White-rot fungi and their lignin modifying enzymes: an effective tool to fight recalcitrant organic pollutants

Agata Sośnicka

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Summary:

In nature species belonging to the white-rot fungi group are responsible degradation of wood components, mainly lignin but also partly cellulose, due to the specific lignin-modifying enzymes they synthesise. Nevertheless, these enzymes tend to act not only upon constituents of wood, but also other macromolecular compounds having within their structure the same bonds as the ones within a lignin and cellulose molecule. It has been reported that with the use of the mentioned enzymes it is possible to break down various recalcitrant organic pollutants, such as polycyclic aromatic hydrocarbons, phenols, biphenyls or heavy metals. This bioremediation technique using fungi as a tool to remove such xenobiotics is called mycoremediation and shows more advantages when compared to bioremediation with the use of bacteria.

Key words: white-rot fungi, mycoremediation, xenobiotics, waste management, environment protection

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Agata Sośnicka: Master of Pharmacy, Department of Drug Technology and Pharmaceutical Biotechnology, Medical University of Warsaw, Banacha Street 1, 02-097 Warsaw, Poland

- Environment contamination with recalcitrant organic compounds being a major issue worldwide
- Enzyme system of white-rot fungi being a promising tool in xenobiotic degradation

Introduction

The white-rot fungi (WRF) group can seem confusing to some researchers at first, as it is not a typical taxonomic group, comprising all the fungi belonging to the same taxonomic ranks. True is it that most white-rotters come from the *Basidiomycota* division (kingdom: Fungi, subkingdom: Dikarya) and many can share similarities in morphology, genetics and biological characteristics. Nevertheless, what makes a species a member of WRF is none of these, the species needs to be capable of synthesising ligninolytic enzymes (Young and Akhtar, 1998). The result of activity of these enzymes, namely lignin peroxidase, manganese peroxidase and laccase, explains the name given to the group of fungi possessing the ability to produce them. The enzymes allow the white-rotters to decompose lignin content of any wooden material, leaving only the cellulose as a partly-digested wood component, which appears as typical white stains on the attacked wood, hence such a name was given (Kang et al., 2007).

In nature WRF degrade wood components in various mechanisms, depending on a species: some white-rotters inhabit only dead wooden material, some colonize living plants eventually causing their death and some can do both (Sośnicka et al., 2018). Only white-rotters are known to effectively and completely degrade lignin to carbon dioxide and water, in this process they gain access to carbon and energy source (Kirk and Farrell, 1987). Lignin is a complex heterogenous polymer that is made of three types of phenylpropane unit (*p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) bonded to each another in many different ways (Du et al., 2013). As mentioned before, the degradation of lignin is an enzymatic process and it involves breaking down the C-C and C-O-C bonds within the lignin structure in a process of an oxidative degradation (Leonowicz et al., 1999). These bonds are present in many other organic molecules with a branched structure, some of them are known as recalcitrant organic pollutants, as they are resistant to most means of degradation and cause an environmental threat when they accumulate. The search for an effective way of dealing with toxic wastes and the discovery of potential that WRF possess became the origin of an idea to employ this fungi group into a remediation technique (Barrech et al., 2018).

Mycoremediation

The technique that is based on using microorganisms to clean up the polluted site (soil, groundwater), eliminate or neutralise toxic contaminants and managing wastes is called bioremediation (Chatterjee et al., 2017). Mycoremediation is a type of bioremediation using fungi, including WRF, for that purpose and it refers to their possibilities as microorganisms of degrading a great number of recalcitrant pollutants and transforming industrial wastes into products (Kulshreshtha et al., 2014). Bacteria have also been used for the same purpose, nevertheless, mushrooms exhibit some valuable advantages over the ones that bacteria can offer. First of all, fungi do not require preconditioning to the

specific pollutant and bacteria mostly have to be pre-exposed to it in order to induce enzymes that can later act upon the pollutant. Furthermore, pollutants need to reach a substantial concentration for the synthesis of enzymes to occur, below which the bacteria will be unable to act (Asamudo et al., 2006).

Recalcitrant xenobiotics

The constant need to develop new methods to deal with environmental pollution is followed by the lack of solutions to apply to the most resistant pollutants. Recently, the contamination with synthetic organic compounds has become a major issue worldwide. These materials, called xenobiotics, are not products created by nature, but by industry and due to this they cannot be easily be degraded by natural forces (Thakur, 2018). Environmental contamination has accelerated, which is due to industrial expansion, extensive chemical usage in agriculture, automobile exhaust, mine explorations, and the improper waste disposal practices of wastes containing high metal concentrations by industry, commercial establishments, and residential communities (Ali et al., 2017) (Fang et al., 2014). These chemicals include polycyclic aromatic hydrocarbons, pentachloro-phenols, polychlorinated biphenyls, 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane, benzene, toluene, ethyl-benzene xylene and trinitrotoluene (Lau et al., 2003) (Verdin et al., 2004). Polycyclic aromatic hydrocarbons (PAH) are highly recalcitrant environmental contaminants, they are a by-product of the burning-off fossil fuels, coal mining, oil drilling and wood burning (Adenipekun and Lawal, 2012). Mushrooms seem to be ideal candidates to be used as a tool in degrading such materials as the results of many pieces of research have shown. To give examples, they are capable of accumulating heavy metals and biodegrading different lignocellulosic substrates (Bennet et al., 2002), they can be used in wastewater treatment (Xu et al., 2017), in degradation of broad-spectrum organochlorine pesticide lindane (Kaur et al., 2016), degradation of common endocrine disrupters (EDCs; bisphenol A, estrone, 17-β-estradiol, estriol, 17-α-ethinylestradiol, triclosan and 4-n-nonylphenol) (Křesinová et al., 2018), they also break down engine oil (Adenipekun and Isikhuemhen, 2008). The applications do not end here and many of them are still to be examined.

Waste-management potential

The variety of possibilities to employ fungi into bioremediation emerges from species diversity. They can effectively use different mechanisms of action to decontaminate polluted sites and stimulate the environment to fight against them (Kulshreshtha et al., 2014). Many papers report the role of mushrooms in bioremediation of pollutants in the process of biodegradation, biosorption and bioconversion (Wu et al., 2008) (Prigione et al., 2008) (Kamei et al., 2006).

Bioconversion gives a possibility of using a variety of waste by-products generated by industries as media for fungi cultivation. Hence it is right to say that the product of bioconversion is a fungus itself (Kulshreshtha et al., 2014). To show examples, the following species have been reported to use bioconversion: *Pleurotus citrinopileatus* to be capable of handmade paper and cardboard industrial waste bioconversion with no genotoxicity shown (Kulshreshtha et al., 2013), *Pleurotus ostreatus* to be able to bioconvert sawdust (Akinyele et al., 2012), *Volvariella volvacea* using some agroindustrial residues such as cassava, sugar beet pulp, wheat bran and apple pomase in bioconversion process (Akinyele et al., 2011), *Lentinula edodes* capable of bioconverting eucalyptus wastes (Brienzo et al., 2007).

Biosorption was defined as "a non-directed physico-chemical interaction that may occur between metal/radio nuclide species and the cellular compounds of biological species" (Shumate and Strandberg, 1985). This process is based on the sorption of metallic ions/xenobiotics from effluent by live or dried biomass which can exhibit a marked tolerance towards metals and other adverse conditions (Gavrilescu, 2004). The mechanism of uptaking xenobiotics consists of two processes, which are bioaccumulation and biosorption. Bioaccumulation refers to transport of a pollutant into to cell and partitioning it into intracellularly located components, while biosorption means binding the pollutant to the biomass without requiring metabolic energy (Kulshreshtha et al., 2014). What is interesting, biosorption can be performed not only by a living organism but also a dead one, and the last one tends to have more advantages. First of all, the dead fungi mass can be easily obtained from industries as it is considered to be waste, contrary to a living fungus that has to be cultivated and maintained in optimal parameters. This is connected with the second reason explaining why dead biomass is easier to handle – it is not sensitive to any operating conditions like pH, temperature, nutrient supply etc. (Mar'in et al., 1997). The reported examples of fungi using biosorption to remove pollutants are: *Lactaricus piperatus* and *Agaricus bisporus* removing cadmium (II) ions (Nagy et al., 2014), *Fomes fasciatus* removing copper (II) (Sutherland and Venkobachar, 2013), *Pleurotus platypus*, *Agaricus bisporus*, *Calocybe indica* removing copper, zinc, iron, cadmium, lead, nickle (Lamrood and Ralegankar, 2013), *Pleurotus tuber-regium* removing heavy metals (Oyetayo et al., 2012).

Biodegradation is the most common and effective process of removing xenobiotics from the contaminated site. It is a process of complete mineralization of the substrate to simple compounds (CO_2, H_2O, NO_3) and other inorganic compounds by living organisms. Fungi

performs biodegradation with the use of a enzymatic system that is thoroughly described in the next chapter.

Ligninolytic complex

The main enzymes of a white-rotter that are capable of lignin mineralisation are called the lignin-modifying enzymes (LMEs), the best characterized of which are: lignin peroxidase (LiP, EC 1.11.1.14), manganese peroxidase (MnP, EC 1.11.1.13) (Orth and Tien, 1995) and laccase (Lac, EC 1.10.3.2) (Thurston, 1994). These enzymes are extracellular which means they are being secreted outside the fungus' cell, so into the environment where they act. The decomposition process of lignin can be enhanced by WRF by producing several oxidoreductases: glyoxal oxidase (EC 1.2.3.5), aryl alcohol oxidase (veratryl alcohol oxidase; EC 1.1.3.7), pyranose 2-oxidase (glucose 1-oxidase; EC 1.1.3.4), cellobiose/quinone oxidoreductase (EC 1.1.5.1), and cellobiose dehydrogenase (EC 1.1.99.18) (Ander and Marzullo, 1997). LME production takes place during secondary metabolism and is induced by limited nutrient levels, particularly nitrogen.

Peroxidases such as LiP, MnP are catalysers for the oxidation of various substrates in the presence of H_2O_2 as electron acceptor, as shown in the reaction below

$$2S + H_2O + 2\,e^- \rightarrow 2S_{ox} + 2H_2O$$

where: S, substrate (electron donor); S_{ox}, oxidized substrate (Falade et al., 2016) including lignin peroxidase, are topical owing to their high redox potential and prospective industrial applications. The prospective applications of lignin peroxidase span through sectors such as biorefinery, textile, energy, bioremediation, cosmetology, and dermatology industries. The litany of potentials attributed to lignin peroxidase is occasioned by its versatility in the degradation of xenobiotics and compounds with both phenolic and non-phenolic constituents. Over the years, ligninolytic enzymes have been studied however; research on lignin peroxidase seems to have been lagging when compared to other ligninolytic enzymes which are extracellular in nature including laccase and manganese peroxidase. This assertion becomes more pronounced when the application of lignin peroxidase is put into perspective. Consequently, a succinct documentation of the contemporary functionalities of lignin peroxidase and, some prospective applications of futuristic relevance has been advanced in this review. Some articulated applications include delignification of feedstock for ethanol production, textile effluent treatment and dye decolourization, coal depolymerization, treatment of hyperpigmentation, and skin-lightening through melanin oxidation. Prospective application of lignin peroxidase in skin-lightening functions through novel mechanisms, hence, it holds high value for the cosmetics sector where it may serve as suitable alternative to hydroquinone; a potent skin-lightening agent whose safety has generated lots of controversy and concern.

What is important, all LME enzymes are non-specific to the substrate, they can catalyse many different reactions, which means they can be used in the mycoremediation process in order to degrade various macromolecular compounds. This a is highly particular phenomenon as many xenobiotics have never before been encountered in nature and mainly WRF are the only organisms able to break them down (Pointing, 2001). Lignin-degrading enzymes has been applied to many different areas such as paper industry, textile industry, wastewater treatment and the degradation of herbicides (Abdel-Hamid et al., 2013).

Lignin peroxidase (LiP)

LiP belongs to a class of haemoprotein peroxidases. The molecule has a globular shape, its molecular weight is in between 38 kDa and 43 kDa and has the isoelectric point in between 3.3 and 4.7 (Piontek et al., 1993) (Kirk et al., 1986) (Glumoff et al., 1990). LiP can oxidise both phenolic and non-phenolic substrates. It is involved in the formation of a radical cation through one electron oxidation which leads to side-chain cleavage, demethylation, intramolecular addition and rearrangements (Falade et al., 2016). LiPs tend to have a stronger redox potential compared to other peroxidases, because their iron is more electron deficient (Millis et al., 1989), and this makes it possible for LiPs to oxidise moderately activated aromatic rings, contrary to other peroxidases, which need a strongly activated aromatic ring in order to act upon it (Abdel-Hamid et al., 2013).

LiP has a common catalytic cycle, which starts with a two-electron oxidation of the native ferric enzyme [LiP]-Fe(III) by H_2O_2 to form a two-electron oxidised form of $[LiP]^{\bullet+}$-Fe(IV) (compound I). Within the next reaction the oxidised form (compound I) first is being reduced by a reducing substrate and then receives an electron to form one-electron oxidised form (compound II). In the last reaction the substrate loses an electron while being reduced, which is being received by the one-electron oxidised form (compound II). This returns the enzyme to the native state and the oxidation cycle is complete (Abdel-Hamid et al., 2013).

LiP has been described widely to be capable of degrading various types of recalcitrant aromatic compounds including three- and four-ring polycyclic aromatic hydrocarbons (Wesenberg et al., 2003), polychlorinated biphenyl (Pease and Tien, 1992), chlorophenols and synthetic dyes (Chivukula et al., 1995), which show it can be successfully applied in remediation (Falade et al., 2016).

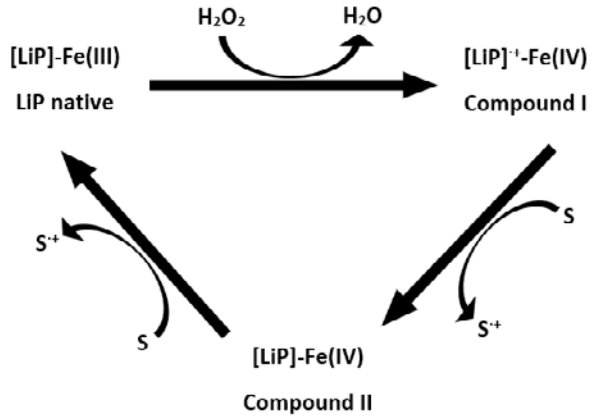

Figure 1. LiP catalytic reaction

Source: adapted from (Abdel-Hamid et al., 2013).

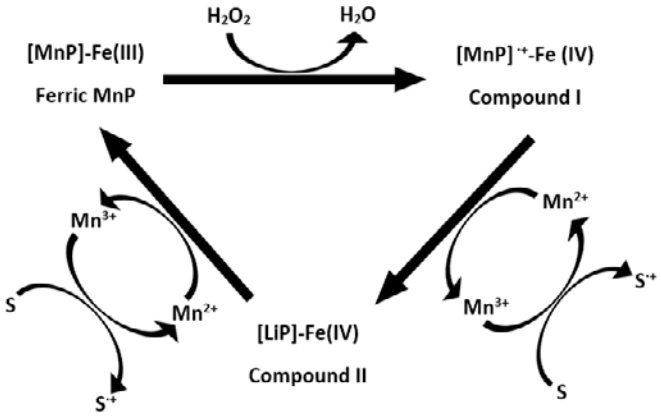

Figure 2. MnP catalytic cycle

Source: adapted from (Abdel-Hamid et al., 2013).

Some of the most widely investigated fungi species capable of synthesising LiP are *Phanerochaete chrysosporium*, *Trametes versicolor*, *Trichoderma reesei*, *Aspergillus niger, Phlebia radiata, Pleurotus ostreatus*, *Pleurotus sajor-caju* (Falade et al., 2016)

Manganese peroxidase (MnP)

MnP is also a haemoprotein of a globular shape, its molecular weight is around 53 kDa and its isoelectric point of about 3.7 (Shin et al., 2005). It oxidizes the one-electron donor Mn^{2+} to Mn^{3+} which then can oxidise a large number of phenolic substrates. The ability of MnP to oxidize Mn^{2+} is due to a Mn-binding site formed by three acidic residues near the internal heme propionate (Martínez, 2002). MnP is regarded as a first enzyme acting upon a phenolic compounds due to Mn^{3+}oxidising different mono- and dimeric phenols.

The catalytic cycle resembles the LiP. It is initiated by the binding reaction of H_2O_2 to the native ferric enzyme [MnP]-Fe(III). This occurs within subsequent cleavage of the peroxide O-O bond which needs a two-electron transfer from the heme and results in formation of the Fe^{4+}-oxo-porphyrin-radical complex- [MnP]$^{\bullet+}$-Fe(IV) (compound I). A Mn^{2+} ion gives away one electron to the porphyrin intermediate to form [MnP]-Fe(IV) (compound II) and is oxidized to Mn^{3+}. The native enzyme is generated from compound II in a similar way in the process of the donation of one electron from Mn^{2+} to form Mn^{3+}. The reduction of compound proceeds in a similar way and another Mn^{3+} is formed from Mn^{2+}, which leads to the emergence of the native enzyme and this completes the catalytic cycle (Wariishi et al., 1988).

The exceptional degradative potential of MnP exceeds lignin decomposition. MnP acts upon modified derivatives of lignin, having an effect on various organopollutants, to which we can classify polyclic aromatic hydrocarbons (PAH) (Bogan and Lamar, 1996), chlorophenols (Hofrichter et al., 1997), nitroaromatic compounds (Van Aken et al., 2000), arsenic-containing (Fritsche et al., 2000) agents and more.

Well known MnP-synthesising WRF species are, among others: *Agaricus bisporus*, *Armillaria mellea*, *Irpex lacteus*, *Lentinula edodes*, *Phanerochaete chrysosporium*, *Phlebia radiata*, *Pleurotus ostreatus*, *Pleurotus sajor-caju*, *Trametes versicolor.*

Laccase (Lac)

Laccase is a member of blue multi-copper oxidases superfamily which means it exhibits another mechanism of action than previously described peroxidases (Morozova et al., 2007). In comparison with peroxidases, oxidases do not use hydrogen peroxide and, due to this reason, they show a greater stability, which allows the use of them more efficiently (Su et al., 2018). Most of the laccases synthesised by WRF are extracellular proteins, nevertheless some intracellular ones have also been reported (Kirk et al., 1986).

The majority of the fungal laccases are monomeric globular proteins, with molecular weight oscillating between 60-70 kDa, having an acidic isoelectric point around 4, moreover, all of them show a similar structure consisting of three sequentially arranged copper domains (Shleev et al., 2004). The enzyme consists of four metal ions classified into three types – T1, T2, and T3, among which T1 copper is responsible for the blue colour (Yaropolov et al., 1994).

Laccases catalyse a one-electron oxidation with the concomitant four-electron reduction of molecular oxygen to water, resulting in reductive cleavage of a dioxygen bond (Giardina et al., 2009). Cu metal atoms of the enzyme structure play a key role in the reduction of O_2 to H_2O. The Cu atoms of laccases include one copper of type 1 (Cu_1 - T1), one of type 2 (Cu_2-T2) and two of type 3 (Cu_3-T3) (Su et al., 2018). Lac catalytic properties can be briefly described in the following three major steps: (1) T1 copper is reduced by accepting electrons from the reducing substrate; (2) Electrons are transferred from T1 copper to the tri-nuclear T2/T3 cluster; (3) Molecular oxygen is activated and reduced to wa-

ter at the tri-nuclear T2/T3 cluster (Su et al., 2018). The overall outcome of the catalytic cycle is the reduction of one molecule of oxygen to two molecules of water and the concomitant oxidation of four substrate molecules to produce four radicals (Claus, 2004). The described direct interaction of the substrate with the copper cluster shows the simplest case of laccase catalytic cycle. Oftentimes it occurs that a substrate cannot get oxidised directly by laccases, for which reasons can vary: a substrate can have a too big molecule to penetrate into the enzyme active site or show a too high redox potential (Riva, 2006). Nevertheless, this limitation can be easily overcome with the presence of mediators- these are compounds acting as intermediate substrates for laccase. The use of certain low-weight compounds, acting as redox mediators, widen the catalytic activity of laccase towards more recalcitrant compounds (Barreca et al., 2003). The most commonly used mediators in literature are 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) and 1-hydroxy- benzotriazole (HBT) (Hilgers et al., 2018).

Laccases exhibit a broad substrate specificity, they can catalyse the oxidation of ortho- and para-diphenols, aminophenols, polyphenols, polyamines, anilines and aromatic thiols, lignins and aryl diamine as well as some inorganic ions (Solomon et al., 1996).

Due to the wide variety of reactions catalysed by laccases, these enzymes hold a great promise for many potential applications.

Laccases are typical to be synthesised by many WRF species, but the ones of a greater importance are: *Polyporus versicolor*, *Neurospora crassa*, *Pleurotus ostreatus*, *Phlebia radiata*, *Trametes versicolor*, *Phanerochaete chrysosporium*, *Armillaria mellea* (Solomon et al., 1996) (Abdel-Hamid et al., 2013) (Sośnicka et al., 2018).

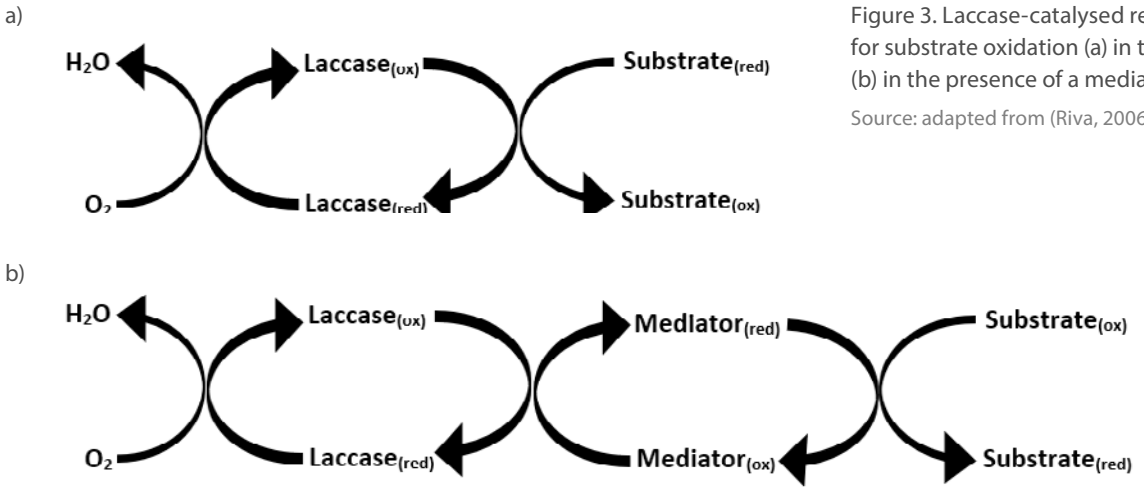

Figure 3. Laccase-catalysed redox cycles for substrate oxidation (a) in the absence, (b) in the presence of a mediator

Source: adapted from (Riva, 2006).

Conclusions

In the age of the high environmental pollution rates, where day by day the number of toxic pollutants accumulate causing a real health threat it seems urgent to look for different solutions that would deal with the wastes we are creating. In order not to turn the forces of nature against ourselves we should start cooperating with it, noticing the help nature itself offers. All the research on the use of fungi for the environment treatment that has been done shows endless applications of the mycoremediation technique. There is no doubt using organisms that are part of environment to fight artificial wastes created by people is an eco-friendly way to achieve the goal – it is a relatively easy process to conduct, it is cheap, safe, and what is more important, becoming more popular.

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Grzyby białej zgnilizny i enzymy przez nie syntetyzowane: skuteczne narzędzie do zwalczania opornych organicznych zanieczyszczeń

Agata Sośnicka

W naturze gatunki należące do grupy *white-rot fungi* (pol. grzyby białej zgnilizny) są odpowiedzialne za rozkład ligniny oraz w niewielkim stopniu celulozy – składników drewna, co jest możliwe dzięki kompleksowi enzymatycznemu, który grzyby z tej grupy posiadają. Jednakże enzymy syntetyzowane przez te gatunki działają nie tylko na ligninę, ale także są w stanie rozłożyć inne wielkocząsteczkowe związki, które w swojej strukturze zawierają te same wiązania chemiczne, co w przypadku cząsteczki ligniny. Literatura podaje, iż enzymy te powodują degradację różnych trudno degradowanych organicznych zanieczyszczeń, takich jak wielopierścieniowe węglowodory aromatyczne, fenole, polichlorowane bifenyle czy metale ciężkie. Technikę bioremediacji, w której używa się grzyby jako narzędzie do walki z zanieczyszczeniami środowiska, nazwano mykoremediacją i wykazuje ona więcej zalet w porównaniu do szeroko stosowanej bioremediacji z użyciem bakterii.

Słowa kluczowe: White-rot fungi, mykoremediacja, ksenobiotyki, gospodarowanie odpadami, ochrona środowiska

