Review Paper

Microbial manganese peroxidase: a ligninolytic enzyme and its ample opportunities in research

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Abstract
Microbial ligninolytic enzymes like laccase, manganese peroxidase, and lignin peroxidase have gained much attention in many industrial applications. Among these, manganese peroxidases are key contributors in the microbial ligninolytic system. It mainly oxidizes Mn(II) ions that remain present in wood and soils, into more reactive Mn^{3+} form, stabilized by fungal chelators like oxalic acids. However, Mn^{3+} acts as a diffusible redox intermediate, a low molecular weight compound, which breaks phenolic lignin and produces free radicals that have a tendency to disintegrate involuntarily. It has a great application potential and ample opportunities in diverse area, such as alcohol, pulp and paper, biofuel, agriculture, cosmetic, textile, and food industries. This review article is focused on the sources, catalytic reaction mechanisms and different biotechnological applications. However, manganese peroxidases have a potential for degradation of many xenobiotic compounds and produce polymeric products formulated them into valuable tools for bioremediation purposes. In addition, microbial MnPs can also convert lignin into biomass so that the sugar can be converted into bio-fuels. Thus, this review article is mainly focused and highlighted the current scenario and updated information on manganese peroxidase enzyme.

Keywords Microbial MnP · Phenolic and non-phenolic compounds · Biotechnological application

1 Manganese peroxidase: an introduction

The ligninolytic enzyme manganese peroxidase (E.C.1.11.1.13. Mn^{2+}: H_2O_2 oxidoreductase) is ubiquitous in nature [1]. This enzyme has more demands in the recent years due to its diverse applications in numerous biotechnological areas [2]. MnP has the most potential, well recognized, and studied enzymatic activities, which is highly adaptable in nature with ample industrial applications [3, 4]. The phenolic and non-phenolic compounds are oxidized during the oxidation of Mn(II) to Mn(III) by the MnP enzyme [1, 5, 6]. MnPs are the extensively disseminated extracellular potential peroxidases formed/produced by fungi (white-rot fungi). It is also with laccases and LiPs, which are considered to play a dynamic role in the lignin depolymerisation process [7–11]. Approximately 20 year ago, these heme-containing glycoproteins were reported to be produced by the fungus *P. chrysosporium* [12]. But, unfortunately in beginning, it had been paid less attention in comparison with LiP, laccase and other peroxidases of *P. chrysosporium* [13]. *P. chrysosporium* is well known and more studied white-rot fungus secretes number of peroxidases and oxidases that are in charge of producing very much reactive and nonspecific free radicals [14, 15]. So far, microorganisms that make adequate amount of ligninolytic enzyme for the biotechnological applications has not been found. Basic Local Alignment Search Tool (BLAST) were used for the determination of MnP isoenzymes in

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which three structurally similar genes (*mnp1*, *mnp2*, and *mnp3*) and two other newly isolated genes were achieved from *P. chrysosporium* [16]. White-rot fungi secrete MnP mainly in multiple types. They are numerous glycoproteins with a molecular weight ranging from 38 to 62.5 kDa, ~ 350 amino acid residues, and have 43% of identity with LiP sequences [17].

The two domains with heminic group in center, one minor helix, ten major helixes, and five disulfide bridges have been responsible for the formation of MnP enzymes. Out of these, one takes part in manganese bonding site. This site is attributed to differentiate MnP from other reported peroxidases [18]. The improved MnP production is important for assisting to create environmentally sound biomass degradation alternatives and diminish the cost of energy and used chemicals in biofuel production industries. MnP has many applications in industrial processes like bio-pulping, bio-bleaching and biodegradation/bioremediation of pollutants [3, 4, 19–21].

The catalytic cycle of MnP is commencement by indigenous ferric enzyme and H_2O_2 to form compound I, which is a Fe^{4+} oxo-porphyrin radical complex, while mono-chelated Mn^{2+} ions give 1 e^- to porphyrin intermediated to compound II by the donation of 1 e^- form Mn^{2+} to form Mn^{3+}. Further, chelated Mn^{3+} ions generated by MnP act as S–S charge transfer mediators, allowing the oxidation of various phenolic substrates like simple phenols, amines, phenolic lignin and several dyes (Fig. 1) [10, 21].

MnP has potential biotechnological as well as several bioremediation applications such as production of natural aromatic flavor, decoloration of various industrial wastewaters such as textile, distillery, pulp and paper, and many other wastewaters [2, 4, 22]. So far, many findings are available on MnP applications, but these are scattered; hence, this review is to compile all important information at a single place.

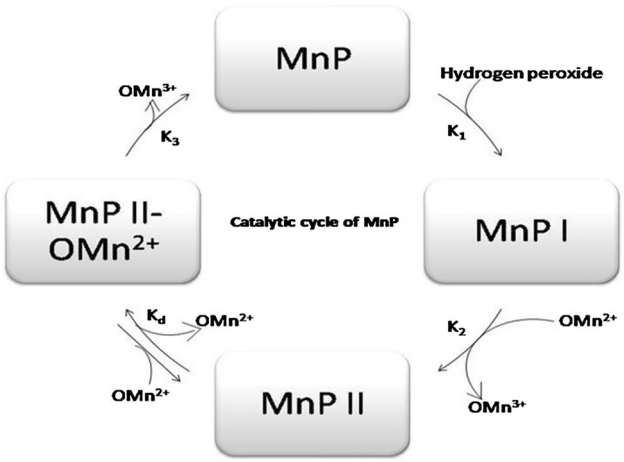

Fig. 1 Catalytic cycle of Manganese peroxidase enzyme

2 Source of MnP

Many researchers have observed that MnPs are found in many microorganisms such as bacteria, fungi, and algae. [23, 24]. A fungus produces/secretes one or more of three extracellular enzymes that are necessary for lignin degradation: LiP, MnP, and laccase. An extracellular MnP produced by *P. sordida, P. chrysosporium, P. radiata, P. rivulosu, C. subvermispora,* and *Dichomeris squalens,* [25]. MnP produced by *P. chrysosporium* BKM-1767 was observed during the growth in several medium and environmental as well as nutritional growth conditions [26]. On the other hand, there is an urgent need to find MnP with higher tolerance to organic solvent and inorganic ions to enhance the degradation potential of xenobiotics. In this context, Qin et al. [27] found that some substrate/mediators such as veratryl alcohol, oxalic acid, 2, 6-Dimethoxyphenol could catalyze the synthesis of MnP in *Irpex lacteus* CD2. In addition, earlier potential strain was characterized as *A. baumanii* based on phylogenetic tree of 16 rRNA sequencing. Above findings have given a number of important microbial strains capable for delignification and biodegradation of recalcitrant compounds by ligninolytic enzymes [28].

Huy et al. [29] found that the wood chips or rice straw can be used as chief carbon source and recognized as inexpensive medium of agricultural residue for the production of MnP from *Fusarium* sp. Further, MnP with molecular mass of 45 kDa was purified from the white-rot fungus *C. unicolor BBP6* and named as MnP-BBP6 with optimum temperature and pH [24]. Now these days, the degradation of lignin and rice straw has great attention especially in Egypt and worldwide due to the accumulation of rice straw as agricultural wastes that cause many environmental problems worldwide.

A. praecox produces extracellular MnP, which mineralizes synthetic lignin. The isolated MnP1 isozyme of *A. praecox* was also characterized, purified, and cloned. Hence, this newly isolated MnP1 may represent a novel group of a typical short-MnP enzyme [30]. MnP production is predominantly found in *Bjerkandera adusta*, *F. fomentarius*, *Cerrena* and *Trametes* genera. Earlier, it was also found that MnP production in *P. chrysosporium* is enhanced by nutrient limitation such as C, N, and also by Mn^{2+}. By contrast, *mnp3* lacks MREs, and it was observed that transcript levels are not disturbed by the addition of Mn^{2+} [31, 32]. *Cupriavidus basilensis* B-8 produces both ligninolytic enzyme laccase and MnP during the lignin biodegradation [33]. *Irpex lacteus* has a great prospective in bio-pretreatment of lignocellulose as well as in biodegradation of xenobiotics.

I. lacteus showed to produce MnP as the main enzyme under many controlled tested conditions [27, 34].

3 Physicochemical and molecular properties of MnP

Ligninolytic enzymes production and activities are affected by many environmental and nutritional parameters such as pH, temperature, carbon, and nitrogen (Table 1). Size exclusion and anion exchange chromatography were used as conventional method for the purification of MnP enzyme. The SDS–PAGE analysis revealed that the purified MnP is a monomeric protein having mol. wt. of 37 kDa with an isoelectric point at 3.55. The optimum pH ranges from 4.0 to 7.0 with a peak at pH 5.5. It was also found that MnP was more active at 5–70 °C with an optimum between 50 and 60 °C. At temperatures above 65 °C, the enzyme quickly vanished activity [46]. In native protein, the heme–iron has high-spin, pentacoordinate form, and ferric state with a His-residue coordinate at the fifth ligands position [49]. MnP has 5 rather than four S–S bond, with the additional bond, Cys341–Cys348, located near the C terminus of the polypeptide chain. The extra S–S bond assists to form Mn(II) binding site, and it is responsible for driving the C terminus part away from the foremost part of protein [50, 51].

Oxidoreductase can catalyze oxidation of an extensive variability of organic compounds using hydrogen peroxide. It is an environmentally low load oxidant and has been used in industry for several purposes such as food processing and oil bio-refining, while in industries the full-scale use of peroxidases is still restricted due to their facile inactivation in the presence of H_2O_2 under supra-physiological conditions. Moreover, peroxidases poor thermal and environmental tolerance reduces the range of practical uses [52]. The reaction of catalytic cycle is initiated with the transfer of 2 e^- from heminic group to H_2O_2, and finally, it form compound I and water. Further, compound I catalyzes the oxidation of one substrate compounds with the formation of free radicals and compound II. However, compound II oxidizes Mn^{2+} to form Mn^{3+}, and the cation is responsible to oxidize aromatic ring containing compounds. It is necessary to know that compound II demands Mn^{2+} presence for its reaction, whereas compound I can oxidize Mn^{2+} or the substrate molecules. Subsequently, Mn^{3+} became stabilized by organic acids; it reacts non-specifically with organic compounds by eliminating 1 e^- and proton from the substrate molecules [17]. MnP is relatively precise for reducing substrates, and only Mn^{2+} efficiently supports enzyme turnover. Direct oxidation of Mn(II) to Mn(III) is characteristic of MnP, although other enzymes can oxidize it via superoxide anion radical. The chelators affect the interaction of Mn ions at the active site of enzyme as shown by kinetic studies [53]. Although the MnP/Mn^{2+} pair is not oxidized non-phenolic lignin model dimers as LiP does, partial depolymerisation of synthetic as well as plant derived lignin has been formed possibly by endwise attack progressing from phenolic components [54]. The enzyme production and activity were determined by following points discussed as below:

- The enzyme yield varies species to species and strain to strain, and assortment of newly isolated microorganisms with large production of these enzymes is possible.
- During the enzyme production process, lignocellulosic materials and C source play an important role.
- The activity of ligninolytic enzymes not only regulated by the aromatic compounds, but it also depends upon the physiological activity of microorganisms.
- Selection and co-cultivation of suitable fungus shows substantial promise as an approach to accelerate/promote the enzyme production [55].

However, after the above-mentioned selection procedure, optimization plays a key role in enzyme production with the selected microorganism. Several studies clearly specified that basidiomycetes showed a wide variety in their response to C sources and their optimum concentration in selected medium [56, 57]. In *P. robustus* kiwi residue stimulates the MnP secretion in compression with wheat barn. Consequently, after the substitution of wheat bran by pericarp laccase/MnP ratio changes from 226 to 2 [55]. In some fungal species like *P. chrysosporium*, the ligninolytic enzyme gene expression is activated only by the diminution of C sources [57]. There are various compounds, like dimethoxyphenol (2,6-DMP), which affects the ligninolytic enzyme activity, and production to the control medium increased the MnP yields twofold. In addition, vanillic acid followed by the ferulic acid and veratric acid and pyrogallol enhances MnP activity more than 50% in *C. unicolor* [55].

4 Effects of various parameters on enzyme activity

Nutritional as well as environmental factors affect the production and activity of ligninolytic enzymes including MnP in various ways (Table 2). The optimum pH and temperature range from organism to organism. Ligninolytic enzyme (Lac, LiP, MnP) activity or production not only depends on the microbial species but also depends on culture conditions, carbon, and nitrogen sources and their concentration [61, 70, 71]. Pedri et al. [72] observed that

Table 1 Various MnP producing microorganisms, growth medium and physiological properties

Microorganism	Microbes growth Source	Molecular mass (kDa)	Used Substrate in assay	Temp. optima of activity (°C)	Temp. stability (°C)	pH optima of activity	pH stability	References
Fungus								
Cerrena unicolor BBP6	Dyes containing agar plates	45	Gallic acid	60	NR	4.5	4.8	[24]
Ganoderma lucidum	Potato dextrose agar	37.72	NR	NR	NR	NR	NR	[35]
Trametes sp.48424	Potato dextrose broth (PDB)	49	Veratric acid	70	NR	5.0	NR	[36]
Ganoderma lucidum IBL-05	Wheat bran	43		30	20–60	4.5	–	[37]
Irpex lacteus F17	Solid-state fermentation medium	–	–	40	–	3.5	–	[38]
Irpex lacteus CD2	Potato dextrose agar	–	Veratryl alcohol	28	40–70	4.5	6.0	[27]
Trametes villosa	Sugarcane bagasse	–	–	–	22	7.0		[39]
Agrocybe praecox	Bark mulch and wood chips	42	–	–	–	4.5	7.0	[30]
Phanerochaete chrysosporium	Wheat Straw	52.8	–	28–38	–	–	–	[40]
P. chrysosporium; Fusarium sp.89; *Fusarium sp.* 82	Rice straw	–	–	–	–	–	–	[41]
Phanerochaete chrysosporium	Agriculture by-products	–	–	–	–	–	–	[42]
P. chrysosporium	Agro-industrial wastes	–	–	35	–	4.5	–	[43]
Schizophyllum commune IBL-06	Banana waste	–	$MnSO_4$	35	–	4.5	–	[44]
C. subvermispora	Japanese beech and cedar wood *Eucalyptus grandis* wood Bamboo culms	–	Phenol red	30	–	–	–	[45]
Irpex lacteus CCBAS238	MEG agar slant	37	–	50–60	65	4–7	5.5	[46]
Phlebia radiata	Wheat straw	68	–	–	–	–	–	[47]
Bacteria								
Acinetobacer baumanii	Rice straw	–	–	–	–	–	–	[28]
Bacillus subtilis	Mineral salt media	68	MnSO4	30	–	–	–	[3]
Alcaligenes faecalis (DQ659619) and *Bacillus cereus* (DQ659620)	GPYM agar plates	43	Phenol red		–	–	–	[48]

NR not reported

maximum concentration of ammonium sulfate and potassium nitrate showed negative effects on enzyme activity, whereas maximum activity was observed in the presence of ammonium sulfate and soyabean. In culture broth, nitrogen source enhances microbial cell growth and also boosts the enzymes expressions [73]. Prasher and Chauhan [74] found that glucose and ammonium oxalate were more effective carbon and nitrogen source, respectively, for the highest manganese peroxidase enzyme activity and production. In recent studies, the maximum activity of lignolytic enzyme was reported at 24 °C temperature and pH from 5 to 9. [74, 75]. In earlier study, it was observed that

Table 2 Factors affecting MnP enzyme activity and their production

Factors	Comments	References
Carbon source	The maximum LiP activities and noticeable levels of MnP, when they used wood as a C source with milled alder as inducer The maximum activities of MnP were obtained in pineapple peel culture	[58]
Nitrogen source	*P. chrysosporium* cultivated in synthetic medium, producer LiP and MnP only under N limited condition. However, it was found that in the presence of ligninolytic substrate, a high N concentration stimulates these enzymes production Several inorganic and organic N sources in submerged fermentation of wheat bran to improve enzyme production by *Ganoderma lucidum*. The maximal valve of laccase activity was revealed in supplementation of culture media with KNO_3. The compound slightly stimulated MnP accumulation	[59–61] [62]
Synthetic inducer	MnP activity was induced by Tween-80. Addition of Tween 80 caused the highest values of MnP activity produced by *P. chrysosporium*	[63–65]
Metal inducers	Manganese (Mn) plays a regulatory role in the expression of LiP, MnP, Lac and in the degradation of lignin. It seems that low concentrations of essential heavy metals are necessary for the development of ligninolytic enzyme system Addition of low concentration of Zn and Cu into the metal free synthetic cultivation medium increased the activity of LiP and MnP of *P. chrysosporium*	[66–68]
pH	MnP and Lac were activity commonly detected in the less acidic (pH > 5.0), whereas no MnP activities are detected in the highly acidic condition. MnP and LiP activities are dependent on pH and independent in the forest floor layer	[69]
Temperature	Temperature is also play an important role during enzyme activity and other related function	[48]

Table 3 Various applications of MnP enzyme

S. No.	Enzyme	Applications	References
1.	MnP	Dye decolorization and denim bleaching	[24]
2.	MnP	Degradation of hydroquinone, pyrocatechol, resorcinol, benzoquinone	[35]
3.	MnP	Adequate treatment of industrial lignin and black liquor	[35]
4.	MnP	Degradation of various types of lignin containing model compound/modification.	[77, 78]
5.	MnP	Degradation of various types of dyes and polycyclic aromatic hydrocarbons (PAHs)	[36]
6.	MnP, laccase	Degradation of lignin and rice straw	[28]
7.	MnP, laccase, LiP	Biodegradation of natural rubber	[3]
8.	MnP	Bio-ethanol production	[79]
9.	MnP	Decolorization and degradation of reactive textile dyes, i.e., Reactive Yellow MERL (7-(4-{4-Chloro-6-[3-(2-Sulfoxy-Ethanesulfonyl)-Phenylamino]-[1,3,5,]Triazin-2-Ylamino}-2-Ureido-Phenylazo)-Napthalene-1,3,6,Trisulfonic Acid) And Reactive red ME4BL(5-{4-Choloro-6-[4-(2-Sulfo-Ehtanesulfonyl)-Phenylamino]- [1, 3, 5] Triazin-2-Ylamino}-3-(1,5-Disulfo-Napthalen-2-Ylazo)-4-Hydroxy-Naphthalena-2,7-Disulfonic Acid	[40]
10.	MnP	Effectively degrade a broad range of synthetic dyes	[27]
11.	MnP, LiP	Used in diagnostic kits	[80]
12.	MnP	Degradation of PAHs degradation of PAHs.	[46]

recombinant MnP (rMnP) showed optimum production at pH 6 and temperature 30 °C in *P. pastoris* [76].

5 Ample applications/opportunities in various sectors

In current scenario, ligninolytic enzymes gain more attention in various types of biotechnological application such as in alcohol, pulp and paper, textile, food, medicals and in cosmetic industry and also for biodegradation of many toxic compounds (Table 3) [55, 82, 83]. In recent years, ligninolytic enzymes have appeared as a new substitute and ample opportunities in various sector, including research detailed discussed in this section (Fig. 2).

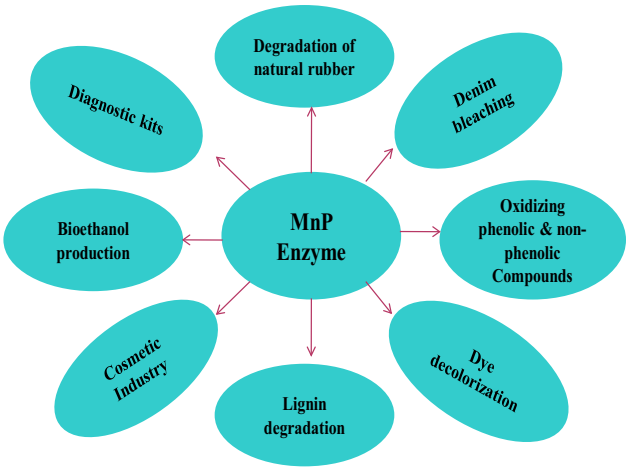

Fig. 2 Manganese peroxidase used in various biotechnological application

5.1 Degradation of phenolic and non-phenolic compounds

Phenolic and non-phenolics compounds are found in different industrial wastewaters, including coal conversion, petroleum refining, resins, plastics, wood preservation, metal coal, dyes and other chemicals, textiles, mining and dressing, and pulp and paper. Most applications have focused on the treatment of phenolic contaminants in the presence of H_2O_2 [5, 84, 85]. MnP-generated Mn(III) chelator can induce the oxidation of phenolic compounds, including phenols, amines, dyes, and also dimers and lignin-containing phenolic structure.

Various researchers found that under physiological conditions Mn(III), chelator acts as mild oxidant and limited to the oxidation of lignin-containing phenolic structures [86, 87]. The Mn(III) formed is separated from the enzyme and stabilized by forming complexes with α-hydroxy acids at a high redox potential of 0.8–0.9 V. There are two optimal chelators, i.e., malonate and oxalate that are produced in significant amount by fungal species [53]. The oxidation by Mn(III) engages the development of reactive radicals for non-phenolic substrate in presence of second mediator [88]. In contrast, LiP catalyzed reaction, which involves e- reduction from the aromatic ring forming a radical cation. In the presence of thiols (R-S–H) such as glutathione, Mn(III) mediates the oxidation of substituted benzyl alcohols and diaryl propane structures into their respective aldehydes [8]. Zhang et al. [36] found that MnP-Tra-48424, which obtained from *Trametes* sp., has the ability to decolorize divers group of dyes such as indigo, anthraquinone, triphenylmethane and azo dyes.

5.2 Pulp and paper industry

Pulp and paper industry is a key contributor in world's economy, but unfortunately it causes various environmental toxicity and health problems. During the paper manufacturing process pulp and paper industry uses huge amount of lignocellulosic materials. Paper manufacturing process involves three main steps like (1) pulping, (2) bleaching and (3) paper production, further pulping divided into three type, i.e., mechanical, chemical and chemi-mechanical or combination pulping (for details see [89]). These processes generate high strength of wastewater, which causes adverse impact on environment. There are several chemical-based treatment technologies available, but are hazardous to living beings, costly and unsafe of green environment, while biological approaches are reported as cost-effective, commercially and environmentally safe approaches for wastewater treatment [90]. For the adequate treatment of discharged wastewater and pollutants, diverse group of microorganism are playing an essential role. Among these, white-rot fungi are found more effective for the degradation of many lignin and other similar wood materials to CO_2 and H_2O [91]. Some of them are potent degrader of lignin rather than cellulose and hemicellulose [92].

A variety of lignocellulosic materials or resources are available for conversion of many value-added bio-products, which increase the research interest in this area [89]. There are problems with the direct use of microbes for degrading lignocellulosic materials, including breaking of cellulosic fibers [93] and long reaction times, extending to long time [94]. Hatakka et al. [95] found that Tween 80, H_2O_2 generating system, and an organic acid assist the chelation of MnP, in the presence of Mn(II). However, Mn(II) is an strong oxidizing agent and an important factor in the delignification system [96]. In pulp and paper industry, enzyme pulping is used for MnP and laccases of *Polyporus* sp., and pectinases from *Rhizopus* sp. 26R in practice. The application of ligninolytic enzymes reduces the amount of chemicals used in basic pulping process such as sodium hydroxide (NaOH) [97]. However, MnP and LiP are reported to play an important role in decolorizing of kraft pulp [98, 99].

5.3 Food industry

Food quality is not a function of nutritional values, but also of the presence of bioactive compounds, which apply positive effects on human and animal health. Microbial ligninolytic enzyme displays great perspective for variety of industrial application like pulp delignification, wastewater treatment, biofuel production, dye decolorization, biosensors, and juice extraction clarification [4, 100]. Bilal

et al. [100] immobilized MnP gives praiseworthy result in which reduction in apple juice color and turbidity was 42.7% and 36.3, respectively. In simultaneous study, it was observed that reduction in color and turbidity 51.5% and 43.6%, respectively. Further, Bilal et al. [101] found that treatment by immobilized ligninolytic enzyme reduces turbidities up to 84.02%, 57.84, 86.14% and 82.13% which was observed for apple, grape, orange and pomegranate juice, respectively. In recent years, MnP have also gained more demands in various applications in food industry. It has great possibility to generate natural aromatic flavors such as vanillin production, ferulic, p-coumaric, syringic and p-hydroxybenzoic [22, 102, 103]. This type of research finding is very imperative because recently special attention in biotechnology has been given to acquire massive quantity of low-cost environment friendly ligninolytic enzymes by use of diverse agriculture and food industry residue; unfortunately, it can call serious environmental problems. The residues present excellent substrate for fungal growth, which are mineralized to low molecular weight (LMW) compounds by various lignocellulolytic enzymes including MnP and other peroxidases. These LMW products are simply absorbed by fungi, better digested by animals, and could be used in the production of high nutritional value food, feeds, and other basic commodities for various industrial uses.

5.4 Alcohol industries

Ligninolytic enzymes play an important role in distillery waste treatment process [23, 82]. Enzymatic degradation/detoxification has been applied in the mitigation of toxicity after different pre-treatments such as steam explosion, strong acids, organosolv, and hot liquid water. In addition, ligninolytic enzyme enhances detoxification, fermentation rates and ethanol production processes in alcohol industry [104]. The enzymatic degradation or decolorization generates an ethanol yields five times more in comparison with ion exchange degradation in sugarcane bagasse [105]. The enzyme has capability to catalyze non-activated alcohols, which is an imperative factor for future degradation or detoxification procedures [106]. For MnP, maximum production was in *Aspergillus niger* TERI DB20 grown on corncob with wastewater. Pant and Adholeya [107] found that *Pleurotus ostreatus* (Florida) Eger EM 1303 achieved color reduction 86.33% of molasses (cane)-based wastewater of distillery industry. Biotechnology treatment encompasses a variety of scientific and engineering treatment methods for applying eco-friendly or biological systems to produce important materials or elimination of problematic, often poisonous, liquid, solid or gaseous wastes.

5.5 Use of lignocellulosic materials and MnP in bio-ethanol production

In recent years, concerning renewable biofuel production and bio-ethanol from lignocellulosic feedstocks is considered the most practicable choice for fossil fuels replacement, since these raw materials do not compete with food or feed crops [108]. Treatment by ligninolytic enzyme of waste biomass could be of precise interest, because it seems to be an environmental friendly method for making bio-ethanol. In future, biorefineries will integrate biomass conversion process to produce fuels, power, heat and value-added chemicals. Due to its low price and wide distribution, lignocellulosic biomass is expected to play an important role toward this goal [20, 109]. To increasing the range of various natural resources scientists have been redirecting their curiosity in biomass-based bio-fuels production, which can be attained from lignocellulosic biomass. They also found that high-performance liquid chromatography (HPLC) analysis is used as promising tool for bio-ethanol production in consecutive saccharification and fermentation [20]. Further, Asgher et al. [2] produced 22.6 g/L ethanol by using *Saccharomyces cerevisiae* with the help of Sequential Saccharification and Fermentation (SSF) process. In recent study, Bilal et al. [110] found that by using extract of ligninolytic enzyme from *G. lucidum* IBL-05 for delignification of newspaper waste followed by saccharification with celluloses extract from *Trichoderma harzianum* and bio-ethanol production by *S. cerevisiae*.

5.6 Miscellaneous and emerging applications

Agostini et al. [111] have purified various potential peroxidase from roots and hairy root cultures of turnip (*Brassica napus*). They develop a diagnostic test kit for determination of uric acid. This assay was based on the following reaction:

$$\text{Uric acid} + O_2 + 2H_2O \longrightarrow \text{Uricaseallantoin} + H_2O_2 + CO_2$$

$$H_2O_2 + 4\text{−aminophenazone} + \text{phenol} \rightarrow \text{peroxidase } p\text{−(benzoquinone)monoamine−phenazone}$$

MnP produced by the basidiomycetes *Bjerkandera adusta* was used in acrylamide polymerization [112]. Styrene (industrial polymer), which is used for wrapping and transporting goods, unfortunately, when discharged into environment, causes serious pollution in for air, water and soil [113]. With proficient direct electron transfer (DET) properties with electrodes, MnP is also act as redox enzyme. It is used in development of biosensors based on DET, biofuel cell, and in synthesis of bioorganic [114]. MnP showed the mineralization of many environmental pollutants, and these are used in bioremediation process.

Due to their potent ability to degrade various dyes, it degrades 1.1.1-tricholoro-2.2-bis-(4-chlorophenyl) ethane (DDT), 2.4.6-trinitrotoluene (TNT) and polycyclic aromatic hydrocarbons (PAHs) [115–119]. Peroxidase has also many practical analytical important applications in diagnostics kits formation, such as quantification of glucose, lactose, cholesterol, and uric acid.

Versatile peroxidases (EC 1.11.1.16) revealed a hybrid molecular building among LiPs and MnPs [120]. They are not specific for Mn(II) as in 3MnPs, but also catalyze the oxidation of phenolic and non-phenolic substrate such as LiPs, in the absence of Mn [121]. In adverse to class I peroxidases, the class II peroxidases have N-terminal signal peptide, four conserved disulfide bridges and calcium in their structure. Versatile peroxidase can oxidize various substrates under different environmental conditions. These are very interesting enzyme due to the fact that they contain unique active sites that are responsible for direct oxidation of many aromatic compounds, including lignin, in addition to the well-known Mn2 binding active site. Peroxidases including MnP predominantly used in ELISA test, in which it is used for labeling an antibody, are most common and consistent method detecting toxins, cancer risk in prostrate and bladder, and in many other analytes [81]. In addition, there are many other prospective applications of MnP such as the development of biosensors based on direct electron transfer (DET), effective biofuels cells and selective bioorganic synthesis [114]. Iwahara et al. [112] found that *Bjerkandera adusta* is used in polymerization of acrylamide. MnP isolated from *P. chrysosporium* can biodegrade styrene, which is an key polymer used as a raw materials for wrapping and shipping goods; it has polluted aquatic, terrestrial as well as atmospheric air [113].

Qin et al. [27] reported decolorization of many dyes such as Remazol Brilliant Violet 5R, indigo carmine, and methyl green as well as decolorization of textile wastewater by CD2-MnP enzyme. Recently, Xu et al. [35] found that MnP isolated from *G. lucidum* 00679 decolorize/detoxify four dyes such as Drimaren Blue CLBR, Drimaren Red K-4B, Drimaren Yellow X-8GN and Disperse Navy Blue HGL. There are also many bacterial strains, which have been reported for the biodegradation of natural rubber by plate assay method [3].

Castillo et al. [122] observed that MnP extracted from white-rot fungus (*P. chrysosporium*) has great potential to biodegrade bentazon in the presence of Mn(II) and Tween-80. In addition, during in vivo and in vitro experiments Castillo et al. [123] found that MnP isolated from *P. chrysosporium* have potential to degraded isoproturon (herbicide). Jiang et al. [76] reported that MnP activity was enhanced by the addition of hemoglobin (Hb) in fermentation medium for *mnp2* overexpressing in *P. pastoris*. In this experiment, it was speculating that the Hb could be assisted to supply biosynthesis of porphyrin in peroxidases. Pizzul et al. [124] reported that glyphosate (herbicide), which was biodegraded by MnP and laccase extracted from *Nematoloma frowardii* and *T. versicolor* in the presence of substrate ABTS [2.2′-azinobis (3-ethylbenzthiazoline-6-sulfonate)].

Many researchers reported that in wastewater many EDCs are present, which resist during the treatment process, and were removed efficiently by the diverse group of oxidative enzymes [83, 125, 126]. Baborová et al. [46] reported that MnP extracted and purified from *I. lacteus* have significant potential for the degradation of PAHs polychlorinated biphenyls and also several pentachlorophenol. In addition, recently the crude MnP enzyme extracted from *I. lacteus* F17 used for the degradation and detoxification of malachite green dye, which is reported as carcinogenic and mutagenic in nature [38]. In addition, various authors have reported that ligninolytic enzyme has great potential in many biotechnological applications, but unfortunately its lower catalytic efficiencies and its working stabilities limit their practical and versatile applications in many areas of the current industrial use [127–135].

6 Conclusion and future prospects

The microbial MnP remains the subject of demanding focused research for their potential applications in broad range of industrial and other biotechnological applications. This enzyme is present in almost all known bacteria and fungi. The bacterial MnP plays an imperative role in bioremediation of industrial wastes because it oxidizes number of xenobiotics compounds as well as nontoxic substrate and also used in industries like food industry, biosensor designing, paper and pulp, textile and distillery industry, diagnostic kits formation and in environmental protection. MnP is reported to catalyze the oxidation of several types of phenolic and non-phenolic compounds, with the aid of small molecules referred to as mediators. However, in recent years a new field of application for MnP is emerging in the cosmetic industry too, because these enzymes are used especially for the synthesis of flavonoids, pigments, cosmetic dyes as well as aromatic aldehydes and heterocyclic compounds, which are active ingredients in cosmetic products.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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