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Enzyme catalyzed oxidative humification reactions (ECOHRs): PFAS remediation and thatch management

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Enzyme-Catalyzed Oxidative Humification Reactions (ECOHRs) are primarily recognized for their involvement in the degradation of lignin. Lignolytic fungi produce extracellular enzymes under nutrient-deficient conditions, which can act directly or indirectly through small-molecule mediators to modify a range of compounds in the environment. The enzymes mediating ECOHRs mainly include laccases, lignin peroxidases (LiP), and manganese peroxidases (MnP), whose properties and catalysis mechanisms are summarized and compared in this review. As an example showcasing the possible environmental application of ECOHRs, the effects of ECOHRs in mediating the transformation of two key per- and polyfluoroalkyl substances (PFAS), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), were discussed. Reports have shown their significant concentration reduction (40%–59%) in systems with ECOHRs induced by amendments with laccases and mediators. Nontarget products identification using high-resolution mass spectrometry suggests that PFOA and PFOS degraded in ECOHR systems primarily through free-radical chain reactions. Reports on the use of laccase to reduce and manage the thatch layer on turf grass are also discussed in this review as another example of ECOHRs application. Laccase application at a rate of 2 U/cm² once per month was found to be as effective as traditional thatch management methods, with the ECOHR effects leading to a reduction in the thatch thickness by 18%–22% in bermudagrass and 21%–30% in zoysiagrass. Overall, this review addresses the concept of ECOHRs, with the major enzymes and systems introduced, and highlights their possible environmental applications exemplified by PFAS remediation and thatch management.

KEYWORDS

enzyme catalyzed humification reactions (ECOHRs), PFAS, dethatching, remediation, laccase-mediator system, laccase, lignin peroxidase (LiP), manganese peroxidase (MnP)

1 Introduction

ECOHRs refer to a class of reactions critically involved in natural organic matter humification processes (Guggenberger, 2005). They are ubiquitous in soil systems and are usually catalyzed by extracellular enzymes produced by certain white/brown rot fungi. One natural function of these fungi is to degrade lignin, an integral part of the plant cell wall (Zavarzina et al., 2010). Lignin is the most persistent natural organic matter, comprising three-dimensional complex heteropolymer of aromatic alcohols. White/brown rot fungi are reported to be the most efficient lignin degraders in nature, with no other microorganisms

being reported with a similar function, and thus play a unique role in plant organic matter turnover and carbon cycling (Atiwesh et al., 2022).

The special capability of white/brown rot fungi in degrading lignin is attributed to the extracellular enzymes that they produce, such as lignin peroxidases, manganese peroxidases, and laccases. These enzymes can effectively convert small-molecule chemicals containing phenolic or anilinic moieties into active intermediates, such as radicals or quinones. These intermediates are highly reactive, and undergo further reactions, including self-coupling and covalent bonding into natural organic matter. In the meantime, the active intermediates may also attack other inert chemicals, such as lignin, and thus cause their degradation and consequently be incorporated into the natural humification process (Abdel-Hamid et al., 2013). The small-molecule chemicals that serve as active intermediates during these enzymatic reactions are also referred to as mediators.

ECOHRs have been investigated for their potential applications, such as pulping, bleaching, dye decolorization, as well as remediation of water and soil contaminated with xenobiotics (Levin et al., 2019; Wei et al., 2021; Falade et al., 2018; Qayyum et al., 2009; Mohajershojaei et al., 2015; Mahmoodi et al., 2014; Mahmoodi and Saffar-Dastgerdi, 2020). It is regarded that the use of fungi or extracellular fungal enzymes in remediation has advantages due to their great resilience in environments of high pollutant concentrations, less stringent substrate specificity, and adaptability to extreme conditions (Chekroun et al., 2014; Aparici-Carratalá et al., 2023; Mehrotra et al., 2021).

This review introduces ECOHRs, including the major enzymes and catalytic mechanisms, and highlights their potential use as a novel strategy to address diverse environmental challenges, with PFAS remediation and turfgrass dethatching as examples. Where appropriate, knowledge gaps are identified with research needs discussed. This review is intended to facilitate new ideas in ECOHRs research and development of ECOHR-based strategies for pollutant remediation and ecosystem management.

2 ECOHRs

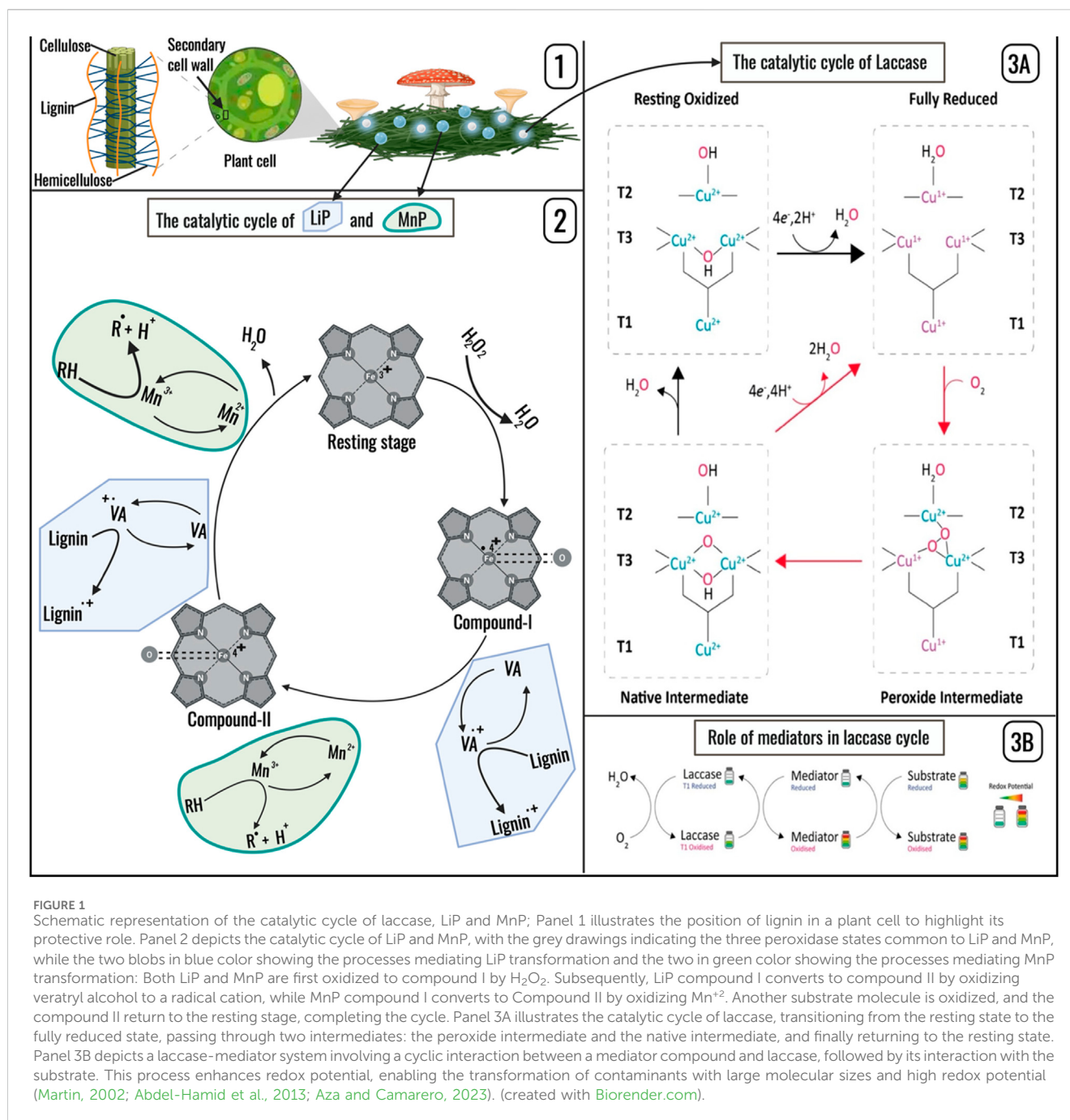
White/brown fungi belong to the second most abundant phylum, *Basidiomycota* (Harms et al., 2011). These fungi shift to secondary metabolism as a defense mechanism or under nutrient-deficient conditions and produce extracellular enzymes as well as small-molecule mediators, which, working together, can decompose complex compounds and are commonly involved in lignin degradation (Dashtban et al., 2009). These extracellular enzymes offer several advantages, including broad substrate specificity, facile harvesting and scalability (Schmidt-Dannert, 2016; Dashtban et al., 2009). Harvesting typically involves fungal fermentation in specific nutrient media that induce extracellular enzyme secretion into the culture broth, after which the broth is filtered and/or centrifuged to separate them from the mycelial biomass (Liu et al., 2016; Nüske et al., 2002). Moreover, purification of ECOHR enzymes is not required for remediation applications as seen in several studies, thereby enhancing cost-effectiveness and applicability (Ding et al., 2022; Luo et al., 2018b; Wen et al., 2010).

Laccase (EC 1.10.3.2) contains four copper atoms covalently bonded to the protein backbone through ten histidine residues and

one cysteine residue, including one Type 1 (T1) copper, one Type 2 (T2) copper, and two Type 3 (T3) copper atoms that are coordinated by six histidine residues (Mot and Silaghi-Dumitrescu, 2012). The T2 and T3 coppers together form a trinuclear cluster (TNC), which is connected to the T1 site via a His-Cys-His triad (Quintanar et al., 2005). The binding pocket at the T1 site enables laccase to bind with a diverse range of substrates. A catalytic cycle with the laccase's four coppers starting in the resting oxidized state is schematically shown in Figure 1 (Panel 3A). The substrate undergoes oxidation at the T1 site, with T1 copper reduced, and the electrons are shuttled until all copper ions reach the fully reduced state (Jones and Solomon, 2015). Subsequently, the trinuclear copper cluster (TNC) interacts with molecular oxygen (O₂), initiating stepwise copper oxidation. T2 and one of the T3 copper ions are first oxidized, leading to the formation of a peroxide intermediate, followed by O–O bond cleavage via electron transfer from T1 and the oxidation of the second T3 copper, assisted by a proton from carboxylate residues near the TNC center, forming the native intermediate (Jones and Solomon, 2015). At this stage, if a substrate is present, it is oxidized by the native intermediate with electrons shuttled to all copper atoms to reach the fully reduced state again, releasing water as a byproduct, forming a catalytic cycle. In the absence of a substrate, the intermediate gradually decays to the resting oxidized form by releasing one water molecule, which may enter the catalytic cycle again when a substrate is present (Jones and Solomon, 2015).

Laccase has a relatively low redox potential (0.4–0.8 V vs. normal hydrogen electrodes) but can interact with mediators to form reactive species that have higher redox potentials and thus enable reactions with a wider range of substrates (Lin et al., 2023). Mediators can be generated by lignin decomposition and are abundant in natural organic matter, such as syringaldehyde, coumaric acid, vanillin, and veratryl alcohol (Cañas and Camarero, 2010; Christopher et al., 2014). The mediators react with laccase to form highly reactive free radicals and/or quinones that can diffuse and oxidize substrates that are otherwise nonreactive to laccase. This process is cyclic, with the mediators continuously oxidized by laccase and the oxidized species reduced by the substrates (Figure 1, Panel 3B). The ideal mediators for laccase-mediator applications are non-toxic, highly effective, and responsive to the enzymatic reactions, to ensure continuous redox cycling. Recent studies have indicated that soybean meal (a soil amendment) contains phenolic compounds, such as vanillin, apocynin, and daidzein, thus providing an ideal, low-cost, natural source of laccase mediators for remediation purposes (Komorowicz et al., 2023; Sebastian et al., 2024; Chia et al., 2024; Liang et al., 2017).

Peroxidases (EC 1.11.1. X) are another class of enzymes able to mediate ECOHRs, for instance lignin peroxidase (LiP) and manganese peroxidase (MnP), which are involved in lignin degradation. Both LiP (EC 1.11.1.14) and MnP (EC 1.11.1.13) are heme-containing oxidoreductases in which Fe (III) is pentacoordinated with four heme tetrapyrrole nitrogens and one amino acid. They share a similar general catalytic mechanism; however, differ in substrate specificity and electron transfer route (Figure 1, Panel 2) (Rahi and Parmar, 2021). The catalytic cycle begins with the oxidation of the resting-state enzyme by H₂O₂, producing Compound I, an unstable two-electron oxidized intermediate characterized as an Fe (IV) = O porphyrin radical cation. This specie forms through electron transfer within the heme



during peroxidase-mediated O–O bond cleavage, which also releases a water molecule. Subsequently, LiP and MnP follow one-electron oxidation, resulting in free radicals of their respective substrates, leading to the reduction of Compound I to Compound II (an Fe (IV) = O porphyrin complex). Finally, Compound II is further reduced back to the resting state upon oxidizing an additional substrate molecule to a free radical, accompanied by the release of another water molecule (Kumar and Chandra, 2020; Rahi and Parmar, 2021). A key difference between LiP and MnP lies in the substrate preference. LiP can directly oxidize aromatic substrates or utilize veratryl alcohol as a mediator to enhance oxidative efficiency (Kulikova et al., 2011), whereas MnP primarily oxidizes Mn^{2+} to Mn^{3+} . Unlike LiP, MnP does not generate any metabolic mediator;

instead, the Mn^{3+} product itself acts as a diffusible mediator after stabilization by organic acids such as oxalate. Another major distinction between LiP and MnP is the presence of a surface-exposed tryptophan residue (Trp171) in LiP, which enables the oxidation of distant aromatic substrates, a feature absent in MnP (Bernini et al., 2012; Kamitsuji et al., 2005). Versatile peroxidase (VP) exhibits qualities of both LiP and MnP which enable it to oxidize Mn^{2+} as well as low and high-molecular-weight substrates. The hybrid nature of VP is attributed to its unique structural feature with two distinct channels that carry out LiP and MnP functions, respectively (Ruiz-Duenas et al., 2009).

The ECOHR enzymes are pivotal in environmental catalysis; however, they also have some notable limitations. Laccase is

TABLE 1 Summary of studies examining PFAS degradation in ECOHRs with an overview of reported experimental conditions, PFAS initial concentrations, and degradation efficiencies.

Study	References	Substrate	Conditions	Total substrate degradation	Starting concentration
1	Luo et al. (2015)	PFOA	1 U/mL laccase, 2 and 20 μM 1-hydroxybenzotriazole (HBT) as mediator	50% in water after 157 days	1 μM
2	Luo et al. (2017)	PFOA	1 U/mL laccase, HBT (0, 20, 100 μM), Cu ⁺² (0.1, 1, 10 mM), Mg ⁺² (0.1, 1, 10 mM), Mn ⁺² (0.1, 1, 10 mM), Fe ⁺² (0.2 mM)	45.7% for 1 μM PFOA and 46.8% for 100 μM after 156 days	1 μM, 100 μM
3	Luo et al. (2018a)	PFOS	1 U/mL laccase, 20 μM HBT, 10 mM metal ions (Cu ⁺² , Mg ⁺²)	59% in water after 162 days	1 μM
4	Mekureyaw et al. (2025)	PFOA	1 and 5 U/mL laccase, 20 μM HBT	95% in water after 55 days	1 μM
5	Luo et al. (2018b)	PFOA	20 U/g laccase every 4 weeks or 60 U/g at once, 50 mg/g soybean meal	40% in soil slurry in 140 days	0.5 μg/g
6	Tseng et al. (2014)	6:2 FTOH	<i>P. Chrysosporium</i> strain, 100 mg lignocellulosic powder, 0.25 mg yeast extract, and 2 mg cellulose with either 10 mg glucose or no glucose	48%–52% after 28 days	1.7 mg/L
7	Merino et al. (2018)	6:2 FTOH	<i>Gloeophyllum trabeum</i> , <i>Trametes versicolor</i> , and six fungal isolates from PFAS contaminated sites, no nutrient addition or 10 mg glucose, 0.25 mg yeast extract and 2 mg cellulose	18–84 mol% removed by different fungi	3 mg/L
8	Merino et al. (2023)	6:2 FTOH	<i>Phanerochaete Chrysosporium</i> , addition or removal of lignocellulose, yeast extract, cellulose, substituting MnSO ₄ with MnCl ₂ , replacing diammonium tartrate with ammonium chloride, nitrilotriacetic acid (NTA) in place of ethylenediaminetetraacetic acid (EDTA), non-ligninolytic nutrient-rich Malt Extract (ME) medium	19.3–93.6 mol% under different nutrient compositions	3 mg/L
9	Zhou et al. (2023)	PFOA	<i>P. chrysosporium</i> strain, 0.04 mM and 40 mM veratryl alcohol	69.23% removal after 35 days	0.002 mM
10	Grimberg et al. (2024)	6:2 FTS	<i>P. ostreatus</i> and <i>T. cervina</i> strains, 75 g/L soybean meal, 1 mg/L Cu ⁺²	50 mol% removed after 30 days	1.15 μg/mL

restricted to low-redox-potential substrates, and requires mediators for non-phenolic oxidation, which can generate toxic byproducts (Gu et al., 2021), while this challenge can be addressed by using natural mediators, such as those from the soybean meal (Liang et al., 2017). LiP and MnP use hydrogen peroxide as the oxidant, which is itself hazardous, and MnP depends on organic acids to stabilize Mn³⁺, restricting the substrate range. Both LiP and MnP exhibit low natural production, limiting their large-scale applicability (Biko et al., 2020; Hofrichter, 2002). Laccase uses oxygen as the oxidant, and it can be produced by fermentation with high productivity, and thus offers great potential for various environmental applications. The environmental application of laccase-induced ECOHRs is discussed below with two examples.

3 ECOHRs application in PFAS remediation

PFAS are defined as fluorinated alkyl substances with at least one fully fluorinated methyl or methylene carbon atom (OECD, 2021), also known as “forever chemicals”. Perfluoroalkyl acids (PFAAs) are

the most persistent subset of PFAS, with all alkyl carbons being fully fluorinated, having extreme thermal and chemical stability because of the strong carbon-fluorine (C-F) bonds (Lemal, 2004) and the protective helical conformation of the perfluorinated carbon chain (Battye et al., 2022; Patch et al., 2022). PFAS are extensively used in industrial and consumer applications, and their persistence has led to global environmental distribution (Wang et al., 2023; O’Hagan, 2008). Their bioaccumulative nature poses serious health risks, including increased incidences of kidney, prostate, and testicular cancers (Panieri et al., 2022; Zhang et al., 2010).

PFAS transformation under ECOHRs has been investigated in aqueous and soil matrices, primarily for PFOA and PFOS, the two most extensively detected PFAS in the environment (Table 1). PFOA, a representative PFAS, was investigated under ECOHRs induced by LMS (laccase-mediator system) (Table 1, Study 1) (Luo et al., 2015). After 157 days of treatment, PFOA exhibited an approximate 50% decrease in concentration, accompanied by 28.3% defluorination.

High-resolution mass spectrometry (HRMS) identified PFOA transformation products, including alcohols, aldehydes, and aromatic compounds, which were either partially fluorinated or

retained a perfluoroalkyl moiety. The reaction proceeds via electron transfer from the carboxyl headgroup to the HBT (1-hydroxybenzotriazole) radical, followed by Kolbe decarboxylation, hydrolysis, and elimination of fluorine to form one-carbon less perfluoroalkyl carboxylic acid (PFCA), and this CF_2 unzipping process goes on until PFCA is mineralized. Products may also form by radical rearrangements, while cross-coupling with nonfluorinated organics generates partially fluorinated products (Luo et al., 2015). Recently, a concern has been raised that the observed PFAS concentration reduction in LMS may not be from their degradation but PFAS adsorption by the enzymes (Steffens et al., 2023). However, the experiments examining PFAS degradation in LMS were carried out with control treatments that had ruled out the contribution by PFAS adsorption (Luo et al., 2015; Luo et al., 2018b). PFOA was further investigated under variable treatment levels in LMS to assess ECOHR efficacy (Luo et al., 2017). Comparable degradation efficiency was observed even at a higher PFOA concentration (100 μM) under identical conditions (Table 1, Study 2). Additionally, increasing the laccase dosage (5 U/mL) (Table 1, Study 4) markedly improved PFOA degradation efficiency (95% in 55 days) (Mekureyaw et al., 2025). However, relatively high mediator concentration (100 μM) resulted in enzyme deactivation due to excess production of the HBT free radicals, which could induce radical quenching by self-coupling and thus reduce PFOA transformation (Table 1, Study 2). In addition, it was found that certain divalent cations, such as Cu^{2+} (10 mM), could enhance the degradation of PFOA by bridging laccase and PFOA, both of which are negatively charged (Luo et al., 2017). Another study (Table 1, Study 3) with PFOS as the model PFAS resulted in 59% degradation over 162 days with 47% defluorination and similar degradation products (Luo et al., 2018b). For the studies presented in Table 1 Study 1–5, it was proposed that the free radicals produced from the mediators by LMS initiated free-radical chain reactions leading to the observed products, involving C-C cleavage, decarboxylation, free radical rearrangements, and cross-coupling, evidenced by products identification with HRMS (Luo et al., 2017; Luo et al., 2015; Luo et al., 2018b). The complexation between multivalent cations and PFAA reduces the C-C bond energy and unravels the helical configuration, making PFAAs more susceptible to free-radical reactions during ECOHRs (Luo et al., 2018b). ECOHRs have also demonstrated effective transformation of PFOA in soil slurry via the amendment of laccase and soybean meal (Table 1, Study 5). Soybean meal contains high concentrations of small molecules that can serve as laccase mediators (Liang et al., 2017) and multivalent metal cations, both factors having been identified as essential to PFAA degradation by ECOHRs (Luo et al., 2018b). The experiment led to a 40% PFOA degradation via free-radical chain reactions similar to those by ECOHRs in the aqueous phase (Luo et al., 2018a).

PFAS transformation by ECOHRs has also been investigated with live fungal species, including wood rot fungi *Trametes versicolor*, *Pleurotus ostreatus*, *Phanerochaete chrysosporium*, *Trametes versicolor*, and *Gloeophyllum trabeum* (Grimberg et al., 2024; Merino et al., 2018; Zhou et al., 2023) (Table 1, Study 6–10). The degradation mechanism involved fungal thallus adsorption followed by biotransformation mediated by extracellular ECOHR enzymes produced by the fungi.

PFAS initially (0–14 days) negatively affected the structure and activity of the enzymes, however in the next phase (14–35 days) fungal defense mechanism was activated to enhance cell survivability. Incubation time and growth medium composition have significant effects on enzyme activity levels and degradation pathways. The highest enzyme activities were observed at day 47 and 53 for Lip and MnP, respectively (Zhou et al., 2023). Limited supply of glucose produced sufficient metabolic energy and reducing power that led to greater production of 5:3 FTCA (fluorotelomer carboxylic acid) from 6:2 FTOH (fluorotelomer alcohol) degradation. Moreover, low glucose coupled with cellulose and yeast extract was able to divert the 6:2 FTOH degradation pathway from forming short PFAS products to 5:3 FTCA (Merino et al., 2023).

A life cycle assessment (LCA) of ECOHR-based remediation of PFAS or any other pollutants has not been reported and is needed in future research. LCA of some other enzymatic treatments has generally shown lower energy use, reduced ozone depletion, and fewer photochemical oxidants, underscoring their sustainability (Gabarrell et al., 2012); and switching electricity to steam for fungal medium sterilization could further improve energy use efficiency (Zhi Fu et al., 2005). ECOHR-based pollutant remediation is expected to benefit similarly as the other enzymatic treatment processes, and using crude enzyme for environmental applications eliminates the need for enzyme purification, further reducing costs (Nüske et al., 2002; Ding et al., 2022). However, a detailed techno-economic analysis is still needed in future research to elucidate capital and operational expenditures, and overall cost-effectiveness under real-world implementation scenarios.

4 ECOHRs applications in thatch management

Thatch forms as a thick organic matter layer between soil and turfgrass when the organic matter accumulation rate exceeds its degradation rate. It restricts hydraulic conductivity, oxygen diffusion, and reduces turfgrass quality. (McCarty et al., 2007; Sidhu et al., 2022; Braun et al., 2024). Lignin, a major structural component of the plant cell wall, forms a protective matrix embedding cellulose and hemicellulose (Figure 1, Panel 1) (Yadav and Chattopadhyay, 2023), thereby contributing substantially to thatch accumulation and limiting the effectiveness of conventional microbial management strategies. Its exceptional recalcitrance arises from a highly heterogeneous and cross-linked structure (Wong, 2009; Yadav and Chattopadhyay, 2023), hydrophobicity, and the abundance of phenolic hydroxyl groups (Zoghalmi and Paës, 2019; Takeda et al., 2017). Functionally, lignin not only acts as a physical barrier but also inhibits cellulolytic enzyme activity, making it the principal rate-limiting factor in the microbial decomposition of organic matter (Brink et al., 2019).

Thatch is commonly managed through cultural practices like core aeration, sand topdressing, or supplementation of microbes and sugars to boost microbial activity. Core aeration and sand topdressing reduce the turf aesthetic and physical quality, leading to financial losses (Sidhu et al., 2022), while primary focus of microbial approach is cellulose and hemicellulose, which are structurally shielded by lignin. Conversely, ECOHRs induced by

laccase application directly transform lignin; i.e., laccase catalyzes electron withdrawal from the phenolic hydroxyl group to form phenoxy radicals that lead to C α -C β cleavage, alkyl-aryl cleavage, and C α oxidation, thus disrupting the complex lignin structure and making labile carbohydrates accessible to microbial degraders (Wong, 2009; Zhao et al., 2025).

ECOHRs for thatch management have been tested in multiple studies at different scales by laccase application (Sidhu et al., 2022). It was found that ECOHRs induced significant dethatching effects, including decreased thatch thickness, reduced organic matter and monosaccharide content, and lower total lignin concentration. These effects led to improved hydraulic conductivity and thus facilitated sustainable, nondestructive thatch management (Sidhu et al., 2013b). Following successful greenhouse trials, a multi-year field study resulted in 18%–22% reduction in thatch layer thickness in bermudagrass and 21%–30% for zoysiagrass and identified the optimal treatment conditions (Sidhu et al., 2013a), demonstrating that a monthly application of 2 U cm⁻² laccase for 6 months annually achieved dethatching efficiencies comparable to those obtained with conventional mechanical methods, thereby confirming the practical applicability of the approach under real-world conditions (Sidhu et al., 2014; Sidhu et al., 2019).

5 Conclusion

ECOHRs have been presented as a sustainable strategy with applications in dethatching and PFAS remediation. It transformed PFOA (40% in soil, ~50% in water), PFOS (59% in water), and 6:2 FTOH (18–93.6 mol% under different conditions), as well as reduced the thatch layer in Bermuda and Zoysia grass by 18%–30%. Their potential for large-scale soil remediation and dethatching offers both environmental and economic benefits. However, field-scale validation of soil remediation with PFAS mixtures, co-contaminants, and variable concentrations remains a critical next step.

Author contributions

UM: Conceptualization, Data curation, Formal Analysis, Investigation, Visualization, Writing – original draft,

Writing – review and editing. YW: Writing – review and editing. QH: Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review and editing.

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