Ligninolytic Enzymes in Environmental Management

12

K.K. Sharma, Deepti Singh, Sapna, Bijender Singh, and Ramesh Chander Kuhad

Abstract

By producing lignocellulose-degrading enzymes, saprotrophic litter-decomposing Basidiomycetes can significantly contribute to the turnover of soil organic matter. The production of lignin- and polysaccharide-degrading enzymes helps in converting the waste litter into value-added compost. White-rot fungi (WRF) have tremendous potential for biodegradation of a variety of industrial pollutants. The capability of WRF for biodegradation of xenobiotics and recalcitrant pollutants has generated a considerable research interest in this area of environmental biotechnology. The broad spectrum for biodegradation of pollutants is due to the extracellular and nonspecific nature of the enzyme system of fungi, comprising mainly of lignin peroxidase (LiP), manganese peroxidase (MnP), versatile peroxidase, and laccase along with other ancillary enzymes. Differential biodegradation capabilities of WRF are mainly due to physiological differences among them, difference in their genetic makeup, and variable pattern and expression of complex lignin-modifying enzymes (LMEs). The activities of the LMEs can be increased by the addition of different low-molecular-mass mediators, mostly secreted by white-rot fungi themselves.

Keywords

Lignin • Laccase • White-rot fungi • Lignin-modifying enzymes • Biodegradation • Bioremediation

Introduction

Fungi are an important and diverse component of soil microbial communities. They provide essential ecosystem functions, such as decomposing organic matter, nutrient cycling, and in the case of mycorrhizal species, also nutrient transfer to plants. In forest ecosystems they are largely

K.K. Sharma (✉) • D. Singh • Sapna • B. Singh
Department of Microbiology, Maharshi Dayanand University, Rohtak 124001, Haryana, India
e-mail: kekul_sharma@yahoo.com

R.C. Kuhad
Lignocellulose Biotechnology Laboratory, Department of Microbiology, University of Delhi South Campus, Benito Juarez Road, New Delhi 110021, India

R.C. Kuhad and A. Singh (eds.), *Biotechnology for Environmental Management and Resource Recovery*, DOI 10.1007/978-81-322-0876-1_12, © Springer India 2013

responsible for breakdown of the abundant large biopolymers cellulose, hemicellulose, lignin, and chitin (Dighton et al. 2005; Kellner and Vandenbol 2010). Recent report suggests the importance of both ascomycetes, as well as Basidiomycetes, in key biogeochemical cycles (Kellner and Vandenbol 2010).

In terrestrial environments, Basidiomycetes are one of the most ecologically significant groups of fungi involved in the breakdown of litter components. They constitute a major fraction of the living biomass responsible for efficient degradation of many recalcitrant organic compounds in soil litter and the humic layer (Dix and Webster 1995; Steffen et al. (2007a, b). An efficient group of litter-degrading organisms are litter-decomposing Basidiomycetes, which produce a wide variety of oxidoreductases and hydrolytic enzymes and are also able to degrade lignin, the most recalcitrant litter component (Steffen et al. 2000). In contrast, Benner et al. (1986), in a study of lignocellulose degradation by microbial samples from two freshwater and two marine habitats, stated that bacteria rather than fungi were the predominant degraders of lignocellulose in aquatic habitat.

Basidiomycetes also have tremendous potential for biodegradation of a variety of industrial pollutants. The broad spectrum for biodegradation of pollutants is due to the extracellular and nonspecific nature of the enzyme system of white-rot fungi (WRF), comprising mainly of lignin peroxidase (LiP), manganese peroxidase (MnP), versatile peroxidase (VP), and laccase along with other accessory enzymes (Table 12.1). The biodegradation capabilities of WRF for different pollutants are variable, mainly due to physiological differences among them and variable pattern and expression of complex lignin-modifying enzymes (LMEs) in the presence of chemically different compounds (Asgher et al. 2008).

Extracellular hydrolases and oxidoreductases are involved in the breakdown of lignocellulose and are produced by many known bacteria, actinomycetes, and ligninolytic fungi. Lignocellulytic enzymes and their biotechnological application have already been discussed in earlier papers, but there is still an ongoing interest, especially in their occurrence and environmental significance. Cellulases, in particular the complex consisting of endoglucanase, cellobiohydrolase, and beta-glucosidase, hydrolyze the long chains of cellulose, resulting in the liberation of cellobiose and finally glucose. Hemicelluloses, such as endo-1,4-β-xylanase or mannanase, are involved in the breakdown of different heterogeneous polysaccharide chains such as xylans and mannans.

Lignin, polysaccharides, and nitrogenous compounds contribute in the formation of humus (Varadachari and Ghosh 1984; Fustec et al. 1989; Inbar et al. 1989). The chemical pathway from organic matter to humus involves complex degradative and condensation reactions. According to Varadachari and Ghosh (1984), lignin is first degraded by extracellular enzymes to smaller units, which are then absorbed into microbial cells where they are partly converted to phenols and quinones. Thereafter, the substances are discharged together with oxidizing enzymes into the environment, where they get polymerized by a free-radical mechanism. Composting is a dynamic process carried out by a rapid succession of mixed microbial consortia including bacteria, actinomycetes, and fungi (Tuomela et al. 2000; Kellner and Vandenbol 2010).

A wide range of bacteria have been isolated from different compost environments, including species of *Pseudomonas, Klebsiella,* and *Bacillus,* e.g., *B. subtilis*, *B. licheniformis,* and *B. circulans* (Nakasaki et al. 1985; Strom 1985a, b; Falcon et al. 1987). Actinomycetes appear during the thermophilic phase as well as the maturation phase of composting and can occasionally become so numerous that they are visible on the surface of the compost. The genera of the thermophilic actinomycetes isolated from compost include *Nocardia*, *Streptomyces*, *Thermoactinomyces*, and *Micromonospora* (Waksman et al. 1939; Strom 1985a).

Lignin Degradation

Lignin-degrading Basidiomycetes, collectively referred to as white-rot fungi, are common inhabitants of forest litter and fallen trees. These are

Table 12.1 Ligninolytic enzymes produced by white-rot fungi

Enzyme	EC no.	Reaction catalyzed	Applications	References
Laccase	1.10.3.2	Phenol oxidation	Spore resistance; rhizomorph formation; pathogenesis; fruit bodies formation; pigments synthesis; lignin degradation	Yaropolov et al. (1994), Mayer and Staples (2002), Claus (2004), Minussi et al. (2007), and Maciel et al. (2010)
Lignin peroxidase	1.11.1.14	Phenol polymerization	Biodegradation of lignin defense of fungi against pathogens	Gold and Alic, (1993), Haglund, (1999), Piontek et al. (2001), Erden et al. (2009), Score et al. (1997), Trejo-Hernandez et al. (2001), and Maciel et al. (2010)
Manganese peroxidase	1.11.1.13	Phenol oxidation; oxidize Mn^{2+} to Mn^{3+}	Degradation of lignin interspecific fungal interactions	Hofrichter (2002), Score et al. (1997), Trejo-Hernandez et al. (2001), and Maciel et al. (2010)
Aryl-alcohol oxidase	1.1.3.7	H_2O_2 production		Martínez et al. (2009)
Glyoxal oxidase	1.2.3.5	H_2O_2 production		Martínez et al. (2009)
Manganese independent peroxidase	1.11.1.7	Activity on aromatic substrates		Wyatt and Broda (1995) and Ruiz-Dueñas et al. (2009)
Versatile peroxidase	1.11.1.16	Oxidizes Mn^{2+}; high redox potential aromatic compounds	Able to efficiently oxidize phenolic compounds and dyes that are the substrates of generic peroxidases and related peroxidases	Ruiz-Dueñas et al. (2009)
Cellobiose dehydrogenase	1.1.99.18	Lignin degradation; unite the hydrolytic and oxidative systems; dispose manganese (MnII) for MnP through precipitate reduction from manganese oxide (MnO_2)		Henriksson et al. (2000a, b), Kersten and Cullen (2007), and Carvalho et al. (2009)

the only microbes that have been convincingly shown to efficiently depolymerize, degrade, and mineralize all components of plant cell walls including cellulose, hemicellulose, and the more recalcitrant lignin. As such, white-rot fungi play an important role in the carbon cycle (Kersten and Cullen 2007).

From the chemical point of view, lignin is a heterogeneous, optically inactive polymer consisting of phenylpropanoid interunits, which are linked by several covalent bonds (e.g., aryl-ether, aryl-aryl, carbon-carbon bonds) (Hofrichter 2002). The polymer arises from laccase- and/or peroxidase-initiated polymerization of phenolic precursors via the radical coupling of their corresponding phenoxy radicals. It is synthesized by higher plants, reaching levels of 20–30% of the dry weight of woody tissue. Because of the bond types and their heterogeneity, lignin cannot be cleaved by hydrolytic enzymes as most other natural polymers. Therefore, lignin is degraded with the help of different nonspecific oxidoreductases which specifically attack the aromatic moieties, preferably phenolic structures. The most widely studied enzymes in this group are laccase, LiP, MnP, and several other peroxidases such as VP (Sharma and Kuhad 2008).

Lignolytic Enzymes and Their Occurrence

Extracellular oxidative enzymes involved in lignin depolymerization include an array of oxidases and peroxidases. These enzymes are responsible for generating highly reactive and nonspecific free radicals that affect lignin degradation. The nonspecific nature and extraordinary oxidation potential of the peroxidases have attracted considerable interest in the development of several bio-processes.

Laccase

Laccase (benzenediol, oxygen oxidoreductases, EC1.10.3.2) is one of the few lignin-degrading enzymes that have been extensively studied since the eighteenth century. Laccases are majorly reported from eukaryotes, e.g., fungi, plants, and insects (Mayer and Staples 2002). However, some evidences for its existence in prokaryotes, with typical features of multicopper oxidase enzyme family, have also been reported (Alexandre and Zulin 2000). The first bacterial laccase was detected in the plant root-associated bacterium, *Azospirillum lipoferum* (Givaudan et al. 1993), where it was shown to be involved in melanin formation (Faure et al. 1994). A typical laccase containing six putative copper binding sites was discovered in marine bacterium *Marinomonas mediterranea*, but no functional role was assigned to this enzyme (Solano et al. 1997; Sanchez-Amat et al. 2001). In insects, laccases have been suggested to be active in cuticle sclerotization (Dittmer et al. 2004). Two isoforms of *laccase 2* gene have been found to catalyze larval, pupal, and adult cuticle tanning in *Tribolium castaneum* (Arakane et al. 2005), and a novel laccase has been isolated and characterized from a bovine rumen metagenome library that neither exhibited any sequence similarity to known laccases nor contained hitherto identified functional laccase motifs (Beloqui et al. 2006).

Recently, Sharma and Kuhad (2009), has reported 22 COGs from Archaea, bacteria, and eukaryotes (http://img.jgi.doe.gov. and http://www.ncbi.nlm.nih.gov/cog). Genome-specific best hit resulted in very exhaustive genomic information of diverse multicopper oxidases. Laccase (CotA) from *B. subtilis* 168 and *B. pumilus* SAFR-032 was found to share a common clade and close ancestry with multicopper oxidase from *Pyrobaculum aerophilum*, an Archaea. Moreover, *P. aerophilum* was also found to be evolutionary related to *E. coli* APEC O1 (laccase) and *Yersinia pestis* KIM (hypothetical protein). Well-known laccases from *T. versicolor* were found to be closely related to *Neurospora crassa* OR74A, *C. neoformans* var. *neoformans* JEC21, and *Drosophila melanogaster*, a common fruit fly. Multicopper oxidases from different yeast, i.e., FET3_Yeast, *Pichia stipitis* CBS6054 (FET3.1), and *Saccharomyces cerevisiae* (FET5), share a common phylogenetic position. An unusual evolutionary history was also established between pathogenic Proteobacteria, i.e., *Burkholderia mallei* and *Burkholderia pseudomallei*, and an archaeal species, i.e., *Haloarcula marismortui* ATCC 43049 and *Natronomonas pharaonis* DSM2160 (Sharma

and Kuhad 2009). Moreover, laccase has been extensively examined since the mid-1970s, and a number of reviews have appeared on the subject (Malkin et al. 1969; Malmstrom et al. 1975; Holwerda et al. 1976; Mayer and Harel 1979; Reinhammar 1984; Thurston 1994; Eriksson 2000; Xu 2005; Morozova et al. 2007; Sharma et al. 2007; Sharma and Kuhad 2008).

Lignin Peroxidase

Lignin depolymerization is catalyzed by extracellular peroxidases of white-rot Basidiomycetes such as *Phanerochaete chrysosporium* (Tien and Kirk 1983). Lignin peroxidase (LiP) was first discovered based on the H_2O_2-dependent C_α–C_β cleavage of lignin model compounds and subsequently shown to catalyze the partial depolymerization of methylated lignin in vitro (Glenn et al. 1983; Tien and Kirk 1983; Gold et al. 1984; Tien and Kirk 1984). Due to their high redox potentials and their enlarged substrate range in the presence of specific mediators, LiPs have great potential for application in various industrial processes (Paice et al. 1995). LiP, being a heme-containing glycoprotein with an unusually low pH optimum (Glumoff et al. 1990), is able to catalyze the oxidation of a variety of compounds with reduction potentials exceeding 1.4 V (vs. normal hydrogen electrode) (Steenken 1998). Contrary to other heme peroxidases, ferric LiP is first oxidized by H_2O_2 to compound I, a two-electron-oxidized intermediate, which is then reduced by one substrate molecule to the second intermediate, compound II. Further reduction back to the resting enzyme can be accomplished either by the same substrate molecule or a second one.

Manganese Peroxidase

Manganese peroxidase (MnP) is considered to be the most common lignin-modifying peroxidase produced by almost all wood-colonizing Basidiomycetes (Tien and Kirk 1983; Martínez et al. 2005). Multiple forms of this glycosylated heme protein with molecular weights normally at 40–50 kDa are secreted by ligninolytic fungi into their microenvironment. There, MnP preferentially oxidizes manganese (II) ions (Mn^{2+}), always present in wood and soils, into highly reactive Mn^{3+}, which is stabilized by fungal chelators such as oxalic acid. Chelated Mn^{3+} in turn acts as low-molecular-weight, diffusible redox mediator that attacks phenolic lignin structures resulting in the formation of instable free radicals that tend to disintegrate spontaneously (Kuwahara et al. 1984; Hofrichter 2002).

Versatile Peroxidase

Versatile peroxidase (VP) has been recently described as a new family of ligninolytic peroxidases, together with lignin peroxidase (LiP) and manganese peroxidase (MnP), both reported for *P. chrysosporium* for the first time. The complete genome of this model fungus has been recently sequenced revealing two families of LiP and MnP genes together with a "hybrid peroxidase" gene. Till date, VP has been reported from the genera *Pleurotus, Bjerkandera, Lepista, Trametes,* and *Panus* (Honda et al. 2006; Rodakiewicz-Nowak et al. 2006). The most noteworthy aspect of VP is that it combines the substrate specificity characteristics of the three other fungal peroxidase families. In this way, it is able to oxidize a variety of (high and low redox potential) substrates including Mn^{2+}, phenolic, and non-phenolic lignin dimers, α-keto-γ-thiomethylbutyric acid (KTBA), veratryl alcohol, dimethoxybenzenes, different types of dyes, substituted phenols, and hydroquinones (Ruiz-Dueñas et al. 2009).

Glyoxal Oxidases

An important component of the ligninolytic system of *P. chrysosporium is* the H_2O_2 that is required as oxidant in the peroxidative reactions. Glyoxal oxidases have been proposed to play a role in this regard (Kirk and Farrell 1987). The temporal correlation of glyoxal oxidase, peroxidase, and oxidase substrate appearances in cultures suggests a close physiological connection between these components (Kersten and Kirk 1987; Kersten 1990). It is a glycoprotein of 68 kDa with two isozymic forms (pI 4.7 and 4.9). The active site of the enzyme has not been characterized, but Cu^{2+} appears to be important in maintaining activity of purified enzyme. Glyoxal oxidase is produced in cultures when *P. chrysosporium* is grown on glucose or xylose, the major sugar components of lignocellulosics. The physiological substrates for glyoxal oxidase, however, are not these

growth-carbon compounds, but their intermediates. A number of simple aldehyde, α-hydroxycarbonyl, and α-dicarbonyl compounds are the known substrates (Cullen and Kersten 1996).

The reversible inactivation of glyoxal oxidase is a property perhaps of considerable physiological significance (Kersten 1990; Kurek and Kersten 1995). Glyoxal oxidase becomes inactive during enzyme turnover in the absence of a coupled peroxidase system. The oxidase is reactivated, however, by lignin peroxidase and non-phenolic peroxidase substrates. Conversely, phenolics prevent the activation by lignin peroxidase. This suggests that glyoxal oxidase has a regulatory mechanism in the presence of peroxidases, their substrates, and their products (e.g., phenolics resulting from ligninolysis). Notably, lignin will also activate glyoxal oxidase in the coupled reaction with LiP (Cullen and Kersten 1996). Cellobiose oxidase (Ayers et al. 1978) and cellobiose: quinone oxidoreductase (CBQase) (Westermark and Eriksson, 1974) may be involved in both lignin and cellulose degradation. Limited proteolysis of cellobiose oxidase indicates that CBQase is probably a breakdown product (Henriksson et al. 1991; Wood and Wood 1992). Cellobiose oxidase has two domains, one containing a flavin and the other containing a heme group. The flavin-containing domain binds cellulose and is functionally similar to CBQase. A role proposed for these oxidoreductases is to prevent repolymerization of phenoxy radicals produced by peroxidases and laccases during lignin oxidation (Eriksson and Goldman 1993; Cullen and Kersten 1996). Moreover the peroxide-generating enzyme, i.e., pyranose oxidase (glucose-2-oxidase), which is intracellular in liquid culture condition of *P. chrysosporium*, plays an additional important role in wood decay (Daniel et al. 1994).

Environmental Significance

Bioremediation technology utilizes the metabolic potential of microorganisms to clean up the environment (Watanabe 2001). Lignin peroxidase (LiP), manganese peroxidase (MnP), laccase, and versatile peroxidase (VPs) are the major LMEs of WRF involved in lignin and xenobiotic degradation by white-rot fungi (Pointing 2001) (Table 12.1). Accessory enzymes such as H_2O_2-forming glyoxal oxidase, aryl-alcohol oxidase, oxalate producing oxalate decarboxylase (ODC), NAD-dependent formate dehydrogenase (FDH), and P450 monooxygenase have also been isolated from many white-rot fungal strains (Doddapaneni et al. 2005; Aguiar et al. 2006). Lignin peroxidases (LiPs) are capable of mineralizing a variety of recalcitrant aromatic compounds (Srivastava et al. 2005). Due to nonspecific nature, lignin-oxidizing enzyme is capable of mineralizing a wide variety of toxic xenobiotics and recalcitrant substrates. In recent years, a lot of work has been done on the development and optimization of bioremediation processes using WRF, with emphasis on the study of their enzyme systems involved in biodegradation of industrial waste (Thurston 1994; Eriksson 2000; Baldrian 2006; Sharma and Kuhad 2008) (Table 12.1).

Bioremediation of Industrial Pollutant

Bioremediation process employs microorganisms or plants to remove the contaminating organic compounds by metabolizing them to carbon dioxide and biomass (Alexander 1994). The purpose of bioremediation is to degrade pollutants to undetectable concentrations or to concentrations that are below the limits established by regulatory agencies. Bioremediation has been used to degrade contaminants in soils, ground water, wastewater, sludges, industrial waste, and gases (Alexander 1994).

Biodegradation of Synthetic Dye

Large amounts of structurally diverse dyestuffs are used for textile dyeing as well as other applications. Based on the chemical structure of the chromophoric group, dyes are classified as azo dyes, anthraquinone dyes, phthalocyanine dyes, etc. (Kuhad et al. 2004). Different dyes and pigments are extensively used in the textile, paper, plastic, cosmetics, pharmaceutical, and food industries (Levin et al. 2005). The involvement of LMEs in the dye decolorization process has been confirmed in several

independent studies using purified cell-free enzymes (Table 12.2). LiP of *P. chrysosporium* has been shown to decolorize azo, triphenylmethane, and heterocyclic dyes in the presence of veratryl alcohol and H_2O_2 (Cripps et al. 1990; Ollikka et al. 1993). Selected Basidiomycetes have been observed to decolorize PolyR-478 (Vasdev and Kuhad 1994) and various triphenylmethane dyes (Vasdev et al. 1995). Laccase can act on chromophoric compounds such as Remazol Brilliant Blue R or triphenylmethane dyes and suggests a potential application in bleaching or decolorization industrial processes (Vasdev et al. 1995).

Further, interest in the biodegradation of synthetic dyes has primarily been prompted by concern over their possible toxicity and carcinogenicity (Maas and Chaudhari 2005; Revankar and Lele 2007). White-rot fungi are better dye degraders than prokaryotes due to their extracellular nonspecific LME system capable of degrading a wide range of dyes (Christian et al. 2005). Most of the earlier dye decolorization studies were based mainly on *P. chrysosporium* and *T. versicolor* (Toh et al. 2003). However, other white-rot fungi including *Phellinus gilvus*, *Pleurotus sajor-caju*, *Pycnoporus sanguineus* (Balan and Monteiro 2001), *Dichomitus squalens*, Irpex flavus, *Daedalea flavida*, *Polyporus sanguineus* (Chander et al. 2004; Eichlerová et al. 2006; Chander and Arora 2007), *Funalia trogii* ATCC200800 (Ozsoy et al. 2005), *Ischnoderma resinosum* (Eichlerová et al. 2006), and *Ganoderma* sp. WR-1 (Revankar and Lele 2007) have been demonstrated to have higher dye decolorization rates than *P. chrysosporium* and *Trametes versicolor* (Table 12.2).

Biodegradation of Polycyclic Aromatic Hydrocarbon

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants that occur in soils, sediments, airborne particles, freshwater, and marine environments (Bumpus 1989). PAHs are nonpolar, neutral, organic molecules that comprise two or more fused benzene rings arranged in various configurations, including linear, angular, and clustered alignments (Collins et al. 1996).

There have been several reports to use bioremediation of PAHs. Eukaryotic microorganisms, such as fungi, cannot use PAHs as a sole carbon source for growth but usually co-metabolize the PAH to dead-end metabolites. In contrast, bacteria can completely degrade many PAHs and use them as the sole carbon and energy source for growth (Sutherland 1992). At present, many microorganisms are known to metabolize the lower-molecular-weight PAHs, but these PAHs tend not to be highly carcinogenic. Less is known about the potential for biodegradation of higher-molecular-weight PAHs, which tend to be more carcinogenic. A microorganism's ability to degrade PAHs is dependent on the bioavailability of the compound (Vandertol-Vanier 2000).

White-rot fungi can completely mineralize some polycyclic aromatic hydrocarbons (PAHs), indicating that complete oxidation of PAHs occurs. However, there are few examples of in vitro oxidation of PAHs by culture supernatants and purified enzymes. The oxidation of anthracene and pyrene by lignin and manganese peroxidases from *P. chrysosporium* and oxidation of many PAHs by the laccases of *T. versicolor* have been reported (Bumpus 1989; Collins et al. 1996). Pickard et al. (1999) have shown that previously uncharacterized fungal strains could metabolize selected PAHs in vivo. *C. gallica* was one of the strains studied and was found to degrade several PAHs. Anthracene concentration decreased by up to 90%; pyrene, up to 20%; and phenanthrene, up to 40% (Vandertol-Vanier 2000) (Table 12.2).

TNT and Other Explosives

The explosives TNT, HMX, and RDX are integral components of many armaments. Degradation of TNT was studied by Donnelly et al. in 1997, using four different strains of white-rot fungi *P. chrysosporium*, *Phanerochaete sordida*, *Phlebia brevispara*, and *Cyathus stercoreus* in liquid medium (Donnelly et al. 1997). They found that within 21 days of incubation, all fungi were able to reduce the TNT concentration (from 90 mg/L) in the liquid medium to below detection limits. *P. sordida* showed a relatively high growth rate and the fastest rate of TNT degradation. White-rot fungi were also found to degrade monoamino-dinitrotoluenes, the major chemical metabolites in the initial transformation of TNT. The studies

Table 12.2 Applications of ligninolytic enzyme producing organism in treatment of environmental pollution

Application	Organism	References
Decolorization of dyes	*Aspergillus* (recombinant)	Soares et al. (2001a)
	Aspergillus (recombinant)	Soares et al. (2001b)
	A. niger	Soares et al. (2002)
	Cerrena unicolor	Michniewicz et al. (2003)
	Coriolopsis gallica	Reyes et al. (1999)
	C. rigida	Gómez et al. (2005)
	Funalia trogii	Ünyayar et al. (2005)
	Ganoderma sp. WR-1	Revankar and Lele (2007)
	Irpex lacteus	Kasinath et al. (2003)
	Laetiporus sulphureus and *Coriolus versicolor*	Mazmanci et al. (2009)
	Myceliophthora thermophila, *Polyporus pinsitus*, *Trametes versicolor*	Claus et al. (2002)
	Pleurotus eryngii, *Pycnoporus cinnabarinus*, *T. versicolor*	Camarero et al. (2004)
	Pleurotus ostreatus	Hou et al. (2004), Palmieri et al. (2005)
	P. cinnabarinus	McCarthy et al. (1999) and Schliephake et al. (2000)
	Sclerotium rolfsii, *Trametes hirsute*	Campos et al. (2001)
	Streptomyces cyaneus	Arias et al. (2003)
	Stereum ostrea	Viswanath et al. (2008)
	S. maltophilia AAP56	Dube et al. (2008)
	T. hirsuta	Abadulla et al. (2000), Domínguez et al. (2005), Moldes et al. (2003), Rodríguez Couto et al. (2004b, 2005, 2006), Rodríguez Couto and Sanromán (2006), Couto and Toca-Herrera (2006a, b), Minussi et al. (2007), Nyanhongo et al. (2002), Levin et al. (2005), and Maceiras et al. (2001)
	T. modesta	Rodríguez Couto et al. (2002)
	T. trogii	Kulys et al. (2003) and Peralta-Zamora et al. (2003)
	T. versicolor	Maceiras et al. (2001), Lorenzo et al. (2002), and Blánquez et al. (2004)
	T. villosa	Potin et al. (2004), Saito et al. (2004), Tavares et al. (2004), Zille et al. (2003), Knutson and Ragauskas (2004), Yamanaka et al. (2008), Ciullini et al. (2008), and Yang et al. (2009)
	Trametes sp. *strain SQ01*	Pickard et al. (1999)
	Strain I-4 of the family *Chaetomiaceae*	Vandertol-Vanier et al. (2002)
Degradation of xenobiotics	*Cladosporium sphaerospermum*	Cho et al. (2002)
	Coprinus cinereus, *Myceliophthora thermophila*, *P. pinsitus*, *Rhizoctonia solani*	Itoh et al. (2000)
	C. gallica	Okazaki et al. (2002), Nicotra et al. (2004), and Casa et al. (2003)
	Coriolus hirsutus	Zavarzina et al. (2004)
	Coriolus versicolor	Eggen (1999) and Hublik and Schinner (2000)
	Myceliophthora thermophila, *Trametes pubescens*	Keum and Li (2004)
	Panus tigrinus	Mougin et al. (2002)

(continued)

Table 12.2 (continued)

Application	Organism	References
	P. ostreatus	Lante et al. (2000) and Carunchio et al. (2001)
	P. ostreatus, *T. versicolor*	Moeder et al. (2004)
	P. cinnabarinus	Niku-Paavola and Viikari (2000)
	Pyricularia oryzae	Böhmer et al. (1988) and Tanaka et al. (2001)
	Rhus vernicifera	Tanaka et al. (2003)
	T. hirsute	Collins et al. (1996) and Johannes et al. (1998)
	Trametes sp.	Majcherczyk et al. (1998) and Johannes and Majcherczyk (2000)
	T. versicolor	Majcherczyk and Johannes (2000) and Castro et al. (2003)
	T. villosa	Dodor et al. (2004), Fabbrini et al. (2001), Fukuda et al. (2001), Kang et al. (2002), Cantarella et al. (2003), and Jung et al. (2003)
	Trichophyton sp. LKY-7	Steffen et al. (2007a, b), Cabana et al. (2007), and Cambria et al. (2008)
	Stropharia rugosoannulata	Calvo et al. (1998)
	Stropharia coronilla	Murugesan (2003)
	Coriolopsis polyzona	D'Annibale et al. (1999)
	Rigidoporus lignosus	D'Annibale et al. (2000)
	Gliocladium virens	D'Annibale et al. (2004)
Effluent treatment	*Lentinula edodes*	Tsioulpas et al. (2002), Aggelis et al. (2003), and Jaouani et al. (2005)
	P. tigrinus	Durante et al. (2004)
	Pleurotus spp.	Jolivalt et al. (2000)
	Pycnoporus coccineus	Edwards et al. (2002)
	R. vernicifera	Lucas et al. (2003)
	Trametes sp. strain AH28-2	Pedroza et al. (2007)
	T. versicolor	Cordi et al. (2007)
	Lentinula edodes	Cordi et al. (2007)
	Botrytis cinerea	Ellouze et al. (2008), Bourbonnais et al. (1997), and Call and Mücke (1997)
	Trametes trogii	Archibald et al. (1997)
	Lentinus tigrinus	Crestini and Argyropoulos (1998)
	Fomes fomentarius, *Ganoderma callosum*, *Lentinus edodes*, *Merulius tremellosus*, *Phlebia radiata*, *P. ostreatus*, *T. versicolor*	Kandioller and Christov (2001)
	C. versicolor	Cordi et al. (2007)
	T. versicolor	Cordi et al. (2007)
Biopulping	*T. versicolor*	Paice et al. (1995) and Cordi et al. (2007)
	Peniophora sp., *Pycnoporus sanguineus*, *T. hirsuta*, *T. versicolor*	Oudia et al. (2008)
	T. versicolor, T. villosa	Balakshin et al. (2001)
	Lentinula edodes	Camarero et al. (2004)
	Botrytis cinerea	Georis et al. (2003)
	C. versicolor	Archibald et al. (1997)
	P. eryngii, P. cinnabarinus, T. versicolor	Bastos and Magan (2009)
	P. cinnabarinus	D'Souza-Ticlo et al. (2009)
Biobleaching	*T. versicolor*	Molina-Guijarro et al. (2009)
	T. versicolor	Punnapayak et al. (2007) and Zhao et al. (2010)

established that white-rot fungi are capable of metabolizing and detoxifying TNT under aerobic conditions in a non-ligninolytic liquid medium. The degradation of TNT by white-rot fungi is a two-step process: the first step was to be degraded to OHADNT and ADNT, and the second step was to DANT (Aken et al. 1999). As reported by Axtell et al. (2000), the strains of *P. chrysosporium* and *P. ostreatus* adapted to grow on high concentrations of TNT thus were able to cause extensive degradation of TNT, HMX, and RDX.

Bioremediation of Contaminated Sites

Many pesticides, xenobiotics, coal substances, and industrial products derived from polycyclic, aromatic, halogenated hydrocarbons, and other organic compounds are hazardous environment pollutants. Using oxidoreductases to detoxify and remove them is attracting active research efforts. Laccase and peroxidase have been used to transform (often in the presence of redox mediators) various xenobiotics, polycyclic aromatic hydrocarbons, and other pollutants found in industrial waste and contaminated soil or water (Xu 2005).

Contrary to most of the research on bioremediation using bacterial strains, fungal bioremediation has attracted in the past few years. White-rot fungi have potential to withstand toxic levels of most organopollutants. Five main genera of white-rot fungi have shown potential for bioremediation, *viz*., *Phanerochaete, Trametes, Bjerkandera, Pleurotus,* and *Cyathus* (Table 12.2). These fungi cannot use lignin as a sole source of energy, however, instead require substrates such as cellulose or other carbon sources. Thus, carbon sources such as corncobs, straw, and sawdust can be easily used to enhance degradation rates by these organisms at polluted sites. Also, the branching, filamentous mode of fungal growth allows for more efficient colonization and exploration of contaminated soil. The main mechanism of biodegradation employed by this group of fungi, however, is the use of lignin degradation system of enzymes. The enzymes LiP, MnP, and laccase involved in lignin degradation are highly nonspecific with regard to their substrate range; this is not surprising considering their mode of action via the generation of radicals (Reddy and Mathew 2001; Kapoor et al. 2005).

Degradation of Medical Waste

Exposure to alkyl-substituted polynuclear aromatic hydrocarbons, stilbenes, genistein, methoxychlor and endocrine-disrupting chemicals (EDC), nonylphenol (NP) and bisphenol A (BPA), and the personal care product ingredient triclosan (TCS) (Asgher et al. 2008) has been associated with a variety of reproductive responses in fish (Kiparisis et al. 2003). Degradation of genistein by *Phanerochaete sordida* YK-624 and detection of the activities of ligninolytic enzymes, MnP, and laccase during treatment show the involvement of WRF extracellular lignolytic system in disappearance of genistein (Tamagawa et al. 2005). MnP, laccase, and the laccase-HBT systems of WRF are also effective in removing the estrogenic activities of bisphenol A (BPA), nonylphenol (NP), 17b-estradiol (E2), and ethinylestradiol (EE2) with production of high-molecular-weight oligomeric metabolites (Asgher et al. 2008; Lee et al. 2005). Further, removal of NP and BPA is associated with the production of laccase by *T. versicolor* and *Bjerkandera* sp. BOL13 (Soares et al. 2005, 2006). The enhanced biocatalytic elimination of nonylphenol (NP), bisphenol A (BPA), and triclosan (TCS) by *Coriolopsis polyzona* by the addition of ABTS (Cabana et al. 2007) also suggested the involvement of laccase-mediator system.

The ligninolytic enzymes of white-rot fungi catalyze the degradation of pollutants by using a nonspecific free-radical mechanism. When an electron is added or removed from the ground state of a chemical, it becomes highly reactive, allowing it to give or take electrons from other chemicals. This provides the basis for the nonspecificity of the enzymes and their ability to degrade xenobiotics, chemicals that have never been encountered in nature (Pointing 2001).

Biodegradation of Rubber Industry Waste

Recycling of spent rubber material is problematic due to the vulcanization, which creates strong sulfur bonds between the rubber molecules (Liu et al. 2000). Different processes for desulfurization of rubber material and to facilitate the reuse of waste rubber have been developed, including biotechnological processes (Bredberg et al. 2002). Microbial devulcanization is a promising way

to increase the recycling of rubber materials. However, several microorganisms tested for devulcanization are sensitive to rubber additives (Christiansson et al. 2000; Asgher et al. 2008). Most of the common rubber additives are aromatic compounds and can be effectively removed by LMEs of WRF. *Resinicium bicolor* is the most effective fungus for detoxification of rubber material, especially the ground waste tire rubber (Bredberg et al. 2002). Treatment of aromatic rubber additives with *R. bicolor* enhances the growth of *Thiobacillus ferrooxidans* bacterium as well as desulfurization compared to the untreated rubber (Asgher et al. 2008).

Control of Pitch in Paper Pulp Manufacturing

Wood extractives cause production and environmental problems in pulp and paper manufacturing. The lipophilic compounds, which form the so-called wood resin, are the most problematic, and they include free fatty acids, resin acids, waxes, fatty alcohols, sterols, sterol esters, glycerides, ketones, and other oxidized compounds. During wood pulping and refining of paper pulp, the lipophilic extractives in the parenchyma cells and softwood resin canals is released, forming colloidal pitch. These colloidal particles can coalesce into larger droplets that deposit in pulp or machinery forming "pitch deposits" or remain suspended in the process waters. Pitch deposition has a detrimental environmental impact when released into wastewaters (Gutiérrez et al. 2001).

The ability to colonize lignified plant material is a characteristic of wood decay fungi, which include white-rot, brown-rot, soft-rot, and sapstain species. The fungi that cause white rot and brown rot are Basidiomycetes and are characterized by their ability to degrade lignin and cellulose, respectively, resulting in white, i.e., cellulose or brown-colored, i.e., lignin-enriched decayed substrates. The typical sapstain fungi, also called "blue-staining fungi," colonize wood vessels and rays (as well as softwood resin canals) penetrating through the cell-wall pits. The growth of sapstain fungi is supported by easily degradable extractives and causes discoloration and minimal weight loss. Wood discoloration is caused by the presence of melanin that has a role in the protection of fungal hyphae against harmful radiation. Because most lipophilic compounds involved in the formation of pitch deposits are concentrated in wood rays and resin canals, the sapstain fungi were the first candidates for the biological control of pitch during wood pulping. Wood-rotting Basidiomycetes have also been investigated for biotechnological application in paper pulp manufacturing. Brown-rot fungi are of little applied interest because they degrade cellulose, the most valuable wood constituent for industrial utilization. Biopulping, in combination with chemical and mechanical treatments, represents an attractive alternative to reduce the consumption of pulping chemicals and energy. White-rot fungi and their enzymes are also of biotechnological interest for pulp bleaching. The advantages of WRF in the degradation of lipophilic extractives have also being realized. The main purpose of biobleaching is to reduce the consumption of the chlorinated reagents traditionally used to bleach pulp, which have a detrimental impact in the water environment (Gutiérrez et al. 2001).

Enzymatic Pulp Bleaching

New environmentally benign, elemental chlorine-free (ECF), and totally chlorine-free (TCF) bleaching technologies are necessary for minimizing the hemicellulose content in dissolving pulp, adjusting the brightness at a high level and improving, simultaneously, the quality of the effluent in terms of toxicity and absorbable organic halogen (AOX). Biological methods of pulp prebleaching using xylanases (Taneja et al. 2002) provide the possibility of selectively removing up to 20% of xylan from pulp and saving up to 25% of chlorine-containing bleaching chemicals. Alternatively, pulp can be bleached with white-rot fungi and their ligninolytic enzymes, enabling chemical savings to be achieved and a chlorine-free bleaching process.

Bjerkandera sp. strain BOS55, *Polyporus ciliatus*, *Stereum hirsutum*, *Phlebia radiata,* and *Lentinus tigrinus* have been found to be efficient biobleachers (Akhtar et al. 1992). Kirk and Yang

(1979) were the first to attempt to bleach pulp with *P. chrysosporium* and some other white-rot fungi. This could lower the kappa number of unbleached softwood kraft pulp up to 75%, leading to reduced requirement for chlorine during the subsequent chemical bleaching. *T. versicolor* could markedly increase the brightness of hardwood kraft pulp. The fungal treatment was carried out in agitated, aerated cultures for 5 days. The kappa number was decreased from 12 to 8, and the brightness increased by 34–48%. *P. cinnabarinus* was found to produce laccase and also its own laccase redox mediator, 3-hydroxy anthranilic acid (3-HAA) (Eggert et al. 1996). The presence of laccase is essential for lignin degradation by *P. cinnabarinus* and that in its absence pulp bleaching is greatly reduced. The biobleaching of kraft with laccase mediator continues to receive strong interest, in part due to the discovery of new mediators for laccase. A number of mediators have recently been used for the use of laccase enzyme in biobleaching, e.g., ABTS 2,2′-azinobis(3-ethylbenzthiazoline-6-sulfonate) (Bourbonnais and Paice 1996), HBT, *N*-acetyl-*N*-phenylhydroxylamine (NHA) and violuric acid (VA) (Chakar and Ragauskas 2004). HBT oxidation leads to the discovery of a new class of mediators with NOH as the reactive species (R-NO). Kraft pulp treatment with laccase and ABTS was found to effectively demethylate and delignify hardwood kraft pulp when the mediator ABTS is present (Bourbonnais and Paice 1996).

Laccase, like other phenol-oxidizing enzymes, such as peroxidases (Huttermann et al. 1980; Haemmerli et al. 1986; Kern and Kirk 1987), preferentially polymerizes lignin by coupling of the phenoxy radicals produced by the oxidation of lignin phenolic groups. When laccase is used alone, the only reaction that can be observed on kraft lignin is polymerization. The fact that ABTS prevents polymerization of kraft lignin by laccase cannot be explained only by inhibition or reduction of the lignin phenoxy radicals produced by laccase, because when ABTS was added after lignin polymerization by laccase, the lignin was effectively depolymerized. It seems likely that ABTS functions as a diffusible electron carrier, because laccase is a large molecule and therefore cannot enter the secondary wall to contact the lignin substrate directly.

Conclusion

The ligninolytic enzymes of white-rot fungi catalyze the degradation of pollutants by using a nonspecific free-radical mechanism. The enzymes LiP, MnP, laccase, and other ancillary enzymes involved in lignin degradation are highly nonspecific with regard to their substrate range. This is not surprising considering their mode of action via the generation of radicals. This provides the basis for the nonspecificity of the enzymes and their ability to degrade xenobiotics and other industrial waste that have never been encountered as a natural substrate and are deleterious to ecosystem. Lignolytic enzyme system holds potential for cleaning the degraded and contaminated sites, using combinatorial, holistic, and ecofriendly approaches.

Acknowledgement The authors acknowledge the research grant from University Grant Commission, New Delhi.

References

Abadulla E, Tzanov T, Costa S, Robra KH, Cavaco-Paulo A, Gübitz G (2000) Decolorization and detoxification of textile dyes with a laccase from *Trametes hirsuta*. Appl Environ Microbiol 66:3357–3362

Aggelis G, Iconomou D, Christouc M, Bokas D, Kotzailias S, Christou G et al (2003) Phenolic removal in a model olive oil mill wastewater using *Pleurotus ostreatus* in bioreactor cultures and biological evaluation of the process. Water Res 37:3897–3904

Aguiar A, de Souza-Cruz PB, Ferraz A (2006) Oxalic acid, Fe^{3+}-reduction activity and oxidative enzymes detected in culture extracts recovered from *Pinus taeda* wood chips biotreated by *Ceriporiopsis subvermispora*. Enzyme Microbial Technol 38(7):873–878

Aken BV, Hofrichter M, Scheibner K, Hatakka AI, Naveau H, Agathos SN (1999) Transformation and mineralization of 2,4,6-trinitrotoluene (TNT) by manganese peroxidase from the white-rot basidiomycete *Phlebia radiata*. Biodegradation 10:83–91

Akhtar M, Attridge MC, Blanchette RA, Myers GC, Wall MB, Sykes MS, Koning Jr JW, Burgess RR, Wegner TH, Kirk T (1992) Biotechnology in pulp and paper

industry. In: Proceedings of the 5th international conference on biotechnology in the pulp and paper industry, University publishers Ltd, Tokyo, pp 3–8
Alexander M (1994) Biodegradation and bioremediation. Academic, San Diego, pp 177–195
Alexandre G, Zulin IB (2000) Laccases are widespread in bacteria. Trends Biotechnol 18:41–42
Arakane Y, Muthukrishnan S, Beeman RW, Kanost MR, Kramer KJ (2005) Laccase 2 is the phenoloxidase gene required for beetle cuticle tanning. Proc Natl Acad Sci USA 102:11337–11342
Archibald FS, Bourbonnais R, Jurasek L, Paice MG, Reid ID (1997) Kraft pulp bleaching and delignification by *Trametes versicolor*. J Biotechnol 53:215–236
Arias ME, Arenas M, Rodríguez J, Soliveri J, Ball AS, Hernández M (2003) Kraft pulp biobleaching and mediated oxidation of a nonphenolic substrate by laccase from *Streptomyces cyaneus* CECT 3335. Appl Environ Microbiol 69:1953–1958
Asgher M, Bhatti HN, Ashraf M, Legge RL (2008) Recent developments in biodegradation of industrial pollutants by white rot fungi and their enzyme system. Biodegradation 19(6):771–783
Axtell C, Johnston CG, Bumpus JA (2000) Bioremediation of soil contaminated with explosives at the Naval Weapons Station Yorktown. Soil Sediment Contam Int J 9:537–548
Ayers AR, Ayers SB, Eriksson KE (1978) Cellobiose oxidase, purification and partial characterization of a hemoprotein from *Sporotrichum pulverulentum*. Eur J Biochem 90:171–181
Balan DSL, Monteiro RTR (2001) Decolorization of textile indigo dye by ligninolytic fungi. J Biotechnol 89(2–3):141–145
Balakshin M, Chen C-L, Gratzl JS, Kirkman AG, Jakob H (2001) Biobleaching of pulp with dioxygen in laccase-mediator system-effect of variables on the reaction kinetics. J Mol Catal B Enzyme 16:205–215
Baldrian P (2006) Fungal laccases: occurrence and properties. FEMS Microbiol Rev 30:215–242
Bastos AC, Magan N (2009) *Trametes versicolor*: potential for atrazine bioremediation in calcareous clay soil, under low water availability conditions. Int J Biodeterior Biodegrad 63:389–394
Beloqui A, Pita M, Polaina J et al (2006) Novel polyphenol oxidase mined from metagenome expression library of bovine rumen: biochemical properties structural analysis and phylogenetic relationship. J Biol Chem 281:22933–22942
Benner R, Moran MA, Hodson RE (1986) Biogeochemical cycling of lignocellulosic carbon in marine and freshwater ecosystems: relative contribution of prokaryotes and eukaryotes. Limnol Oceanogr 31:89–100
Blánquez P, Casas N, Font X, Gabarrell M, Sarrá M, Caminal G (2004) Mechanism of textile metal dye biotransformation by *Trametes versicolor*. Water Res 38:2166–2172
Böhmer S, Messner K, Srebotnik E (1988) Oxidation of phenanthrene by a fungal laccase in the presence of 1-hydroxybenzotriazole and unsaturated lipids. Biochem Biophys Res Commun 244:233–238
Bourbonnais R, Paice MG (1996) Enzymic delignification of kraft pulp using laccase and a mediator. Tappi J 79:199–204
Bourbonnais R, Paice MG, Freiermuth B, Bodie E, Borneman S (1997) Reactivities of various mediators and laccases with kraft pulp and lignin model compounds. Appl Environ Microbiol 63:4627–4632
Bredberg K, Andersson BE, Landfors E, Holst O (2002) Microbial detoxification of waste rubber material by wood-rotting fungi. Bioresour Technol 83:221–224
Bumpus J (1989) Biodegradation of polycyclic aromatic hydrocarbons by *Phanerochaete chrysosporium*. Appl Environ Microbiol 55:154–158
Cabana H, Jiwan JL, Rozenberg R, Elisashvili V, Penninckx M, Agathos SN, Jones JP (2007) Elimination of endocrine disrupting chemicals nonylphenol and bisphenol A and personal care product ingredient triclosan using preparation from the white rot fungus *Coriolopsis polyzona*. Chemosphere 67:770–778
Call HP, Mücke I (1997) History, overview and applications of mediated lignolytic systems, especially laccase-mediator systems (LignozymR process). J Biotechnol 53:163–202
Calvo AM, Copa-Patiño JL, Alonso O, González AE (1998) Studies of the production and characterization of laccase activity in the basidiomycete *Coriolopsis gallica*, an efficient decolorizer of alkaline effluents. Arch Microbiol 171:31–36
Camarero S, Garcia O, Vidal T, Colom J, del Rio JC, Gutierrez A et al (2004) Efficient bleaching of non-wood high-quality paper pulp using laccase-mediator system. Enzyme Microb Technol 35:113–120
Cambria MT, Minniti Z, Librando V, Cambria A (2008) Degradation of polycyclic aromatic hydrocarbons by *Rigidoporus lignosus* and its laccase in the presence of redox mediators. Appl Biochem Biotechnol 149:1–8
Campos R, Kandelbauer A, Robra KH, Cavaco-Paulo A, Gübitz GM (2001) Indigo degradation with purified laccases from *Trametes hirsute* and *Sclerotium rolfsii*. J Biotechnol 89:131–139
Cantarella G, Galli C, Gentili P (2003) Free radical versus electron-transfer routes of oxidation of hydrocarbons by laccase/mediator systems. Catalytic or stoichiometric procedures. J Mol Catal B Enzyme 22:135–144
Carunchio F, Crescenzi C, Girelli AM, Messina A, Tarola AM (2001) Oxidation of ferulic acid by laccase: identification of the products and inhibitory effects of some dipeptides. Talanta 55:189–200
Carvalho W, Canilha L, Ferraz A, Milagres A (2009) Uma visão sobre a estrutura, composição e biodegradação da madeira. Química Nova 32(8):1–5
Casa R, D'Annibale A, Pieruccetti F, Stazi SR, Giovannozzi SG, LoCascio B (2003) Reduction of the phenolic components in olive-mill wastewater by an enzymatic treatment and its impact on durum wheat (*Triticum durum* Desf.) germinability. Chemosphere 50:959–966

Castro AIRP, Evtuguin DV, Xavier AMB (2003) Degradation of biphenyl lignin model compounds by laccase of *Trametes* versicolor in the presence of 1 hydroxybenzotriazole and heteropolyanion [SiW11VO40]5−. J Mol Catal B Enzyme 22:13–20

Chakar FS, Ragauskas AJ (2004) Biobleaching chemistry of laccase-mediator systems on high-lignin-content kraft pulps. Can J Chem Rev Can Chim 82(2):344–352

Chander M, Arora DS (2007) Evaluation of some white-rot fungi for their potential to decolorize industrial dyes. Dyes Pigments 72:192–198

Chander M, Arora DS, Bath HK (2004) Biodecolourisation of some industrial dyes by white-rot fungi. J Ind Microbiol Biotechnol 31:94–97

Cho SJ, Park SJ, Lim JS, Rhee YH, Shin KS (2002) Oxidation of polycyclic aromatic hydrocarbons by laccase of *Coriolus hirsutus*. Biotechnol Lett 24:1337–1340

Christiansson M, Stenberg B, Holst O (2000) Toxic additives - a problem for microbial waste rubber desulfurisation. Res Environ Biotechnol 3:11–21

Ciullini I, Tilli S, Scozzafava A, Fabrizio B (2008) Fungal laccase, cellobiose dehydrogenase, and chemical mediators: combined actions for the decolorization of different classes of textile dyes. Bioresour Technol 99:7003–7010

Claus H (2004) Laccases: structure, reactions, distribution. Micron 35(1–2):93–96

Claus H, Faber G, König H (2002) Redox-mediated decolorization of synthetic dyes by fungal laccases. Appl Microbiol Biotechnol 59:672–678

Collins PJ, Kotterman MJJ, Field JA, Dobson ADW (1996) Oxidation of anthracene and benzo[a]pyrene by laccases from *Trametes versicolor*. Appl Environ Microbiol 62:4563–4567

Cordi L, Minnussi RC, Freire RS, Duran N (2007) Fungal laccase: copper induction, semi-purification, immobilization, phenolic effluent treatment and electrochemical measurement. Afr J Biotechnol 6:1255–1259

Couto RS, Toca-Herrera JL (2006a) Laccases in the textile industry. Biotechnol Mol Biol Rev 1:115–120

Couto SR, Toca-Herrera JL (2006b) Industrial and biotechnological applications of laccases: a review. Biotechnol Adv 24:500–513

Crestini C, Argyropoulos DS (1998) The early oxidative biodegradation steps of residual kraft lignin models with laccase. Bioorg Med Chem 6:2161–2169

Cripps C, Bumpus JA, Aust SD (1990) Biodegradation of azo and heterocyclic dyes by *Phanerochaete chrysosporium*. Appl Environ Microbiol 56(4):11–14

Cullen D, Kersten PJ (1996) Enzymology and molecular biology of lignin degradation. In: Bramble R, Marzluf G (eds) The Mycota III. Springer, Berlin/Heidelberg/New York, pp 297–314

Daniel G, Volc J, Kubatova E (1994) Pyranose oxidase, a major source of H_2O_2 during wood degradation by Phanerochaete chrysosporium, Trametes versicolor, and Oudemansiella mucida. Appl Environ Microbiol 60:2524–2532

D'Annibale A, Stazi SR, Vinciguerra V, Di Mattia E, Giovannozzi SG (1999) Characterization of immobilized laccase from *Lentinula edodes* and its use in olive-mill wastewater treatment. Process Biochem 34:697–706

D'Annibale A, Stazi SR, Vinciguerra V, Giovannozzi SG (2000) Oxirane-immobilized *Lentinula edodes* laccase: stability and phenolics removal efficiency in olive mill wastewater. J Biotechnol 77:265–273

D'Annibale A, Ricci M, Quaratino D, Federic F, Fenice M (2004) *Panus tigrinus* efficiently removes phenols, color and organic load from olive-mill wastewater. Res Microbiol 155:596–603

D'Souza-Ticlo D, Sharma D, Raghukumar C (2009) A thermostable metal-tolerant laccase with bioremediation potential from a marine-derived fungus. Marine Biotechnol 11:725–737

Dighton J, White JF, Oudemans P (2005) The fungal community: its organization and role in the ecosystem. Taylor & Francis, Boca Raton, 936 p

Dittmer NT, Suderman RJ, Jiang H, Zhu YC, Gorman MJ, Kramer KJ, Kanost MR (2004) Characterization of cDNA encoding putative laccase-like multicopper oxidases and developmental expression in the tobacco hornworm, *Manduca sexta*, and the malaria mosquito, *Anopheles gambiae*. Insect Biochem Mol Biol 34:29–41

Dix NJ, Webster J (1995) Fungal ecology. Chapman & Hall, London

Doddapaneni H, Chakraborty R, Yadav JS (2005) Genome-wide structural and evolutionary analysis of the P450 monooxygenase genes (P450ome) in the white rot fungus *Phanerochaete chrysosporium*: evidence for gene duplications and extensive gene clustering. BMC Genom 6:92–116

Dodor DE, Hwang HM, Ekunwe SIN (2004) Oxidation of anthracene and benzo[a] pyrene by immobilized laccase from *Trametes versicolor*. Enzyme Microb Technol 35:210–217

Domínguez A, Rodríguez Couto S, Sanromán MA (2005) Dye decolourization by *Trametes hirsuta* immobilised into alginate beads. World J Ind Microbiol Biotechnol 21:405–409

Donnelly KC, Chen JC, Huebner HJ, Brown KW, Autenrieth RL, Bonner JS (1997) Utility of four strains of white-rot fungi for the detoxification of 2,4,6-trinitrotoluene in liquid culture. Environ Toxicol Chem 16:1105–1110

Dube E, Shareck F, Hurtubise Y, Daneault C, Beauregard M (2008) Homologous cloning, expression, and characterization of a laccase from *Streptomyces coelicolor* and enzymatic decolourization of an indigo dye. Appl Microbiol Biotechnol 79:597–603

Durante D, Casadio R, Martelli L, Tasco G, Portaccio M, De Luca P et al (2004) Isothermal and non-isothermal bioreactors in the detoxification of waste waters polluted by aromatic compounds by means of immobilised laccase from *Rhus vernicifera*. J Mol Catal B Enzyme 27:191–206

Edwards W, Leukes WD, Bezuidenhout J (2002) Ultrafiltration of petrochemical industrial wastewater using immobilised manganese peroxidase and laccase:

application in the defouling of polysulphone membranes. J Desalin 149:275–278

Eggen T (1999) Application of fungal substrate from commercial mushroom production *Pleuorotus ostreatus* for bioremediation of creosote contaminated soil. Int Biodeterior Biodegrad 44:117–126

Eggert C, Temp U, Eriksson KE (1996) The ligninolytic system of the white rot fungus *Pycnoporus cinnabarinus*: purification and characterization of the laccase. Appl Environ Microbiol 62: 1151–1158

Eichlerova I, Homolka L, Nerud F (2006) Synthetic dye decolorization capacity of white rot fungus *Dichomitus squalens*. Bioresour Technol 97:2153–2159

Ellouze M, Aloui F, Sayadi S (2008) Detoxification of Tunisian landfill leachates by selected fungi. J Hazard Mater 150:642–648

Erden E, Ucar CM, Gezer T, Pazarlioglu NK (2009) Screening for ligninolytic enzymes from autochthonous fungi and applications for decolorization of Remazole Marine Blue. Braz J Microbiol 40(2):346–353

Eriksson JE, Goldman RD (1993) Protein phosphatase inhibitors alter cytoskeletal structure and cellular morphology. Adv Protein Phosphatases 7:335–357

Eriksson K-EL (2000) Lignocellulose, lignin, ligninases. In: Encyclopedia microbiol, vol III, II edn. Academic

Fabbrini M, Galli C, Gentili P, Macchitella D (2001) An oxidation of alcohols by oxygen with the enzyme laccase and mediation by TEMPO. Tetrahedron Lett 42:7551–7553

Falcon MA, Corominas E, Perez ML, Perestelo F (1987) Aerobic bacterial populations and environmental factors involved in the composting of agricultural and forest wastes of the Canary Islands. Biol Wastes 20:89–99

Faure D, Bouillant ML, Bally R (1994) Isolation of *Azospirillum lipoferum* 4T Tn5 mutants affected in melanization and laccase activity. Appl Environ Microbiol 60:3413–3415

Fukuda T, Uchida H, Takashima Y, Uwajima T, Kawabata T, Suzuki M (2001) Degradation of bisphenol a by purified laccase from *Trametes villosa*. Biochem Biophys Res Commun 284:704–706

Fustec E, Chauvet E, Gas G (1989) Lignin degradation and humus formation in alluvial soils and sediments. Appl Environ Microbiol 55(4):922–926

Georis J, Lomascolo A, Camarero S, Dorgeo V, Herpoel I, Asther M (2003) *Pycnoporus cinnabarinus* laccases: an interesting tool for food or non-food applications. Meded Fac Landbouwkd Toegep Biol Wet 68: 263–266

Givaudan A, Effose A, Faure D, Potier P, Bouillant M-L, Bally R (1993) Polyphenol oxidase in *Azospirillum lipoferum* isolated from rice rhizosphere: evidence for laccase activity in non-motile strains of *Azospirillum lipoferum*. FEMS Microbiol Lett 108:205–210

Glenn JK, Morgan MA, Mayfield MB, Kuwahara M, Gold MH (1983) An extracellular H_2O_2-requiring enzyme preparation involved in lignin biodegradation by the white rot basidiomycete *Phanerochaete chrysosporium*. Biochem Biophys Res Commun 114(3): 1077–1083

Glumoff T, Harvey PJ, Molinari S, Goble M, Frank G, Palmer JM, Smit JDG, Leisola MSA (1990) Lignin peroxidase from *Phanerochaete chrysosporium*. Molecular and kinetic characterization of isozymes. Eur J Biochem 187(3):515–520

Gold MH, Enoki A, Morgan MA, Mayfield MB, Tanaka H (1984) Degradation of the γ-carboxyl-containing diarylpropane lignin model compound 3-(4,-Ethoxy-3,-Methoxyphenyl)-2-(4″-Methoxyphenyl) Propionic acid by the basidiomycete phanerochaete chrysosporium. Appl Environ Microbiol 47(4):597–600

Gold MH, Alic M (1993) Molecular biology of the lignin-degrading basidiomycete *Phanerochaete chrysosporium*. Microbiol Rev 57(3):605–622

Gómez J, Pazos M, Rodríguez Couto S, Sanromán MA (2005) Chestnut shell and barley bran as potential substrates for laccase production by *Coriolopsis rigida* under solid-state conditions. J Food Eng 68:315–319

Gutiérrez A, del Río JC, Martínez MJ, Martínez AT (2001) The biotechnological control of pitch in paper pulp manufacturing. Trends Biotechnol 19(9):340–348

Haemmerli SD, Leisola MSA, Fiechter A (1986) Polymerisation of lignins by ligninases from *Phanerochaete chrysosporium*. FEMS Microbiol Lett 35:33–36

Haglund C (1999) Biodegradation of xenobiotic compounds by the white-rot fungus *Trametes trogii*. Molecular Biotechnology Programme, Uppsala University School of Engineering, Uppsala, 30 p

Henriksson G, Pettersson G, Johansson G, Ruiz A, Uzcategui E (1991) Cellobiose oxidase from *Phanerochaete chrysosporium* can be cleaved by papain into two domains. Eur J Biochem 196:101–106

Henriksson G, Johansson G, Pettersson G (2000a) A critical review of cellobiose dehydrogenases. J Biotechnol 78(2):93–113

Henriksson G, Zhang L, Li J, Ljungquist P, Reitberger T, Pettersson G, Johansson G (2000b) Is cellobiose dehydrogenase from *Phanerochaete chrysosporium* a lignin degrading enzyme? Biochim Biophys Acta (BBA) Protein Struct Mol Enzymol 1480(1–2):83–91

Hofrichter M (2002) Review: lignin conversion by manganese peroxidase (MnP). Enzyme Microb Technol 30(4):454–466

Holwerda RA, Wherland S, Gray HB (1976) Electron transfer reactions of copper proteins. Annu Rev Biophys Bioeng 5:363

Honda Y, Watanabe T, Watanabe T (2006) Exclusive overexpression and structure-function analysis of a versatile peroxidase from white-rot fungus, *Pleurotus ostreatus*. Sustain Humanosphere 2:2–6

Hou H, Zhou J, Wang J, Du C, Yan B (2004) Enhancement of laccase production by *Pleurotus ostreatus* and its use for the decolorization of anthraquinone dye. Process Biochem 39:1415–1419

Hublik G, Schinner F (2000) Characterization and immobilization of the laccase from *Pleurotus ostreatus* and

its use for the continuous elimination of phenolic pollutants. Enzyme Microb Technol 27:330–336

Huttermann A, Herche C, Haars A (1980) Polymerization of water-insoluble lignins by *Fomes Annosus*. Holzforschung 34:64–66

Inbar Y, Chen Y, Hadar Y (1989) Solid-state Carbon-13 nuclear magnetic resonance and infrared spectroscopy of composted organic matter. Soil Sci Soc Am J 53:1695–1701

Itoh K, Fujita M, Kumano K, Suyama K, Yamamoto H (2000) Phenolic acids affect transformations of chlorophenols by a *Coriolus versicolor* laccase. Soil Biol Biochem 32:85–91

Jaouani A, Guillen F, Penninckx MJ, Martinez AT, Martinez MJ (2005) Role of *Pycnoporus coccineus* laccase in the degradation of aromatic compounds in olive oil mill wastewater. Enzyme Microb Technol 36:478–486

Johannes C, Majcherczyk A (2000) Natural mediators in the oxidation of polycyclic aromatic hydrocarbons by laccase mediator systems. Appl Environ Microbiol 66:524–528

Johannes C, Majcherczyk A, Huttermann A (1998) Oxidation of acenaphthene and acenaphthylene by laccase of *Trametes versicolor* in a laccase-mediator system. J Biotechnol 61:151–156

Jolivalt C, Brenon S, Caminade E, Mougin C, Pontié M (2000) Immobilization of laccase from *Trametes versicolor* on a modified PVDF microfiltration membrane: characterization of the grafted support and application in removing a phenylurea pesticide in wastewater. J Membr Sci 180:103–113

Jung H, Hyun K, Park Ch (2003) Production of laccase and bioremediation of pentachlorophenol by wood-degrading fungus *Trichophyton* sp. LKY-7 immobilized in Ca-alginate beads. Polpu Chongi Gisul 35:80–86

Kandioller G, Christov L (2001) Evaluation of the delignification and bleaching abilities of selected laccases with HBT on different pulps. In: Argyropoulos DS (ed) Oxidative delignification chemistry fundamentals and catalysis, vol 785, ACS symposium series. Oxford University Press, New York, pp 427–443

Kang KH, Dec J, Park H, Bollag JM (2002) Transformation of the fungicide cyprodinil by a laccase of *Trametes villosa* in the presence of phenolic mediators and humic acid. Water Res 36:4907–4915

Kapoor RK, Sharma KK, Kuhar S, Kuhad RC (2005) Diversity of lignin degrading microorganisms, lignolytic enzymes and their biotechnological applications. In Satyanarayana T, Johri BN (eds) Microbial diversity: current perspectives and potential applications. I. K. International Pvt. Ltd., New Delhi, pp 815–84

Kasinath A, Svobodová NK, Patel KC, Šašek V (2003) Decolorization of synthetic dyes by *Irpex lacteus* in liquid cultures and packed-bed bioreactor. Enzyme Microb Technol 32:167–173

Kellner H, Vandenbol M (2010) Fungi unearthed: transcripts encoding lignocellulolytic and chitinolytic. Enzym Forest Soil 5(6):e10971

Kern HW, Kirk TK (1987) Influence of molecular size and ligninase pretreatment on degradation of lignins by *Xanthomonas* sp. Appl Environ Microbiol 53: 2242–2246

Kersten PJ, Kirk TK (1987) Involvement of a new enzyme, glyoxal oxidase, in extracellular H_2O_2 production by *Phanerochaete chrysosporium*. J Bacteriol 169:2195–2201

Kersten PJ (1990) Glyoxal oxidase of *Phanerochaete chrysosporium*: its characterization and activation by lignin peroxidase. Proc Natl Acad Sci USA 87:2936–2940

Kersten P, Cullen D (2007) Extracellular oxidative systems of the lignin-degrading Basidiomycete *Phanerochaete chrysosporium*. Fungal Genet Biol 44(2):77–87

Keum YS, Li QX (2004) Fungal laccase-catalyzed degradation of hydroxyl polychlorinated biphenyls. Chemosphere 56:23–30

Kiparisis Y, Balch GC, Metcalfe TL, Metcalfe CD (2003) Effects of the isoflavones genistein and equol on the gonadal development of Japanese medaka (*Oryzias latipes*). Environ Health Perspect 111:1158–1163

Kirk TK, Yang HH (1979) Partial delignification of unbleached kraft pulp with ligninolytic fungi. Biotechnol Lett 1:347–352

Kirk TK, Farrell RL (1987) Enzymatic combustion: the microbial degradation of lignin. Annu Rev Microbiol 41:465–505

Knutson K, Ragauskas A (2004) Laccase-mediator biobleaching applied to a direct yellow dyed paper. Biotechnol Prog 20:1893–1896

Kuhad RC, Kapoor M, Rustagi R (2004) Enhanced production of an alkaline pectinase from *Streptomyces* sp. RCK-SC by whole-cell immobilization and solid-state cultivation. World J Microbiol Biotechnol 20:257–263

Kulys J, Vidziunaite R, Schneider P (2003) Laccase-catalyzed oxidation of naphthol in the presence of soluble polymers. Enzyme Microb Technol 32:455–463

Kurek B, Kersten PJ (1995) Physiological regulation of glyoxal oxidase from *Phanerochaete chrysosporium* by peroxidase systems. Enzyme Microb Technol 17:751–756

Kuwahara M, Glenn JK, Morgan MA, Gold MH (1984) Separation and characterization of two extracellular H_2O_2-dependent oxidases from ligninolytic cultures of *Phanerochaete chrysosporium*. FEBS Lett 169: 247–250

Lante A, Crapisi A, Krastanov A, Spettoli P (2000) Biodegradation of phenols by laccase immobilised in a membrane reactor. Process Biochem 36:51–58

Lee Y, Yoon J, Gunten UV (2005) Kinetics of the oxidation of phenols and phenolic endocrine disruptors during water treatment with ferrate (Fe(VI)). Environ Sci Technol 39:8978–8984

Levin L, Forchiassin F, Viale A (2005) Ligninolytic enzyme production and dye decolorization by *Trametes trogii*: application of the Plackett–Burman experimental design to evaluate nutritional requirements. Process Biochem 40:1381–1387

Liu HS, Mead JL, Stacer RG (2000) Environmental effects of recycled rubber in light-fill applications. Rubber Chem Technol 73:551–564

Lorenzo M, Moldes D, Rodríguez Couto S, Sanromán A (2002) Improving laccase production by employing different lignocellulosic wastes in submerged cultures of *Trametes versicolor*. Bioresour Technol 82:109–113

Lucas M, La D, Rubia T, Martinez J (2003) Oxidation of low molecular weight aromatic components of olive-mill wastewaters by a *Trametes versicolor* laccase. Polyphenols Actual 23:36–47

Maas R, Chaudhari S (2005) Adsorption and biological decolourization of azo dye Reactive Red 2 in semicontinuous anaerobic reactors. Process Biochem 40(2):699–705

Maceiras R, Rodríguez Couto S, Sanromán A (2001) Influence of several inducers on the synthesis of extracellular laccase and in vivo decolourisation of Poly R-478 by semi-solid-state cultures of *Trametes versicolor*. Acta Biotechnol 21:255–264

Maciel MJM, Silva AC, Ribeiro HCT (2010) Industrial and biotechnological applications of ligninolytic enzymes of the basidiomycota: a review. Electron J Biotechnol 13(6):14–15

Majcherczyk A, Johannes C (2000) Radical mediated indirect oxidation of a PEG-coupled polycyclic aromatic hydrocarbon (PAH) model compound by fungal laccase. Biochim Biophys Acta 1474:157–162

Majcherczyk A, Johannes C, Hüttermann A (1998) Oxidation of polycyclic aromatic hydrocarbons (PAH) by laccase of *Trametes versicolor*. Enzyme Microb Technol 22:335–341

Malkin R, Malmstrom BG, Vanngard T (1969) The reversible removal of one specific copper (II) from fungal laccase. Eur J Biochem 7:253

Malmstrom BG, Andreason LE, Reinhammar R (1975) In: Boyer PD (ed) The enzymes, vol 12B, 3rd edn. Academic, New York, p 507

Martínez AT, Speranza M, Ruiz-Duenas FJ, Ferreira P, Guillén F, Martínez MJ, Gutiérrez A, del Rio CJ (2005) Biodegradation of lignocellulosics: microbial, chemical, and enzymatic aspects of the fungal attack of lignin. Int Microbiol 8:195–204

Martínez AT, Ruiz-Dueñas FJ, Martínez MJ, Del Rio JC, Gutiérrez A (2009) Enzymatic delignification of plant cell wall: from nature to mill. Curr Opin Biotechnol 20(3):348–357

Mayer AM, Harel E (1979) Polyphenol oxidases in plants. Phytochemistry 33:765–767

Mayer AM, Staples RC (2002) Laccase: new functions for an old enzyme. Phytochemistry 60(6):551–565

Mazmanci MA, Ali U, Erkurt EA, Arkey NB, Bilen E, Ozyurt M (2009) Colour removal of textile dyes by culture extracts obtained from white rot fungi. Afr J Microbiol Res 3:585–589

Mccarthy JT, Levy VC, Lonergan GT, Fecondo JV (1999) Development of optimal conditions for the decolourisation of a range of industrial dyes using *Pycnoporus cinnabarinus* laccase. Hazard Ind Waste 31:489–498

Michniewicz A, Ledakowicz S, Jamroz T, Jarosz-Wilkolazka A, Leonowicz A (2003) Decolorization of aqueous solution of dyes by the laccase complex from *Cerrena unicolor*. Biotechnologia 4:194–203

Minussi RC, Miranda MA, Silva JA, Ferreira CV, Aoyama H, Marangoni S, Rotilio D, Pastore GM, Durán N (2007) Purification, characterization and application of laccase from *Trametes versicolor* for colour and phenolic removal of olive mill wastewater in the presence of 1-hidroxybenzotriazole. Afr J Biotechnol 6(6):1248–1254

Moeder M, Martin C, Koeller G (2004) Degradation of hydroxylated compounds using laccase and horseradish peroxidase immobilized on microporous polypropylene hollow fiber membranes. J Membr Sci 245:183–190

Moldes D, Gallego PP, Rodríguez Couto S, Sanromán A (2003) Grape seeds: the best lignocellulosic waste to produce laccase by solid state cultures of *Trametes hirsuta*. Biotechnol Lett 25:491–495

Molina-Guijarro JM, Perez J, Munoz-Dorado J, Guillen F, Moy R, Hernandez M, Arias ME (2009) Detoxification of azo dyes by a novel pH-versatile, salt-resistant laccase from *Streptomyces ipomoea*. Int Microbiol 12:13–21

Morozova OV, Shumakovich GP, Shleev SV, Yaropolov Ya I (2007) Laccase–mediator systems and their applications: a review. Appl Biochem Microbiol 43(5):523–535

Mougin C, Jolivalt C, Malosse C, Chaplain V, Sigoillot JC, Asther M (2002) Interference of soil contaminants with laccase activity during the transformation of complex mixtures of polycyclic aromatic hydrocarbons in liquid media. Polycycl Aromat Compd 22:673–688

Murugesan K (2003) Bioremediation of paper and pulp mill effluents. Indian J Exp Biol 41:1239–1248

Nakasaki K, Sasaki M, Shoda M, Kubota H (1985) Characteristic of mesophilic bacteria isolates isolated during thermophilic composting of sewage sludge. Appl Environ Microbiol 49:42–45

Nicotra S, Cramarossa MR, Mucci A, Pagnoni UM, Riva S, Forti L (2004) Biotransformation of resveratrol: synthesis of trans-dehydrodimers catalyzed by laccases from *Myceliophthora thermophyla* and from *Trametes pubescens*. Tetrahedron 60:595–600

Niku-Paavola M-L, Viikari L (2000) Enzymatic oxidation of alkenes. J Mol Catal B Enzyme 10:435–444

Nyanhongo GS, Gomes J, Gübitz G, Zvauya R, Read JS, Steiner W (2002) Production of laccase by a newly isolated strain of *Trametes modesta*. Bioresour Technol 84:259–263

Okazaki S-Y, Michizoe J, Goto M, Furusaki S, Wariishi H, Tanaka H (2002) Oxidation of bisphenol A catalyzed by laccase hosted in reversed micelles in organic media. Enzyme Microb Technol 31:227–232

Oudia A, Queiroz J, Simoes R (2008) The influence of operating parameters on the biodelignification of *Eucalyptus globules* Kraft pulps in a laccase-violuric acid system. Appl Biochem Biotechnol 149:149–3

Ozsoy S, Altunatmaz K, Horoz H, Kasikcle G, Alkan S, Bilat T (2005) The relationship between lameness, fertility and aflatoxin in a dairy cattle herd. Turk J Vet Anim Sci 29:981–986

Paice MG, Bourbonnais R, Reid ID (1995) Bleaching kraft pulps with oxidative enzymes and alkaline hydrogen peroxide. Tappi J 78:161–169

Palmieri G, Cennamo G, Sannia G (2005) Remazol brilliant blue R decolourisation by the fungus *Pleurotus ostreatus* and its oxidative enzymatic system. Enzyme Microb Technol 36:17–24

Pedroza AM, Mosqueda R, Alonso-Vante N, Rodriguez-Vazquez R (2007) Sequential treatment via *Trametes versicolor* and UV/TiO2/Ru(x)Se(y) to reduce contaminants in waste water resulting from the bleaching process during paper production. Chemosphere 67:793–801

Peralta-Zamora P, Pereira CM, Tiburtius ERL, Moraes SG, Rosa MA, Minussi RC (2003) Decolorization of reactive dyes by immobilized laccase. Appl Catal B Environ 42:131–144

Pickard MA, Roman R, Tinoco R, Vazquez-Duhalt R (1999) Polycyclic aromatic hydrocarbon metabolism by white rot fungi and oxidation by *Coriolopsis gallica* UAMH 8260 laccase. Appl Environ Microbiol 65:3805–3809

Piontek K, Smith AT, Blodig W (2001) Lignin peroxidase structure and function. Biochem Soc Trans 29(2): 111–116

Pointing SB (2001) Feasibility of bioremediation by white-rot fungi. Appl Microbiol Biotechnol 57(1–2):20–33

Potin O, Veignie E, Rafin C (2004) Biodegradation of polycyclic aromatic hydrocarbons (PAHs) by *Cladosporium sphaerospermum* isolated from an aged PAH contaminated soil. FEMS Microbiol Ecol 51:71–78

Punnapayak H, Prasongsuk S, Messner K, Danmek K, Lotrakul P (2007) Polycyclic aromatic hydrocarbons (PAHs) degradation by laccase from a tropical white rot fungus *Ganoderma lucidum*. Afr J Biotechnol 8:5897–5900

Reddy CA, Mathew Z (2001) In: Gadd GM (ed) Bioremediation potential of white rot fungi. Cambridge University Press, Cambridge, p 250

Reinhammar B (1984) Laccase. In: Lontie R (ed) Copper proteins and copper enzymes, vol 3. CRC Press, Boca Raton, pp 1–35

Revankar MS, Lele SS (2007) Synthetic dye decolorization by white rot fungi, *Ganoderma* sp. WR-1. Bioresour Technol 98:775–780

Reyes P, Pickard MA, Vazquez-Duhalt R (1999) Hydroxybenzotriazole increases the range of textile dyes decolorized by immobilized laccase. Biotechnol Lett 21:875–880

Rodakiewicz-Nowak J, Jarosz-Wilkołazka A, Luterek J (2006) Catalytic activity of versatile peroxidase from *Bjerkandera fumosa* in aqueous solutions of water-miscible organic solvents. Appl Catal A Gen 308:56–61

Rodríguez Couto S, Sanromán MA (2006) Effect of two wastes from groundnut processing on laccase production and dye decolourization ability. J Food Eng 73:388–393

Rodríguez Couto S, Gundín M, Lorenzo M, Sanromán A (2002) Screening of supports for laccase production by *Trametes versicolor* in semisolid - state conditions. Determination of optimal operation conditions. Process Biochem 38:249–255

Rodríguez Couto S, Rosales E, Gundín M, Sanromán MA (2004) Exploitation of a waste from the brewing industry for laccase production by two *Trametes* sp. J Food Eng 64:423–428

Rodríguez Couto S, Sanromán MA, Gübitz GM (2005) Influence of redox mediators and metal ions on synthetic acid dye decolourization by crude laccase from *Trametes hirsuta*. Chemosphere 58:417–422

Rodríguez Couto S, López E, Sanromán MA (2006) Utilisation of grape seeds for laccase production in solid-state fermentors. J Food Eng 74:263–267

Ruiz-Dueñas FJ, Morales M, García E, Miki Y, Martínez MJ, Martínez AT (2009) Substrate oxidation sites in versatile peroxidase and other basidiomycete peroxidases. J Exp Bot 60(2):441–452

Saito T, Kato K, Yokogawa Y, Nishida M, Yamashita N (2004) Detoxification of bisphenol A and nonylphenol by purified extracellular laccase from a fungus isolated from soil. J Biosci Bioeng 98:64–66

Sanchez-Amat A, Lucas-Elio P, Fernandez E, Garcia-Borron JC, Solano F (2001) Molecular cloning and functional characterization of a unique multipotent polyphenol oxidase from *Marinomonas mediterranea*. Biochim Biophys Acta 1547:104–116

Schliephake K, Mainwaring DE, Lonergan GT, Jones IK, Baker WL (2000) Transformation and degradation of the diazodye Chicago Sky Blue by a purified laccase from Pycnoporus cinnabarinus. Enzyme Microb Technol 27:100–107

Score AJ, Palfreyman JW, White NA (1997) Extracellular phenoloxidase and peroxidase enzyme production during interspecific fungal interactions. Int Biodeter Biodegr 39(2–3):225–233

Sharma KK, Kuhad RC (2008) Laccase: enzyme revisited and functions redefined. Indian J Microbiol 48: 309–316

Sharma KK, Kuhad RC (2009) An evidence of laccase in archaea. Indian J Microbiol 49:142–150

Sharma P, Goel R, Capalash N (2007) Bacterial laccases. World J Microbiol Biotechnol 23:823–832

Soares GMB, Costa-Ferreira M, Pessoa de Amorim MT (2001a) Decolorization of an anthraquinone-type dye using a laccase formulation. Bioresour Technol 79:171–177

Soares GMB, Pessoa de Amorim MT, Costa-Ferreira M (2001b) Use of laccase together with redox mediators to decolourize Remazol Brilliant Blue R. J Biotechnol 89:123–129

Soares GMB, Pessoa Amorim MT, Hrdina R, Costa-Ferreira M (2002) Studies on the biotransformation of novel disazo dyes by laccase. Process Biochem 37: 581–587

Soares A, Jonasson K, Terrazas E, Guieysse B, Mattiasson B (2005) The ability of white-rot fungi to degrade the endocrine-disrupting compound nonylphenol. Appl Microbiol Biotechnol 66:719–725

Soares A, Guieysse B, Mattiasson B (2006) Influence of agitation on the removal of nonylphenol by the white-rot fungi *Trametes versicolor* and *Bjerkandera* sp. BOL 13. Biotechnol Lett 28:139–143

Solano F, Garcia E, Perez D, Egea E, Sanchez-Amat A (1997) Isolation and characterization of strain MMB-1 (CECT 4803), a novel melanogenic marine bacterium. Appl Environ Microbiol 63:3499–3506

Srivastava V, Negi AS, Kumar JK, Gupta MM, Khanuja SPS (2005) Plant-based anticancer molecules: a chemical and biological profile of some important leads. Bioorg Med Chem 13:5892–5908

Steenken S (1998) Lifetime, reduction potential and base-induced fragmentation of the veratryl alcohol radical cation in aqueous solution. Pulse radiolysis studies on a ligninase "Mediator". J Phys Chem A 102:7337–7342

Steffen KT, Hofrichter M, Hatakka A (2000) Mineralisation of 14C-labelled synthetic lignin and ligninolytic enzyme activities of litter decomposing basidiomycetous fungi. Appl Microbiol Biotechnol 54:819–825

Steffen KT, Schubert S, Tuomela M, Hattaka A, Hofrichter M (2007a) Enhancement of bioconversion of high-molecular mass polycyclic aromatic hydrocarbons in contaminated non-sterile soils by litter-decomposing fungi. Biodegradation 18:359–363

Steffen TK, Cajthaml T, Šnajdr J, Baldrian P (2007b) Differential degradation of oak (*Quercus petraea*) leaf litter by litter-decomposing basidiomycetes. Res Microbiol 158:447–455

Strom PF (1985a) Effect of temperature on bacterial species diversity in thermophilic solid-waste composting. Appl Environ Microbiol 50:899–905

Strom PF (1985b) Identification of thermophilic bacteria in solid- waste composting. Appl Environ Microbiol 50:907–913

Sutherland JB (1992) Detoxification of polycyclic aromatic hydrocarbons by fungi. J Ind Microbiol 9:53–62

Tamagawa Y, Hirai H, Kawai S, Nishida T (2005) Removal of estrogenic activity of endocrine-disrupting genistein by ligninolytic enzymes from white rot fungi. FEMS Microbiol Lett 244:93–98

Tanaka T, Tonosaki T, Nose M, Tomidokoro N, Kadomura N, Fujii T (2001) Treatment of model soils contaminated with phenolic endocrine-disrupting chemicals with lactase from *Trametes* sp. in a rotating reactor. J Biosci Bioeng 92:312–316

Tanaka T, Nose M, Endo A, Fujii T, Taniguchi M (2003) Treatment of nonylphenol with laccase in a rotating reactor. J Biosci Bioeng 96:541–546

Taneja K, Gupta S, Kuhad RC (2002) Properties and application of a partially purified alkaline xylanase from an alkalophilic fungus *Aspergillus nidulans* KK-99. Bioresour Technol 85(1):39–42

Tavares APM, Gamelas JAF, Gaspar AR, Evtuguin DV, Xavier AMRB (2004) A novel approach for the oxidative catalysis employing polyoxometalate–laccase system: application to the oxygen bleaching of kraft pulp. Catal Commun 5:485–489

Thurston CF (1994) The structure and function of fungal laccases. Microbiology 140:19–26

Tien M, Kirk K (1983) Lignin-degrading enzyme from the hymenocete *Phanerochaete chrysosporium*. Science 221:661–663

Tien M, Kirk TK (1984) Lignin-degrading enzyme from *Phanerochaete chrysosporium*: purification, characterization, and catalytic properties of a unique H_2O_2-requiring oxygenase. Proc Natl Acad Sci USA 81(8):2280–2284

Toh Y-C, Yen JJL, Obbard JP, Ting Y-P (2003) Decolourisation of azo dyes by white-rot fungi (WRF) isolated in Singapore. Enzym Microb Technol 33(5):569–575

Trejo-Hernandez MR, Lopez-Munguia A, Quintero Ramirez R (2001) Residual compost of *Agaricus bisporus* as a source of crude laccase for enzymatic oxidation of phenolic compounds. Process Biochem 36(7):635–639

Tsioulpas A, Dimou D, Iconomou D, Aggelis G (2002) Phenolic removal in olive oil mill wastewater by strains of *Pleurotus* spp. In respect to their phenol oxidase (laccase) activity. Bioresour Technol 84:251–257

Tuomela M, Vikman M, Hatakka A, Itavaara M (2000) Biodegradation of lignin in a compost environment: a review. Bioresour Technol 72:169–183

Ünyayar A, Mazmanci MA, Ataçağ H, Erkurt EA, Coral G (2005) A Drimaren Blue X3LR dye decolorizing enzyme from *Funalia trogii* one step isolation and identification. Enzyme Microb Technol 36:10–16

Vandertol-Vanier HA (2000) The role of laccase from C*oriolopsis gallica* in polycyclic aromatic hydrocarbon metabolism, PhD thesis Faculty of Graduate Studies and Research, Dept. of Biological Sciences, University of Alberta, Canada

Vandertol-Vanier HA, Vazquez-Duhalt R, Tinoco R, Pickard MA (2002) Enhanced activity by poly(ethylene glycol) modification of *Coriolopsis gallica* laccase. J Ind Microbiol Biotechnol 29:214–20

Varadachari V, Ghosh K (1984) On humus formation. Plant Soil 77:305–313

Vasdev K, Kuhad RC, Saxena RK (1995) Decolorization of triphenylmethane dyes by *Cyathus bulleri*. Curr Microbiol 30(5):269–272

Vasdev K, Kuhad RC (1994) Induction of Laccase production in *Cyathus bulleri* under shaking and static conditions. Folia Microbiol 39(4):326–330

Viswanath B, Chandra MS, Kumar KP, Rajasekhar-reddy B (2008) Production and purification of laccase from *Stereum ostrea* and its ability to decolorize textile dyes. Dyn Biochem Process Biotechnol Mol Biol 2:19–25

Waksman SA, Cordon TC, Hulpoi N (1939) Influence of temperature upon the microbiological population and decomposition processes in composts of stable manure. Soil Sci 47:83–114

Watanabe K (2001) Microorganisms relevant to bioremediation. Curr Opin Biotechnol 12:237–241

Wood J, Wood P (1992) Evidence that cellobiose: quinine oxidoreductase from *Phanerochaete chrysosporium* is

a breakdown product of cellobiose oxidase. Biochem Biophys Acta 1119:90–96

Wyatt AM, Broda P (1995) Informed strain improvement for lignin degradation by *Phanerochaete chrysosporium*. Microbiology 141:2811–2822

Xu F (2005) Applications of oxidoreductases: recent progress. Ind Biotechnol 1:38–50

Yamanaka R, Soares CF, Matheus DR, Machado KMG (2008) Lignolytic enzymes produced by *Trametes villosa* CCB 176 under different culture conditions. Braz J Microbiol 39:78–84

Yang XQ, Zhao XX, Liu CY, Zheng Y, Qian SJ (2009) Decolorization of azo, triphenylmethane and anthraquinone dyes by a newly isolated *Trametes* sp. SQ01 and its laccase. Process Biochem 44:1185–1189

Yaropolov AI, Skorobogat'ko OV, Vartanov SS, Varfolomeyev SD (1994) Laccase: properties, catalytic mechanism, and applicability. Appl Biochem Biotechnol 49(3):257–280

Zavarzina AG, Leontievsky AA, Golovleva LA, Trofimov SY (2004) Biotransformation of soil humic acids by blue laccase of *Panus tigrinus*: an *in vitro* study. Soil Biol Biochem 36:359–69

Zhao YC, Yi XY, Zhang M, Liu L, Ma WJ (2010) Fundamentals of degradation of dichlorodiphenyltrichloroethane in soil by laccase from white rot fungi. Int J Environ Sci Technol 7:359–366

Zille A, Tzanov T, Guebitz GM, Cavaco-Paulo A (2003) Immobilized laccase for decolourization of Reactive Black dyeing effluent. Biotechnol Lett 25:1473–1477