Chapter 6
Extracellular Fungal Peroxidases and Laccases for Waste Treatment: Recent Improvement

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6.1 Introduction

Fungi are widespread eukaryotic microorganism exploit subsidiary living conditions through their unusual extracellular enzymes capable of utilizing variable sources as substrates. Mostly, these extracellular enzymes degrade complex organic substances including cellulose, hemicellulose, lignin, phenols, pesticides, hydrocarbons, etc. into simple molecules for their carbon, energy, and nutrition (Burns et al. 2013). Among the various organic substances, lignin, hemicelluloses, and phenolic compounds are the major wastes as environmental pollutants. Due to the chemical complexity, lignins take a long time to its natural degradation. In nature, majority of the fungi in the phylum Basidiomycota have the enzymes such as laccases and peroxidases to actively degrade the lignin containing polyphenol waste from the environment, which have potential biotechnological applications.

Three phenotypic groups of fungi specifically white-rot, brown-rot, and soft-rot fungi are the predominant groups which degrade lignin compounds variably. Among them, white-rot fungi execute complete lignin degradation with the ability to cleave Cα- Cβ, β-aryl, and C1-Cα bonds, including aromatic C-C bonds degradation c, but brown-rot fungi partially degrade lignin compounds by Fenton/Haber Weiss chemistry (Arantes et al. 2012). However, white-rot fungi produce a special group of extracellular enzymes like laccases and peroxidases which entirely degrade lignin

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compounds. Also, fungal laccases and peroxidases have enormous potentials in environmental detoxification and bioremediation of phenolic compounds. Using these enzymes, the white-rot fungi can convert wood, paints, pesticides, and plastics etc. into nutrients, and it has lots of industrial application. Laccases have been regarded as a "Green Tool," because they require molecular oxygen (O_2) as the only co-substrate for biocatalysis and not hydrogen peroxide (H_2O_2) (Surwase et al. 2016). In this chapter, the structure, functional properties, applications, and their recent advancements are being discussed.

6.2 Laccases

Laccases (EC 1.10.3.2; 1,4-benzenediol: oxygen oxidoreductases) are extracellular copper-containing monomeric glycoproteins, which come under multicopper oxidase family (Solomon et al. 1996). It is otherwise called as polyphenol oxidase and blue multicopper oxidases. It oxidizes several aromatic and non-aromatic compounds especially phenols as well as diamines and hexacyanoferrate by using molecular oxygen as an electron acceptor. It was first demonstrated in the sap of the Japanese lacquer tree *Toxicodendron vernicifluum* (formerly *Rhus vernicifera*); hence, it is named as laccase. Its molecular weight ranges from 50 kDa to 100 kDa (Galhaup and Haltrich 2001).

6.3 Sources of Laccases

Laccases have been generally present as extracellular and intracellular enzymes in several organisms ranging from microbes to higher plants. It was first discovered in plants by Yoshida in 1883. It is widely distributed in all plants, but not yet studied properly, because of the existence of several isoenzymes of laccase in lignified plant tissues (Gavnholt et al. 2002) and difficulties of their detection and purification from crude plant extracts (Ranocha et al. 1999), but it was well documented in fungi. Fungi are unique important class of eukaryotic microorganisms and synthesize unusual enzymes capable of performing chemically tricky reactions (Viswanath et al. 2008; Shraddha et al. 2011). Many fungal species are of great value and can remove toxic recalcitrant compounds in an environment-friendly manner. Laccases play an important role in bioremediation of toxic phenolic compounds (Singh et al. 2011) and degradation of recalcitrant xenobiotic compounds. The presence of laccase enzyme in fungi was first reported by Laborde in 1897 (Mayer and Harel 1979). Laccases are found in a wide range of fungi generally in white-rot fungi (Brijwani et al. 2010; Mayer and Staples 2002).

Generally, paper and pulp industry effluents contain a large amount of chlorinated phenolic compounds that is formed from incomplete breakdown of lignin during pulp bleaching process. Different groups of fungi can remove such lignin

and phenol from the effluent by producing extracellular enzymes like laccase, manganese peroxidase, and lignin peroxidase. Several studies suggested that filamentous fungi are the best choice than bacteria for the removal of soil pollutants because fungi can reach the pollutant efficiently than bacteria (Rubilar et al. 2008; Kour et al. 2019; Yadav et al. 2018). For example, laccase activity was detected in the cultures of fungi belonging to Basidiomycetes, Ascomycetes, and Deuteromycetes family (Table 6.1). The highest amount of laccase is produced by white-rot fungi (Leonowicz et al. 1997). Laccase enzyme has been reported in many fungal species such as *Trichoderma reesei* (Levasseur et al. 2010), *Xylaria polymorpha* (Nghi et al. 2012), *Lentinus tigrinus* (Pozdnyakova et al. 2006), *Pleurotus ostreatus* (Zhao et al. 2017), *Cerrena unicolor* (Kim et al. 2002) *T. versicolor* (Minussi et al. 2007; Rogalski et al. 1991), *Trametes pubescens* (Shleev et al. 2007) *Melanocarpus albomyces* (Kiiskinen et al. 2002), *Magnaporthe grisea* (Iyer and Chattoo 2003), *Aspergillus flavus* PUF5 (Priyanka and Uma 2017), *Trametes hirsuta* (Tapia-Tussell et al. 2011), *Trametes ljubarskyi* (Goh et al. 2017), *Aspergillus flavus* (Kumar et al. 2016), etc. Further, Abd El Monssef et al. (2016) reported that the genus *Alternaria*, *Aspergillus*, *Cladosporium*, *Penicillium*, *Rhizopus*, and *Trichoderma* also produce laccases.

Table 6.1 Examples of laccase producing fungi

Class and division	Source	References
Agaricomycetes	*Trametes versicolor*	Bourbonnais and Paice (1992)
Agaricomycetes	*Phanerochaete chrysosporium* BKM-F-1767	Srinivasan et al. (1995)
Agaricomycetes	*Pleurotus pulmonarius*	Marques de Souza et al. (2002)
Sordariomycetes (*Ascomycota*)	*Chalara* (syn. *Thielaviopsis*) *paradoxa* CH 32	Robles et al. (2002)
Agaricomycetes	*Trametes pubescens*	Galhaup and Haltrich (2001); Rodriguez Couto et al. (2004); Osma et al. (2007)
Agaricomycetes	*Phanerochaete chrysosporium* ME-446	Kapich et al. 2004
Agaricomycetes	*Trametes hirsuta*	Rodríguez Couto et al. (2006)
Agaricomycetes	*Phanerochaete chrysosporium* NCIM 1197	Gnanamania et al. (2006)
Agaricomycetes	*Pycnoporus sanguineus*	Vikineswary et al. (2006)
Agaricomycetes	*Ganoderma lucidum*	Murugesan et al. (2007)
Eurotiomycetes (*Ascomycota*)	*Aspergillus* carbonarius	Sanjay et al. (2007)
Sordariomycetes (*Ascomycota*)	*Trichoderma harzianum* WL1	Sadhasivam et al. (2008)
Agaricomycetes (*Basidiomycota*)	*Pleurotus ostreatus, Trametes pubescens, Cerrena unicolor, and Trametes versicolor*	Osma et al. (2011)
Sordariomycetes (*Ascomycota*)	*Trichoderma* spp.	Kalra et al. (2013)

Other than fungi and plants, laccase enzyme has been reported from bacteria (Santhanam et al. 2011) (Yadav et al. 2016, 2019a, b), lichens (Laufer et al. 2009) and sponges (Li et al. 2015a). Moreover, polyphenol oxidases with laccase-like activity have been found in oysters (Luna-Acosta et al. 2010) and insect cuticles (Lang et al. 2012). Functions of laccase enzymes are based on their source and the stage of life of the organism producing them.

6.3.1 Structure of Laccases

Laccases are glycoproteins synthesized as monomer and containing four copper atoms (Fig. 6.1). After synthesis, laccase was modified with mannose which is accountable for about 10–50% of total weight of laccase. Carbohydrate may contribute structural stability of laccases (Mayer and Staples 2002). Glycosylation of laccases confers copper retention, susceptibility to proteolytic degradation, thermal stability, and secretion. The copper atoms of laccase are divided into three types. They are (i) Type 1 (T1) (ii) Type 2 (T2) and (iii) Type 3 (T3). Laccase contains one T1 and T2 and two T3 copper atoms. The catalytic mechanism of the laccase starts with the donation of an electron to the substrate by the T1 copper site, followed by an internal electron transfer from the reduced T1 to the T2 and T3 copper sites. During oxidation of substrate, molecular oxygen is reduced to water (Jones and Solomon 2015). The reduction reaction takes place at trinuclear cluster which is formed by the association of T2 and T3 copper atoms (Fig. 6.1). Type 1 copper confers blue color to the enzyme because of maximum absorbance around at 600 nm which is the result of the covalent copper–cysteine bond (Matera et al. 2008). However, in fungal laccases, the axial ligand is leucine or phenylalanine, which possibly provides the mechanism for the regulation of enzyme activity (Claus 2004; Kumar et al. 2003; Enguita et al. 2003; Garavaglia et al. 2004). Type 2 is a non-blue copper and showed weak absorption in the visible spectrum (Niku-Paavola et al. 2004). Type 2 copper is coordinated by two histidine residues and is strategically

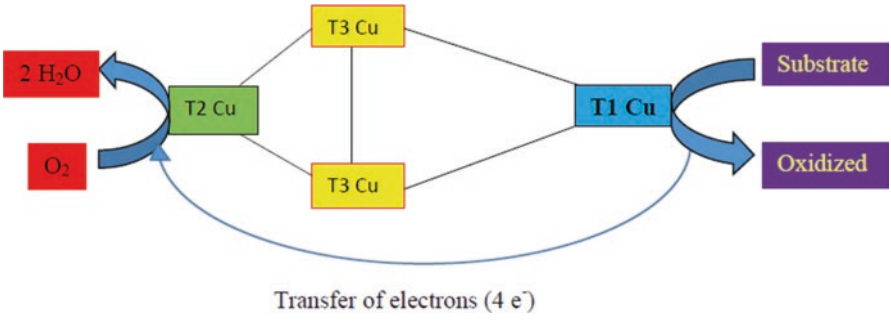

Fig. 6.1 Catalytic mechanism of laccase

positioned close to Type 3 copper. Type 3 copper is a binuclear center that showed maximum absorbance at 330 nm in its oxidized form (Matera et al. 2008; Decker and Terwilliger 2000). Laccase molecular weight was determined to be in the range of 60–390 kDa (Kalme et al. 2009). The pH values vary between pH 4.32–6.51 and pH 5.32–6.19 (Cázares-García et al. 2013; Moreno et al. 2017). The catalytic domain of laccase is moderately conserved in diverse fungal species, and the rest of the enzyme structure shows high diversity (Gochev and Krastanov 2007; Moreno et al. 2017). However, laccases with variants in the active site are also reported in *Pleurotus ostreatus* (Palmieri et al. 1997). In this fungus, enzymes lacking the maximum absorption around 600 nm are usually classified as "yellow" or "white" laccases. Difference in the active center might confer these laccases have different functional properties of interest. Similar white laccase has also been reported in Deuteromycete fungus and *Myrothecium verrucaria* NF-05 (Zhao et al. 2012). These white laccases contain only one Cu, one Fe and two Zn atoms (Palmieri et al. 1997; Zhao et al. 2012), but laccase enzyme of *Phellinus ribis* has one manganese atom instead of T1 copper atom (Min et al. 2001). Many fungi have variable number of laccase genes and they are typically inducible.

6.3.2 Mechanism of Laccase Activity

Laccases have wide range of substrate-specific activity on ortho- and para-diphenol groups, as well as mono-, di-, and polyphenols, aminophenols, methoxyphenols, ascorbate, and aromatic amines with the linked four-electron reduction of oxygen to water (Bourbonnais and Paice 1990; Bourbonnais et al. 1995; Madhavi and Lele 2009). Oxidation of aromatic compounds occurs with the concurrent reduction of one O_2 molecule to H_2O. After four cycles of single-electron oxidation of aromatic compounds, it leads to formation of free radicals and reduction of one molecule of oxygen into two molecules of H_2O (Fig. 6.1). Initially, the free radical is unstable and converted to a quinone in a second enzyme-catalyzed step. Alternatively, oxidized phenol-containing polymers may be partially degraded by nonenzymatic radical reactions. Partial degradation is due to the breaking of covalent bonds that join the monomer (Strong and Claus 2011). In the presence of small molecules, known as redox mediators, laccases improve their substrate specificity. Redox mediators are low molecular weight and small-sized molecules that are used as enhancer in the real electron transfer steps of enzymatic degradations process. It is a stable and reusable molecule. It increases the capability of an enzyme to react toward uncommon substrates (Majeau et al. 2010). The following mediators are frequently used for laccase activity. (1) 2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), (2) 1-hydroxy-benzotriazole, (HBT) (3) 1-nitroso-2-naphthol-3,6-disulfonic acid (NNDS), (4) syringaldehyde, (5) 4-Acetylamino-TEMPO 4-hydroxy-TEMPO, (6) violuric acid (VIO), and (7) p-coumaric acid (Majeau et al. 2010).

6.3.3 Applications of Laccases

Laccases have several biological functions such as lignification of plant cell walls (O'Malley et al. 1993), lignin biodegradation, detoxification of lignin (Baldrian 2006), virulence factors (Williamson et al. 1998), and copper and iron homeostasis (Stoj and Kosman 2003). Further, laccases have potential applications in bioremediation, paper pulp bleaching, finishing of textiles, biofuel cells, etc. Laccases exhibit transformation reactions like oxidation of functional groups to the heteromolecular coupling for production of new antibiotics derivatives or the catalysis of key steps in the synthesis of complex natural products (Xenakis et al. 2016). However, fungal laccases are largely used for removal of phenols which present in wastewater (Pang et al. 2016). The following are the significant areas of laccase applications.

6.3.3.1 Environmental Applications

Extensive use of chemicals in agriculture and industrialization leads to release of different persistent, hazardous, bioactive, and bioaccumulative chemicals to the environment that causes pollution in land and water. These toxic chemicals create adverse effects on both human and other flora and fauna of soil and aquatic environment. Naturally, phenol and its derivatives are ever-present pollutants that arrived as wastewater from the effluents of industrial activities, such as pulp, petrochemicals, coal refineries, pharmaceuticals, production of resins, paints, and textiles (Rastegari et al. 2019; Yadav et al. 2017). They are highly toxic to aquatic organisms, including fish and shellfishes. The toxic effects of phenol are based on its chemical complexity and the range of free radical formation. It causes acute toxicity, with an effect of damaging DNA or enzymes inducing mutagenicity, carcinogenicity, and hematotoxic and hepatotoxic effects toward humans and other living organisms (Michałowicz and Duda 2007). Therefore, removal of phenol is essential to protect the environment and individual. Most of the conventional oxidation method (chemical method) removes the chemicals but has several drawbacks such as (i) use of hazardous chemicals for oxidation (ii) nonspecific, and (iii) undesirable side reactions. In the present scenario, biological treatment methods (enzymatic oxidation) are most suitable and widely used due to specific and biodegradable catalysts and enzyme reactions are carried out in mild conditions (Rodríguez Couto and Toca Herrera 2006).

Laccases are capable of oxidizing, polymerizing, or transforming different xenobiotics including phenolic pesticides into less toxic molecules. Hence, it is a more apt enzyme in water (Majeau et al. 2010) and soil bioremediation. Laccase-based bioremediation has been proposed to remove toxins from textile, paper and pulp, food, distillery, pharmaceutical, printing, paint, and cosmetic industrial effluents. For the remediation, laccase could be used as (1) free enzyme, (2) immobilized enzyme, and (3) laccase containing cells to remove the pollutants from water (Mugdha and Usha 2012).

6.3.3.1.1 Direct Use of Laccase Producing Fungi

The growing fungi are used for waste (harmful pollutants) treatment. In this method, the fungal cells can adapt in the pollutant containing environment, utilize the harmful pollutants as carbon and energy requirements by synthesizing the specialized degradative enzyme, and digest or transform the pollutants to harmless. The introduced organisms produced enzyme that co-metabolized the targeted contaminants (Mugdha and Usha 2012). White-rot fungus *Trametes versicolor* is able to remove humic acids from a real humic-rich industrial-treated wastewater of a food-processing plant (Mostafa Zahmatkesh et al. 2017).

6.3.3.1.2 Cell-Free Laccase Enzyme

Enzymes extracted from organisms are used to treat toxic pollutants as a pure form or crude extract. This method is advantageous, because of the following: (1) there is no need of acclimatization of source organisms to the toxic environment, (2) additional nutrients are not essential, (3) growth supportive environment is not required, (4) the growth rate of the source organism does not affect the amount of available enzyme to treat the effluent, (5) usage of cell-free enzyme makes it easier to standardize optimum treatment conditions, and (6) it is easy to handle and monitor the process (Karam and Nicell 1997). Crude enzyme extract is the least processed but contains active form of the enzyme. It is used to treat large-scale effluent treatment. Although usage of pure enzyme is highly expensive, crude enzyme preparation at larger volume should be used for industrial effluent treatment. In general, enzyme function is based on their conformation, under extreme conditions such as very high or low pH and temperature, high ionic strength, high concentrations of reactants, and presence of inhibitors; the structure of free enzyme may be modified and the enzyme becomes nonfunctional (Karam and Nicell 1997). Besides, use of free enzyme is hard to be taken from the residual reaction system for reuse (Wang et al. 2008). Therefore, immobilized preparation of enzymes and the whole-cell biomass for repeated long-time usage have been developed.

6.3.3.1.3 Immobilized Laccase Enzyme

Immobilization of enzyme provides an increasing availability of enzyme to the substrate with better turnover over a significant period of time. The practice of immobilized enzymes in effluent treatment overcomes the cell-free enzyme because of the following reasons: (1) high stability, (2) easy to handle, (3) reusability, and (4) cost-effectiveness. Immobilization of laccase was done using different materials and used for bioremediation process (Table 6.2). Several immobilization techniques have been developed and adapted in enzyme immobilization for different applications. Theoretically, enzyme immobilizations are done by two basic methods: they are physical (entrapment, encapsulation, and cross-linking) and chemical

Table 6.2 Immobilization of laccase enzyme and their applications

Organisms name	Support	Method of immobilization	Applications	References
Trametes versicolor	Porous glass beads	Entrapment	Dye decolorization	Champagne and Ramsay (2010)
Trametes versicolor	Microfibers	Encapsulation	Dye decolorization	Dai et al. (2010)
Aspergillus	Green coconut fiber	Adsorption	Dye decolorization	Cristovao et al. (2011)
Trametes versicolor	Carbon-based mesoporous magnetic composites	Adsorption	Phenol removal	Liu et al. (2012)
Trametes versicolor	Gold electrode	Covalent bonding	Biosensor for Phenolic compounds in industrial effluents	Sarika et al. (2014)
Coriolopsis gallica	Calcium alginate beads	Entrapment	Remazol Brilliant Blue R, Reactive Black 5, and Bismarck Brown R	Daassi et al. (2014)
T. versicolor	Nanostructured bacterial cellulose	Physical adsorption and cross-linking with glutaraldehyde	Biosensors and establishment of bioreactors	Chen et al. (2015)
Cyathus bulleri	Polyvinyl alcohol	Entrapment	Decolorization of azo dye acid red 27	Chhabra et al. (2015)
Cercospora sp. SPF-6	Alginate	Entrapment	Dye decolorization	Vikram et al. (2015)
Cyathus bulleri	Polyvinyl alcohol	Entrapment	Acid red 27	Chhabra et al. (2015)
Trametes versicolor	ZnO/SiO_2 nano-composite	Adsorption	Remazol Brilliant Blue B and Acid Blue 25	Li et al. (2015b)
Trametes versicolor	Poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate)	Covalent bonding	Bisphenol A	Melo et al. (2017)
Trametes versicolor	Chitosan macrobeads	Covalent bonding	Anthracene	Azzurra Apriceno et al. (2017)
Trametes versicolor	Magnetic nanoparticles	Polymerization	4-chlorophenol	Zhang et al. (2017)
Trichoderma harzianum strain HZN10	Sol–gel matrix	Entrapment	Dye decorization	Zabin et al. (2017)
Cerrena sp	Cross-linked enzyme aggregates	Cross-linking	Malachite green	Yang et al. (2017a)
	Functionalized methacrylate–acrylate microspheres	Covalent bonding	Biosensor for Tartrazine	Mazlan et al. (2017)

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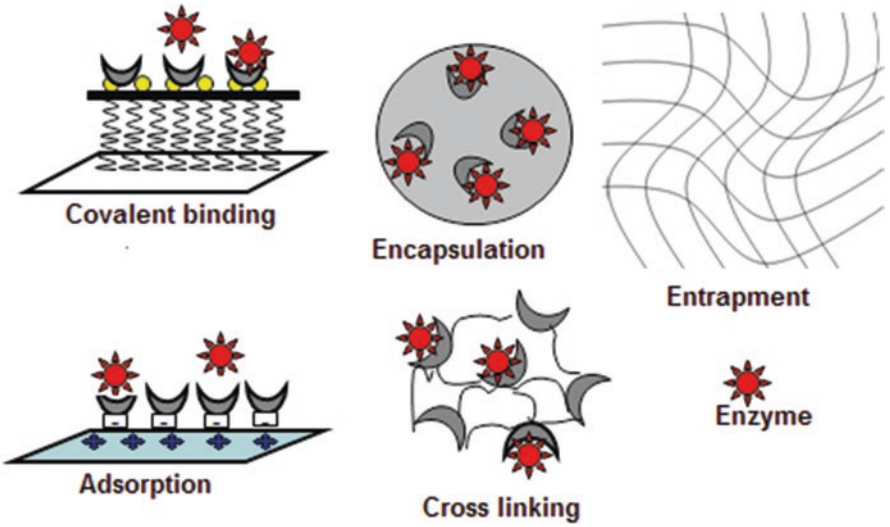

Fig. 6.2 Enzyme immobilization methods

(adsorption, covalent binding) interactions with enzyme-supportive matrix (Matijosyte et al. 2010) (Fig. 6.2).

(i) Entrapment is defined as the preservation of enzymes in a porous solid matrix, such as polyacrylamide, collagen, alginate, or gelatin (Dayaram and Dasgupta 2008; Lu et al. 2007; Niladevi and Prema 2008; Phetsom et al. 2009).

(ii) In encapsulation, enzymes are protected in a semi-permeable polymer materials such as polyethyleneimine, sol–gel silica matrix, SiO_2, and poly(GMA-co-nBA) microspheres (Qiu and Huang 2010; Rochefort et al. 2008; Crestini et al. 2010; Mazlan and Hanifah 2017).

(iii) In the adsorption method, the enzyme immobilized onto a support is based on ionic and/or other weak forces of attraction. Adsorption is based on the pH and ionic strength of the medium and the hydrophobicity of the support (Xu et al. 2009; Fang et al. 2009; Forde et al. 2010). Adsorbents like Mobil Composition of Matter (MCM), cyano-modified silica (CNS), and Santa Barbara Amorphous (SBA-15) (Forde et al. 2010) and ion-exchange resins such as dextran, agarose, and chitosan (Cordova et al. 2009; Çorman et al. 2010; Ibrahim et al. 2007) are used for laccase immobilization.

(iv) Covalent attachment is widely used enzyme immobilization method in which the chemical groups on the support surface are activated and react with nucleophilic groups on the protein (Arroyo 1998; Brady and Jordaan 2009). For example, silica-based supports such as kaolinite or mesoporous silica nanoparticles and GLU-activated silica nanoparticles (Champagne and Ramsay 2007; Liu et al. 2008; Salis et al. 2009), epoxy-activated resins such as Eupergit and Sepabeads (Berrio et al. 2007; Russo et al. 2008), Alumina and Granocel (Crestini et al. 2010), and electrodes based on carbon, glass, gold, silver or graphite (Balland et al. 2008; Rahman et al. 2008; Szamocki et al. 2009) have been frequently used for laccase.

(v) In cross-linked method, enzyme immobilization is possible with the use of bifunctional cross-linkers (Brady and Jordaan 2009). For example, dialdehydes, diiminoesthers, diisocyanates, and diamines activated by carbodiimide (Arroyo 1998) have been used.

6.3.3.2 Textile Effluent Treatment

Colors and dyes are commonly used in textile, paper, food, cosmetics, and pharmaceutical industries. There are above 1,00,000 different human-made synthetic dyes available on the market, and worldwide, its production is around 7,00,000 tons/year (Hao et al. 2000). Wastewater from textile industries carries 10% of the dye stuffs which has been a significant cause of environmental pollution. Most of the synthetic dyes are lethal to living organisms due to their toxic and carcinogenic properties. The removal of dyes from industrial wastewaters could be very important due to their toxicity and carcinogenicity. The structural complexity of dyes makes effluent treatment difficult by conventional physicochemical methods due to their high cost and low effectiveness. Laccases are promising tools for the detoxification of dyes (Table 6.3) because it has shown efficient decolorization of different industrial dyes at low concentrations (Rodriguez et al. 1999; Reyes et al. 1999) without generation of harmful aromatic amines (Chivukula and Renganathan 1995; Wong and Yu 1999).

Dye degradation ability of laccase depends on physiochemical parameters such as cell aging, concentration of dye, immobilized cells, etc. (He et al. 2004; Kalyani et al. 2008). Laccase from *Polyporus rubidus* showed efficient decolorization of industrially important synthetic textile dyes in broad range of concentration without the use of redox mediators (Bayoumi et al. 2014). Immobilized laccase of *Paraconiothyrium variabile* has pH and thermal stability and exhibited efficient decolorization of Acid Blue 25 and Acid Orange 7 (Mirzadeh et al. 2014). Complete decolorization of malachite green was achieved with *Cerrena* sp. laccase CLEAs (cross-linked enzyme aggregates) at 60 °C (Yang et al. 2017a). *Trametes versicolor* CBR43 can decolorize different types of dyes such as acid disperse and reactive textile dyes by producing laccase and Mn-dependent peroxidase (Yang et al. 2017b). Laccase enzyme from *Cerrena unicolor* strain GSM-01has been purified and identified that laccase is a monomeric protein of 63.2 kDa, their optimal pH and temperature is 2.6 and 45 °C, respectively and effectively decolorize bromothymol blue, evans blue, methyl orange, and malachite green (Wang et al. 2017).

6.3.3.3 Paper Industries

Large amount of phenolic compounds such as lignin and their derivatives containing effluent has been discharged from the paper industries. Commonly, chemical bleaching method is used to remove lignin. In this process, chlorine is used, but chlorine formed bond with lignin and produce toxic organochloro-complexes like chlorolignins, chlorophenols, chloroguiacols, and chloroaliphatics. Large volume

Table 6.3 Decolorization of various dyes by laccase

Organism name	Dye name	References
Ganoderma lucidum	Ramazol Black B and Ramzol Orange 16	Murugesan et al. (2009)
Trametes versicolor	Orange G	Casas et al. (2010)
Aspergillus ochraceus NCIM-1146	Methyl Orange	Telke et al. (2010)
Paraconiothyrium variabile	Bromophenol blue	Vinoth Kumar et al. (2011)
Trametes versicolor	Reactive Black 5	Bibi and Bhatti (2012)
Armillaria sp. F022	Reactive Black 5	Hadibarata et al. (2012)
Trametes trogii	Acid Orange 51	Dalel Daassi et al. (2013)
Coprinopsis cinerea	Methyl Orange	Tian et al. (2014)
Aspergillus niger	Basic fuchsin	Rani et al. (2014)
Cerrena sp. *circulans BWL1061*	Malachite Green	Yang et al. (2015)
Ganoderma sp.	Direct Blue E	Iyer et al. (2016)
Pleurotus ostreatus MTCC 142	Congo Red	Das et al. (2016)
Paraconiothyrium variabile	Acid Orange 67, Disperse Yellow 79, Basic Yellow 28, Basic Red 18, Direct Yellow 107, and Direct Black 166	Forootanfar Hamid et al. (2016)
Talaromyces funiculosum (M2F)	Reactive Magenta HB	Ankita Chatterjee et al. (2017)
Marasmiellus palmivorus	Reactive blue 220 (RB)and Acid blue 80 (AB)	Cantele Cantele et al. (2017)
Marasmius cladophyllus	Remazol Brilliant Blue R, Orange G, and Congo red	Ngieng Ngui Sing et al. (2017)

of dark colored wastewater is produced at the end of bleaching process. Dark colored, toxic wastewater of paper industry are highly hazardous and also create environment pollution. Physical and chemical methods such as ultrafiltration, ion exchange, lime precipitation and aerated lagoons, and activated sludge methods are used to treat wastewater, but they are ineffective and expensive. This triggers the use of microbial laccase enzymes which fulfills the whole requirement and delignification, separates wood into its constituent fibers and lessens the toxic wastewater formation. Laccase-mediated delignification was introduced in the 1900 and uses mediators to oxidize the phenolic compound, lignin.

The laccase enzyme itself can effectively break phenolic compound due to its high redox potential. The incorporation of mediator along with laccase increases the availability and dimension of the enzyme against non-aromatic ring-containing compounds. Several mediators ABTS, HBT, N-hydroxyacetanilide (NHA), and violuric acid have been used in delignification process. Effective mediators commonly

possess N-OH functional group, and it should be biodegradable, specific, and economically feasible. Paper recycling reduces usage of source material and also cost. Laccase facilitated bleaching of old newsprint pulp with improved brightness by removing the lignin component (Hakala 2011; Xu et al. 2007, 2009). Combined action of laccase and hemicellulolytic enzyme exhibited efficient deinking and biobleaching of the pulp. The combination of xylanase and laccase is an effective tool for lessening the amount of lignin and related molecules from the pulp (Valls and Roncero 2009; Saxena and Chauhan 2016). Old newsprint is efficiently recycled with high brightness and low effective residual ink concentration (ERIC) content through a combination of the physical methods like sonication and microwaving and enzymatic method (laccase and xylanase) (Virk et al. 2013). Pure laccase enzyme from *T. versicolor* decolorized the paper and pulp mills effluent to a clear light-yellow solution (Karimi et al. 2010), and various structurally different industrial dyes (Dhillon et al. 2012). The expression of delignifying enzymes only commenced complete glucose depletion (Girard et al. 2013). *B. adusta* and *P. chrysosporium* have showed 100% delignification of industrial pulp and paper mill wastewater in 8–10 days, independent from pH control, with a significant reduction of total organic carbon (TOC) of the solution (Costa et al. 2017).

6.3.3.4 Bioremediation of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are xenobiotic compounds and consist of a benzene ring arranged linearly, angularly or in clusters (Zeng et al. 2011; Li et al. 2010; Yadav et al. 2018). Rapid industrialization and widespread use of pesticides for better agricultural output liberates large amount of PAHs, the main pollutant of soil, air, or aquatic environment. PAHs and their derivatives such as polychlorinated biphenyls (PCBs); benzene, toluene, ethylbenzene, and xylene (BTEX); polycyclic aromatic hydrocarbons (PAHs); trinitrotoluene (TNT); pentachlorophenol (PCP); and 1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane (DDT) are highly toxic for humans as well as carcinogenic to living beings. PAHs are less soluble in water and are resistant to biodegradation (Ihssen et al. 2015). Laccase enzyme may convert polycyclic aromatic hydrocarbons to their quinines and then carbon dioxide. Laccase converts acenaphthylene to 1, 2- acenapthalenedione and 1,8-napthelic acid when used along with mediator HBT (Madhavi and Lele 2009). Laccase-mediated removal of PAHs is an economically feasible, ecofriendly, and efficient bioremediation process. Polychlorinated biphenyls (PCB) are recalcitrant toxic substances, presently banned in most countries but used as pesticides and wood preservatives. *T. versicolor* degraded PCP efficiently after the initial uptake by the mycelia (Pallerla and Chambers 1998). Laccase-mediated degradation rate of PCBs is inversely proportional to number of chlorine. The 4–6-chlorine substituted hydroxyl-PCB is degraded by laccase in the presence of the mediator 2,2,6,6-tetramethylpiperidine-N-oxy radical (Keum and Li 2004). Heterologously expressed *Trametes sanguineus* laccase in *Trichoderma atroviride* efficiently removed phenolic compounds present in industrial wastewater, bisphenol A (an endocrine disruptor) from the culture medium, benzo[a]pyrene, and phenanthrene (Balcázar-López et al. 2016).

Enzyme immobilized on mesoporous nanofibers that were prepared by Vinyl-modified poly (acrylic acid)/SiO_2 nanofibrous membranes exhibited a better triclosan removal (Xu et al. 2014). Laccase enzyme from *Trametes versicolor* and *Myceliophthora thermophile* could degrade the hormones and endocrine disrupting compounds (EDCs) (Dennis Becker et al. 2017). Phenolic compounds present in industrial wastewater and bisphenol A (an endocrine disruptor) from the culture medium was removed effectively by the heterologously expressed *Trametes sanguineus* laccase in *Trichoderma atroviride* (Balcázar-López et al. 2016). *Bjerkandera adusta* has the ability to degrade aromatic xenobiotics (Sodaneath et al. 2017) and extractives (Kinnunen et al. 2017) have raised its biotechnological importance in wastewater treatments for lignin removal.

The immobilization of *Trametes versicolor* laccase on carbon-based mesoporous magnetic composites was done by an adsorbing laccase into bimodal carbon-based mesoporous magnetic composites. Adsorption effects of the support were responsible for the quick removal rate in the first hour, and up to 78% and 84% of phenol and p-chlorophenol were removed in the end of the reaction, respectively, indicating that the magnetic bimodal mesoporous carbon is a promising carrier for both immobilization of laccase and further application in phenol removal (Liu et al. 2012).

6.3.3.5 Biosensor for Detection of Pollutants

Researchers concentrated to device a system for deduction of phenolic compounds in the environment, food, and biomedical components by a user-friendly and cost-effective approach. Biosensors are suitable for monitoring contaminated area continuously with high specificity and sensitivity. Among the various biosensors, enzymatic biosensor has increased eventually, due to its substrate-specific catalytic activities. There are more number of biosensors available to detect phenolic compounds, in particular, horseradish peroxidase (Jaafar et al. 2006), and tyrosinase. However, those enzyme biosensors have some disadvantages due to their lower structural stability and sensitive to reaction products (Rodríguez-Delgadoa et al. 2015). On the other hand, laccase shows a strong claimant as a biosensor, having selective advantages over other enzymes including stability, catalytic efficacy (electron transfer reaction), and oxidized phenol and related compounds in the presence of O_2 without any cofactors (Munteanu et al. 1998).

Laccase can react with wide range of phenolic compounds; therefore, it has been used in biosensor technology to detect the presence of various phenolic compounds, oxygen, aromatic amines, morphine, codeine, catecholamines, and plant flavonoids even at low concentration (Leite et al. 2003; Jarosz-Wilkołazka et al. 2004; Ferry and Leech 2005). The smaller and more efficient biosensors are developed through controlled deposition and specific adsorption of laccase on different types of surfaces, at the micro and nanometer scale. There are two types of laccase biosensors: the first type monitors spectrum variation (at an absorbance of 600 nm) of the enzyme, and the second type monitors voltage changes from a modified oxygen electrode (Madhavi and Lele 2009). Immobilized alkali-tolerant laccase on nitrocellulose membrane can react with different substrates (syringaldazine, catechol,

catechin, and L- DOPA) at their low concentrations (Singh et al. 2010). Oktem et al. (2012) immobilized laccase enzyme on Whatman filter paper No. 1 with coloring agent MBTH (3-methyl-2-benzothiazolinone) that is used for the identification of oxidation products of phenols by developing maroon-green colors.

6.4 Peroxidase

Peroxidases (EC 1.11.1.7) are glycoproteins with a hematin compound as cofactor. This heme protein has iron (III) protoporphyrin IX as the prosthetic group. They catalyze hydrogen peroxide (H_2O_2)-dependent oxidization of the different organic and inorganic compounds. Its molecular weights range between 30 and 150 kDa (Bansal and Kanwar 2013). It is widely distributed in all living organisms like bacteria, fungi, algae, plants, and animals. Peroxidases have been applied to reduce pollution in environment. They have the potential to oxidize phenols, cresols, and chlorinated phenols and synthetic textile azo dyes in water. Phenolic compounds are degraded by lignin peroxides (LiPs) in the presence of H_2O_2 (co-substrate) and veratryl alcohol (mediator). In this degradation, H_2O_2 is reduced to H_2O by accepting an electron from LiP (which can oxidize itself). The oxidized LiP returns to its native form (reduced) by gaining an electron from veratryl alcohol thereby veratryl aldehyde is formed. Veratryl aldehyde gets reduced back to veratryl alcohol by receiving an electron from the substrate (Karigar and Rao 2011).

6.4.1 Peroxidases Classification

Peroxidases are classified into two types based on the presence or absence of heme group. They are (1) heme peroxidases and (2) non-heme peroxidases (Passardi et al. 2007a, b). Most of the known peroxidase are heme-containing peroxidases (>80%). Small proportion of the non-heme peroxidases such as thiol peroxidase, alkylhydroperoxidase, and NADH peroxidase existed. Heme peroxidases have further been classified into two superfamilies. They are (i) peroxidase-cyclooxygenase superfamily (PCOXS) and (ii) peroxidase-catalase superfamily (PCATS) (Passardi et al. 2007a, b; Zamocky and Obinger 2010) (Fig. 6.3).

6.4.1.1 Peroxidase-Cyclooxygenase Superfamily (PCOXS)

Animal peroxidases like myeloperoxidase (MPO), eosinophil peroxidase (EPO), lactoperoxidase (LPO), and thyroid peroxidase (TPO) come under this peroxidase-cyclooxygenase superfamily. They revealed major role in the innate immunity, defense responses etc. (Dick et al. 2008; Soderhall 1999). In this superfamily peroxidase, the heme (prosthetic) group is covalently joined with the apoprotein (Pandey et al. 2017).

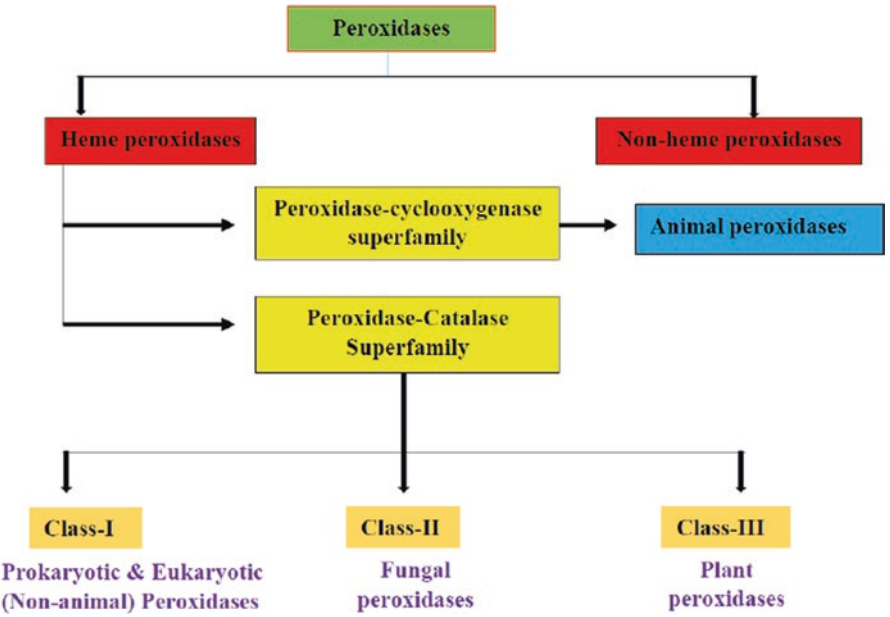

Fig. 6.3 Classification of peroxidases

6.4.1.2 The Peroxidase–Catalase Superfamily (PCATS)

Non-animal (plant, fungal, and bacterial) heme peroxidases come under this superfamily. At first, based on the sources of peroxidase, this superfamily peroxidase was called as the plant, fungal and bacterial heme peroxidase. But, the name of this superfamily was altered as peroxidase–catalase superfamily after identification of new cnidarians peroxidase. The non-animal peroxidases are further divided into three classes. They are Class I, II, and III peroxidases (Pandey et al. 2017).

Class-I: They are intracellular peroxidases. It includes cytochrome c peroxidase (CCP1), ascorbate peroxidases and catalase peroxidase.

Class-II: They are extracellular fungal peroxidases, like the lignin (LiP) and manganese (MnP) peroxidase. Both are secreted by white-rot fungi and involved in the degradation of lignin. Versatile peroxidases (VP; EC 1.11.1.16) displayed a hybrid molecular structure between LiPs and MnPs (Pérez-Boada et al. 2005). This group of peroxidases plays a major role in lignin biodegradation.

Class-III: They are extracellular plant peroxidases. This includes horseradish peroxidases (HRP), peanut peroxidase (PNP), soybean peroxidase (SBP), etc. They play a major role in plant physiological processes such as cell wall metabolism, lignification, suberization, auxins metabolism, wound healing, etc. Class II and Class III peroxidases contain a N-terminal signal peptides, disulfide bridges, glycans, and calcium in their structure (Pandey et al. 2017).

6.4.1.3 Fungal Peroxidase (Class II Peroxidase)

6.4.1.3.1 Peroxidase Structure

Fungal peroxidases have a high-spin protoporphyrin IX (heme b) prosthetic group. It is located in-between the proximal (C-terminal) and distal (N-terminal) domains. The Fe group of this peroxidase is pentacoordinated form which is associated with the four pyrrole nitrogens in the imidazole group of the proximal histidine. The active site containing Fe coordination of peroxidases is highly conserved. At the active site, distal histidine assisted by an asparagine residue participate transfer of electrons from H_2O to the heme. Redox potentials of the enzyme are determined by the length of Fe-imidazolic nitrogen (Fe–Ne_2) bond. A higher basicity of the imidazole group gives a higher redox potential, except few (Choinowski et al. 1999). In general, the change of basicity is dependent on the electron extraction from the imidazolic nitrogen to the surrounding (proximal histidine) (Sinclair et al. 1992). This may differ in peroxidases such as LiP and MnP. Active site residues such as Ser177 and Asp201 weaken the basicity charges of imidazolic nitrogen bond.

The peroxidases enzymes have four disulfide bonds; it was identified in LiP, ARP, and T. versicolor peroxidases (Kunishima et al. 1994; Limongi et al. 1995; Poulos et al. 1993), but MnP have fifth SH linkage extracellular peroxidases containing both N- and O-glycans; however, the glycosylation may be different in various peroxidases, which determines its isozymes (Kjalke et al. 1992). In addition, extracellular peroxidases contain two highly conserved, Ca^{2+}-binding sites which have been located at the proximal and distal domains (Kunishima et al. 1994; Poulos et al. 1993). Presence of Ca^{2+}-binding sites gives structural stability of the extracellular form of peroxidases (Banci 1997), and it gives more strength to the active site. Being extracellular enzymes, fungal peroxidases are synthesized with an N-terminal signal peptide. The LiP has eight Cys residues, all forming disulfide bridges. The enzyme molecule consists of eight major and eight minor α-helices and a limited β structure in the proximal domain.

6.4.1.3.2 Mechanisms of Peroxidase Activity

Peroxidase catalyzes the oxidation of several of organic and inorganic compounds by using hydrogen peroxide which acts as the electron acceptor. The native form of enzyme (E) is oxidized to an active intermediate enzymatic form termed compound I (EI) with concurrent reduction of hydrogen peroxide (H_2O_2) to water molecule. Compound I oxidizes a phenol molecule to phenol-free radical and becomes compound II (EII). Compound II oxidizes another one phenol molecule to phenol free radical and returns to its original state (E) (Fig. 6.4). The formed free radical polymerizes and forms insoluble polyaromatic products which are precipitated by solid–liquid operations (Nicell 1994).

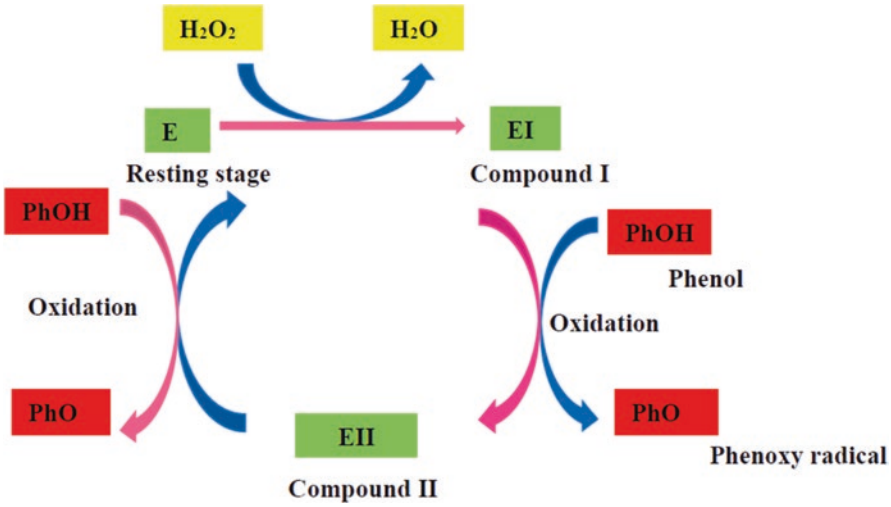

Fig. 6.4 Steps involved in peroxidase catalytic activity

6.4.1.4 Lignin Peroxidase

Lignin peroxidase (EC 1.11.1.14) comes under oxidoreductases family (Higuchi 2004; Martínez et al. 2005; Hammel and Cullen 2008). It was first observed in the basidiomycete fungi *Phanerochaete chrysosporium* by Burdsall in 1983 (Glenn et al. 1983; Tien and Kirk 1988). LiP is an extracellular H_2O_2-dependent heme protein (Gold and Alic 1993; Haglund 1999; Piontek et al. 2001; Erden et al. 2009). LiP enzyme contains 343–345 amino acids preceded by a 27-or 28-residue leader sequence (Gold and Alic 1993). LiP has less substrate specificity, reacting with different phenolic compounds. LiP is capable of oxidizing a variety of reducing substrates including polymeric substrates. It can oxidize methoxylated aromatic rings without a free phenolic group and produce cation radicals that undergo ring opening, demethylation, and phenol dimerization (Haglund 1999). LiP needs H_2O_2 to initiate the reaction, but not mediators to decompose high redox potential compounds. It is used for various industrial application and bioremediation process because of their wide substrate specificity and high redox potentials (Erden et al. 2009). Phenolic compounds are degraded by lignin peroxidase (LiP) in the presence of H_2O_2 (co-substrate) and veratryl alcohol (mediator). In this degradation, H_2O_2 is reduced to H_2O by accepting an electron from the LiP (which can oxidize itself). The oxidized LiP returns to its native form (reduced) by gaining an electron from veratryl alcohol; thus veratryl aldehyde is formed. Veratryl aldehyde gets reduced back to veratryl alcohol by accepting an electron from the substrate (Fig. 6.5). White-rot fungi secreted lignin and manganese peroxidases degrade lignin. Lignin-degrading peroxidases are identified in a number of basidiomycetous fungi: *Phanerochaete chrysosporium, Trametes versicolor, Pleurotus* spp., *Phlebia radiata, Coprinus* spp., *Bjerkandera adusta, Ceriporiopsis subvermispora, Dichomitus*

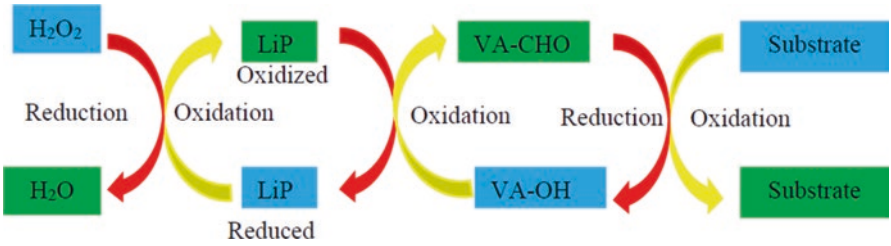

Fig. 6.5 Catalytic cycle of a LiP-mediator oxidation system. VA-OH veratryl alcohol, VA-CHO veratryl aldehyde

squalens and Arthromyces ramosus, *Cylindrobasidium evolvens*, and *Daedaleopsis septentrionalis* (Kimura et al. 1990; Pelaez et al. 1995; Varela et al. 2000; Kinnunen et al. 2016).

6.4.1.5 Manganese Peroxidases

Manganese peroxidases (EC 1.11.1.13) also belong to oxidoreductase family (Higuchi 2004; Martínez et al. 2005; Hammel and Cullen 2008). It is a lignin-degrading enzyme and was discovered in the fungus *Phanerochaete chrysosporium* following the discovery of LiP (Glenn and Gold 1985). MnP is present in all white-rot fungi than lignin peroxidase (Hammel and Cullen 2008). MnPs are present mostly in white-rot fungi, such as *Phanerochaete chrysosporium, Ganoderma* sp., *Pleurotus* sp., *Trametes* sp., and *Irpex lacteus* (Manavalan et al. 2015; Janusz et al. 2013), *Phyllosticta*, *Aspergillus*, *Fusarium*, and *Penicillium* (Pant and Adholeya 2007), *Hyphodontia* sp., *Pleurotus pulmonarius* and *Trametes ochracea* (Kinnunen et al. 2016).

The MnP enzyme is made up of 330–370 amino acids and has a leader peptide that consists of 21–29 amino acids (Li et al. 1999). It is a glycosylated heme protein; molecular weight is ranging from 38 to 62.5 kDa, and averaging at 45 kDa (Hofrichter 2002). Compared to LiP, MnP redox potential is low and oxidizes the substances with the use H_2O_2 which act as oxidant. Manganese acts as a mediator in the MnP catalytic cycle. Manganese peroxidase (MnP) activity involves the oxidation of Mn^{2+} ions to Mn^{3+}. The Mn^{3+} is highly reactive and chelated with organic molecules such as oxalate and malates which are produced by the fungus (Kishi et al. 1994; Galkin et al. 1998; Mäkelä et al. 2002). Chelated Mn^{3+} oxidizes phenolic structures to phenoxyl radicals (Hofrichter 2002).

6.4.1.6 Versatile Peroxidase

Versatile peroxidase (VP) (EC 1.11.1.16) is a heme-containing ligninolytic peroxidase and, as the name suggests, has the catalytic activities of both MnP and LiP and is able to oxidize Mn^{2+} similar of MnP and high redox potential non-phenolic

compounds like LiP. It was first identified in the white-rot fungus *Pleurotus eryngii* (Martinez et al. 1996). It was first purified from the fungi B*jerkandera* (Moreira et al. 2007) and can transform lignin even in the absence of an external mediator. It is found in *Physisporinus vitreus* (Kong et al. 2017), *Phlebia radiata*, *P. pulmonarius*, and *Galerina marginata* (Kinnunen et al. 2016). VPs can oxidize wide range of substrates with low and high redox potentials. Generally, VPs have hybrid molecular structures of LiP and MnP and provide multiple binding sites for the substrates (Camarero et al. 1999). VPs are superior than other peroxidases, because VPs efficiently oxidize phenolic compounds without the use of veratryl alcohol or Mn(II) that are needed for LiPs and MnPs activity, respectively (Ruiz-Duenas et al. 2009). Because of the catalytic versatility, VPs have been involved in the different biotechnological applications. VP can oxidize not only Mn (II), but also veratryl alcohol, phenolic, non-phenolic and high molecular weight compounds, including dyes in Mn-independent reactions (Asgher et al. 2008; Wong 2009). Like MnP, commercial applications of VPs are limited, because of their unavailability in large quantities which can be overcome by the use of DNA recombinant technology (Ruiz-Duenas et al. 2009).

6.4.2 Applications of Fungal Peroxidases

Ligninolytic extracellular enzymes especially lignin peroxidase and manganese peroxidase have shown capability toward the degradation of various xenobiotics including dyes, chlorophenols, polycyclic aromatic hydrocarbons (PAHs), organophosphorus compounds, and phenols (Wesenberg et al. 2003), improve the digestibility of wood or straw for animal feed (Valmaseda et al. 1991), and reduce costs for the pulp and paper industry (Martinez et al. 1994) (Table 6.4). The other applications of LiP are delignification of feedstock for ethanol production, textile effluent treatment and dye decolorization, coal depolymerization, treatment of hyperpigmentation, and skin-lightening through melanin oxidation. The lignin peroxidase–graphite electrode biosensor systems have been established for recognition of recalcitrant aromatic compounds because of their effective bioelectrocatalysis (Ferapontova et al. 2006). The applications of peroxidases on various industries are given below.

6.4.2.1 Textile Industry

Dye is a synthetic colored substance and is used by various industries to color paper, cotton, polyester, nylon, silk, leather, plastics, hair, etc. to which the dye binds and becomes an integral part. When unbound synthetic dyes are released into water, they cause pollution and cause skin allergy, cancer, and chromosomal aberrations for human beings and also affect plants that reduce photosynthetic activity by reflecting sunlight and affect germination rate of plants. Fungi can rapidly become

Table 6.4 Applications of LiP and MnP enzymes

Organism	Enzyme type	Compound removal	References
Phanerochaete chrysosporium	LiP	Anisyl alcohol (Monomethoxylated Aromatic Compounds)	Valli et al. (1990)
Trametes versicolor	MnP	Pulp Bleaching (oxidation of phenolic lignin substructures)	Paice et al. (1993)
Phanerochaete chrysosporium	MnP & LiP	Bentazon (3-isopropyl-1H-2,1,3 benzothiadiazin-4(3H)-one 2,3-dioxide) and MCPA (4-chloro-2-methylphenoxyacetic acid)	Castillo (1997)
Phanerochaete chrysosporium	LiP	Procion Brilliant Blue HGR, Ranocid Fast Blue, Acid Red 119, and Navidol Fast Black MSRL	Verma and Madamwar (2002)
Fungal strain L-25	MnP	Azo, diazo, and anthraquinone dyes	Kariminia et al. (2007)
P. chrysosporium Burds BKM-F-1767	LiP	Catechol derivative	Cohen et al. (2009)
Phanerochaete chrysosporium	MnP	Orange II	Sharma et al. (2009)
P. chrysosporium RP78	LiP & MnP	Azo dyes	Ghasemi et al. (2010)
Anthracophyllum discolor	MnP	Phenanthrene, anthracene, fluoranthene, pyrene and benzo(a)pyrene	Acevedo et al. (2011)
P. floridensis	LiP	Coracryl brilliant blue	Chander and Kaur (2015)
Phanerochaete chrysosporium	LiP	Paper and pulp industry effluent treatment (Color and lignin removal)	Singh et al. (2016)
Phanerochaete chrysosporium	MnP	Congo Red	Bosco et al. (2017)

accustomed to varying nutritional sources because they can produce a significant number of intra- and extracellular enzymes that are needed to degrade several complex organic pollutants such as dye stuffs, polyaromatic compounds, organic waste, and steroids (Gadd 2001; Humnabadkar et al. 2008). The fungal system can be utilized in the treatment of colored and metallic textile effluents (Ezeronye and Okerentugba 1999) because they can produce nonspecific enzymes such as lignin peroxidase (LiP), manganese peroxidase (MnP) and laccase (Christian et al. 2005) that can mineralize dyes. Direct participation of fungal ligninolytic enzymes is necessary for the mineralization of dyes (Park et al. 2007). Versatile peroxidases (VPs) have shown effective direct oxidation of high redox potential dyes Reactive Black 5. Reactive Black 5 is oxidized by LiP only in the presence of veratryl alcohol, redox mediators (Heinfling et al. 1998). It can oxidize phenols, including hydroquinones (Gomez-Toribio et al. 2001). Fungi produce enzymes extracellularly that confer decolorization ability of dyes. Lignin peroxidase of *P. prosopidis* degrades scarlet RR dye (Fernandes et al. 2008). LiP degrades dye by the following steps

initial asymmetric cleavage, demethylation and denitrification and form N-ethyl-1 l3-chlorinin-2-amine which is further degraded by laccase. *Pleurotus ostreatus* can decolorize Remazol Brilliant Blue by producing peroxidase extracellularly (Shin et al. 1997).

Ganoderma lucidum, a white-rot basidiomycete, could be capable of the decolorization of four dyes (Drimaren Blue CLBR, Drimaren Yellow X-8GN, Drimaren Red K-4B and Disperse Navy Blue HGL) and degradation of phenol with the aid of manganese peroxidase. Manganese peroxidase (MnP) from *Ganoderma lucidum* was expressed in *Pichia pastoris* and recombinant MnP can also degrade four textile dyes and phenol (Xu et al. 2017). Similarly, *Pleurotus* species have been reported for the production of lignin peroxidases, manganese peroxidases, and laccases enzymes, which play a vital role in the biodegradation and bioremediation (Pandey et al. 2012) of textile effluents. White-rot fungi, *Pleurotus flabellatus*, *P. ostreatus*, *and P. citrinopileatus*, are used effectively and efficiently for dye decolorization and bioremediation of recalcitrant substances (Singh and Srivastava 2016).

MnP of *Pleurotus pulmonarius* could be able to decolorize the anthraquinonic dye Remazol Brilliant Blue R and the azo dye Congo Red. The enzyme is strictly dependent on Mn^{2+} for oxidizing phenolic and non-phenolic compounds. MnP of *Pleurotus pulmonarius* can be used for textile dye effluent treatment (da Silva et al. 2017). Agrawal et al. (2018) reported that *Ganoderma lucidum* will be an effective phenanthrene and pyrene degrader by producing ligninolytic enzymes (laccase, lignin peroxidase, and manganese peroxidase).

6.4.2.2 Paper and Pulp Industry

Humic substances (HS) are formed from microbial breakdown of dead plant matter, mainly from lignin. HS tend to be polydisperse polymers of aromatic and aliphatic units that have been synthesized from the polymerization of intermediate lignin degradation products (Abdel-Hamid et al. 2013), and the polymer is physically and chemically structurally complex (Niladevi 2009). HS are existing in soil, marine, and groundwater environments and wastewater from industrial and municipal water treatment (Abdel-Hamid et al. 2013). In the pulp and paper industry, HS are produced from the chemical treatment of wood and removed using membrane filters during wastewater treatment, but they form biopolymer and produce blockage of filter leads to decrease of filtration flux rates (Sutzkover-Gutman et al. 2010). The enzymes are applied to remove the HS in ecofriendly method with low cost (Cavicchioli et al. 2011). Peroxidases catalyze H_2O_2-dependent oxidation of aromatic polymers, including HS, by generating radicals which can break aromatic rings, ether and carbon–carbon bonds, and by causing demethoxylation (Wong 2009; Abdel-Hamid et al. 2013). Versatile peroxidase oxidizes complex polymeric humic substances (HS) derived from lignin (humic and fulvic acids) and industrial wastes (Siddiqui et al. 2014).

6.4.2.3 Bioremediation of Toxic Agrochemicals

The herbicide atrazine was converted to the less toxic compounds desethyl atrazine and hydroxyatrazine (N-dealkylated and hydroxylated metabolites, respectively), by the fungus *Phanerochaete chrysosporium*. Atrazine removal corresponded to the production of LiP and MnP from the fungus (Mougin et al. 1994). LiP and MnP of white-rot fungus *P. chrysosporium* can degrade the herbicide and isoproturon in in vitro and in vivo conditions (Del Pilar et al. 2001). MnPs from *P. chrysosporium* have the ability to break bentazon in the presence of mediators like Mn(II) and Tween 80. The herbicide glyphosate was oxidized by MnP that is produced by *Nematoloma frowardii* (Pizzul et al. 2009). This information evidently indicates the prospective application of lignin-degrading enzymes in the treatment of herbicides contaminated soil and water. Polycyclic aromatic hydrocarbons (PAHs) such as anthracene and pyrene are highly hydrophobic, but they are oxidized by MnP and LiP of wood rotting fungus *Nematoloma frowardii*. In the presence of low molecular mediator substances, the substrate range and the oxidation rate of LiP, MnP is increased (Günther et al. 1998). When endocrine-disrupting chemicals and trace organic contaminants like pharmaceuticals and personal care products are released into water, it leads to bioaccumulation, acute, and chronic toxicity to aquatic living organisms and also causes severe effect on human health. *Podoscypha elegans* degrades lignin and organic pollutant by producing nonspecific extracellular lignin-olytic enzymes such as laccase, lignin peroxidase (LiP) and manganese peroxidase (MnP). It can be used for the removal of pollutants from the environment (Nikki Agrawal et al. 2017). MnP from *Pleurotus ostreatus* could detoxify aflatoxin B1 (AFB1) depending on the enzyme concentration and incubation period (Yehia Ramy Sayed 2014). Non-lignolytic filamentous fungus *Penicillium* sp. CHY-2 can degrade different aliphatic and aromatic hydrocarbons. *Penicillium* sp. CHY-2 efficiently degrades decane than octane, dodecane, ethylbenzene, butylbenzene, naphthalene, acenaphthene, and benzo[a]pyrene by producing MnP enzyme. The relative molecular mass of MnP enzyme from *Penicillium* sp. CHY-2 is estimated to be 36 kDa, and the native form of MnP is a monomer (Govarthanan et al. 2017).

6.5 Conclusion and Future Prospects

Fungal laccases and peroxidases are a promising biocatalyst, used as a better alternative for conventional chemical processes in the treatment of lignin degradation, wastewater treatment, decolorization, and detoxification of textile dyes and biosensor preparation to detect the environmental pollutant. Their substrate range is fairly wide and immobilization technology increases enzyme stability and to achieve its reuse.

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