



Biotechnological Applications of Manganese Peroxidases for Sustainable Management

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Microbial manganese peroxidases (MnPs) are ligninolytic enzymes primarily responsible for degrading lignin, but they are also capable of degrading dyes, organic pollutants, and emerging contaminants in wastewater. They have been isolated and characterized from many white-rot fungi and few bacteria. For microbial MnPs, the optimum pH range is between 3.5 and 9.0; the optimum temperature range is between 25°C and 70°C. Their molecular weights range between 25 kDa and 68 kDa. By oxidizing Mn^{2+} to Mn^{3+} , they can oxidize a wide range of phenolic and non-phenolic substrates. MnPs can be used in a wide range of industrial applications, including delignification of pulp, wastewater treatment, biofuel production, dye removal, biopulping, biobleaching, and juice extract clarification. The purpose of this review is to summarize biotechnological applications of manganese peroxidases.

Keywords: bioethanol, textile dye, bioremediation, biopulping, biobleaching

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INTRODUCTION

Manganese peroxidase (MnP, EC 1.11.1.13) is a H_2O_2 -dependent glycoprotein peroxidase that comprises heme as a cofactor and belongs to the oxidoreductase family. The MnP enzyme is found in most white-rot fungi and some bacteria (Qin et al., 2017). This enzyme was first discovered in the fungus *Phanerochaete chrysosporium* (Paszczynski et al., 1985). The range of its molecular mass is from 25kDa to 68 kDa. Different MnPs exist in nature with different properties. Based on the lengths of their C-terminal tail, MnPs can be classified as short, long, or extra-long types in white-rot fungi (Fernández-Fueyo et al., 2014; Chang et al., 2021). In Agaricales, three different subfamilies of the fungal MnP were described based on residues found in their Mn^{2+} -binding sites: MnP-ESD (Glu/Ser/Asp Mn^{2+} -oxidation site), MnP-DGD (Asp/Gly/Asp Mn^{2+} -oxidation site), and MnP-DED (Asp/Glu/Asp Mn^{2+} -oxidation site) (Chang et al., 2021; Ruiz-Dueñas et al., 2021). Mn^{2+} -binding sites are not unique in MnPs. Those peroxidases, which were originated from MnPs, also contain structures identical to the Mn^{2+} -binding site and can oxidize Mn^{2+} to Mn^{3+} (Ayuso-Fernández et al., 2018; Chang et al., 2021).

MnPs need hydrogen peroxidase and Mn^{2+} for oxidation of various aromatic and phenolic compounds (Bermek et al., 2004; Asgher et al., 2014). MnPs have the greatest capacity for enzymatic actions, and they are extraordinarily flexible in nature with a wide variety of industrial uses (Nayanashree and Thippeswamy, 2015a). MnP has biotechnological applications in the treatment of textile waste effluents (Bilal and Asgher, 2015). Various kinds of environmental pollutants can be found in textile effluents, such as synthetic dye residues that are toxic and can cause cancer. Based on their eco-toxicological properties, textile effluents containing dyes have been extensively studied for their potential ecological hazards (Iqbal and Bhatti, 2014; Bilal and Asgher, 2015). MnP can be used to oxidize aromatic amines and phenolic compounds in wastewater through

TABLE 1 | List of sources and characteristics of fungal MnPs.

Fungal source	Culture medium	Molecular mass (kDa)	Optimum pH	Optimum temperature (°C)	References
<i>Agaricus bisporus</i>	Semi-solid rye bran medium	—	—	—	Hilden et al. (2013)
<i>Penicillium</i> sp. CHY-2	Potato dextrose broth	36	5.0	30	Govarthanam et al. (2017)
<i>Phanerochaete chrysosporium</i> BKM-F 1767	Malt agar plates	—	4.5	37	Urek and Pazarlioglu, (2007)
<i>Bjerkandera</i> sp. BOS55	Basal medium	—	—	—	Mester and Field, (1997)
<i>Trametes versicolor</i>	Czapek-Dox medium	—	—	—	Shi et al. (2021)
<i>Schizophyllum commune</i>	Czapek-Dox medium	—	—	—	Shi et al. (2021)
<i>Anthracoophyllum discolor</i>	Glucose malt extract agar plates	—	—	—	Acevedo et al. (2010)
<i>Phanerochaete chrysosporium</i>	Nitrogen-limited broth medium	—	—	—	Emami et al. (2020)
<i>Pseudolagarobasidium</i> sp. PP17-33	Dye-containing agar plates	—	—	—	Thamvithayakorn et al. (2019)
<i>Penicillium chrysogenum</i>	Mineral salt medium	45	—	—	Nayanashree and Thippeswamy, (2015a)
<i>Galactomyces reessii</i>	Malt extract agar	—	—	—	Chajjak et al. (2018)
<i>Fusarium</i> strain ZH-H2	Mineral salt medium	—	—	—	Zhang et al. (2020)
<i>Irpex lacteus</i> F17	Solid-state fermentation	—	3.5	40	Yang et al. (2016)
<i>Echinodontium taxodii</i> 2,538	Solid-state fermentation	53.4	3.5	55	Kong et al. (2016)
<i>Pleurotus ostreatus</i>	Glucose peptone yeast extract medium	42	—	—	Kamitsuji et al. (2004)
<i>Trametes</i> sp. 48424	Potato dextrose broth (PDB)	49	5.0	70	Zhang et al. (2016)
<i>Cerrena unicolor</i> BBP6	Dye-containing agar plates	45	4.5	60	Zhang et al. (2018)
<i>Bjerkandera adusta</i> strain CX-9	O-dianisidine dihydrochloride-containing potato dextrose agar	30	3.0	70	Bouacem et al. (2018)
<i>Trametes pubescens</i> strain i8	O-dianisidine dihydrochloride-containing potato dextrose agar	55.2	5.0	40	Rekik et al. (2019)
<i>Irpex lacteus</i> CD2	Basal liquid medium	42	5.5	70	Qin et al. (2014)
<i>Schizophyllum commune</i> IBL-06	Banana stalk-containing solid-state fermentation	--	4.5	35	Irshad and Asgher, (2011)
<i>Phanerochaete chrysosporium</i> IBL-03	Wheat straw, rice straw, banana stalks, corncobs, corn stover, and sugarcane bagasse	—	4.5	35	Muhammad et al. (2011)
<i>Ganoderma lucidum</i> IBL-05	Wheat bran-containing solid-state medium	43	5.0	40	Bilal et al. (2015)
<i>Ceriporiopsis subvermispora</i>	Japanese beech and Japanese cedarwood	—	—	30	Tanaka et al. (2009)
<i>Agrocybe praecox</i>	Bark mulch and wood chips	42	4.5	—	Hilden et al. (2014)
<i>Trametes polyzona</i> KU-RNW027 (MnP1)	Kirk's liquid medium containing Remazol brilliant dye	44	4.5	50	Lueangjaroenkit et al. (2019)
<i>Trametes polyzona</i> KU-RNW027 (MnP2)	Kirk's liquid medium containing Remazol brilliant dye	42	4.5	70	Lueangjaroenkit et al. (2019)
<i>Penicillium oxalicum</i> isolate-1	Basal medium	46	5.0	—	Jha and Patil, (2011)

the use of one-electron oxidation and produce more reactive free radicals (Heinzkill et al., 1998). In nature, the MnP enzyme catalyzes the depolymerization of plant lignin and is a constituent of the lignin-degrading enzyme complex. It can degrade lignin most commonly, as well as hemicellulose, cellulose, and lignin in agriculture (Torres and Ayala, 2010). In addition, it can degrade recalcitrant aromatic contaminants, including industrial dyes, polycyclic aromatic hydrocarbons, chlorophenols, and antibiotics, which may be hazardous to human health (Qin et al., 2014). Recently, this enzyme has been widely studied in terms of its potential to perform the wastewater treatment. It can be applied to dye decolorization, biopulping, biobleaching, clarifying juices, bioethanol production, and degradation of various xenobiotic compounds (Asgher and Iqbal, 2013; Nousiainen et al., 2014; Nayanashree and Thippeswamy, 2015b).

MnP is a versatile enzyme with numerous applications in many industries, such as pulp and paper, textile, food, and

biofuel. Only a few review articles have been published on MnP-catalyzed wastewater treatment. Chowdhary et al. (2019) presented an overview of the current scenario on MnPs. Chang et al. (2021) discussed decolorization of textile dyes by MnPs. Currently, their wide range of applications is rarely reviewed. This review discusses the industrial and biotechnological applications of MnPs.

SOURCES OF MnPs

MnPs are produced by fungi and bacteria (Champagne and Ramsay, 2005; Chowdhary et al., 2019). In this section, we described various fungal and bacterial sources of MnPs.

Fungal MnPs

MnPs are produced and characterized from a number of fungi that belong to the class Basidiomycetes (Tello et al., 2000; Dong

et al., 2014). Examples are *Agaricus bisporus* (Hilden et al., 2013), *Irpex lacteus* F17 (Yang et al., 2016), *Trametes* sp. 48424 (Zhang et al., 2016), *Echinodontium taxodii* 2538 (Kong et al., 2016), *Ganoderma lucidum* IBL-05 (Bilal et al., 2015), *Fusarium* sp. strain ZH-H2 (Muhammad et al., 2011), *Agrocybe praecox* (Hilden et al., 2014), *Penicillium* sp. (Oliveira et al., 2009), *Irpex lacteus* CD2 (Qin et al., 2014), *Trametes versicolor* (Shi et al., 2021), *Phlebia radiata* (Hakala et al., 2006), *Ceriporiopsis subvermispora* (Tanaka et al., 2009), *Pleurotus ostreatus* (Kamitsuji et al., 2004), and *Pseudolagarobasidium* sp. PP17-33 (Thamvithayakorn et al., 2019). A list of MnP-producing fungi is presented in **Table 1**.

Fungal MnPs exhibited the highest activity between pH 3.0 and 5.5. The optimum temperature for fungal MnPs is 30–70°C. Immobilization may increase their thermostability. For example, the chitosan-immobilized MnP from *Trichoderma harzianum* exhibited stability at 50°C (El-Shora et al., 2017). A fungal MnP has a molecular weight ranging from 36 kDa to 55.2 kDa. *Penicillium chrysogenum* produces MnP with a molecular weight of 45 kDa that is used in the degradation of natural rubber (Nayanashree and Thippeswamy, 2015a). *Galactomyces reessii* a subterranean termite-associated yeast species was used for phenol removal from palm oil mill effluents due to its MnP and laccase activities (Chaijak et al., 2018). The MnP from *Bjerkandera adusta* strain CX-9 named MnP BA30 showed high solvent stability and dye decolorization efficiency (Bouacem et al., 2018). Similarly, *Trametes pubescens* strain i8 produced MnP TP55 with a molecular weight of 55.2 kDa, which could be used to produce cleaners, decolorize textile dyes, and degrade lignin (Rekik et al., 2019). *Trametes polyzona* KU-RNW027 produced two MnPs which play essential roles in biodegradation of dyes and pharmaceutical products (Lueangjaroenkit et al., 2019). The main disadvantages of fungal MnPs are their low yields and poor stability.

Bacterial MnPs

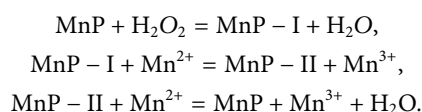
A number of advantages of bacterial MnPs over fungal MnPs have emerged in recent years from the industrial point of view, including their ability to work in wide ranges of temperatures and pH with a high stability toward inhibitory agents, easy production in a short period of time, broad substrate specificity, and ease of cloning and expression in host cells with appropriate manipulation (Chauhan et al., 2017; Xu et al., 2018). Examples of MnP-producing bacteria include *Bacillus subtilis* (Nayanashree and Thippeswamy, 2015b), *B. amyloliquefaciens* SL-7 (Mei et al., 2020), *B. aryabhatai* (Zainith et al., 2019), *B. cereus* 11778 (Khelil et al., 2015), and *Lactobacillus kefir* (Omar et al., 2021). For bacteria, MnPs show their optimum activity between pH 5.0 and 9.0. For bacterial MnPs, the optimum temperature ranges from 25 to 70°C. The molecular weight of bacterial MnPs ranges from 25 kDa to 68 kDa. Recently, *Bacillus velezensis* AI-Dhabi 140 produces MnPs of 46 kDa that could degrade tetracycline antibiotic using the fibrous bed reactor (Al-Dhabi et al., 2021). The MnPs from *Klebsiella pneumoniae* strains have been utilized in the manufacturing of ethanol using rice and wheat bran biomass as substrates (Gaur et al., 2018). A list of MnP-producing bacteria is summarized in **Table 2**.

CRYSTAL STRUCTURE OF MnP

The crystal structure of MnP refined at 0.93 Å resolution is presented in **Figure 1**. The active site of MnP is composed of one heme propionate and the side chains of Glu35, Glu39, and Asp179 (Sundaramoorthy et al., 2010). Two calcium ions are essential components of MnP that provide thermal stability. In MnPs, five disulfide bridges are present to stabilize them, which are formed by 10 cysteine amino acid residues (Chang et al., 2021). Heme propionate is found in the internal hydrophobic cavity of the enzyme, and Mn²⁺ binds to the center of the active site. As a resting-state structure, MnP contains a penta-coordinated Fe³⁺ structure integrated with the porphyrin ring of the heme cofactor and a proximal histidine (Chang et al., 2021). At the distal end, a catalytic His and an Arg residue form a peroxide-binding pocket (Sundaramoorthy et al., 2010). This structure is highly conserved among heme peroxidases. Minor variations are due to the Phe residues that are Trp in intercellular peroxidases, cytochrome c, and ascorbate peroxidase (Chang et al., 2021). The Asp242–His173 pair is also conserved (Sundaramoorthy et al., 2010).

CATALYTIC MECHANISM OF MnP

The catalytic cycle of MnP begins when the heme group of MnP transfers two electrons to hydrogen peroxidase in its resting state, resulting in the production of water and compound I (Hofrichter, 2002). In the next step, compound I oxidizes Mn²⁺ and produces compound II, a free radical, and Mn³⁺. Compound II then catalyzes the oxidation of Mn²⁺ to form Mn³⁺, allowing MnP to revert to its original form (**Figure 2**). These catalytic biochemical reactions of MnP are summarized as follows:



FACTOR AFFECTING PRODUCTION AND ACTIVITY OF MnPs

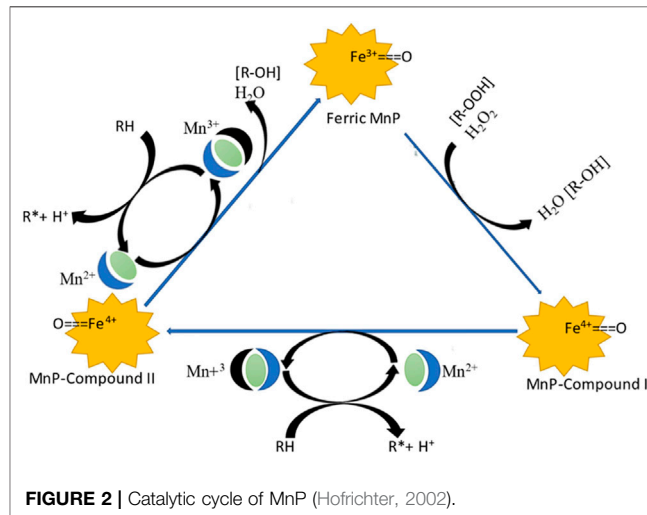
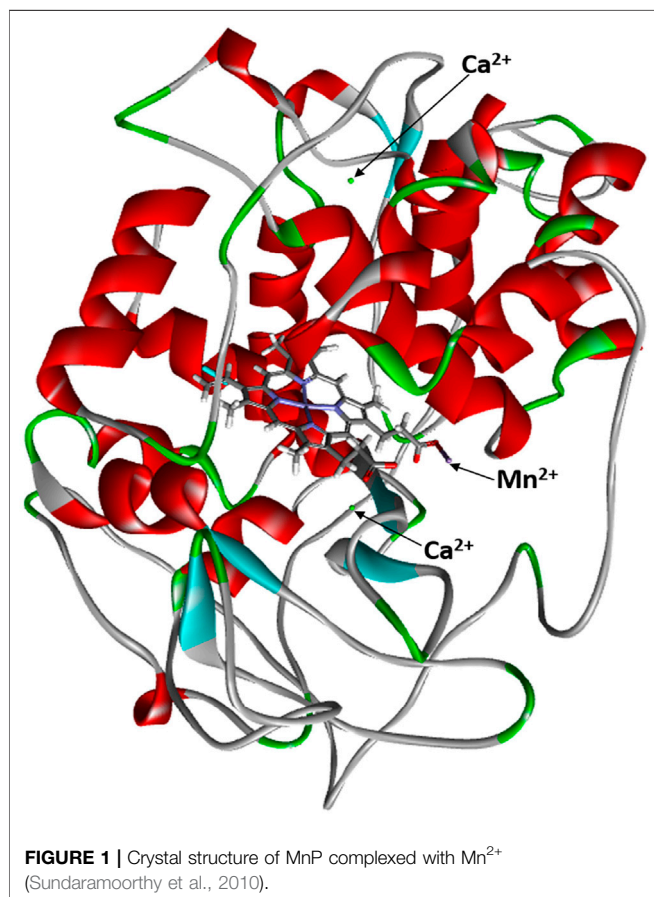
The growth conditions and culture media composition influence the gene expression and total enzyme activity of microbial MnPs (Zhang et al., 2021). It varies from species to species and strain to strain. In this section, we described the effect of various factors on the MnP's activity and production.

Effect of Carbon Sources

MnP is likely to be produced more efficiently with appropriate carbon sources. Glycerol and walnut pericarp, for example, provided the highest MnP activity compared to other carbohydrates (such as glucose, xylose, and sucrose) in *Cerrena unicolor* (Zhang et al., 2021). In contrast, in *Phanerochaete chrysosporium*, glucose is the preferred carbon source (Urek and Pazarlioglu, 2007; Zhou et al., 2013). The most

TABLE 2 | List of sources and characteristics of bacterial MnPs.

Bacterial source	Culture medium	Molecular mass (kDa)	Optimum pH	Optimum temperature (°C)	References
<i>Bacillus amyloliquefaciens</i> SL-7	Lignin-containing special medium	—	—	—	Mei et al. (2020)
<i>Klebsiella pneumoniae</i> strains	Lignin basic medium	48	5.0	70	Gaur et al. (2018)
<i>Bacillus</i> sp. R2	Waste newspaper	—	—	—	Khellil et al. (2015)
<i>Bacillus cereus</i> 11778	Waste newspaper	—	—	—	Khellil et al. (2015)
<i>Salmonella enterica</i>	Glucose peptone yeast medium agar plates	—	8.1	37	Kumar and Chandra, (2018)
<i>Enterobacter aerogenes</i>	Glucose peptone yeast medium agar plates	—	8.1	37	Kumar and Chandra, (2018)
<i>Enterobacter cloacae</i>	Glucose peptone yeast medium agar plates	—	8.1	37	Kumar and Chandra, (2018)
<i>Bacillus velezensis</i> strain Al-Dhabi 140	Minimal medium containing tetracycline	46	7.0	35	Al-Dhabi et al. (2021)
<i>Lactobacillus kefir</i>	Melanoidin modified glucose peptone yeast medium	—	—	—	Omar et al. (2021)
<i>Bacillus aryabhatai</i>	Lignin amended mineral salt medium	—	—	—	Zainith et al. (2019)
<i>Acinetobacter iwoffii</i>	Mineral salt medium lignin agar plate	—	—	—	Ayeronfe et al. (2019)
<i>Lysinibacillus</i> sp	Mineral salt medium (MSM) lignin agar plate	—	—	—	Ayeronfe et al. (2019)
<i>Bacillus subtilis</i>	Mineral salt medium	68	—	—	Nayanashree and Thippeswamy, (2015b)
<i>Bacillus</i> sp	Mineral salt medium lignin agar plate	—	—	—	Ayeronfe et al. (2019)
<i>Bacillus pumilus</i> CBMAI 868	Medium containing birch-wood xylan	25	8.0	25	Oliveira et al. (2009)
<i>Paenibacillus</i> sp. CBMAI 868	Medium containing birch-wood xylan	40	9.0	35	Oliveira et al. (2009)



effective carbon source for the MnP enzyme activity in *Trichoderma harzianum* is sucrose rather than any other carbon source.

Effect of Nitrogen Sources

High nitrogen concentration in the medium suppresses the MnP activity of several fungal species, including *P. chrysosporium* (Leatham and Kirk, 1983; Janusz et al., 2013). In contrast, higher amounts of MnP are produced in *P. ostreatus* and *Trametes trogii* in the presence of high concentration of nutrient nitrogen (Levin et al., 2002; Levin et al., 2010).

Meanwhile, MnP from *Dichomitus squalens* cultures is secreted under both high- and low-nitrogen conditions (Perie and Gold, 1991). The nitrogen source also effects the production and activities of MnPs. The optimum production of MnP by four *Pleurotus* species occurred using $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 as the inorganic nitrogen source (Stajić et al., 2006). The enzyme activity of *Trichoderma harzianum* is optimum when yeast extract is used as a nitrogen source (El-Shora et al., 2017). As a nitrogen source, peptone has been shown to be extremely effective in MnP production under solid state fermentation by many fungi including *Cerrena unicolor* strain IBB 62, *Bjerkandera adusta*, *Bjerkandera* sp. strain BOS55, *Lentinus edodes*, *P. ostreatus*, and *P. chrysosporium* (Kaal et al., 1995; Elisashvili et al., 2001; Janusz et al., 2013).

Effect of Metal Ions

Increases in Mn^{2+} ions in the culture medium enhance the production of the MnP enzyme by activating the transcription of the *mnp* gene (Urek and Pazarlioglu, 2007; El-Shora et al., 2017). MnP of *Trametes* sp. 48424 is strongly resistant to metal ions such as Ni^{2+} , Li^+ , Ca^{2+} , K^+ , and Mn^{2+} (Zhang et al., 2016), whereas Mn^{2+} , Ca^{2+} , Co^+ , Cu^{2+} , Li^+ , and K^+ enhance the production of MnP BA 30 of the *Bjerkandera adusta* strain CX-9 (Bouacem et al., 2018). The activity of MnP TP55 of *Trametes pubescens* strain i8 is induced by Mn^{2+} , Fe^{2+} , Cu^{2+} , and Mg^{2+} whereas it was completely inhibited by Cd^{2+} , Ni^{2+} , and Hg^{2+} (Rekik et al., 2019).

Effect of Synthetic Inducers and Hydrogen Peroxide (H_2O_2)

Synthetic inducers such as Tween 80 when added in low quantities into the growth medium stimulate the enzyme activity in comparison to control by increasing the surface area for the microbial growth (Urek and Pazarlioglu, 2007; Muhammad et al., 2011). The initial concentration of hydrogen peroxide increases the MnP activity whereas the latter exerts the inhibitory effect on the MnP enzyme activity (Vrsanska et al., 2015; Rekik et al., 2019).

Effect of Phenylmethylsulphonyl Fluoride

Phenylmethylsulphonyl fluoride (PMSF), an inhibitor of serine protease, when supplemented to a growth medium suppresses the protease production that participates in the regulation of the MnP activity, resulting in inhibiting the MnP activity (Urek and Pazarlioglu, 2007).

Effect of Inhibitors

Sodium azide, L-cysteine, sodium sulfate, β -mercaptoethanol, potassium cyanide, ethylenediaminetetraacetic acid (EDTA), sodium dodecyl sulfate (SDS), and hydroxylamine have inhibitory effects on enzyme activity (Kong et al., 2016; Bouacem et al., 2018; Gaur et al., 2018; Rekik et al., 2019). Sodium azide can break the disulfide bonds that maintain the active site of the enzyme. SDS removes the hydrophobic interactions that are present in protein, resulting in the degradation of tertiary and quaternary structures. EDTA, a

chelating agent of metals, has the property to form complexes with complex or metal ions, resulting in the decreased activity of the enzyme.

Effect of Organic Solvents

Enzyme activity decreases with the increase in the concentration of organic solvents such as methanol, ethanol, DMSO, ethylene glycol, iso-propyl alcohol, butanediol, and glycerine (Kong et al., 2016; Liu et al., 2020).

Effect of Chelators

Chelators such as oxalate, malate, malonate, and lactate are added to the growing media; these chelators stabilized the Mn^{2+} ions by chelating them, hence increasing the MnP enzyme activity (El-Shora et al., 2017).

Effect of pH and Temperature

The MnP enzyme is affected by temperature and pH. MnPs from different species and strains of microorganisms responded differently to temperature and pH. Each MnP has its own optimal temperature and pH range.

BIOTECHNOLOGICAL APPLICATIONS OF MnPs

MnPs may degrade several toxic dyes, antibiotics, phenolic compounds, and polycyclic aromatic hydrocarbons under peroxide-dependent conditions, making them a better biocatalyst for the biodegradation of harmful environmental pollutants in wastewater (Singh et al., 2021). In addition, MnPs may be used for delignification of lignin, clarifying juices, and bioethanol production. In this section, various applications of MnPs are summarized.

MnP-Mediated Textile Dye Decolorization

MnPs act as biocatalysts for decolorizing dyes in wastewater. Several MnPs have been purified and characterized for their ability to decolorize dyes. Two MnPs isolated from *Trametes polyzona* KU-RNW027 degraded Remazol brilliant blue (25 mg/L) in 10–30 min and showed high degradation activities toward Remazol navy blue and Remazol brilliant yellow (Lueangiaroenkit et al., 2019). Both of these MnPs were found to be highly stable and were activated by various organic solvents and metal ions. Rekik et al. (2019) purified the MnP (named MnP TP55) from the fungus *Trametes pubescens* strain i8. Several types of dyes were degraded using MnP TP55, including anthraquinone dyes (Remazol Brilliant Blue Reactif and Cibacet Brilliant Blue BG), triphenylmethane dye (methyl green), indigo dye (indigo carmine), azo dyes (Direct Red 5B and Remazol Brilliant Violet 5R), polymeric dye (Poly R-478), and acid dye (Acid Blue 158). The degradation efficiency of MnP TP55 varied from dye to dye and ranged from 42 to 95% when the dye concentration was 50 μM . Emami et al. (2020) studied the effects of various stabilizers including manganese (IV) dioxide (MnO_2), veratryl alcohol (VA), dimethyl sulfoxide (DMSO), polyethylene glycol (PEG), and iron (III) oxide (Fe_2O_3) on production, stability, and

decolorization efficiency of MnP produced by *Phanerochaete chrysosporium*. The Fe₃O₄-containing calcium alginate beads increased MnP production by 67%. Furthermore, PEG and DMSO boosted the decolorization efficiency of MnP toward Acid Orange 7 and crystal violet. Gomathy et al. (2021) reported that MnP produced by an alkaliphilic bacterial strain *Pseudomonas mendocina* was able to degrade mixed azo dyes at alkaline pH. Furthermore, immobilization of this alkaline MnP with the Luffa fibers increased the dye decolorization efficiency. Bouacem et al. (2018) reported that MnP from *Bjerkandera adusta* strain CX-9 (called MnP BA30) decolorized various dyes including indigo carmine, Remazol Brilliant Violet 5R, Remazol Brilliant Blue Reactif, Poly R-478, Cibacet Brilliant Blue BG, and Acid Blue 158 dyes with decolorization percentages of 42, 70, 38, 80, 77, and 91 within 12 h. In Mn²⁺-independent processes, MnPs from *Bjerkandera adusta* strain DSM 11310 and *Pleurotus eryngii* strain ATCC 90787 decolorized four azo and two phthalocyanine dyes by their direct interaction with the dye (Heinfling et al., 1998).

MnP-Mediated Biopulping and Biobleaching of Pulp in the Paper Industry

MnPs may reduce the amount of lignin components and chemicals in the paper industry wastewater through the process of biopulping and pulp biobleaching.

Biopulping is the process of treating wood chips with lignin-degrading fungus or MnPs before pulping. By pre-treating the composted wood with fungi before mechanical pulping, we can reduce electrical energy consumption during the refining process, improve paper strength, and reduce pitch (extractives) content, thereby reducing the environmental impact of the pulping process (Viikari et al., 2009). In biopulping, MnPs from white-rot fungi can be used to degrade lignin partially and loosen lignin structures. Jha and Patil (2011) demonstrated that MnP obtained from *Penicillium oxalicum* isolates-1 was effective in de-lignifying paper pulp and kraft liquor.

Biobleaching is the process of bleaching pulps with enzymes or lignolytic fungi, thereby reducing the quantity of the chemical bleach required (Kumar, 2021). Chemicals such as H₂SO₄, Cl₂, ClO₂, NaOH, and H₂O₂ are used during bleaching (Kumar, 2021). By reacting with lignin and carbohydrates, these chemicals generate a substantial amount of pollutants in bleach effluents. The pulp and paper industry generates high-strength, dark brown-colored wastewater during various stages of the paper-making process which is discharged into the environment.

In addition to reducing the level of lignin within the pulp, MnPs are generally used in pulp and paper industries as biobleaching agents. Kaneko et al. (1995) reported biobleaching of oxygen-alkaline-treated hardwood kraft pulp using a fungal MnP. In the presence of Tween 20, ISO brightness was improved by five points, while without Tween 20, ISO brightness did not improve significantly. Tween 20 could prevent mechanical inactivation of MnP caused by agitation or reduce the absorption of enzymes that would result in enzyme inactivation. Kondo et al. (1994) reported bleaching of hardwood

kraft pulp using MnP from fungus *Phanerochaete sordida* YK-624 in the presence of MnSO₄, Tween 80, and sodium malonate. In comparison to the untreated pulp, the brightness of the pulp increased by approximately 10 points, and the Kappa number decreased by approximately six points. In addition, multiple MnP treatments increased pulp brightness by 43 points to 75.5%. Harazono et al. (1996) investigated effects of various manganese chelators (oxalate, malonate, or gluconate) on MnP-mediated bleaching of hardwood kraft pulp, and they concluded that the brightness of the pulp was increased by about 10 points when oxalate was present in 2 mM. To enhance the bleaching effect of MnP on pulp, Bermek et al. (2002) investigated the effects of a large number of organic compounds such as organic acids, thiol-containing compounds, and their combinations on pulp bleaching. The pulp bleaching effect of linoleic acid, linolenic acid, and some unsaturated fatty acids was better than that of Tween 80. The bleaching power of MnP pulp was higher when Tween 80 and carboxylic acid were combined. Masarin et al. (2016) investigated the degradation of lignin in milled *Eucalyptus grandis* wood and kraft pulp by MnP from the fungus *Ceriporiopsis subvermispota*. The MnP-mediated elemental chlorine-free bleaching of eucalyptus kraft pulp resulted in a reduction of 3.7 kg/ton of ClO₂, with an increase in ISO brightness from 88 to 90 points. MnP produced by *Trametes versicolor* during pulp bleaching, demethylates and delignifies kraft pulp and oxidizes mainly the phenolic lignin structures (Paice et al., 1993). Sasaki et al. (2001) developed a chlorine-free pulp-biobleaching system using MnP immobilized with mesoporous silica. There was 88% improvement in brightness when MnP treatment and pulp bleaching were performed in a two-stage reactor at temperatures of 39°C and 70°C, respectively.

By biobleaching of pulp, pulp can be of higher quality without using chlorine-based chemicals in large amounts (Kumar, 2021). When pulp is pretreated with MnPs, the kappa number of the pulp is reduced, and brightness is improved. Biobleaching of pulp has also resulted in improved physical strength properties and pulp viscosity (Kumar, 2021).

MnP-Mediated Delignification of Lignin

Lignin and lignin-like compounds are either discharged from agricultural waste or from the pulping and paper-making industries into water (De los Santos Ramos et al., 2009). Lignin is the second most abundant organic material after cellulose. It occurs in combination with other carbohydrates such as hemicellulose and cellulose at the cell wall level. It is a polymer with a high molecular mass, which makes it resistant to degradation by diverse types of microorganisms in the environment (Wang et al., 2011). Chemically, lignin is a heterogeneous polymer with phenylpropanoid units that are connected *via* a variety of linkages, e.g., carbon-carbon, aryl-aryl, and aryl-ether (Mohammad et al., 2020). In addition, lignin may be used as a feedstock for the production of chemical compounds such as substituted aromatics (Ragauskas et al., 2006). This type of valorization would require controlled depolymerization of lignin, which is hampered by its high level of resistance to biodegradation (Martinez et al., 2005). There are a

variety of lignin degradation methods, such as pyrolysis, hydrogenation, and selective oxidation, as well as degradation under hydrothermal and supercritical conditions (Ma et al., 2015; Dai et al., 2016). Nevertheless, many of these processes are hazardous, environmentally unfriendly, and require large amounts of energy (Ward and Singh, 2002). Most of the processes use expensive chemical catalysts containing metals such as molybdenum or palladium (Chauhan, 2020). Therefore, it is essential to find a cheap and eco-friendly method for bioremediation or degradation of lignin. Hence, microbial enzymes appear to be a better and more suitable alternative to be used in these methods to solve the problems mentioned earlier. By using enzymes specific to their substrate, the selectivity of reactions can be increased and byproducts can therefore be minimized (Janusz et al., 2017; Chauhan, 2020). White-rot fungi have received extensive attention in recent years for their ability to degrade lignin through MnPs.

Pretreatment of lignin by biological means (microorganisms or MnPs) is an emerging method for biodelignification. In these methods, either fungi or bacteria are directly applied to the lignin treatment, or MnPs are used in enzymatic treatments. The white-rot fungi depolymerize lignin more efficiently than bacteria. Examples of lignin-depolymerizing fungi are *Trametes pubescens* strain i8 (Rekik et al., 2019), *Pleurotus ostreatus* (Kamitsuji et al., 2004), *Echinodontium taxodii* 2538 (Kong et al., 2016), *Phanerochaete chrysosporium* IBL-3 (Muhammad et al., 2011), *Trametes versicolor* (Shi et al., 2021), and *Schizophyllum commune* (Shi et al., 2021). Delignification is highly variable, depending on the species of fungi and the carbohydrates in the lignocellulose raw material (Suryadi et al., 2022). Although microorganism-mediated pretreatment boasts numerous advantages, it is still plagued with problems such as lengthy processing times, large space requirements, and regular monitoring of microbial growth (Suryadi et al., 2022).

In contrast to using fungi directly, MnP-mediated degradation of lignin has several advantages (Suryadi et al., 2022). These include the ability to overcome challenges related to large-scale growth, long incubation processes, penetration of the mycelium into the substrate, excessive polysaccharide consumption which causes carbohydrate degradation, and contamination issues. MnPs can be used for direct lignocellulose treatment, which minimizes the problems encountered in fungal pretreatment. Due to its ability to operate in a short reaction time, it only requires a few hours, and it requires fewer nutrients for enzymatic reactions; this method is well-suited for further exploration (Suryadi et al., 2022).

MnP-Mediated Fruit Juice Clarification

MnP is crucial in fruit juice clarification to decompose phenolic compounds. The use of MnP in the clarification of fruit juices showed its future utility in food and beverage processing. Manavalan et al. (2015) reported clarification of various fruit juices using a solvent-tolerant MnP isolated from *Ganoderma lucidum*. They reported that pomegranate, lemon, and apple juices pretreated with MnP exhibited significant reductions in phenolic compounds up to 89, 85, and 78%, respectively. Immobilization of MnP may increase its stability and

effectiveness in clarifying juices. For example, Bilal et al. (2016) used gelatin-immobilized MnP to de-bitter apple juice by reducing the color by 42.7%, as well as reducing turbidity by 36.3%. Moreover, Bilal et al. (2017a) found that treating apple, grape, orange, and pomegranate juices with an immobilized ligninolytic enzyme reduced turbidity by 84.02%, 57.84%, and 82.13%, respectively.

MnP-Mediated Bioethanol Production

Agricultural wastes (e.g., wood, straw, alfalfa, switch grass, and sugarcane bagasse) are raw materials for production of bioethanol due to presence of carbohydrates. The carbohydrates must be converted into simple sugars (glucose) before they can be fermented into ethanol. Since lignin and cellulose are present in these agri-wastes, pretreatment with lignolytic enzymes such as laccase and MnPs is a pre-requisite for ethanol production. Asgher et al. (2014) pre-treated biomass of wheat straw with ligninolytic enzymes including MnPs, laccase, and lignin peroxidase and produced 22.6 g/L of ethanol through sequential saccharification and fermentation (SSF) using *Saccharomyces cerevisiae*. Bilal et al. (2017b) observed that *S. cerevisiae* was able to synthesize bioethanol from de-lignified newspaper waste using ligninolytic enzymes from *Ganoderma lucidum* IBL-05 followed by saccharification using cellulose extract from *Trichoderma harzianum*. Gaur et al. (2018) produced bioethanol from wheat and rice bran biomass using the ligninolytic enzymes of *Klebsiella pneumoniae* strains.

MnP-Mediated Oxidation of Phenolic and Non-Phenolic Compounds

MnPs may degrade phenolic and non-phenolic compounds in wastewater. Kong et al. (2016) isolated MnP from *Echinodontium taxodii* and tested its ability to oxidize three phenols and three non-phenols present in lignin. It was observed that MnP degrades three lignin phenolic compounds more effectively than non-phenolic compounds. MnP degraded phenolic compounds 4-hydroxy-3-methoxy cinnamic acid, 4-hydroxy cinnamic acid, and 4-hydroxy-3,5-dimethoxy cinnamic acid by 97.79, 28.35, and 99.92%, respectively. The degradative rate of n-cinnamic acid, 3-methoxy cinnamic acid, and 3,5-dimethoxycinnamic acid were 26.19, 30.03, and 44.84% for MnP, respectively.

MnP-Mediated Degradation of Mycotoxins

MnP catalyzed the degradation of mycotoxins in foods. Wang et al. (2019) studied degradation of four major mycotoxins (aflatoxin B1, zearalenone, deoxynivalenol, and fumonisin B1) by the eight MnPs, which belong to four lignocellulose-degrading fungi (five from *Irpex lacteus*, one from *Phanerochaete chrysosporium*, one from *Ceriporiopsis subvermisporea*, and another from *Nematoloma frowardii*). MnP-mediated mycotoxin degradation is only possible in the presence of a dicarboxylic acid malonate, where free radicals play a major role. MnPs from *C. subvermisporea* and *I. lacteus* transformed mycotoxins similarly, outperforming those from *P. chrysosporium* and *N. frowardii*. The ability to degrade multiple mycotoxins is

not exclusive to any one MnP but is shared by many MnPs with different sequences.

RECOMBINANT MnPs AND THEIR APPLICATIONS

Recombinant MnPs are constructed to improve their stability, efficiency, and yields using both homologous and heterologous expression systems. The MnP-coding genes of various white-rot fungi were isolated, and then, they were cloned into the appropriate vectors and expressed in the appropriate host strains. An example of this is the MnP gene cloned from *Ganoderma lucidum* 00679 (GluMnP1), which was expressed in *Pichia pastoris* SMD1168H. This recombinant MnP (r-GluMnP1) was capable of degrading four dyes and phenol (Xu et al., 2017). Similarly, Zhang et al. (2020) expressed the MnP gene from *Cerrena unicolor* BBP6 in *Pichia pastoris* X33 to produce recombinant MnP (rMnP3-BBP6) that plays a significant role in denim bleaching and dye decolorization. Cortés-Espinosa et al. (2011) expressed the MnP gene (*mnp1*) from *Phanerochaete chrysosporium* in *Aspergillus niger* SBC2-T3. This recombinant fungus degraded phenanthrene. Lee et al. (2016) expressed MnP genes from *Peniophora incarnata* KUC8836 in *Saccharomyces cerevisiae* and confirmed that the recombinant yeast had improved anthracene degradation. Liu et al. (2020) cloned a MnP gene from *Aspergillus* sp. TS-A and expressed it in *Pichia pastoris* GS115. Recombinant MnP (GS115-MnP) was more efficient at degrading dyes. Chen et al. (2015) expressed the MnP gene (*imnp*) from *Irpex lacteus* F17 in *Escherichia coli* Rosetta (DE3). Recombinant MnP exhibited improved pH stability and dye degradation efficiency.

Pech-Canul et al. (2020) used a new approach to obtain a functional recombinant MnP1 (rMnP1) from *P. chrysosporium* (Chang et al., 2021). A chemically synthesized *mnp1* gene was

cloned into a pTXB1 vector using NdeI/SapI restriction sites and then transferred into *Escherichia coli* DH5 α cells. The rMnP1 was expressed as a fusion protein, which was recovered from inclusion bodies and was then purified by intein-based protein purification techniques followed by affinity chromatography.

CONCLUSION AND FUTURE PROSPECTS

MnPs were isolated and characterized from a variety of white-rot fungi and bacteria and play a significant role in decolorizing dyes, bio-pulping, pulp biobleaching, removing mycotoxins, making ethanol, de-lignifying lignin, and clarifying fruit juices. It was possible to produce recombinant MnPs in large quantities with improved stability, production, and degradation efficiency. The immobilization of MnPs also improved their stability and capability.

Delignification of various lignocellulose materials using purified MnPs should be further investigated. The application of MnPs in dye decolorization and wastewater treatment should be carried out on a large scale. Genetic engineering should be used to develop more efficient MnPs in order to increase biodegradability. The CRISPR/Cas9-mediated genome editing in microorganisms may be used in order to improve industrial applications of MnPs.

AUTHOR CONTRIBUTIONS

AK wrote the manuscript, and PKA checked and edited it.

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