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REVIEW PAPER

Recent developments in biodegradation of industrial pollutants by white rot fungi and their enzyme system

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Abstract Increasing discharge and improper management of liquid and solid industrial wastes have created a great concern among industrialists and the scientific community over their economic treatment and safe disposal. White rot fungi (WRF) are versatile and robust organisms having enormous potential for oxidative bioremediation of a variety of toxic chemical pollutants due to high tolerance to toxic substances in the environment. WRF are capable of mineralizing a wide variety of toxic xenobiotics due to non-specific nature of their extracellular lignin mineralizing enzymes (LMEs). 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 pollutants. Many new strains have been identified and their LMEs isolated, purified and characterized. In this review, we have tried to cover the latest developments on enzyme systems of WRF, their low molecular mass mediators and their potential use for bioremediation of industrial pollutants.

Keywords Industrial pollutants · Bioremediation · White rot fungi · Lignin mineralizing enzymes · Low molecular mass mediators

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Introduction

In view of the extensive contamination of the environment by persistant and toxic chemical pollutants originating from industrial wastewaters, it is imperative to develop cost effective and efficient methods for their remediation. Bioremediation is a popular and attractive technology that utilizes the metabolic potential of microorganisms to clean up the environment (Watanabe 2001). Recently, the capability of white rot fungi (WRF) for biodegradation of xenobiotics and recalcitrant pollutants has generated a considerable research interest in this area of industrial/environmental microbiology.

WRF are physiological group comprizing fungi that are capable of biodegrading lignin and the name white rot derives from the white appearance of the wood attacked by WRF, where lignin removal gives a bleached appearance (Pointing 2001). Taxanomically, WRF are mostly basidiomycetes, although few ascomycetes are also capable of white-rot decay (Eaton and Hale 1993). The extracellular and non-specific lignin

mineralizing enzymes (LMEs) and low-molecular-mass mediators enhance the bioavailability of pollutants to WRF (Pointing 2001). Property of WRF to withstand a wide range of pH further enhances their pollutant degradation capabilities (Verma and Madamwar 2002).

Many reviews (Kirk and Farrell 1987; Cullen and Kersten 1992; Gold and Alic 1993; Barr and Aust 1994; Hatakka 1994, 2001; Reddy 1995; Pointing 2001; Hofrichter 2002; Martínez 2002; Shah and Nerud 2002; Wesenberg et al. 2003) are available on different aspects of WRF and their enzyme systems. This review will focus on recent developments in biodegradation of industrial pollutants by WRF and their enzyme system.

Enzyme system of white rot fungi

Lignin peroxidase (LiP), mangnese peroxidase (MnP), laccase and versatile peroxidase (VPs) are the major LMEs of WRF involved in lignin and xenobiotic degradation by WRF (Pointing 2001; Wesenberg et al. 2003). 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 WRF strains (Wesenberg et al. 2003, 2005; Doddapaneni et al. 2005; Aguiar et al. 2006).

Lignin peroxidases (LiPs) are capable of mineralizing a variety of recalcitrant aromatic compounds (Shrivastava et al. 2005). The molecular mass of LiPs from different WRF strains varies from 37 to 50 kDa (Asgher et al. 2006; Hirai et al. 2005). pH and temperature activity profiles of LiPs from different sources vary significantly with optimum activities shown between pH 2–5 and 35–55°C, respectively (Yang et al. 2004; Asgher et al. 2007). Immobilization of LiP has been found to enhance its pH and temperature optima as well as thermostability and catalytic properties (Asgher et al. 2007). The natural fungal secondary metabolites veratryl alcohol (VA) and 2-chloro-1,4-dimethoxybenzene act as redox mediators to stimulate the LiP catalyzed oxidation of a wide range of recalcitrant substrates (Teunissen and Field 1998; Christian et al. 2005). Oxidation of VA by YK-LiP2 from *P. chrysosporium* and other LiPs reveal ordered bi–bi ping–pong mechanisms rather than peroxidase bi–bi ping–pong kinetics shown by Pc-LiP (Liu et al. 2003; Hirai et al. 2005). Kinetic analysis suggests that cationic radical of VA accelerates the catalytic cycle of LiP possibly by conversion of LiP (II) and/or LiP(III) to LiP (Lan et al. 2006). Cationic surfactant cetyltrimethylammonium bromide (CTAB) is an inhibitor for LiP; it lowers the V_{max} and causes K_M of H_2O_2 to decrease dramatically and that of VA to increase possibly by modifying the enzyme conformation (Liu et al. 2003). *Phanerochaete chrysosporium* LiP is also inhibited by ethylenediamine tetraacetic acid (EDTA) and *N-N-N′-N′*-tetramethylenediamine (TEMED). However, in the presence of excess Zn^{2+} and other metal ions, the EDTA and TEMED mediated non-competitive inhibition of LiP catalyzed veratryl alcohol oxidation can be reversed (Chang and Bumpus 2001). The oxidation by LiP depends on the optimum molar ratio of H_2O_2 to pollutant. At lower concentrations, H_2O_2 is an activator of *Phanerochaete chrysosporium* LiP (Pc-LiP), while at higher concentrations it is an inhibitor and rapidly deactivates the enzyme (Yu et al. 2006; Lan et al. 2006).

Manganese peroxidases (MnPs) are extracellular glycoproteins with an iron protoporphyrin IX (heme) prosthetic group with molecular weights varying between 32 and 62.5 kDa, optimum pH of 4–7 and optimum temperature of 40–60°C (Ürek and Pazarlioglu 2004; Baborová et al. 2006). MnPs are secreted in multiple isoforms in carbon and nitrogen limited media supplemented with Mn^{2+} and VA (Hakala et al. 2005; Cheng et al. 2007). The marked differences in structure and characteristics (pI 3.4 & 3.9; molecular masses 47 & 52 kDa) and differential regulation of two different MnP encoding genes MnPA and MnPB in *Physiisporinus rivulosus* T24li and their variable properties also confirm the expression of MnP isoforms (Hakala et al. 2005, 2006).

Mn^{2+} performs the role of mediator for MnP. High resolution crystal structure has revealed that MnP catalyzes the peroxide dependent oxidation of Mn^{2+} to Mn^{3+} and Mn^{3+} is released from the enzyme in complex with oxalate or with other chelators (Sundramoorthy et al. 2005). Along with pyrophosphate, the various Mn^{2+} chelators that enhance the activity are malonate, oxalate, L-tartrate, oxaloacetate, L-malate, and methylmalonate (Mäkelä et al. 2005). MnP can also utilize both H_2O_2 and various organic

hydroperoxides, such as peracetic acid, *m*-chloroperoxybenzoic acid, and *p*-nitroperoxybenzoic acid, as its source of oxidizing equivalents. MnP activity is inhibited by NaN_3, ascorbic acid, β-mercaptoethanol and dithreitol (Ürek and Pazarlioglu 2005), whereas the activity can be enhanced in the presence of cooxidants such as glutathione, unsaturated fatty acids and Tween 80 (Hofrichter 2002; Ürek and Pazarlioglu 2005). The stability of MnP can be improved by immobilization with sodium alginate, gelatin or chitosan as carriers and glutaraldehyde as crosslinking agent (Cheng et al. 2007).

Laccases are *N*-glycosylated extracellular blue multicopper oxidases (Wells et al. 2006) with molecular masses varying from 58 to 90 kDa (Murugesan et al. 2006; Salony et al. 2006; Zouari-Mechichi et al. 2006; Quaratino et al. 2007). Purified laccases from *Cyathus bulleri* and *Panus tigrinus* CBS577.79 have shown 16% and 6.9% (high mannose type) glycation, respectively (Salony et al. 2006; Quaratino et al. 2007). The pH and temperature optima of laccases from different WRF vary from 2 to 10 and 40 to 65°C, respectively (Lu et al. 2005; Ullrich et al. 2005; Murugesan et al. 2006; Zouari-Mechichi et al. 2006; D'Souza et al. 2006; Quaratino et al. 2007). Two laccase isozymes LacI and LacII have been identified in *Physisporinus rivulosus* T241i (pI 3.1 & 3.3; MW 66 & 68 kDa), *Trametes trogii* (pI 4.3 & 4.5; MW around 62 kDa; optimum pH 2.0 & 2.5; optimum temperature around 50°C), *Cerrena unicolor* 137 (pI 3.6 & 3.7; MW 64 & 57 kDa; optimum pH 7 & 10; optimum temperature around 60°C) and *Panus tigrinus* (identical optimum pH 7.0 and 60–65°C temperature) (Cadimaliev et al. 2005; Lorenzo et al. 2006; Mäkelä et al. 2006; Michniewicz et al. 2006; Zouari-Mechichi et al. 2006). Two different laccase encoding genes Pr-lac1 and Pr-lac 2 in *Phlebia radiata* 79 are differentially expressed and regulated (Mäkelä et al. 2006). The Pr-lac 2 gene has a very high (66%) sequence similarity with *Trametes versicolor* laccase.

Various fungal metabolites such as *N*-hydroxyacetanilide (NHA), *N*-(4-cyanophenyl)acetohydroxamic acid (NCPA), 3-hydroxyanthranilate, syringaldehyde, ABTS (2,2′-azino-bis(3-ethylbenzthiazoline-6-sulphonate), 2,6-dimethoxyphenol (DMP), violuric acid, 1-hydroxybenzotriazole (HBT), 2,2,6,6-tetramethylpipperidin-*N*-oxide radical, acetovanillone (AV), acetosyringone and acetohydroxamic acid perform the role of mediators of laccase and enhance pollutant degradation (Geng et al. 2004; Cho et al. 2006; Lu et al. 2007; Minussi et al. 2007; Quaratino et al. 2007). However, *Trametes versicolor* laccase was more effective for denim washing without a mediator as compared to a commercial laccase (Pazarlioglu et al. 2005). Addition of Cu, Cd, Ni, Mo and Mn increase the activity of WRF laccase, in most cases, whereas Ag, Hg, Pb, Zn, sodium azide, sodium chloride and H_2O_2 inhibit its activity (Ullrich et al. 2005; Murugesan et al. 2006). However, laccase from *Trametes trogii* is not affected by Cd, Al, Li and Ca (Zouari-Mechichi et al. 2006), whereas the activity of *Pleurotus ostreatus* laccase is enhanced by Pb and Zn (Baldrian et al. 2005). Immobilization of laccase in alginate-chitosan microcapsules increases stability and catalytic activity of the enzyme for repeated use in dye decolorization (Lu et al. 2007).

Versatile peroxidase (VP) is a heme containing structural hybrid between MnPs and LiPs, since they can oxidize not only Mn^{2+} but can also oxidize veratryl alcohol, phenolic and nonphenolic and high-molecular weight aromatic compounds including dyes in manganese-independent reactions (Kamitsuji et al. 2004; Pogni et al. 2005; Shrivastava et al. 2005). VPs have been described in species of *Pleurotus* and *Bjerkandera* (Mester and Field 1998; Kamitsuji et al. 2005a, b; Pogni et al. 2005; Honda et al. 2006; Rodakiewicz-Nowak et al. 2006). The deduced amino acid sequence of MnP2 isolated from *P. ostreatus* and VP (VAXPDGVNTA) from a novel strain of *Bjerkandera* sp. (MW 45 kDa) is more than 95% identical to that of a typical VP (VP-PS1) from *P. eryngii* (Moreira et al. 2006). A homologous enzyme, MnP-GY, from recombinant strains *P. ostreatus* ATCC66376 (Kamitsuji et al. 2004) and MnP2 from *P. ostreatus* TM2-10 (Tsukihara et al. 2006) can directly oxidize veratryl alcohol and high-molecular weight compounds, such as Poly R-478 and RNaseA, although much less efficiently than it oxidized Mn^{2+} in the absence of a mediator suggesting that the enzyme is a VP having properties of both LiP and MnP.

The molecular architecture of VP from *Bjerkandera adusta* and *Pleurotus eryngii* includes an exposed neutral tryptophan 172 (Trp 172) radical near to the heme prosthetic group, that is responsible for aromatic substrate oxidation and is a putative Mn^{2+} oxidation site (Pogni et al. 2007; Tinoco et al. 2007). However, high resolution crystal structure and

side chain orientation studies have shown that Trp164 is the site involved in long-range electron transfer for aromatic substrate oxidation (Pogni et al. 2006). The crystal structures (solved up to 1.3 Å) of *Pleurotus eryngii* VP, before and after exposure to Mn^{2+}, showed a variable orientation of the Glu36 and Glu40 side chains that, together with Asp175, contribute to Mn^{2+}coordination (Ruiz-Dueñas et al. 2007). *Bjerkandera adusta* VP requires Ca^{2+} for long range electron transfer during oxidation of pollutants. Inactivation of VP by Ca^{2+}-depletion at optimum pH 4.5 due to the differences in the Fe^{3+} spin states suggested that Ca^{2+}-depleted VP is able to form the active intermediate compound I but its long range electron transfer is disrupted (Verdín et al. 2006). The decrease in medium polarity by the addition of organic solvents like acetonitrile, dimethylsulfoxide (DMSO), ethanol, and *n*-propanol leads to inhibition of *Bjerkandera fumosa* VP (Rodakiewicz-Nowak et al. 2006). Oxidizing mediators like veratryl alcohol, acetosyringone and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) enhance the VP catalyzed decolorization of some textile dyes by *Bjerkandera adusta* (Tinoco et al. 2007).

Bioremediation of industrial pollutants by WRF

Biodegradation of bleach plant effluents

Bleach plant effluents (BPEs) from the pulp and paper industry generated during bleaching with chlorine-containing chemicals contain toxic chloroorganics and colored compounds that are difficult to decolorize and cause serious environmental problems (D'Souza et al. 2006). Extracellular LMEs from WRF have the potential to degrade highly toxic phenolic compounds from BPEs (Minussi et al. 2007). BPE-decolorizing and dechlorination/detoxification activities of *Phanerochaete chrysosporium, Trametes versicolor, Fomes lividus* and *Thelephora* sp. and the enzyme systems have been elucidated (Selvam et al. 2002, 2006). It has been demonstrated that laccase and not MnP or LiP plays the major role in decolorizing and detoxifying effluents from pulp and paper industry by WRF (D'Souza et al. 2006; Font et al. 2006). However, some studies indicate that laccase and MnP are the enzymes responsible for BPE decolorization by *Coriolus versicolor*. This decolorization is directly proportional to the initial color intensities and addition of glucose stimulates color removal (Driessel and Christov 2001).

Immobilization of *Trametes versicolor* in nylon and polyurethane foam cubes causes only 36% reduction in colour, 54% reduction in aromatic compounds and up to 5.7 fold reduction in toxicity as compared to *Trametes versicolor* pellets causing 84.8% colour removal and 70.2% aromatic compounds reduction with laccase as the major enzyme activity (Font et al. 2006). It suggests that immobilization of the fungus causes a significant reduction in laccase production/activity. Acetohydroxamic acid is very efficient mediator for *Trametes versicolor* laccase catalyzed bioremediation of BPEs, reducing 70% and 73% of the total phenol and total organic carbon, respectively as compared to 23% phenol reduction in the presence of HBT or in the absence of any mediator (Minussi et al. 2007).

Biodegradation/decolorization of dyestuffs

Different dyes and pigments are extensively used in the textile, paper, plastic, cosmetics, pharmaceutical and food industries (Levin et al. 2005). Interest in the biodegradation of synthetic dyes has primarily been prompted by concern over their possible toxicity and carcinogenicity (Maas and Chaudhari 2005; Salony et al. 2006; Revankar and Lele 2007). WRF are better dye-degraders than prokaryotes due to their extracellular non-specific 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 *Phanerochaete chrysosporium* and *Trametes versicolor* (Toh et al. 2003). However, other WRF 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* ATCC 200800 (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 decolourization rates than *P. chrysosporium* and *Trametes versicolor*.

LME-producing profiles and patterns of their expression vary among different WRF cultures depending upon the chemical structure and functional groups of the dyes being degraded (Table 1) and this

Table 1 Lignolytic enzymes of white rot fungi involved in biodegradation of different dyestuffs

WRF strain	Dyestuff	Enzymes	References
Coriolus versicolor f. antarcticus	Malachite Green, Azure B, Poly R-478, Anthraquinone Blue, Congo Red, Xylidine	Laccase	Levin et al. (2004))
Cerrena unicolor (Bull. ex Fr.) Murr. 137	Acid Blue 62, Acid Blue 40, Reactive Blue 81, Direct Black 22, Acid Red 27	Laccase	Michniewicz et al. (2008)
Daedalea quercina	Chicago Sky Blue, Poly B-411, Remazol Brilliant Blue R, Trypan Blue, Reactive Blue 2	Laccase	Baldrian (2004)
Funalia trogii	Reactive BLack 5	Laccase	Mazmanci and Ünyayar (2005)
Funalia trogii	Remazol Brillant Blue Royal (RBBR), Drimaren Blue CL-BR	Laccase	Erkurt et al. (2007)
Irpex lacteus	Reactive Blue 19 (RBBR), Reactive Black 5	MnP, laccase	Máximo and Costa-Ferreira (2004)
Irpex lacteus	Reactive Orange 16 and Remazol Brilliant Blue R.	Laccase	Svobodová et al. (2008)
Irpex lacteus (immobilized)	Reactive Orange 16	Laccase, MnP	Tavcar et al. (2006)
Lentinula (Lentinus) *edodes*	Remazole Brilliant Blue R	MnP	Boer et al. (2004)
Phanerochaete chrysosporium (immobilized on $ZrOCl_2$-activated pumice)	Direct Blue 15	MnP	Pazarlioglu et al. (2005)
Phanerochaete chrysosporium (immobilized on Kissiris)	Mythylene Blue	MnP	Karimi et al. (2006)
Phanerochaete chrysosporium BKM-F1767	Direct Blue 15, Direct Green 6, Congo Red	MnP	Ürek and Pazarlioglu (2005)
Pleurotus pulmonarius	Amido Black, Congo Red, Trypan Blue, Methyl Green, Remazol Brilliant Blue R, Methyl Violet, Ethyl Violet, Brilliant Cresyl Blue, Methylene Blue, Poly R-478	Laccase	Tychanowicz et al. (2004)
Pleurotus ostreatus	Phenol Red, Orthocresol Red, Meta-cresol Purple, Bromophenol Red, Bromocresol Purple, Bromophenol Blue, Bromocresol Green	MnP, MiP	Shrivastava et al. (2005)
Scyzophyllum commune IBL-06	Solar golden yellow R	MnP, laccase	Asgher et al. (2008)
Trametes trogii	Malachite Green, Xylidine, Ponceau 2R, Anthraquinone Blue	Laccase, MnP, GOx	Levin et al. (2005)
Trametes versicolor	Remazol Brilliant Blue R	LiP	Christian et al. (2005)
Trametes versicolor CNPR8107	Remazol Brilliant Blue RR, Remazol Red RR, Remazol Yellow RR	MnP, laccase	Toh et al. (2003)

appears to be of most interest for practical applications (Boer et al. 2004; Kariminiaae-Hamedaani et al. 2007). Mechanisms of biodegradation and profiles of biodegradation products of different dyes have also been determined (Zhao et al. 2005, 2006; Gavril and Hodson 2007; Zhao and Hardin 2007). Decolorization of Direct Blue 15 by *Phanerochaete chrysosporium* immobilized on $ZrOCl_2$-activated pumice follows the first-order kinetics with respect to initial dye concentration and MnP plays the major role in decolorization with mycelial adsorption being the minor mechanism (Pazarlioglu et al. 2005). MnP

was also the major enzyme with minor acticvities of laccase and LiP involved in decolorization of Solar golden yellow R by Schyzophyllum commune.

Low molecular mass redox mediators like ABTS are necessary for laccase-catalyzed decolorization of most of the dyes (Lu et al. 2005, 2007). However, *Pleurotus pulmonarius* and *Lentinula edodes* SR-1 have been reported to produce only exracellular laccase to decolorize dyes of different spectra without any mediators (Nagai et al. 2002). MnP mediated decolorization of azo dyes Direct Blue 15, Direct Green 6, and Congo red by *Phanerochaete chrysosporium can be* enhanced by the addition of Tween-80 (Ürek and Pazarlioglu 2005) and copper (Tychanowicz et al. 2006).Whereas, LiP produced by *Trametes versicolor* can decolorize Remazol Brilliant Blue R (RBBR) in the presence as well as in the absence of VA (Christian et al. 2005). The decolorization ability of WRF can be substantially increased by carefully optimizing the operational conditions such as initial dye concentration, nutrient content of the media, age of fungus and carbon and nitrogen sources (Ozsoy et al. 2005; Nilsson et al. 2006; Sanghi et al. 2006). Addition of glucose as carbon source caused a dramatic increase in decolorization of Solar golden yellow R by *Schyzophyllum commune* IBL-06, whereas additional nitrogen sources were inhibitory to MnP formation and dye decolorization (Asgher et al. 2008).

Bioremediation of olive oil mill wastewater

Olive oil extraction produces huge volume of wastewater, known as olive mill wastewater (OMWW) and dry residues of olives (ADOR). Both have high organic load, acidic pH and contain recalcitrant and toxic substances such as phenolic and lipidic compounds that is a serious concern of the olive industry (Ahmadi et al. 2006; Aranda et al. 2006). OMWW has high chemical oxygen demand (COD) of up to 200 g l^{-1} and organic fraction includes sugars, tannins, polyphenols, polyalcohols, pectins and lipids. Some of these substances (mainly sugars and polyalcohols) can be used as carbon and energy sources for microbial growth. Conventional biological wastewater treatments are ineffective for OMWW treatment since phenolics possess antimicrobial activity (Ahmadi et al. 2005). Most of the studies have been focused on bioremediation as a means of reducing the polluting effect of OMWW and its bio-transformation into valuable products (Ramos-Cormenzana et al. 1995). There are reports (Sanjust et al. 1991; Zervakis et al. 1996; Kalmis and Sargin 2004) on the cultivation of *Pleurotus* spp., *Pleurotus sajor-caju* and *P. cornucopiae* var. citrinopileatus using wheat straw moistened with mixtures containing 25% and 50% OMWW.

The removal of total phenols from OMWW relative to the total organic load consumed indicates the highest capability for free as well as loofah-immobilized *Phanerochaete chrysosporium* (Garcia et al. 2004; Ahmadi et al. 2005). OMWW can be detoxified through removal of organic matter, decreasing COD/BOD ratio by *Phanerochaete chrysosporium* or *Trametes versicolor* in the presence of complex microbial consortia in combined aerobic/anaerobic systems for its reuse and biogas production on industrial scale (Dhouib et al. 2006). *Pycnoporus coccineus*, *Pleurotus sajor-caju*, *Coriolopsis polyzona* and *Lentinus tigrinus*, are also very active in color and COD removal of OMWW at 50 and 75 g l^{-1} COD (Jaouani et al. 2003). At 100 g l^{-1} COD only *Pycnoporus coccineus* and *Pleurotus sajor-caju* are effective. *Panus trigrinus* CBS577.79 gives better COD reduction (60.9%), dephenolization (97.2%) and decolorization (75%) of OMWW in bubbled column bioreactor (BCB) as compared to stirred tank reactors (STR) due to possible occurrence of shear stress (D′Annibale et al. 2006).

A better decolourisation of OMWW by *Coriolopsis polyzona* has been reported (Jaouani et al. 2006) under LiP induction conditions (5 mM veratryl alcohol addition) than when LiP was repressed (100 μM Mn^{2+} addition). High levels of laccase have a detrimental effect on OMWW decolourisation concomitant to the formation of soluble polymeric aromatic compounds. However, high laccase activity produced by *Pleurotus* spp. in the growth medium reflected a close relationship between the amount of laccase produced and decrease in phenol content (Tsioulpas et al. 2002). *Pycnoporus cinnabarinus* and *Coriolopsis rigida* also produce high laccase activities responsible for 73% phenol reduction of ADOR in 15 days (Aranda et al. 2006).

Biodegradation of molasses based wastewater

Fermentation processes using sugarcane molasses yield large volumes of dark brown and highly toxic molasses wastewater (MWW) that contains

considerable amounts of organic compounds. Although most of the organic matter of MWW is removed by means of conventional biodegradation treatments, the removal of dark color due to the presence of melanoidin-type high molecular weight compounds is only marginal (Vahabzadeh et al. 2004). WRF are however, capable of catalyzing degradation of numerous recalcitrant organic compounds often present in MWW (Fu and Viraraghavan 2001; Lacina et al. 2003). The color removal ability of *Phanerochaete chrysosporium* is correlated to the activity of ligninolytic enzymes LiP and MnP (Vahabzadeh et al. 2004). The color reduction in the presence of VA is lower than in its absence, thus confirming the major role of MnP. Increased expression of laccase genes in *Trametes* sp. I-62 (lcc1 & lcc2) and basidiomycetous fungus NIOCC #2a upon exposure to MWW accompanied by enhanced color removal, suggested the involvement of laccase in the melanoidins metabolism (D'Souza et al. 2006; González et al. 2007).

Molasses spent wash (MSW) or digested spent wash (DSW) or alcohol distillery wastewater (WAD) is another wastewater from molasses-based alcohol distilleries (Raghukumar 2002; Chopra et al. 2004). The brown color of MSW is due to the presence of melanoidin pigments, which are highly recalcitrant to biodegradation. These pigments, polycyclic aromatic hydrocarbons (PAHs) like benzo(a)pyrenes and phenols are the causes of its toxicity (Raghukumar et al. 2004; Chairattanamanokorn et al. 2005). Several species of WRF have been reported to remove about 70–80% of the color present in MSW based effluents (Fahy et al. 1997; Raghukumar 2002; D'Souza et al. 2006). Immobilized mycelia of *Pycnoporus coccineus* on polyurethane foam removed nearly twofold higher WAD color and threefold higher total phenol content than did free mycelia (Chairattanamanokorn et al. 2005). Decolorization of MSW using free and immobilized mycelia of *Flavodon flavus* is accompanied by simultaneous detoxification and decrease in PAH contents of the MSW possibly via the action of glucose oxidase, accompanied by the production of H_2O_2 that acts as a bleaching agent in the process (Raghukumar and Rivonkar 2001; Raghukumar et al. 2004). Decolorization and COD reduction (52%) of DSW by *Coriolus versicolor* is dependent on the carbon source and addition of organic/inorganic nitrogen has no enhancing effect on decolorization and COD reduction (Chopra et al. 2004).

Biodegradation of byproducts of rubber industry and waste rubber

The extensive use of rubber products, mainly tyres, and the huge amount of waste rubber material produced as a byproduct is an environmental problem of great concern (Bredberg et al. 2002). Natural rubber waste serum (NRWS) is obtained as a by-product during coagulation of latex and is a major pollutant from the rubber industry (Lau and Subramaniam 1991). Although NRWS is being used as nitrogen and potassium supplement in fertilizers, and as a source of quebrachitol and hevealipin, it is still a menace in rubber-producing countries. Recycling of spent rubber material is problematic due to the vulcanisation, 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 (Christiansson et al. 1998; Bredberg et al. 2001). Microbial devulcanisation is a promising way to increase the recycling of rubber materials. However several microorganisms tested for devulcanisation are sensitive to rubber additives (Christiansson et al. 2000). However, WRF have the potential to bioremediate NRWS (Atagana et al. 1999). 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 *Resinicium bicolor* enhances the growth of *Thiobacillus ferrooxidans* bacterium as well as desulfurization compared to the untreated rubber. The co-cultures of aromatic additive degrader WRF with desulfurizing bacteria can thus be an attractive option for developing a potentially viable process for biodegradation of wastes from rubber industry.

Biodegradation of hormone disrupting compounds

Exposure to alkylsubstituted polynuclear aromatic hydrocarbons (Fragoso et al. 1998), stilbenes (Burnison et al. 1999), genistein (Kiparissis et al. 2003), methoxychlor (Lee et al. 2006) and endocrine disrupting chemicals (EDC), nonylphenol (NP) and bisphenol A

(BPA) and the personal care product ingredient triclosan (TCS) (Lee et al. 2005; Cabana et al. 2007) has been associated with a variety of reproductive responses in fish (Kiparisis et al. 2003). Degradation of genistein by *Phanerochaete sordida* YK-624 and dectecion of the activities of ligninolytic enzymes, MnP and laccase during treatment shows the involvement of WRF extracelluar 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), ethinylestradiol (EE2) with production of high molecular weight oligomeric metabolites through radical polymerization mechanism and formation of C–C and C–O bonds (Tsutsumi et al. 2001; Suzuki et al. 2003; Lee et al. 2005).

Stereum hisrsutum has high resistance to methoxychlor and is capable of degrading it by dechlorination and dehydrogenation with a significant reduction in its estrogenic activity (Lee et al. 2006). 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 laccasse/mediator system.

Conclusions and future prospects

WRF have tremendous potential for biodegradation of a variety of industrial pollutants. The broad spectrum for biodegradation of pollutants is due to the extracellular and non-specific nature of the enzyme system of WRF, comprising mainly of LiP, MnP, VP, laccase along with other accessory enzymes. The biodegradation capabilities of WRF for different pollutants are variable, mainly due to physiological differences among them, difference in their genetic make up and variable pattern and expression of complex LMEs in the presence of chemically different compounds. The major LMEs from different WRF sources vary widely regarding the number of amino acids, their moleculas masses, prosthetic group, low molecular mass mediator requirements, catalytic properties and mechanisms of action on different types of pollutants in performing their role in bioremediation. The activities of the LMEs can be increased by the addition of different low molecular mass mediators, mostly secreted by WRF themselves. The biodegradation efficiency of WRF can be further enhanced by addition of supplementary nutrients and proper process optimization. Isolation, characterization, immobilization and engineering of LMEs for their hyperactivation and thermostabilization, and their direct use in industrial processes are the area of potential future research.

References

Aguiar A, Souza-Cruz PBD, 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 Microb Technol 38:873–878

Ahmadi M, Vahabzadeh F, Bonakdarpour B, Mofarrah E, Mehranian M (2005) Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation. J Hazard Mater 123:187–195

Ahmadi M, Vahabzadeh F, Bonakdarpour B, Mehranian M, Mofarrah E (2006) Phenolic removal in olive oil mill wastewater using loofah-immobilized *Phanerochaete chrysosporium*. World J Microbiol Biotechnol 22:119–127

Aranda E, Sampedro I, Ocampo JA, García-Romera I (2006) Phenolic removal of olive-mill dry residues by laccase activity of white-rot fungi and its impact on tomato plant growth. Int Biodet Biodeg 58:176–179

Asgher M, Shah SAH, Ali M, Legge RL (2006) Decolorization of some reactive textile dyes by white rot fungi isolated in Pakistan. World J Microbiol Biotechnol 22:89–93

Asgher M, Asad MJ, Bhatti HN, Legge RL (2007) Hyperactivation and thermostabilization of *Phanerochaete chrysosporium* lignin peroxidase by immobilization in xerogels. World J Microbiol Biotechnol 23:525–531

Asgher M, Kausar S, Bhatti HN, Shah SAH, Ali M (2008) Optimization of medium for decolorization of Solar golden yellow R direct textile dye by *Schizophyllum commune* IBL-06. Int Biodet Biodeg 61:189–193

Atagana HI, Ejechi BO, Ayilumo AM (1999) Fungi associated with degradation of wastes from rubber processing industry. Environ Monit Assess 55:401–408

Baborová P, Moder M, Baldrian P, Cajthamlová K, Cajthaml T (2006) Purification of a new manganese peroxidase of the white-rot fungus *Irpex lacteus* and degradation of polycyclic aromatic hydrocarbons by the enzyme. Res Microbiol 157:248–253

Balan DSL, Monteiro RTR (2001) Decolorization of textile indigo dye by ligninolytic fungi. J Biotechnol 89:141–145

Baldrian P (2004) Purification and characterization of laccase from the white-rot fungus *Daedalea quercina* and decolorization of synthetic dyes by the enzyme. Appl Microbiol Biotechnol 63:560–563

Baldrian P, Valaskova V, Meerhautova V, Gabriel J (2005) Degradation of lignocellulose by *Pleurotus ostreatus* in the presence of copper, manganese lead and zinc. Res Microbiol 156:670–676

Barr DP, Aust SD (1994) Mechanisms white rot fungi use to degrade pollutants. Environ Sci Technol 28:78–87

Boer CG, Obici L, Giatti C, De Souza CG, Rosane M, Peralta M (2004) Decolorization of synthetic dyes by solid-state cultures of *Lentinula* (*Lentinus*) *edodes* producing manganese peroxidase as the main ligninolytic enzyme. Biores Technol 94:107–112

Bredberg K, Persson J, Christiansson M, Stenberg B, Holst O (2001) Anaerobic desulfurization of ground rubber with the thermophilic archaeon *Pyrococcus furiosus*-a new method for rubber recycling. Appl Microbiol Biotechnol 55:43–48

Bredberg K, Andersson BE, Landfors E, Holst O (2002) Microbial detoxification of waste rubber material by wood-rotting fungi. Biores Technol 83:221–224

Burnison BK, Comba ME, Carey JH, Parrott J, Sherry JP (1999) Isolation and tentative identification of compound in bleached-kraft mill effluent capable of causing mixed-function oxygenase induction in fish. Environ Toxicol Chem 18:2882–2887

Cabana H, Jiwan J-LH, 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 enzyme preparation from the white rot fungus *Coriolopsis polyzona*. Chemosphere 67:770–778

Cadimaliev DA, Revin VV, Atykyan NA, Samuilov VD (2005) Extracellular oxidases of the lignin-degrading fungus *Panus tigrinus*. Biochemistry (Moscow) 70:703–707

Chairattanamanokorn P, Imai T, Kondo R, Sekine M, Higuchi T, Ukita M (2005) Decolorization of alcohol distillery wastewater by thermotolerant white rot fungi. Appl Biochem Microbiol 41:662–667

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

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

Chang HC, Bumpus JA (2001) Inhibition of lignin peroxidase-mediated oxidation activity by ethylenediamine tetraacetic acid and *N-N-N′-N′*-tetramethylenediamine. Proc Natl Sci Counc Rep China Part B Life Sci 25:26–33

Cheng X-B, Jia R, Lip S, Zhu Q, Tu S-Q, Tang W-Z (2007) Studies on the properties and co-immobilization of manganese peroxidase. Chin J Biotechnol 23:90–96

Cho NS, Jarosa-Wilkolazka A, Luterek J, Cho H-Y, Ohga S, Leonowicz A (2006) Effect of fungal laccase and low molecular weight mediators on decolorization of Direct Blue dye. J Fac Agric Kyushu Univ 51:219–225

Chopra P, Singh D, Verma V, Puniya AK (2004) Bioremediation of melanoidin containing dig-ested spent wash from cane-molasses distillery with white rot fungus *Coriolus versicolor*. Ind J Microbiol 44:197–200

Christian V, Shrivastava R, Shukla D, Modi H, Rajiv B, Vyas M (2005) Mediator role of veratryl alcohol in the lignin peroxidase-catalyzed oxidative decolorization of Remazol Brilliant Blue R. Enzyme Microb Technol 36:426–431

Christiansson M, Stenberg B, Wallenberg LR, Holst O (1998) Reduction of surface sulfur upon microbial devulcanization of rubber materials. Biotechnol Lett 20:637–642

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

Cullen D, Kersten P (1992) Fungal enzymes for lignocellulose degradation. In: Kinghorn JR, Turner G. Glasgow (eds) Applied molecular genetics of filamentous fungi. Blackie Academic and Professional, Chapman & Hall, pp 100–l31

D′Annibale A, Quaratino D, Federici F, Fenice M (2006) Effect of agitation and aeration on the reduction of pollutant load of olive mill wastewater by the white-rot fungus *Panus tigrinus*. Biochem Eng J 29:243–249

Dhouib A, Ellouz M, Aloui F, Sayadi S (2006) Effect of bioaugmentation of activated sludge on olive mill wastewater detoxification with white-rot fungi. Lett Appl Microbiol 42:405–411

Doddapaneni H, Subramanian V, Yadav JS (2005) Physiological regulation, xenobiotic induction, and heterologous expression of P450 monooxygenase gene pc-3 (CYP63A3), a new member of the CYP63 gene cluster in the white-rot fungus *Phanerochaete chrysosporium*. Curr Microbiol 50:292–298

Driessel BV, Christov L (2001) Decolorization of bleach plant effluent by mucoralean and white-rot fungi in a rotating biological contactor reactor. J Biosci Bioeng 92:271–276

D′Souza DT, Tiwari R, Sah AK, Raghukumar C (2006) Enhanced production of laccase by a marine fungus during treatment of colored effluents and synthetic dyes. Enzyme Microb Technol 38:504–511

Eaton RA, Hale MDC (1993) Wood: decay, pests and protection. Chapman and Hall, London

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

Erkurt EA, Ünyayar A, Kumbur H (2007) Decolorization of synthetic dyes by white rot fungi involving laccase enzyme in the process. Proc Biochem 42:1429–1435

Font X, Caminal G, Gabarrell X, Vicent T (2006) Treatment of toxic industrial wastewater in fluidized and fixed-bed batch reactors with *Trametes versicolor*: influence of immobilization. Environ Technol 27:845–854

Fragoso NM, Parrott JL, Hahn ME, Hodoson PV (1998) Chronic retene exposure causes sustained induction of CYP1A activity and protein in rainbow trout (*Oncorhynchus mykiss*). Environ Toxicol Chem 17:2347–2353

Fu Y, Viraraghavan T (2001) Fungal decolourization of dye wastewater: a review. Biores Technol 79:251–262

Garcia IG, Pena PRJ, Venceslada JLB, Martin AM, Santos MAM, Gomez ER (2004) Removal of phenol compounds from olive mill wastewater using *Phanerochaete chrysosporium*, *Aspergillus niger*, *Aspergillus terreus* and *Geotrichum candidum*. Proc Biochem 35:751–758

Gavril M, Hodson PV (2007) Chemical evidence for the mechanism of the biodecoloration of Amaranth by *Trametes versicolor*. World J Microbiol Biotechnol 23: 103–124

Geng X, Li K, Xu F (2004) Investigation of hydroxamic acids as laccase-mediators for pulp bleaching. Appl Microbiol Biotechnol 64:493–496

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

González T, Terrón MC, Yagüe S, Junca H, Carbajo JM, Zapico EJ, Silva R, Arana-Cuenca A, Téllez A, González AE (2007) Melanoidin-containing wastewaters induce selective laccase gene expression in the white rot fungus *Trametes* sp. I-62. Res Microbiol. doi: 10.1016/j.resmic.2007.10.005

Hakala TK, Lundell T, Galkin S, Maijala P, Kalkkinen S, Hatakka A (2005) Manganese peroxidases, laccase and oxalic acid from the selective white-rot fungus *Physisporinus rivulosus* grown on spruce wood chips. Enzyme Microb Technol 36:461–468

Hakala TK, Hildén K, Maijala P, Olsson C, Hatakka A (2006) Differential regulation of manganese peroxidases and characterization of two variable MnP encoding genes in the white-rot fungus *Physisporinus rivulosus*. Appl Microbiol Biotechnol 73:839–849

Hatakka A (1994) Lignin-modifying enzymes from selected white-rot fungi: production and role in lignin degradation. FEMS Microbiol Rev 13:125–135

Hatakka A (2001) Biodegradation of lignin. In: Steinbüchel A, Hofrichter M (eds) Biopolymers. Lignin, humic substances, and coal, vol 1. Wiley-VCH, Weinheim, pp 129–180

Hirai H, Sugiura M, Kawai S, Nishida T (2005) Characteristics of novel lignin peroxidases produced by white-rot fungus *Phanerochaete sordida* YK-624. FEMS Microbiol Lett 246:19–24

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

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

Jaouani A, Sayadi S, Vanthournhout M, Penninckx MJ (2003) Potent fungi for decolorization of olive oil mill wastewater. Enzyme Microb Technol 33:802–809

Jaouani A, Tabka MG, Penninckx MJ (2006) Lignin modifying enzymes of *Coriolopsis polyzona* and their role in olive oil mill wastewaters decolourisation. Chemosphere 62:1421–1430

Kalmis E, Sargin S (2004) Cultivation of two *Pleurotus* species on wheat straw substrates containing olive mill wastewater. Int Biodet Biodeg 53:43–47

Kamitsuji H, Honda Y, Watanabe T, Kuwahara M (2004a) Production and induction of manganese peroxidase isozymes in a white rot fungus *Pleurotus ostreatus*. Appl Microbiol Biotechnol 65:287–294

Kamitsuji H, Honda Y, Watanabe T, Kuwahara M (2005a) Direct oxidation of polymeric substrates by multifunctional manganese peroxidase isozyme from *Pleurotus ostreatus* without redox mediators. Biochem J 386: 387–393

Kamitsuji H, Honda Y, Watanabe T, Kuwahara M (2005b) Mn^{2+} is dispensable for the production of active MnP2 by *Pleurotus ostreatus*. Biochem Biophys Res Commun 327:871–876

Karimi A, Vahabzadeh F, Bonakdarpour B (2006) Use of *Phanerochaete chrysosporium* immobilized on Kissiris for synthetic dye decolourization: involvement of manganese peroxidase. World J Microbiol Biotechnol 22:1251–1257

Kariminiaae-Hamedaani H-R, Sakurai A, Sakakibara M (2007) Decolorization of synthetic dyes by a new manganese peroxidase-producing white rot fungus. Dyes Pigm 72:157–162

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

Lacina C, Germin G, Spiros A (2003) Utilization of fungi for biotreatment of new wastewater: a review. Afr J Biotechnol 2:620–635

Lan J, Wang F, Huang X-R, Li Y-Z, Qu Y-B, Gao P-J (2006) Studies on the hydrogen peroxide regulated veratryl alcohol mediated oxidation of Pyrogallol red catalyzed by lignin peroxidase. Acta Chimi Sin 64:463–468

Lau CM, Subramaniam A (1991) Recovery and applications of waste solids from natural rubber latex. In: Proceedings of rubber growers conf., Kuala Lumpur, Malaysia, pp 24–26

Lee SM, Koo BW, Choi JW, Choi DH, An BS, Jeung EB, Choi IG (2005) Degradation of bisphenol A by white rot fungi *Stereum hirsutum* and *Heterobasidium insulare*, and reduction of its estrogenic activity. Biol Pharm Bull 28:201–207

Lee JW, Lee SM, Hong EJ, Jeung EB, Kang HY, Kim MK, Choi IG (2006) Estrogenic reduction of styrene monomer degraded by *Phanerochaete chrysosporium* KFRI20742. J Microbiol 44:177–184

Levin L, Papinutti L, Forchiassin F (2004) Evaluation of four Argentinean white rot fungi; their ability to produces lignin-modifyng enzymes and decolorize industrial dyes. Biores Technol 2:169–176

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

Liu A, Huang X, Song S, Wang D, Lu X, Qu Y, Gao P (2003) Kinetics of the H_2O_2-dependent ligninase-catalyzed oxidation of veratryl alcohol in the presence of cationic surfactant studied by spectrophotometric technique. Spectrochim Acta Part A Mol Biomol Spectrosc 59:2547–2551

Lorenzo M, Moldes D, Sanromán MA (2006) Effect of heavy metals on the production of several laccase isoenzymes by *Trametes versicolor* and on their ability to decolourise dyes. Chemosphere 63:912–917

Lu R, Shen XL, Xia LM (2005) Studies on laccase production by *Coriolus versicolor* and enzymatic decoloration of dye.

Linchan Huaxue Yu Gongye/Chem Ind Forest Prod 25:73–76
Lu L, Zhao M, Wang Y (2007) Immobilization of laccase by alginate-chitosan microcapsules and its use in dye decolorization. World J Microbiol Biotechnol 23:159–166
Maas R, Chaudhari S (2005) Adsorption and biological decolorization of azo dye Reactive Red-2 in semicontinuous anaerobic reactors. Proc Biochem 40:699–705
Mäkelä MR, Galkin S, Hatakka A, Lundell TK (2005) Production of organic acids and oxalate decarboxylase inlignin-degrading white rot fungi. Enzyme Microb Technol 30:542–549
Mäkelä MR, Hildén KS, Hakala TK, Hatakka A, Lundell TK (2006) Expression and molecular properties of a new laccase of the white rot fungus *Phlebia radiata* grown on wood. Curr Genet 50:323–333
Martínez AT (2002) Molecular biology and structure-function of lignin-degrading heme peroxidases. Enzyme Microb Technol 30:425–444
Máximo C, Costa-Ferreira M (2004) Decolorization of reactive textile dyes by *Irpex lacteus* and lignin modifying enzymes. Proc Biochem 39:1475–1479
Mazmanci MA, Ünyayar A (2005) Decolourisation of Reactive Black 5 by *Funalia trogii* immobilised on *Luffa cylindrica* sponge. Proc Biochem 40:337–342
Mester T, Field JA (1998) Characterization of a novel manganese peroxidase-lignin per-oxidase hybrid isozyme produced by *Bjerkandera* species strain BOS55 in the absence of manganese. J Biol Chem 273:15412–15417
Michniewicz A, Ullrich R, Ledakowicz S, Hofrichter M (2006) The white-rot fungus *Cerrena unicolor* strain 137 produces two laccase isoforms with different physicochemical and catalytic properties. Appl Microbiol Biotechnol 69:682–688
Michniewicz A, Ledakowicz S, Ullrich R, Hofrichter M (2008) Kinetics of the enzymatic decolorization of textile dyes by laccase from *Cerrena unicolor*. Dyes Pigm 77:295–302
Minussi RC, Pastore GM, Durán N (2007) Laccase induction in fungi and laccase/N–OH mediator systems applied in paper mill effluent. Biores Technol 98:158–164
Moreira PR, Bouillenne F, Almeida-Vara E, Xavier Malcata F, Frère JM, Duarte JC (2006) Purification, kinetics and spectral characterisation of a new versatile peroxidase from a *Bjerkandera* sp. isolate. Enzyme Microb Technol 38:28–33
Murugesan K, Arulmani M, Nam I-H, Kim Y-M, Chang Y-S, Kalaichelvan PT (2006) Purification and characterization of laccase produced by a white rot fungus *Pleurotus sajor-caju* under submerged culture condition and its potential in decolorization of azo dyes. Appl Microbiol Biotechnol 72:939–946
Nagai M, Sato T, Watanabe H, Saito K, Kawata M, Enei H (2002) Purification and characterization of an extracellular laccase from the edible mushroom *Lentinula edodes*, and decolorization of chemically different dyes. Appl Microbiol Biotechnol 60:327–335
Nilsson I, Moller A, Mattiasson B, Rubindamayugi MST, Welander U (2006) Decolorization of synthetic and real textile wastewater by the use of white-rot fungi. Enzyme Microb Technol 38:94–100
Ozsoy HD, Unyayar A, Mazmanci MA (2005) Decolourisation of reactive textile dyes Drimarene Blue X3LR and Remazol Brilliant Blue R by Funalia trogii ATCC 200800. Biodegradation 16:195–204
Pazarlioglu NK, Sariisik M, Telefoncu A (2005) Laccase production by *Trametes versicolor* and application to denim washing. Proc Biochem 40:1673–1678
Pogni R, Baratto MC, Giansanti S, Teutloff C, Verdin J, Valderrama B, Lendzian F, Lubitz W, Vazquez-Duhalt R, Basosi R (2005) Tryptophan-based radical in the catalytic mechanism of versatile peroxidase from *Bjerkandera adusta*. Biochemistry 44:4267–4274
Pogni R, Baratto MC, Teutloff C, Giansanti S, Ruiz-Dueñas FJ, Choinowski T, Piontek K, Martínez AT, Lendzian F, Basosi R (2006) A tryptophan neutral radical in the oxidized state of versatile peroxidase from *Pleurotus eryngii*: a combined multifrequency EPR and density functional theory study. J Biol Chem 281:9517–9526
Pogni R, Teutloff C, Lendzian F, Basosi R (2007) Tryptophan radicals as reaction intermediates in versatile peroxidases: multifrequency EPR, ENDOR and density functional theory studies. Appl Magn Reson 31:509–526
Pointing SB (2001) Feasibility of bioremediation by white-rot fungi. Appl Microbiol Biotechnol 57:20–33
Quaratino D, Federici F, Petruccioli M, Fenice M, D′Annibale A (2007) Production, purification and partial characterisation of a novel laccase from the white-rot fungus *Panus tigrinus* CBS577.79. Antonie Van Leeuwenhoek Int J Genet Mol Microbiol 91:57–69
Raghukumar C (2002) Bioremediation of colored pollutants by terrestrial versus facultative marine fungi. In: Hyde KD (ed) Fungi in marine environments. Fungal Diversity Research Series, vol 7. pp 317–344
Raghukumar C, Rivonkar G (2001) Decolorization of molasses spent wash by the white-rot fungus *Flavodon flavus*, isolated from a marine habitat. Appl Microbiol Biotechnol 55:510–514
Raghukumar C, Mohandass C, Kamat S, Shailaja MS (2004) Simultaneous detoxification and decolorization of molasses spent wash by the immobilized white-rot fungus *Flavodon flavus* isolated from a marine habitat. Enzyme Microb Technol 35:197–202
Ramos-Cormenzana A, Monteoliva-Sanchez M, Lopez MJ (1995) Bioremediation of alpechin. Intl Biodet Biodeg 35:249–268
Reddy CA (1995) The potential for white-rot fungi in the treatment of pollutants. Curr Opin Biotechnol 6:320–328
Revankar MS, Lele SS (2007) Synthetic dye decolorization by white rot fungus, *Ganoderma* sp. WR-1. Biores Technol 98:775–780
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
Ruiz-Dueñas FJ, Morales M, Pérez-Boada M, Choinowski T, Martínez MJ, Piontek K, Martínez ÁT (2007) Manganese oxidation site in *Pleurotus eryngii* versatile peroxidase: a site-directed mutagenesis, kinetic, and crystallographic study. Biochemistry 46:66–77
Salony SM, Bisaria VS (2006) Production and characterization of laccase from *Cyathus bulleri* and its use in

decolorization of recalcitrant textile dyes. Appl Microbiol Biotechnol 71:646–653

Sanghi R, Dixit A, Guha S (2006) Sequential batch culture studies for the decolorisation of reactive dye by *Coriolus versicolor*. Biores Technol 97:396–400

Sanjust E, Pompei R, Resciggno A, Augusto R, Ballero M (1991) Olive milling wastewater as medium for growth of four *Pleurotus* species. Appl Biochem Biotechnol 31: 223–235

Selvam K, Swaminathan K, Myung Hoon Song MH, Chae K (2002) Biological treatment of a pulp and paper industry effluent by *Fomes lividus* and *Trametes versicolor*. World J Microbiol Biotechnol 18:523–526

Selvam K, Swaminathan K, Rasappan K, Rajendran R, Pattabhi S (2006) Decolourization and dechlorination of a pulp and paper industry effluent by *Thelephora* sp. Ecol Environ Conserv 12:223–226

Shah V, Nerud F (2002) Lignin degrading system of white-rot fungi and its exploitation for dye decolorization. Can J Microbiol 48:457–870

Shrivastava R, Christian V, Vyas BRM (2005) Enzymatic decolorization of sulfonphthalein dyes. Enzyme Microb Technol 36:333–337

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

Sundramoorthy M, Yougs HL, Gold MH, Poulos TL (2005) High resolution crystal structure of manganese peroxidase:substrate and inhibitor complexes. Biochemistry 44:6463–6470

Suzuki K, Hirai H, Murata H, Nishida T (2003) Removal of estrogenic activities of 17*b*-estradiol and ethinylestradiol by ligninolytic enzymes from white rot fungi. Water Res 37:1972–1975

Svobodová K, Majcherczyk A, Novotný C, Kües U (2008) Implication of mycelium-associated laccase from *Irpex lacteus* in the decolorization of synthetic dyes. Biores Technol 99:463–471

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 Microb Lett 244:93–98

Tavcar M, Svobodová K, Kuplenk J, Novotný C, Pavko A (2006) Biodegradation of azo dye RO16 in different reactors by immobilized *Irpex lacteus*. Acta Chim Slovenica 53:338–343

Teunissen PJM, Field JA (1998) 2-Chloro-1,4-dimethoxybenzene as a mediator of lignin peroxidase catalyzed oxidations. FEBS Lett 439:219–223

Tinoco R, Verdin J, Vazquez-Duhalt R (2007) Role of oxidizing mediators and tryptophan 172 in the decoloration of industrial dyes by the versatile peroxidase from *Bjerkandera adusta*. J Mol Catal B Enzyme 46:1–7

Toh Y, Jia J, Yen L, Obbard JP, Ting Y (2003) Decolorization of azo dyes by white-rot fungi (WRF) isolated in Singapore. Enzyme Microb Technol 33:569–575

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. Biores Technol 84:251–257

Tsukihara T, Honda Y, Watanabe T, Watanabe T (2006) Molecular breeding of white rot fungus *Pleurotus ostreatus* by homologous expression of its versatile peroxidase MnP2. Appl Microbiol Biotechnol 71:114–120

Tsutsumi Y, Haneda T, Nishida T (2001) Removal of estrogenic activities of bisphenol A and nonylphenol by oxidative enzymes from lignin-degrading basidiomycetes. Chemosphere 42:271–276

Tychanowicz GK, Zilly A, Giatti C, Marques de Souza M, Peralta RM (2004) Decolorization of industrial dyes by solid-state cultures of *Pleurotus pulmonarius*. Proc Biochem 39:855–859

Tychanowicz GK, De Souza DF, Souza CGM, Kadowaki MK, Peralta RM (2006) Copper improves the production of laccase by the white-rot fungus *Pleurotus pulmonarius* in solid state fermentation. Brazil Arch Biol Technol 49:699–704

Ullrich R, Le MH, Nguyen LD, Hofrichter M (2005) Laccase from the medicinal mushroom *Agaricus blazei*: production, purification and characterization. Appl Microbiol Biotechnol 67:357–363

Ürek RO, Pazarlioglu NK (2004) Purification and partial characterization of manganese peroxidase from immobilized *Phanerochaete chrysosporium*. Proc Biochem 39:2061–2068

Ürek RO, Pazarlioglu NK (2005) Production and stimulation of manganese peroxidase by immobilized *Phanerochaete chrysosporium*. Proc Biochem 40:83–87

Vahabzadeh F, Mehranian M, Saatari AR (2004) Color removal ability of *Phanerochaete chrysosporium* in relation to lignin peroxidase and manganese peroxidase produced in molasses wastewater. World J Microbiol Biotechnol 20:859–864

Verdín J, Pogni R, Baeza A, Baratto MC, Basosi RB, Vázquez-Duhalt R (2006) Mechanism of versatile peroxidase inactivation by Ca^{2+} depletion. Biophys Chem 121: 163–170

Verma P, Madamwar D (2002) Production of lignolytic enzymes for dye decolorization by co-cultivation of white rot fungi *Pleurotus ostreatus* and *Phanerochaete chrysosporium* under solid state fermentation. Appl Biochem Biotechnol 102–103:109–118

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

Watanabe T, Hattori T, Tengku S, Shimada M (2005) Purification and characterization of NAD-dependent formate dehydrogenase from the white-rot fungus *Ceriporiopsis subvermispora* and a possible role of the enzyme in oxalate metabolism. Enzyme Microb Technol 37:68–75

Wells A, Teria M, Eve T (2006) Green oxidations with laccase-mediator systems. Biochem Soc Trans 34:304–308

Wesenberg D, Kyriakides I, Agathos SN (2003) White-rot fungi and their enzymes for the treatment of industrial dye effluents. Biotechnol Adv 22:161–187

Yang JS, Yuan HL, Chen WX (2004) Studies on extracellular enzymes of lignin degrading fungus *Penicillium* sp. P6. China Environ Sci 24:24–27

Yu G, Wen X, Li R, Qian Y (2006) In vitro degradation of a reactive azo dye by crude ligninolytic enzymes from non-immersed liquid culture of *Phanerochaete chrysosporium*. Proc Biochem 41:1987–1993

Zervakis G, Yiatras P, Balis C (1996) Edible mushrooms from olive oil mill waste. Int Biodet Biodeg 38:237–243

Zhao X, Hardin IR (2007) HPLC and spectrophotometric analysis of biodegradation of azo dyes by *Pleurotus ostreatus*. Dyes Pigm 73:322–325

Zhao X, Yiping Lu Y, Hardin I (2005) Determination of biodegradation products from sulfonated dyes by *Pleurotus ostreatus* using capillary electrophoresis coupled with mass spectrometry. Biotechnol Lett 27:69–72

Zhao X, Hardin IR, Hwang H-M (2006) Biodegradation of a model azo disperse dye by the white rot fungus *Pleurotus ostreatus*. Int Biodet Biodeg 57:1–6

Zouari-Mechichi H, Mechichi T, Dhouib A, Sayadi S, Martínez AT, Martínez MJ (2006) Laccase purification and characterization from *Trametes trogii* isolated in Tunisia: decolorization of textile dyes by the purified enzyme. Enzyme Microb Technol 39:141–148