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Review

White-rot fungi-mediated bioremediation as a sustainable method for xenobiotic degradation

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Abstract

Xenobiotics are hazardous compounds that are foreign to natural ecosystems. The production and use of xenobiotic compounds continue to increase worldwide, which in turn causes environmental pollution and has adverse effects on humans. Degradation of such compounds, therefore, needs urgent awareness and attention. The physicochemical approaches to treat the contaminants are expensive. Bioremediation is a concept that exploits organisms to manage the environment with less manpower and time. White-rot fungi-mediated bioremediation offers inexpensive, environmentally sustainable and potential degradation mechanisms for different recalcitrant chemicals. White-rot fungi secrete lignolytic enzymes that have extensive substrate specificities and are involved in the transformation and solubilization of lignin-like structural contaminants. The main lignolytic enzymes occurring in white-rot fungi are laccases, lignin peroxidase, manganese peroxidase, and other peroxidases. Such lignolytic enzymes permit white-rot fungi to endure high toxic levels. This review describes the opportunities to use white-rot fungi and their enzyme systems in the biodegradation of multiple xenobiotic contaminants.

Key words: biodegradation, lignolytic enzymes, mycoremediation, white-rot fungi, xenobiotics.
Abbreviations: BTEX, benzene, toluene, ethylbenzene and xylene; DyP, dye-decolourizing peroxidase; LiP, lignin peroxidase; MnP, manganese peroxidase; PAHs, polyaromatic hydrocarbons; PCBs, polychlorinated biphenyls; PCPs, pentachlorophenols; TNT, 2,4,6-trinitrotoluene; YMG, yeast-malt-glucose

Introduction

Xenobiotics are toxic chemicals that are exotic to living organisms and have an affinity to persist in the biosphere (Sinha et al. 2009). These compounds have synthetic chemical composition, and species have not adapted to these in evolution (Gren 2012). The residues of xenobiotic substances persist in the ecosystem over a long period and have negative effects on the microflora and the fertility of the soil (Gianfreda, Rao 2008). Therefore, polluting the environment with recalcitrant chemicals, which often are xenobiotics, is one of the major environmental issues with global focus and recognition (Tišma et al. 2010). The pollution created by xenobiotics disrupts natural ecosystems, causes changes in climatic conditions, reduces water levels and has other negative impacts (Gursahani, Gupta 2011). The main sources of xenobiotics enter into the environment from pharmaceutical industries (ibuprofen, paracetamol), agriculture (pesticides, herbicides, insecticides), the paper industry (paper and pulp effluent), food industry (food additives such as vinegar, lecithin), plastic industry (polyvinyl chloride), consumer industry (coatings, dyes) and petroleum industries (benzene, xylene) (Mishra et al. 2019). Humans are exposed to xenobiotics through inhalation, adsorption by skin (cosmetic products) or ingestion (medicines, vegetables, fruits). They can cause severe health hazards such as heart defects, neurodegeneration, defects in the central nervous system and adverse reproductive problems. Hence, xenobiotic degradation in the environment is essential (Phale et al. 2019).

Physico-chemical approaches involved in the control of organic pollutants include ion exchange, chemical flocculation, adsorption, irradiation, oxidation, precipitation and ozonation (Aksu 2005). The physico-chemical approaches are very costly and often yield adverse intermediate metabolites that are harmful and need further secondary treatment. To overcome these, several other environmentally friendly processes have been described, such as bioremediation, phytoremediation, etc. (Varsha et al. 2011). Bioremediation is a technology in which biological organisms (algae, bacteria, fungi and plants) are employed to minimize the accumulation and harmfulness of environmental contaminants (Gnanasalomi et al. 2013). Xenobiotic microbial depletion is an effective strategy for eliminating toxic pollutants from the environment.

The ability of microorganisms to break down xenobiotic substances is considered an important means of removing toxic materials (Sridevi et al. 2011). Some fungi are resilient organisms compared to bacteria and are typically less susceptible to high levels of pollutants. This is why fungi were extensively studied regarding their bioremediation capabilities in the mid-1980s (Ellouze, Sayadi 2016).

Fungi play a crucial role in all environments including soil and marine habitats as decomposers and symbionts. They are especially suitable for bioremediation because of their robust morphological structure and various biochemical capabilities. Mycoremediation is a component of bioremediation that employs fungus for intrinsic and extrinsic management of polluted areas. Mycoremediation is a cost-effective and environmentally reliable option for removing, transporting and storing hazardous waste. Mycelia may destroy these contaminants within the soil before they move through food chains (Ramachandran, Gnanadoss 2013). Further, attention has been given to the distinct ability of fungi to remove these contaminants by using a variety of extracellular and intracellular enzyme systems for detoxification and bioremediation (Deshmukh et al. 2016). The objective of this review paper is to emphasize the significant properties of white-rot fungi in degrading different xenobiotic compounds like polymers, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pentachlorophenols (PCPs), antibiotics, 2,4,6-trinitrotoluene (TNT), benzene, toluene, ethylbenzene and xylene (BTEX), pesticides and dyes.

White-rot fungi

White-rot fungi possess the remarkable ability to biodegrade lignin and hence the name white-rot comes from the white surface of timber invaded by white-rot fungi, where the evacuation of lignin gives a faded impression (Pointing 2001). Systematically, white-rot fungi include specific basidiomycetes, and very few ascomycete families like Xylariaceae are associated with white-rot decay (Eaton, Hale 1993). The utilization of fungi for the cleaning of contaminated soil was initially demonstrated during the mid-1980s, when the white-rot fungus *Phanerochaete chrysosporium* was found to degrade a high diversity of natural contaminants (Bumpus, Aust 1987). This ability was later exhibited for diverse species such as *Trametes versicolor* and *Pleurotus ostreatus* (Ghani et al. 1996), *Lentinus subnudus* (Adenipekun, Fasidi 2005), *Psathyrella candolleana* LCJ 178 and *Myrothecium gramineum* LCJ 177 (Gnanasalomi, Gnanadoss 2013), *Porostereum spadiceum* (Tigini et al. 2013), *Pleurotus floridanus* LCJ155, *Leucocoprinus cretaceous* LCJ164, and *Agaricus* sp. LCJ169 (Jebapriya, Gnanadoss 2014), *Dentipellis* sp. (Park et al. 2019), *Ganoderma lucidium* (Coelho-Moreira et al. 2018) and *Bjerkandera adusta* (Dhiman et al. 2020). White-rot fungi degrade all timber components, for example, cellulose, hemicellulose and lignin, whereas other fungi destroy lignin predominantly. The former is called a non-selective white-rot degraders and the latter are known as specific white-rot degraders. The specific white-rot degraders are extremely intriguing from the biotechnology perspective as they remove lignin leaving the lucrative cellulose unaltered (Dashtban et al. 2010). Potential benefits of using white-rot fungi to remove ecological contaminants are due to their ubiquitous existence, ability to break down assorted classes of destructive foreign substances and to adjust the pH of their characteristic substrate (Christian et al. 2005).

Enzyme systems in white-rot fungi

White-rot fungi usually produce one or multiple lignolytic enzymes in various amounts, on the basis of which they can be divided into four classes (Nerud, Misurcova 1996) namely: (a) laccase, manganese peroxidase (MnP) and lignin peroxidase (LiP), (b) laccase and any of the peroxidases, (c) laccases only, (d) peroxidases only. The most widely recognized lignolytic enzymes present in white-rot fungi incorporate laccases and MnP and the least common are LiP and versatile peroxidase. These lignolytic enzymes can work together or independently, yet additional enzymes like glyoxal oxidase, aryl alcohol oxidase, cellobiose dehydrogenase, pyranose 2-oxidase, and others are fundamental to accomplish the cycle of lignocellulose or xenobiotic degradation. In addition, an intracellular enzyme cytochrome P450 monooxygenase and low molecular weight oxidants like hydroxyl radicals and Mn^{3+} were demonstrated to be powerful in eliminating lignocellulosic materials and various xenobiotics. Recently, dye decolourising peroxidase (DyP), which is involved in the decolouration of dyestuffs, and aromatic peroxygenases has been found to be associated in catalysis of oxygen transfer reactions that bring about the ester cleavage, is also recognized as a lignolytic enzyme that corresponds with white-rot fungi (Rodríguez-Couto, 2016).

Laccase

Laccase is a copper protein that has its position in blue oxidases. Copper, which occurs at the dynamic site of the enzyme, plays an integral role in catalytic reactions. The catalytic center of the enzyme consists of four copper atoms. Laccase catalyzes four single electron oxidations of the substrate into four electron reductive bond cleavages. Degradation of various aromatic mixtures can be catalyzed by an associative reduction of oxygen to water. Moreover, in the presence of key substrates [2,20-azinobis-3-ethylbenzothiazoline-6-sulphonicacid or 1-hydroxybenzotriazole] working as electron transfer mediators, the substrate spectrum is further extended to degrade non-phenolic mixtures (Kılıç et al. 2016). Laccase was first recognized in 1883 by Yoshida, when he separated the exudates from *Rhus vernicifera* (Thurston 1994).

They are derived from natural sources and often occur in plants and microorganisms (Dwivedi et al. 2011) and also in a few insects (Xu 1999). Fungal sources of laccase have been isolated from different groups of fungi like deuteromycetous, ascomycetous and basidiomycetous. Of these, white-rot fungi and other litter degrading organisms are the most prominent sources of the laccase enzyme. In specific, laccase production by basidiomycetous taxa such as *Trametes, Pleurotus, Agaricus, Phanerochaete, Pycnoporus*, and *Lentinus* has been broadly explored as they are easy to grow in *in vitro* (Rodríguez-Couto, 2019). White-rot fungal species that synthesize laccase are *Polyporus sanguineus, Phlebia brevispora, Daedalea flavida* and *Phlebia radiata* (Arora, Gill 2001), *Phanerochaete chrysosporium, Trametes hirsuta, Marasmius* sp. and *Trametes versicolor* (Risdianto et al. 2012), *Pleurotus florida, Pleurotus ostreatus* and *Pleurotus sajor-caju* (Radhika et al. 2013), *Agaricus* sp. LCJ262 (Jose, Joel 2014), *Trametes orientalis* (Zheng et al. 2017), *Cerrena unicolor* strain GSM-01 (Wang et al. 2017), and *Myrothecium gramineum* LCJ 177 (Gnanasalomi, Gnanadoss 2019). Laccases from white-rot fungi are associated with lignin removal and are resilient at different pH and temperatures. High purity of laccase can be obtained by suitable optimizing parameters (Gnanasalomi, Gnanadoss 2013). Laccase-mediator methods have enormous potential for lignin removal, biosensor application, biofuel and organic synthesis, bioremediation of some toxic chemical wastes, pharmaceutical and nanobiotechnology applications (Singh, Gupta 2020).

Lignin peroxidase

LiP is a heme enzyme from the oxidoreductase family, which is primarily secreted by white-rot basidiomycetes during the formation of secondary metabolites. LiP plays a key part in removing the lignin portion of the plant cell wall. LiP assists in the biodegradation of lignin and other phenolic molecules with H_2O_2 as a substrate and veratryl alcohol as a mediator (Singh et al. 2019). LiP has been reported in various white-rot fungi like *Coriolus versicolor* f. *antarcticus* (Levin et al. 2004), *Phanerochaete chrysosporium* (Wang et al. 2008), *Ganoderma lucidium* (Sasidhara et al. 2014), *Pleurotus ostreatus, Pleurotus sapidus, Pleurotus florida* (Kunjadia et al. 2016), *Porodaedalea pini* (Tanabe et al. 2016), *Podoscypha elegans* (Agarwal et al. 2017), *Coriolopsis gallica, Pleurotus sajor-caju* and *Lentinula edodes* (Ding et al. 2019). LiP is exploited for numerous industrial uses and bioremediation processes due to its immense substrate specificity and high redox potential (Erden et al. 2009).

Manganese peroxidase

As LiP, MnP is also placed under the same family of oxidoreductases described in *Phanerochaete chrysoporium* as another lignolytic enzyme (Paszczyńskib et al. 1985). MnP seems to more prevalent in white-rot fungi than LiP (Hammel, Cullen 2008). In contrast to LiP, MnP has a low redox potential and oxidizes the compounds with H_2O_2 performing as oxidant and manganese performing as a mediator in the MnP catalytic process. The function of MnP is the conversion of Mn^{2+} ions to Mn^{3+}. Mn^{3+} is extremely reactive and chelates with biomolecules such as oxalate and malate formed by the fungus (Shanmugapriya et al. 2019). Chelated Mn^{3+} stimulates the degradation of phenolic compounds to phenoxy radicals (Hofrichter 2002). A few examples of MnP from white-rot fungi are *Bjerkandera* sp. (Mester, Field 1997), *Irpex flavus, Polyporus sanguineus* and *Dichomitus squalens* (Gill, Arora 2003), *Physisporinus rivulosus* (Hakala et al. 2005), *Pleurotus ostreatus, Coriolus versicolor* and *Phlebia tremellosa* (Robinson et al. 2011), *Cerrena unicolor* (Zhang et al. 2018) and *Pseudolagarobasidium* sp. (Thamvithayakorn et al. 2019). MnP finds wide applications in the industries such as food, textile, paper and pulp industries, pharmaceutical and bioremediation (Singh et al. 2019).

Versatile peroxidase

Versatile peroxidase is a hybrid peroxidase that comprises the catalytic activities of MnP and LiP (Dosoretz, Reddy 2007). Similar to MnP, it have a strong affinity for Mn^{2+} and initiates the conversion of Mn^{2+} to Mn^{3+} and it also metabolizes non-phenolic and phenolic molecules without Mn^{2+} like LiP. This enzyme seems to be expressed mostly in fungal genera such as *Pleurotus, Bjerkandera*, and *Lepista* and may also be present in *Panus* and *Trametes* (Yadav, Yadav 2015). Versatile peroxidase has distinctive characters compared to other lignolytic peroxidases and is suitable for utilization in various applications like the paper and pulp industry, biofuel production, ruminant nutrition, bioremediation, and the textile industry (Ravichandran, Sridhar 2016).

Dye-decolourising peroxidase

DyP is a novel group of heme peroxidases that were molecularly identified and are well-known in bacteria and fungi. They lack structural and sequence resemblances with traditional flora and fauna peroxidases. As the name specifies, DyP can use H_2O_2 to detoxify different groups of azo and anthraquinone-based artificial dyes, substrates that are less susceptible to oxidation by members of other classical heme peroxidases. Also, specific DyP were described to oxidize compounds of the phenol lignin type, thus providing the enzymatic ability for this category of heme peroxidase to support the transformation of lignocellulosic materials for downstream production of biofuel (Chaplin et al. 2019). DyP was initially identified from *Bjerkandera adusta* culture (formerly reported as *Geotrichum candidum*) (Fernández-Fueyo et al. 2015). DyP producing white-rot fungi include *Termitomyces albuminosus* (Johjima et al. 2003), *Pleurotus ostreatus* (Faraco et al. 2007), *Marasmius scorodonius* (Pühse et al. 2009), A*uricularia auricula-judae* (Liers et al. 2010),

Exidia glandulosa, Mycena epipterygia (Liers et al. 2013), *Irpex lacteus* (Salvachúa et al. 2013), *Funalia trogii* (Kolwek et al. 2018), *Trametes versicolor* (Amara et al. 2018), and *Pleurotus sapidus* (Krahe et al. 2020).

Cytochrome P450 monooxygenase

Cytochrome P450 monooxygenase is a main intracellular enzyme that fits the class of oxygenases that helps in the degradation of xenobiotics via oxygen. They also have heme-comprising enzymes that incorporate one or several oxygen molecules to break down aromatic rings and even stabilize the compound (Baker et al. 2019). The importance of cytochrome P450 monooxygenase mechanisms in detoxification of endogenous and exogenous molecules has been shown (Ichinose et al. 2013). Increased removal of PAHs was achieved by the initial application of cytochrome P450 monooxygenase in degradation experiments. Improved elimination of contaminants was obtained through molecular methods for efficient and oversupply of cytochrome P450 enzyme (Deshmukh et al. 2016).

Xenobiotic degradation process by white-rot fungi

The capability of white-rot fungal species in eliminating xenobiotic compounds from ecosystems is dependent on their ability to biodegrade lignin, as it is close to the structure of different xenobiotics (Fig. 1). Therefore, the identical methodologies that provide white-rot fungi the potential to degrade lignin are being used to remove a large range of xenobiotic contaminants. Most of the xenobiotics

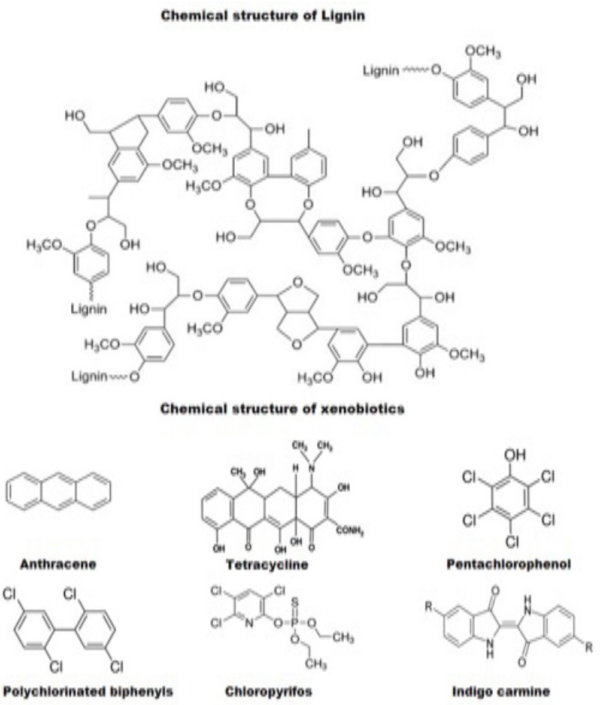

Fig. 1. Structure of lignin in comparison with the chemical structure of diverse xenobiotic compounds.

are oxidized and mineralized to various sizes using white-rot fungi under the lignolytic conditions (Field et al. 1993). The xenobiotic degradation process is shown in Fig. 2.

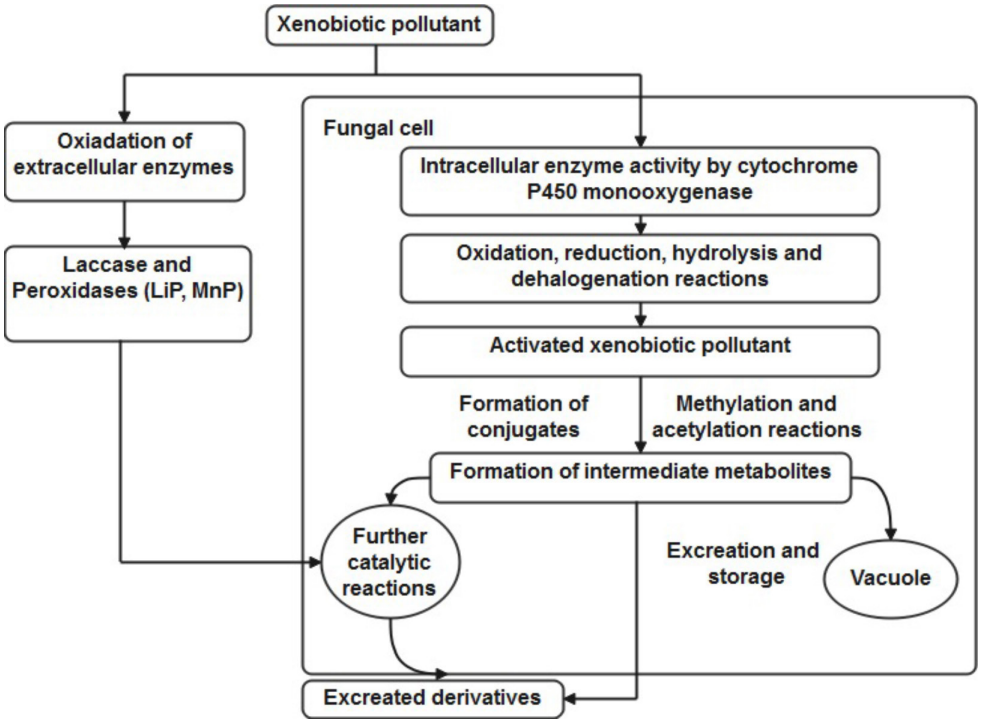

Fig. 2. Schematic diagram representing the degradation mechanism of xenobiotic compounds using white-rot fungi.

Applications of white-rot fungi in xenobiotic degradation

Degradation of polymers using white-rot fungi

Plastic is typically a polymer that is composed of various elements such as carbon, hydrogen, silicon, oxygen, chloride and nitrogen (Seymour 1989). Linking the monomers using chemical bonds forms plastic. Polythene contains about 64% of plastic, a continuous hydrocarbon polymer comprising elongated strands of ethylene monomers. The overall equation for polyethylene is C_nH_2n, where *n*, represents the total number of carbon molecules (Sangale et al. 2012). The worldwide usage of plastic is rising rapidly at a rate of 12% per year and approximately 0.15 billion units of synthetic materials are developed globally every year (Das, Kumar 2014). Every year, the ecosystem accumulates 25 million metric tons of polymer waste (Kaseem et al. 2012).

Biodegradation of many synthetic polymers with different chemical compositions has been reported, but several of them involved degradation using white-rot fungi-mediated lignin enzymes (Pointing 2001). Nylon-6 polymer degradation initially using white-rot fungus *Bjerkandera adusta* has been described (Friedrich et al. 2007). Synthetic materials including polyvinyl chloride, nylon, acrylamide, etc. that are degraded by different white-rot fungi have been documented (Kale et al. 2015). Removal of biopolymers like lignin, hemicellulose and cellulose is also possible by white-rot fungi. In comparison to other groups of microorganisms, lignin removal through white-rot fungi is more promising (Woiciechowski et al. 2013). *Phellinus pini, Phanerochaete chrysosporium, Phlebia* sp., *Pleurotus* sp., *Heterobasidion annosum, Ceriporiopsis subvermispora, Irpex lacteus* and *Trametes veriscolor* are specific white-rot fungi that preferably invade lignin more effectively than cellulose and hemicellulose. They secrete different classes of lignolytic enzymes that facilitate the degradation of aromatic organic compounds, producing aromatic radicals, and modify the structure of lignin- and lignocellulose-derived products (Andlar et al. 2018). Study on the oxidation of the biopolymer lignin from the paper industry was conducted to determine the capacity for degradation by five white-rot fungi (*Lentinus edodes, Pleurotus ostreatus, Trametes versicolor, Phanerochaete chrysosporium* and S22). Among these five isolates, three white-rot fungi (*Phanerochaete chrysosporium, Pleurotus ostreatus* and S22) showed a high level of lignin degradation at pH 9.0 to 11.0 (Wu et al. 2005).

Degradation of PAHs using white-rot fungi

PAHs are organic substances that mostly lack colour or are pale yellow solids. They are an omnipresent class of many chemically related compounds that persist in the environment with complex structures and toxicity (Abdel Shafy et al. 2016). Some white-rot fungi including BKM-F-1767, *Bjerkandera adusta* CBS 595.78, *Trametes versicolor* Paprican 52, *Phanerochaete chrysosporium* and *Trametes versicolor* has been tested for ability to degrade hydrocarbons (Field et al. 1992). All white-rot fungi significantly degraded anthracene, as well as nine of the strains effectively degraded benzo(a)pyrene. Of those, *Bjerkandera* sp. Bos 55 seems to be new species and was deemed an effective degrader of anthracene (99.2 %) and benzo(a)pyrene (83.1%) molecules within 28 days respectively. The genus *Phanerochaete* and *Bjerkandera* transformed anthracene into anthraquinone, which is an end metabolite. Further, this analysis showed *Trametes* sp. degraded anthracene with no substantial accumulation of quinone (Field et al. 1992).

The removal of PAHs by means of white-rot fungi is affected by temperature, the composition of the medium, dissolved oxygen and soil moisture content (Chen et al. 2005). The biological removal of PAHs such as phenanthrene, fluorine and pyrene was achieved using thermotolerant *Trametes polyzona* RYNF13. This fungus exhibited PAH degradation at 100 mg L^{-1}. Complete removal of phenanthrene was detected in mineral salt glucose medium at 30 °C after an incubation period of 18 days while 52% of pyrene and 90% of fluorine could be removed under similar conditions. This fungus is still capable of surviving at a high temperature of about 42 °C and degrades phenanthrene (68%), fluorine (48%) and pyrene (30%) respectively within 32 days. Thus, this strain has potential for PAH degradation specifically in the tropical area where even air temperature can be more than 40 °C (Teerapatsakul et al. 2016). It was shown that the most efficient laccase-producing white-rot fungi *Pycnoporus sanguineus* can remove phenanthrene (45.6%) and benz(a)anthracene (90.1%) in *in vivo* conditions (Li et al. 2018). They also transformed phenanthrene into 2-dibenzofuranol by the cytochrome P450 monooxygenase enzyme or 9,10-phenanthrenedione through extracellular laccase and benz(a)anthracene into benz(a)anthracene-7,12-dione through extracellular laccase. Various PAHs that are degraded by diverse white-rot fungi are represented in Table 1.

Degradation of PCBs using white-rot fungi

PCBs are widespread organic molecules that were used as coolant liquids in transformers and electric motors during the 20th century (Borja et al. 2005). Although their application and production were prohibited in the last decade, they survive in ecosystems and lead to severe consequences for living organisms (Colvin, Nelson 1990). Eaton (1985) was the first researcher to study PCBs (Aroclor® 1254 mixture) degradation using *Phanerochaete chrysosporium*. In this experiment, Aroclor® 1254 was mineralized into CO_2 with the removal of water-soluble organic compounds and irreversible attachment to cells. The results obtained have been validated by the absence of gas chromatographic peaks.

Table 1. Degradation of various PAHs by different white-rot fungi

PAH compounds	White-rot fungi	Reference
Acenapthene	*Phanerochaete chrysoporium*	Bishnoi et al. 2008
Anthracene	*Pleurotus ostreatus, Coriolopsis polyzona, Phanerochaete chrysosporium, Trametes versicolor*	Vyas et al. 1994
	Trametes pocas, Trametes cingulate	Tekere et al. 2005
	Irpex lacteus	Baborová et al. 2006
	Anthracophyllum discolor	Acevedo et al. 2011
Chrysene	*Bjerkandera* sp.	Valentin et al. 2007
	Polyporus sp.	Hadibarata et al. 2009
	Pleurotus ostreatus	Nikiforova et al. 2010
	Pleurotus sajor-caju	Saiu et al. 2018
Dibenzothiophene	*Coriolopsis gallica*	Bressler et al. 2000
	Bjerkandera sp.	Valentin et al. 2007
	Agrocybe aegerita, Coprinellus radians	Aranda et al. 2009
Fluoranthene	*Bjerkandera* sp.	Valentin et al. 2007
	Phanerochaete chrysosporium	Bishnoi et al. 2008
	Pleurotus pulmonarius	Wirasnita, Hadibarata 2016
Fluorene	*Agrocybe* sp.	Chupungars et al. 2009
	Pleurotus eryngii	Hadibarata, Kristanti 2014
	Polyporus sp.	Lazim, Hadibarata 2016
	Trametes sp.	Zhang et al. 2016
	Ganoderma sp.	Torres-Farradá et al. 2019
Napthalene	*Phlebia lindtneri*	Mori et al. 2003
	Trametes versicolor	Bautista et al. 2010
	Armillaria sp.	Hadibarata et al. 2012
	Pleurotus ostreatus	Sukor et al. 2012
	Pleurotus eryngii	Hadibarata et al. 2013
	Ganoderma sp.	Torres-Farradá et al. 2019
Phenanthrene	*Trametes versicolor*	Han et al. 2004
	Bjerkandera sp..	Terrazas-Siles et al. 2005
	Phanerochaete chrysoporium	Bishnoi et al. 2008
	Anthracophyllum discolor	Acevedo et al. 2011
	Ganoderma lucidum	Agarwal et al. 2018
	Pycnoporus sanguineus	Li et al. 2018
Pyrene	*Dichomitus squalens, Pleurotus* sp..	Martenz, Zadrazil 1996
	Phlebia brevispora	Lee et al. 2016
	Coriolopsis brysina	Agarwal, Shahi 2017
	Pleurotus sajor-caju	Saju et al. 2018
Quinoloine	*Pleurotus ostreatus*	Zhang et al. 2007

PCB congener degradation by *Ceriporia* sp. was carried out by Hong et al. (2012). In this analysis, four PCB congeners (4,4'-dichlorobiphenyl, 2,2',4,4',5,5'-hexachloro-biphenyl, 2,3',4',5-tetrachlorobiphenyl and 2,2',4,5,5'-pentachloro-biphenyl) were examined. The biodegradation rate of 4,4'-dichlorobiphenyl on the 13th day was reported to be around 34.03% whereas the biodegradation rate of 2,2',4,4',5,5'-hexachlorobiphenyl on the 17th day was nearly 40.05%. This shows that extremely chlorinated biphenyls can be reduced by *Ceriporia* sp. The immobilized laccase obtained from *Coprinus comatus* on wood biochar from diverse species can degrade chlorinated biphenyl in wastewater (Li et al. 2018). *Pleurotus ostreatus, Trametes versicolor, Phlebia brevispora, Pycnoporus cinnabarinus*, and *Pleurotus sajor-caju* are few other white-rot fungi explored for PCBs degradation.

Degradation of PCPs using white-rot fungi

PCPs are lethal compounds that extensively occur in the industrial output of pesticides and wood preservatives (Czaplicka 2004). The usage of PCPs was forbidden in several countries owing to their high toxicity in the late 1980s but still, they are used in a few countries. The harmfulness of pentachlorophenol has been broadly reported as a recalcitrant and global pollutant in the soil and water (Varela et al. 2017). Degradation of PCPs is

achieved in three ways: via oxygenolysis, hydroxylation or reductive dehalogenation (Field, Sierra-Alvarez 2008). Fungal remediation of PCPs gained interest in the last forty years. White-rot fungi can degrade PCPs and transform the respective PCPs compounds through methylation and dechlorination reactions. PCPs degradation under both lignolytic and non-lignolytic conditions using three white-rot fungi (*Trametes* sp., *Pleurotus* sp., and *Phanerochaete chrysosporium*) were studied (Ryu et al. 2000). The activity of lignolytic enzymes was detected in *Pleurotus* and *Trametes* cultures, but not in *Phanerochaete chrysosporium*. This proves that PCP degradation can be carried out in two conditions (lignolytic and non-lignolytic) using white-rot fungi. *Phlebia acanthocystis*, a white-rot fungus, was capable of degrading 100% and 76% of PCPs (25 µM concentration) in low nitrogen as well as potato dextrose broth culture media, respectively, during incubation for approximately 10 days (Xiao, Kondo 2020).

The reduction of PCPs in *Phlebia acanthocystis* culture is followed by the production of two metabolites (*p*-tetrachlorohydroquinone and pentachloroanisole) through oxidative metabolism. The metabolism of both molecules is closely linked to *Phlebia acanthocystis* extracellular enzymes. Further, the breakdown of PCPs to p-tetrachlorohydroquinone is carried out by cytochrome P450 monooxygenase (Xiao, Kondo 2020). The white-rot fungi with ability to degrade PCPs are *Trametes versicolor* (Walter et al. 2004), *Anthracophyllum discolor* (Rubilar et al. 2007), *Bjerkandera adusta, Fomes fomentarius, Ganoderma applantum, Pleurotus ostreatus*, and *Laetiporus cincinnatus* (Ramesh, Pattar 2009) and *Phlebia acanthocystis* (Xiao, Kondo 2020).

Degradation of TNT using white-rot fungi

TNT is often utilized as an explosive by the military and can cause pollution to soil and water at TNT production and storage sites. It is mutagenic and harmful to many organisms in that environment. Based on animal studies, TNT can be a carcinogen for humans (Honeycutt et al. 1996). Most of the white-rot fungi can convert TNT to dinitrotoluenes and further, result in mineralization to CO_2 (Pointing 2001). TNT degradation (50 mg L^{-1}) was studied using seven white-rot species in two different media: yeast-malt-glucose (YMG) medium and nutrient-rich YMG medium (Kim, Song 2000). The degradation rate was higher in nutrient-rich YMG medium than in the limited nutrient YMG medium. Hydroxylamino-dinitrotoluene isomers have been recognized as the first TNT metabolites to be detected and these compounds are converted into amino-dinitrotoluenes during further incubation. It was observed that TNT (90 mg L^{-1}) was degraded in nutrient broth during 21 days by four white-rot fungal species: *Phanerochaete chrysosporium* (67%), *Phanerochaete sordida* (87%), *Phlebia brevispora* (90%), and *Cyathus stercoreus* (94%). The TNT degradation from culture was evaluated by high-performance liquid chromatography and the cytotoxicity of pollutants in the medium was calculated by *Salmonella*/microsome bioassay. This study showed that white-rot fungi can degrade and detoxify TNT compounds in aerobic conditions in non-lignolytic nutrient broth (Donnelly et al. 1997). TNT degradation was examined by several other white-rot fungi like *Irpex lacteus* (Kim, Song 2003), *Hypholoma fasciculare* (Perkins et al. 2005), *Trametes versicolor* (Cheong et al. 2006), *Kuehneromyces mutabilis*, and *Stropharia* sp. (Serrano-González et al. 2018).

Degradation of BTEX compounds using white-rot fungi

BTEX compounds like benzene, toluene, ethylbenzene, and xylenes are a vital class of organic contaminants that are constituents of petroleum fuels and they are often used in various industries as industrial solvents (Smith 1990). The first study of white-rot fungi degradation of BTEX compounds was reported by Yaddav, Reddy (1993). Waste mushroom biomass from *Ganoderma lucidum* and *Pleurotus ostreatus* was used as a substrate (10%) to decontaminate Esfahan Oil Refinery's petroleum hydrocarbon contaminated soil (Mohammadi-Sichani et al. 2019). Petroleum hydrocarbons at the contamination site were oxidized by waste mushroom biomass of *Pleurotus ostreatus* (69.5%) as well as *Ganoderma lucidum* (57.7%) and also reduced the soil toxicity in 3rd month respectively. BTEX compound degradation using white-rot fungi has been less explored.

Degradation of antibiotics using white-rot fungi

Antibiotics are substances that help to treat communicable diseases in animals, humans, cattle and aquacultures around the globe. The discharge of a high proportion of vaccines into water sources and soil creates a potential threat to all microbes in these surroundings (Cycoń et al. 2019). The production of antibiotics is continuously increasing and their usage has extended from 100 000 to 200 000 tons worldwide (Gelband et al. 2015). Almost all antibiotics are not entirely processed in humans and animal bodies. A large number of therapeutic drugs are discharged into soil and water bodies by community wastewater, livestock manure, sludge from sewage and nitrogenous wastes that are often used to irrigate and enhance farmlands (Bouki et al. 2013). Usually, the traditional treatment process is not effective in treating many pharmaceutical products (Heberer 2002). The white-rot fungi-mediated bioremediation technique is therefore a simple and economical method to eliminate antibiotics.

An in vitro study was conducted on use of LiP obtained from *Phanerochaete chrysosporium* for the removal of two drugs (carbamazepine and diclofenac) that are commonly found in water bodies. It showed that the LiP entirely removed diclofenac at pH 3.0 to 4.5 and 3 to 24 ppm H_2O_2. The efficacy of carbamazepine degradation is generally below 10% (Zhang, Geißen 2010). A study on ciprofloxacin degradation using *Pleurotus ostreatus* (Singh et al. 2017) showed that the highest degradation rate occurred at

a concentration of 500 ppm due to maximum enzyme production. The degradation rate of ciprofloxacin after 14 days of culture at this concentration was evaluated by three assays: titrimetric (68.8%), indigo carmine (94.25%) and methyl orange (91.34%). Elimination of ciprofloxacin was additionally demonstrated by high-performance liquid chromatography, which showed 95.07% degradation and the microbiological experiment exhibited reduced biological activities of degraded products against pathogenic bacteria i.e. *Staphylococcus aureus, Escherichia coli* and *Streptococcus pyogenes. Trametes hirsuta* efficiently degraded higher concentrations of chloramphenicol (10 mg L^{-1}) in the existence of a laccase mediator system like syringaldehyde, vanillin, 2,20-azinobis-3-ethylbenzothiazoline-6-sulphonic acid and α-naphthol. The availability of mediators enhanced the degradation percentage from 10 to 100% during 48 h. Liquid chromatography mass spectrometry confirmed the chloramphenicol degradation. The production of chloramphenicol aldehyde after the breakdown was non-pathogenic to microorganisms (Navada, Kulal 2019). Magnetic cross-linked enzyme aggregates of *Cerrena* laccase have been demonstrated to be effective in the biodegradation of antibiotics such as tetracycline, oxytetracycline, ampicillin, sulfamethoxazole and erythromycin (Yang et al. 2017). For example, at 40 U mL^{-1} *Cerrena* laccase removed tetracycline antibiotic (100 μg mL^{-1}) at pH 6 and temperature at 25 °C during 48 h without redox mediators. Numerous studies revealed that white-rot fungi have the potential to degrade antibiotics (Table 2).

Degradation of pesticides using white-rot fungi

In modern-day farming, pesticide application is more common to increase crop produce and reduce post-harvest losses (Hai et al. 2012). About 5% of applied pesticides exterminate the specific pest organisms whereas the remnants pass through surface and groundwater (Nawaz et

Table 2. Degradation of different antibiotics by various white-rot fungi

Antibiotics	White-rot fungi	Reference
Amoxicillin	*Trametes polyzona*	Lueangjaroenkit et al. 2019
Ampicillin	*Verticillium leptobactrum*	Kumar et al. 2013
Carbamazepine	*Trametes versicolor*	Hata et al. 2010a
	Phanerochaete chrysosporium	Zhang, Geißen 2010
	Stropharia rugosoannulata, Gymnopilus luteofolius, Ganoderma lucidum, Irpex lacteus, Agrocybe erebia	Castellet-Rovira et al. 2018
Chloramphenicol	*Trametes hirsuta*	Navada, Kulal 2019
Ciprofloxacin	*Trametes versicolor*	Prieto et al. 2011
	Pleurotus ostreatus	Singh et al. 2017
	Ganoderma lucidum	Chakraborty, Abraham 2017
	Pycnoporus sanguineus, Phanerochaete chrysosporium	Gao et al. 2018
	Xylaria longipes	Rusch et al. 2018
Dichlofenac	*Phanerochaete sordida*	Hata et al. 2010b
	Trametes trogii, Phanerochaete chrysosporium	Aracagök et al. 2018
	Pleurotus ostreatus	Chapple et al. 2019
Erythromycin	*Trametes versicolor, Bjerkandera adusta*	Aydin et al. 2016
Ibuprofen	*Trametes versicolor, Irpex lacteus, Ganoderma lucidum, Phanerochaete chrysosporium*	Marco-Urrea et al. 2009
Lamotrigine	*Pleurotus ostreatus*	Chefetz et al. 2019
Naproxen	*Trametes versicolor*	Borràs et al. 2011
Norfloxacin	*Trametes versicolor*	Prieto et al. 2011
	Irpex lacteus, Panus tigrinus, Dichomitus squalens, Pleurotus ostreatus	Čvančarová et al. 2015
	Ganoderma lucidum	Chakraborty, Abraham 2017
Ofloxacin	*Trametes hirsute*	Haroune et al. 2014
	Trametes versicolor, Irpex lacteus, Panus tigrinus, Dichomitus squalens, Pleurotus ostreatus	Čvančarová et al. 2015
Sulfamethoxazole	*Phanerochaete chrysosporium*	Guo et al. 2014
	Pleurotus ostreatus, Pleurotus pulmonarius, Trametes sp.	de Araujo et al. 2017
	Trametes versicolor	Alharbi et al. 2019
Tetracycline	*Phanerochaete chrysosporium*	Wen et al. 2009
	Trametes versicolor	Suda et al. 2012
	Cerrena sp.	Yang et al. 2017
	Pycnoporus sp.	Tian et al. 2020

al. 2011). The existence of agropesticides in the biosphere has becomes a threat to flora, fauna, microbes and humans (Hussain et al. 2015). The removal of lindane pesticides was accomplished by *Cyathus bulleri* and *Phanerochaete sordida*. Among these two species, *Cyathus bulleri* degraded more effectively than *Phanerochaete sordida*. During the time of degradation, two degradable intermediate metabolites (tetrachlorocyclohexene and tetrachlorocyclohexanol) were observed in *Phanerochaete sordida* culture. Tetrachlorocyclohexanol was the first detected degradation product in *Cyathus bulleri* culture (Singh, Kuhad 2000). Bending et al. (2002) studied the degradation potential of nine white-rot fungi against monoaromatic pesticides like diuron, metalaxyl, atrazine or terbuthylazine in liquid culture. The highest level of pesticide degradation was reported in *Hypholoma fasciculare, Stereum hirsutum* and *Coriolus versicolor*. The rate of degradation of terbuthylazine, diuron and atrazine was 86% while for metalaxyl the degradation rate was below 44%. The capability of three *Phlebia* species to degrade dieldrin and aldrin was also examined (Xiao et al. 2011). After 42 days of treatment, the three *Phlebia* sp. could degrade approximately 50% of dieldrin in a low nitrogen medium. Three oxidized products were identified as dieldrin metabolites in *Phlebia* species; oxidation reactions might play an effective role in removing dieldrin. Further, aldrin showed high degradation activity and after 28 days of culture, 90% of aldrin was degraded. Transformed metabolites (two carboxylic acid products and 9-hydroxyaldrin) were identified in the fungal cultures. This showed that the methyl group of pesticides such as aldrin and dieldrin might be susceptible to oxidative attack by white-rot fungi. Clothianidin pesticide degradation was tested using *Phanerochaete sordida* in nitrogen-limited broth. Approximately 37% of clothianidin was degraded at 30 °C after an incubation period of 20 days. N-(2-chlorothiazol-5-yl-methyl)-N'-methylurea was the transformed metabolite during clothianidin degradation, identified by analyzing the supernatant culture with high-resolution electrospray ionisation mass spectrometry and nuclear magnetic resonance (Mori et al. 2017). Some common pesticides that are degraded by various white-rot fungi are shown in Table 3.

Degradation of dyes using white-rot fungi

Artificial dyes are broadly exploited in various industries like food, cosmetics, pharmaceutical, textiles and leather, etc. (Couto 2009). From 1856, over 105 different dyes have been produced globally with a yearly production of about 7×10^5 metric tons (Chen et al. 2003). Globally, approximately 28 000 tons of textile dyestuffs are released into textile industrial effluent each year (Jin et al. 2007). Unprocessed dye effluents in water bodies cause severe environmental and health threats (Shedbalkar et al. 2008). Developing a cost-effective biological method to remove synthetic colours is essential.

White-rot fungi are a class of fungi that synthesize

Table 3. Degradation of different pesticides by various white-rot fungi

Pesticide	White-rot fungi	Reference
Atrazine	*Pleurotus pulmonarius*	Masaphy et al. 1996
	Anthracophyllum discolor	Elgueta et al. 2016
Carbofuran	*Phlebia* sp., *Irpex lacteus*	Li et al. 2020
Chlorpyrifos	*Phlebia* sp., *Lenzites betulinus, Irpex lacteus*	Wang et al. 2020
Clothianidin	*Phanerochaete sordida*	Mori et al. 2017
Dichlorophen	*Bjerkandera adusta*	Davila-Vazquez et al. 2005
Dichlorophenoyacetcid	*Lentinula edodes*	Tsujiyama et al. 2013
	Lentinus crinitus	Serbent et al. 2020
Diuron	*Agrocybe semiorbicularis, Auricularia auricola, Flammulina velupites, Dichotomitus squalens, Coriolus veriscolor, Hypholoma fasciculare, Phanerochaete velutina, Pleurotus ostreatus, Stereum hirsutum*	Bending et al. 2002
	Ceriporia lacerata, Phanerochaete chrysosporium, Phanerochaete sordida, Trametes versicolor	Mori et al. 2018
Endrin	*Phlebia acanthocystis, Phlebia brevispora*	Xiao, Kondo 2019
Fipronil	*Trametes versicolor*	Wolfand et al. 2016
Lindane	*Cyathus bulleri, Phanerochaete sordida*	Singh, Kuhad 2000
	Ganoderma australe	Dritsa et al. 2005
	Pleurotus ostreatus	Papadopoulou et al. 2006
	Ganoderma lucidum	Kaur et al. 2016
Parathion	*Bjerkandera adusta, Pleurotus ostreatus, Phanerochaete chrysosporium*	Jauregui et al. 2003
1,1'-(2,2,2-Trichloroethane-1,1-diyl)bis(4-chlorobenzene) (DDT)	*Phlebia lindineri, Phlebia brevispora*	Xiao et al. 2011

enzymes able to decompose dyes in aerobic conditions (Nozaki et al. 2008). They produce several oxidoreductases that can biodegrade lignin and their associated aromatic compounds. The capacity for dye degradation differs for fungal species and enzymes (Nyanhongo et al. 2002). Four different mechanisms are involved in the decolouration of dye using white-rot fungi: biodegradation, biosorption, bioreactor and immobilized lignin modified enzymes (Jebapriya, Gnanadoss 2013). The biosorption mechanism involves the adsorption of dyes by fungal biomass. However, dye removal by adsorption was found to be restricted to 50% (Knapp et al. 2001). Biodegradation has a key role in dye decolourization, as it secretes extracellular lignolytic enzymes to oxidize the dyes (Jayasinghe et al. 2008). Laccase producing white-rot fungi *Pleurotus floridanus* LCJ155, *Leucocoprinus cretaceous* LCJ164, and *Agaricus* sp. LCJ169 were effective in degrading synthetic dyes such as bromophenol blue, methyl red, phenol red, Congo red and brilliant green (Jebapriya, Gnanadoss 2014). *Bjerkandera adusta* cultured in potato dextrose broth medium in an airlift bioreactor. After 10- to 15-h treatment, there was 90% of dye decolourization for both acid and reactive colourants. These results suggested that a bioreactor employed with a white-rot fungal strain is promising for dye effluent removal (Sodaneath et al. 2017). The decolourization of erichrome black T and Congo red dyes by *Pleurotus ostreatus* was studied (Gnanadoss et al. 2013). The highest degradation rate of dyes was observed when *Pleurotus ostreatus* culture was immobilized on polyurethane foam.

The LiP enzyme obtained from *Ganoderma lucidum* (GRM117) and *Pleurotus ostreatus* (PLO9) immobilized on carbon nanotubes is a promising biocatalyst for dye removal (Oliveira et al. 2018). Biosorption of remazol brilliant blue R and indigo carmine dyes was studied using immobilized biomass of white-rot fungus *Psathyrella candolleana* LCJ178. Polyurethane foam, stainless steel sponge, luffa sponge, scotch brite and white nylon sponge were used as supporting materials for immobilization of *Psathyrella candolleana* LCJ178 biomass. Of these, stainless steel sponge was found effective in binding to the culture without causing any operational difficulties. This study revealed that the selection of suitable support material, culture condition (shaking) and other physical aspects were critical for enhancing the process of dye removal (Gnanasalomi et al. 2016). Several reviews on the dye removal by means of white-rot fungi have already been published (Shah, Nerud 2002; Wesenberg et al. 2003; Asgher et al. 2008; Tišma et al. 2010; Jebapriya, Gnanadoss 2013; Sen et al. 2016; Chaturvedi et al. 2019; Periasamy et al. 2019).

Conclusions

Xenobiotic compounds are anthropogenic substances generated from multiple industries that have negative environmental consequences if they are released without proper pretreatment. Xenobiotics are noxious to living organisms; therefore they need to be removed quickly before entering into the environment. However, the physical and chemical methodologies are not feasible enough to degrade xenobiotic compounds. Subsequently, an alternative remediation technology is needed to combat xenobiotic compounds. Bioremediation technology is more promising in xenobiotic degradation owing to its cost-effective and eco-friendly approach.

White-rot fungi are thought to be efficient bio-degraders of organic pollutants probably owing to their metabolic enzymes with extensive substrate specificities. Different white-rot fungi have different biodegradation abilities for different xenobiotic compounds primarily due to their unique morphology, culture and environmental aspects as well as the nature of the enzymes produced. The characteristic features of lignolytic enzymes differ between taxa of white-rot fungi. They are well explored in the biodegradation of diverse xenobiotics like dyes, hydrocarbons, and phenolic compounds on a laboratory scale. Still, many studies are required to explore the scope of white-rot fungi at the industrial level. Additionally, screening of new white-rot fungal isolates often with promising enzyme activity is required for the bioremediation of new toxic chemicals due to increased industrial contamination. White-rot fungi in combination with biotechnological tools such as genetic engineering can produce novel strains with ideal properties for the disintegration of numerous xenobiotic pollutants.

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