduced in slag samples that were HF or $HNO_3$ treated | (Nishimoto et al., 2013) |
| • $MnO_2$<br>• $Fe_2O_3$<br>• $Al_2O_3$ | 0.3 g/125 mL | Polyphenol reaction | Catechin | • The order of catechin polymerization degree is $MnO_2 > Fe_2O_3 > Al_2O_3$<br>• The order of HA and FA formation is $MnO_2 > Fe_2O_3 > Al_2O_3$<br>• The order of humic polymers adsorbed on the residual sediments after extraction with water: $Fe_2O_3 > MnO_2 > Al_2O_3$<br>• The order of total humic polymers in the system is $Fe_2O_3 > MnO_2 > Al_2O_3$ | (Chen et al., 2010) |
| • $MnO_2$<br>• $Fe_2O_3$<br>• $Al_2O_3$ | 25 mg/mL | Maillard Reaction/Integrated Polyphenol- | Glucose + glycine<br>Catechol + glucose + glycine | • The order of catalytic activity is $MnO_2 > Fe_2O_3 > Al_2O_3$<br>• The humic products produced by $MnO_2$ had the most aliphatic carboxylic in nature compared to $Fe_2O_3$ and $Al_2O_3$ | (Hardie et al., 2010) |

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| | | Maillard reaction | | | |
| • Kanuma soil (allophanic soil)<br>• Zeolite<br>• Bentonite<br>• Aluminum silicate | 2 g/150 mL | Polyphenol-amine reaction | Catechol + glycine | • Allophanic soil, which has a surface area of 36.30 ± 0.05 $m^2$/g, showed higher humification potential than clays with lower surface area, such as bentonite (34.73 ± 0.07 $m^2$/g) and zeolite (26.82 ± 0.04 $m^2$/g)<br>• In contrast, kaolin and aluminum silicate have low humification potential<br>• Fe and Ti in clays contribute more to humification than other elements, such as Al or Si<br>• $Ca^{2+}$ in clays was also correlated with the rate of humification reaction | (Miura et al., 2009) |
| Allophanic soil | 2 g/150 mL | Polyphenol-amine reaction | Catechol + glycine | • Allophanic soil effectively enhanced humification reaction | (Fukushima et al., 2009) |
| Nontronite | 1 g/75 mL | Polyphenol reaction | Hydroquinone | • Nontronite has higher humification potential than montmorillonite and hectorite<br>• The nontronite's interlayers have been deposited with humic macromolecules | (Wang and Huang, 1986) |
| Mg/Fe-LDH | 2 g/L | Integrated Polyphenol-Maillard reaction | Catechol + glucose + glycine | • Fe(III)-catechol is produced by the combination of catechol and iron released from Mg/Fe-LDH.<br>• Without light illumination, the reaction of humification accelerated by Mg/Fe-LDH was more effective | (Zhang et al., 2021) |
| Zn/Al-LDH-$Fe_3O_4$ composite | 5 mg/mL | Integrated Polyphenol-Maillard reaction | Catechol + glucose + glycine | • The humification conversion can reach up to 65% and 668 mg/g of HS<br>• The obtained HS showed good performance on toxic metal adsorption | (Li et al., 2019) |

**Table S4.** Effects of different catalysts on humification during composting

| Additives | Dose | Scale | Compost Materials | Remarks/Impact | Ref. |
|---|---|---|---|---|---|
| $MnO_2$ | 0.05% of $MnO_2$ | Lab scale: 35 L | Chicken manure (CM)/Rice straw (RS): 5/1 | • The production of highly humified components was accelerated by $MnO_2$ (79.2% for component 2 and 45.8% for component 3)<br>• The percentage of the primary bacteria responsible for FA transformation increased due to $MnO_2$ | (Qi et al., 2021a) |
| $MnO_2$ | 0.05% of $MnO_2$ | Lab scale: 35 L | Chicken manure (CM)/Rice straw (RS): 5/1 | • $MnO_2$ increased the OM degradation (34% compared to 29% of the control sample)<br>• FA and HA concentrations were not significantly impacted by $MnO_2$.<br>• FA and HA structure was affected by $MnO_2$.<br>• $MnO_2$ slows the rate at which the bacterial community regenerates | (Qi et al., 2021b) |
| $MnO_2$ | 0.5% | N/A | Chicken manure (CM)/<br>Corn straw (CS) | • CS:<br>○ $MnO_2$ reduced the sugar concentration (84.0%) in 5 days and increased HS by 38.7% compared with control<br>○ $MnO_2$ primarily served as an abiotic catalyst to encourage HS production<br>• CM:<br>○ The promoting effect of $MnO_2$ is weaker than that of CS<br>○ $MnO_2$ reshaped the bacteria community and stimulated them to use OM during CM composting | (Wu et al., 2018) |
| $Fe_xO_y$ | 10 mg/kg | Lab scale: 65 L | Rice straw, vegetable leaves, soil, and bran | • The number of thermophilic microorganisms required to break down OM increased due to $Fe_xO_y$<br>• The amino acid metabolism was accelerated by $Fe_xO_y$ | (Zhang et al., 2022) |
| $Fe_3O_4$ + *P. chrysosporium* | 1% $Fe_3O_4$ + 1% oxalic acid + 10 mL *P.* | N/A | Sediment/Rice straw (RS): 4/5 | • $Fe_3O_4$ improved HA generation and HM remediation<br>• $Fe_3O_4$ improved Pb's bioavailability, but only slightly improved Cd and Cu's | (Chen et al., 2021) |

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|---|---|---|---|---|---|
| | *chrysosporium* (2.0 × $10^6$ CFU/mL) | | | | |
| Tertiary-amine bentonite (TAB) | 0–10% | Lab scale: 100 L | Chicken manure (CM)/Wheat straw (WS): 5/1 | • TAB concentrations increased, leading to increases in HA content and polymerization of 11.71–27.08% and 3.40–47.0%, respectively<br>• TAB reduced the evaporation of $N_2O$ and $CH_4$ while increasing $CO_2$ emission; the 10% TAB treatment has a global warming potential score of only 108.99 | (Ren et al., 2019) |
| Clay | 10% | Lab scale: 80 L | Sawdust (SD)/Pig manure (PM): 1/2 | • A 45.88% decrease in $CH_4$ emissions and an 86.79% decrease in $NO_2$ emissions<br>• Enhancing OM degradation<br>• Accelerating HA formation<br>• Promoting aliphatic carbon oxidation and the creation of aromatic carbon compounds<br>• Facilitating the breakdown of tyrosine and tryptophan and the production of HS, increasing humification<br>• The HA/FA and HIX were rose by 14.44% and 1.96%, respectively, compared to the control treatment | (Ren et al., 2020) |
| Biochar/Montmorillonite | 10% | N/A | Chicken manure (CM)/Rice hull (RH) | • The humification degree of compost was increased<br>• HA, FA, and DOC are linked with Cu and Zn speciation<br>• The modifications broadened the range of bacteria with Cu resistance/actor and Zn actor properties<br>• The transformation of FA into HA reduces the HMs' toxicity | (Song et al., 2021) |
| Thermally treated montmorillonite (M-)/Illite(I-) | 7.5% | N/A | Chicken manure (CK)/Rice straw | • M- and I- enhanced the microbial diversity and compost quality<br>• Normal clays (M and I) increased the HA formation via abiotic pathways<br>• M- and I- encouraged the development of the HA by combining biotic and abiotic pathways | (Pan et al., 2021) |

| | | | | | |
|---|---|---|---|---|---|
| | | | | • HS level rose by 11.5%, 39.3%, 32.7%, 30.9%, and 27.6% during control, M-, M, I-, and I composting, respectively | |
| Zeolite + Lime ($Ca(OH)_2$) | 10%/15%/30% of zeolite + 1% of lime | Lab scale: 130 L | Biosolids/Wheat Straw (WS): 5/1 | • The zeolite and lime mixture had the highest enzymatic and humification<br>• The HMs' bioavailability (Cu and Zn) was decreased | (Awasthi et al., 2018) |
| BC + zeolite | 10% of BC + 4% of zeolite | Lab scale: 130 L | Pig manure (PM)/wheat straw (WS): 2/1 | • $NH_3$ and $NO_2$ emissions are reduced (63.4% and 78.13%, respectively).<br>• OM reduction was 15.57%, higher than single treatment (14.30% for zeolite and 13.22% for BC)<br>• DOC reduction rate was 60.04%, higher than single treatment (58.60% for BC and 58.37% for zeolite)<br>• The mixture resulted in the highest increase in HA production: 104.5%<br>• HA/FA: 2.95 (2.43 for BC and 2.01 for zeolite as a single treatment)<br>• Total nitrogen loss was 19.72%, which was lower than the single treatment | (Wang et al., 2017) |

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