# **Chapter 7 Exploiting Marine Fungi in the Removal of Hazardous Pollutants and Biomass Valorisation**



### Dushyant R. Dudhagara, Bhumi M. Javia, and Anjana K. Vala

Abstract The environment and human health are now seriously threatened by pollution. Organic contaminants have a long half-life in the environment and possess hydrophobic, mutagenic, and cytotoxic properties. Hence, they are a big challenge to the health of environment. Due to their hydrophobic and persistent character, non-biodegradable and recalcitrant chemicals have an adverse effect on terrestrial and aquatic ecosystems. According to current pollution management methods, biodegradation and bioremediation using various microorganisms is an efficient, reliable, and eco-friendly approach to combat the pollutants. Marine-derived fungi play a significant role in the remediation of organic pollutants because their unique morphological and physiological properties including survival in the extreme conditions and a diverse metabolic capability. This chapter highlights the role and mechanisms of marine-derived fungi in removal of various pollutants as polyaromatic hydrocarbons (PAHs), heavy metals, dyes, and the biomass valorization. Fungi can oxidize PAHs, alkanes, and other complex hydrocarbons using various intracellular and extracellular enzymatic machineries including monooxygenases and lignin-modifying enzymes. Marine-derived fungi act as biosorbents to remove heavy metal contaminants through active and passive mechanisms. Both living and non-living fungal biomass can be used to detoxify and degrade dyes from the contaminated environment. Furthermore, fungal biomass valorization facilitates the sustainable development of value-added products such as biofuels, enzymes, amino acids, organic acids, alcohol, pigments etc. Thus, the chapter emphasizes to understand the mechanisms of marine-derived fungi in degradation of organic pollutant, metabolic pathways, and enzymes responsible for degradation of organic compounds which would help to develop the future

e-mail: akv@mkbhavuni.edu.in

D. R. Dudhagara · B. M. Javia

Department of Life Sciences, Bhakta Kavi Narsinh Mehta University, Junagadh, India

A. K. Vala (🖂)

Department of Life Sciences, Maharaja Krishnakumarsinhji Bhavnagar University, Bhavnagar, India

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mycoremediation policies and production of value-added products for sustainable future development.

**Keywords** Organic pollutants · Bioremediation · Biomass valorization · Valueadded products · Sustainable development

## 7.1 Introduction

Pollution is a matter of grave concern in this age. The condition of environment directly influences the quality of life in the ecosystem on earth. Industrialization and growing affluence in the developed world along with population explosion and rapid development in the developing countries has resulted in accelerated environmental degradation on a large-scale. Major sources of pollutants include industrial effluents, injudicious use of fertilizers, insecticides, pesticides, mining activities, sewage sludge, etc. Pollutants can be divided into two major types: biodegradable and non-biodegradable pollutants. Non-biodegradable pollutants cause hazardous effect on environment. Non-biodegradable pollutant includes heavy metals, pesticides, polyaromatic compounds and radionuclear material etc. (Peng et al. 2008). Many conventional physico-chemical methods of treatment/removal of these compounds, though effective, are not feasible for application on a large scale. Hence, there is need to develop treatments that can minimize or even eliminate such pollutants from environment. In recent years, the application of microorganisms which degrade or convert hazardous pollutants to less toxic compounds have become popular. Fungi proved to have high potential in the degradation of high molecular weight compounds and therefore are used widely to remediate environmental pollution (Akcil et al. 2015; Deshmukh et al. 2016; Varjani 2017).

Fungi are eukaryotic, chemoheterotrophic, parasitic or saprophytic, unicellular or multicellular filamentous organisms that include molds, yeasts, and mushrooms. The kingdom Fungi includes eight phyla. Fungi are found in variety of habitats like soil, fresh, and marine waters (Anastasi et al. 2013). Fungi produce secondary metabolites, enzymes, biosurfactants, and polysaccharides and applied in bioremediation of pollutants. Fungi have been efficiently used to treat water samples contaminated with micropollutants (Badia-Fabregat et al. 2015). Marine fungi are able to sustain high saline conditions and extreme pH this trait provides biological advantage over terrestrial fungi (Thatoi et al. 2013; Singh et al. 2019).

Marine fungi are found in oceans and colonize different niches. They act as parasites, saprobes, or symbionts and associated with organisms (Wang et al. 2012). Marine fungi can be isolated from different samples such as sediment, seawater, mangrove detritus, decaying wood, seaweeds, and invertebrates (Pang et al. 2016). Marine fungi have capacity to produce different pharmacological metabolites (Imhoff 2016). Marine fungi are source of novel antibacterial, antiviral, anticancer, antiplasmodial, and anti-inflammatory compounds (Bovio et al. 2019), enzymes, biosurfactant (Cicatiello et al. 2016; Nicoletti and Andolfi 2018) and are also useful in the bioremediation of pollutants (Bovio et al. 2017). Marine fungi tolerate high

concentrations of heavy metals such as copper and lead (Gazem and Nazareth 2013). Role of marine fungi in heavy metals, dyes, and hydrocarbons degradation has been well documented. Furthermore, enzymes from marine fungi can be used for paper, pulp, textile, leather, biofuel industries, food and beverages, for animal feed, for pharmaceutical, cosmetic, and environmental applications (Damare et al. 2012; Bonugli-Santos et al. 2015; Deshmukh et al. 2016).

It has been reported that marine fungi have capacity to bioremediate highly recalcitrant pollutants. Bioremediation is a process in which living organisms degrade or convert harmful organic contaminants to less toxic compounds. Mycoremediation is the process in which fungi are used for bioremediation. Mycoremediation is eco-friendly and effective method to combat increasing pollution of soil and water (Arun et al. 2008). Fungi are ideal candidates for remediation of pollutants due to their unique traits including ability to withstand fluctuation in temperature and pH, heavy metal resistance, high surface area to volume ratio, mycelial growth, hyphal network, and extracellular ligninolytic enzymes (Khan et al. 2019). Fungi produce variety of intracellular as well as extracellular enzymes including peroxidase and cytochrome P450, respectively, for detoxification and biodegradation of pollutants (Durairaj et al. 2015). The diversity of habitats and ability for secreting multitude of enzymes makes fungi potential candidates for bioremediation at various locations (Divya et al. 2014).

In this chapter, the role of marine fungi in degrading various recalcitrant, persistent, and harmful pollutants like polycyclicaromatic hydrocarbons (PAHs), heavy metals, dyes, and mechanisms behind the mycoremediation of these pollutants are summarized with process of biomass valorization. An attempt is made to understand how the process of degradation can be accelerated and the future strategy to overcome the existing limitations is discussed.

## 7.2 Hydrocarbon Degradation by Marine Fungi

Hydrocarbon contamination from petrochemical industry is the major environmental problem faced by humanity. Leakage and accidental spillage of petroleum products are to the tune of 2,00,000–6,00,000 metric tons per year (Kvenvolden and Cooper 2003; Das and Chandran 2011). These organic pollutants are carcinogenic and neurotoxic which cause the harmful effects on animal and plant.

Bioremediation or biodegradation by application of natural populations of microorganisms is one of the mechanisms by which hydrocarbon and other pollutants can be removed from the environment (Ulrici 2000). Biodegradation of petroleum hydrocarbons is a complex process which depends on the environment and the amount of the pollutants present in the site. Petroleum hydrocarbons are divided into four classes: saturates, aromatics, the asphaltenes (ketones, phenols, porphyrins, esters and fatty acids), and the resins (sulfoxides, amides, pyridines, carbazole, and quinolones). Hydrocarbons differ in their degradation susceptibility to microbial attack. The susceptibility of hydrocarbons to microbial degradation is linear alkanes > branched alkanes > small aromatics > cyclic alkanes (Ulrici 2000). Some compounds such as high molecular weight containing polycyclic aromatic hydrocarbon may be difficult to be degraded (Atlas 1995) but many fungal species are capable to degrade this recalcitrant hydrocarbon-containing pollutants. It has been observed that fungi present in polluted environment have developed adaptive mechanisms by which they are able to utilize hydrocarbons as the sole source of carbon (Dacco et al. 2020).

Chaillan et al. (2004) isolated fungi *Amorphotheca*, *Talaromyces*, *Neosartorya*, and *Graphium* from the soil contaminated by petroleum and have higher efficiency in the degradation of petroleum hydrocarbons. Some terrestrial fungi *Aspergillus*, *Penicillium*, and *Cephalosporium* are reported as idea candidate for the degradation of crude oil (Singh 2006; Das and Chandran 2011). The different hydrocarbon degrading pathways and their mechanisms operated by fungi are mentioned below.

## 7.2.1 Degradation Process of Alkane

Alkane is a saturated hydrocarbon with all single bonds in its structure and cycloalkane is a saturated hydrocarbon with several carbon rings in its structure. Alkane degradation can be catalyzed by some enzymes such as oxidase, dehydrogenase and converted into fatty acids, and followed by acetyl coA and which can be further mineralized as  $CO_2$  and  $H_2O$  (Singh 2006). It has been observed that in the process of Alkane degradation many enzymes played an important role such as alkane monooxygenase, fatty alcohol dehydrogenase, fatty aldehyde dehydrogenase, etc. Biological degradation of alkane is a subterminal oxidation process. In the primary step, cycloalkane is oxidized into alcohols by n-alkane monooxygenase type of oxidizing enzymes. Then, alcohols are converted into fatty acid. Cyclohexane is converted into corresponding compound, followed by cyclohexanol, cyclohexanone, and fatty acids. At last, the compound is mineralized and form  $CO_2$  and  $H_2O$  along with fungal biomass production as the end product (Fig. 7.1) (Dacco et al. 2020).

# 7.2.2 Degradation Process of Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAH) are widely distributed in the environment and may persist for extended period of time. PAHs are composed of two or more fused benzene rings and are formed during combustion of organic molecules (Haritash and Kaushik 2009). Polycyclic aromatic hydrocarbons have carcinogenic, mutagenic, and teratogenic properties. Forest, oil seep, volcanic eruption and

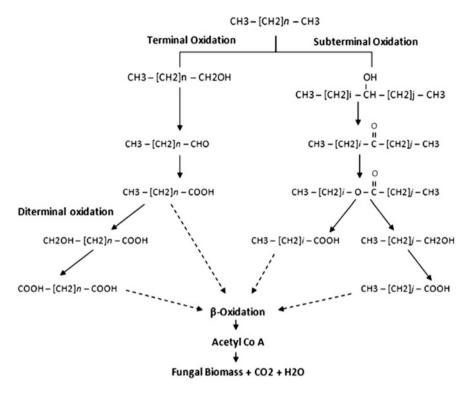


Fig. 7.1 Degradation shows the terminal, diterminal, and subterminal pathways for the n-alkane (modified from Dacco et al. 2020)

exudates from trees are natural sources of PAHs. Anthropogenic sources include fossil fuel burning, coal tar, wood, garbage, lubricating oil, municipal waste incineration and petroleum spills, etc., are the major source of pollutants (Kaushik and Haritash 2006). Most important and ecologically damaging components of pollution are the PAHs and cause depletion of the ozone layer and affect Earth's heat balance, adding acidic air pollutants to atmosphere and reduce visibility (Chauhan et al. 2000).

According to Yumoto et al. (2002), PAHs can be degraded by enzymes and catalyzed into glycol or catechol, then decomposed into succinic acid or acetyl coA. In degradation pathway, PAHs are gradually degraded into epoxide, trans diol, phenol, and trans dihydro 2 phenol by monooxygenase enzyme of yeast. In another study of Mills et al. (2004), PAHs can be degraded by dioxygenase into cis dihydro 2 phenol, epoxide, cis diol etc. The final metabolites in both pathways are  $co_2$  and water. The ligninolytic and monooxygenase system of cytochrome P-450 may be involved in polycyclic aromatic hydrocarbon degradation by filamentous fungi. Induction of the monooxygenase before application in degradation of hydrocarbon could result in enhanced removal of PAHs (Haritash and Kaushik 2009). Fungal cytochrome P-450 Monooxygenase from white rot fungi *Phenerochaete* 

*chrysosporium* have capacity to oxidize pollutants like aliphatic hydrocarbons, crude oil, n-alkane, polyaromatic hydrocarbons alkylphenol, etc.

PAHs degradation depends on solubility, number of benzene rings, the species and number of substituent species, the properties of heterocyclic atom of PAHs. Asphalt is very difficult to be degraded by biodegradation due to its most complicated structure. Many researches indicated that the PAH can be degraded only in aerobic conditions. While it has been observed that PAH can be degraded in anaerobic condition as well like sulfate reduction, denitrification, or methanogenic fermentation. Though rate of aerobic degradation of PAHs is higher than the rate of anaerobic degradation. (Meckenstock Rainer 2004).

Ligninolytic fungi are capable of oxidizing PAH by non-specific extracellular enzymatic complexes, normally used to depolymerize lignin. These lignindegrading enzymes include laccase, lignin peroxidase, manganese peroxidase, etc. (Peng et al. 2008). A novel PAH metabolic pathway in fungi involves hydroxylation by cytochrome P-450 monooxygenase enzyme through a sequence of reactions mammalian metabolism (Capotorti et al. 2004). similar to In many non-ligninolytic fungi, this pathway occurs to effectively degrade hydrocarbons (Ravelet et al. 2000). Many researchers have studied that purified fungal laccase enzyme can be used for the oxidation of PAH. Laccase enzyme of T. versicolor, C. hirsutus, P. ostreatus, and Coriolopsis gallica was the most studied in the fungi. It has been reported that activity of enzyme in T. versicolor fungi is 29 times higher than other microorganisms (Margot et al. 2013). For example, T. versicolor laccase, in combination with 1-hyrdoxybenzotriazole (HBT), was capable to oxidize two PAHs, acenaphthene and acenaphthylene; Laccasewithout mediator oxidized about 35% of the acenaphthene and only 3% of acenaphthylene. The end products obtained after incubation were 1,2-acenaphthenedione and 1,8-naphthalic acid anhydride (Johannes et al. 1998).

Kirk and Gordon (1988) explained that 14 strains of obligate marine fungi belonging to genus, *Varicosporina, Dendryphiella, Lulworthia*, and *Corollospora* species can grow using alkenes and alkanes as a sole source of carbon and mineralized into n-hexadecane. The study has shown that the 14 lignicolous and arenicolous strains utilized pristine, 1-hexadecene and some degree of tetradecane as a sole source of carbon. Raikar et al. (2001) isolated*Thraustochytrids* fungi from several oil spills polluted sites in Goa and they were capable of degrading tar-balls added to peptone broth and degradation was observed up to 30% in 7 days as estimated by gas chromatography and gravimetry. *A.sclerotiorum* showed 99.7% pyrene 2 mg in 30 mL and 76.6% benzo pyrene 1 mg in 30 mL degradation after 8 and 16 days, respectively (Passarini et al. 2011). Two non- identified marine-derived fungi were able to remove phenanthrene from a media by adsorption through fungal mycelium. Fungus *Aspergillus* sp. BAP14 isolated from marine sediment showed degradation of benzopyrene and removed approx 30% BaP after 3 days (Raghukumar et al. 2006; Damare et al. 2012).

In the degradation process of aromatic hydrocarbons, aromatic hydrocarbon is oxidized by oxidase into dihydrodiol. Then, the dihydrodiol is degraded into o-dihydroxybenzene. Dihydroxybenzene is degraded by following two processes,

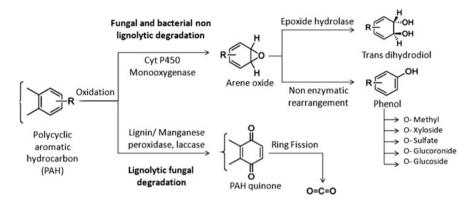


Fig. 7.2 Degradation of polycyclic aromatic hydrocarbons by fungi

which are ortho position ring opening and meta position ring opening reaction. Then, these compounds are oxidized into long chain compounds and gradually metabolized into acetyl coA. Degradation process by microorganisms such as bacteria and fungi are comparatively different from each other. In bacteria, aromatic hydrocarbon is oxidized by two oxygen atoms and converted into cis-dihydrodiol. While in fungi, aromatic hydrocarbon is oxidized and converted into trans-dihydrodiol (Fig. 7.2) (Xue et al. 2015; Kadri et al. 2017).

## 7.3 Heavy Metal Removal by Marine Fungi

Heavy metals are considered as one of the most hazardous pollutants having a specific density of more than 5 gm/cm<sup>3</sup>. Heavy toxic metals are directly or indirectly released into environment and as a result, annual worldwide release of heavy metals reached 13,50,000 tons of zinc, 9,39,000 tons of copper, 22,000 tons of cadmium and 7,83,000 tons of lead (Singh et al. 2003). Metals like iron, zinc, copper, and manganese are essential for biological process. While mercury, cadmium, and nickel have no physicological role but these metals can cause harmful disorders at high concentration (Lenin et al. 2014). High concentration of heavy metals can cause serious environmental as well as health problems. Unlike organic contaminants, pollutants from heavy metals are non-biodegradable these and cause bioaccumulation in food chain. Conventional physico-chemical treatment technologies become less effective and more expensive when metal concentrations are in the higher range (1–100 ppm) (Dermont et al. 2008).

Marine fungi can tolerate high concentration of heavy metals and its their interaction to metal ions can be used to remove heavy metal pollutants from environment (Lopez Errasquín and Vázquez 2003). Marine fungi can remove toxic metals from the environment by adsorption as well as their metabolic activities (Davis et al. 2003). Living as well as dead fungal biomass has been recognized for the removal of heavy metals through absorption (Bishnoi and Garima 2005). Fungi can be used as a biosorbent for the removal of heavy metals with excellent metal uptake and recovery (Fu et al. 2012). Rehman et al. (2008) isolated yeast *Lodderomyces elongisporus* from metal-contaminated site and found to tolerate various heavy metals. Damare et al. 2012 stated that the fungus *Thraustochytrids* from shallow water hydrothermal vents have efficiency to withstand high concentration of heavy metals. Majeau et al. (2010) reported that psychrophilic fungi, *Cryptococcus* sp. found in deep-sea sediments have capability to tolerate high concentration of heavy metals such as ZnSO<sub>4</sub>, CuSO<sub>4</sub>, Pb (CH<sub>3</sub>COO)<sub>2</sub> and CdCl<sub>2</sub> up to 100 mg/L.

Vala et al. (2004) while searching for new sources of marine fungi for the removal and tolerance of heavy metal confirmed two seaweeds associated fungi *Aspergillus flavus* and *A. niger* for their tolerance potential against hexavalent chromium. Both the confirmed fungi had remarkable chromium tolerance and removal capability. Chromium removal (mg/g dry wt) was noticed to increase with increasing chromium concentrations.

Khambhaty et al. (2009) isolated three marine-derived aspergilli viz. *Aspergillus niger*, *A. wentii* and *A. terreus* from Gujarat coastal area and were examined for their hexavalent chromium (Cr(VI))removal capacity. Out of the three, *A. niger* was monitored as the most potential candidate for Chromium removal. Complete analyses of biosorption and sorption capability discovered 117.33 mg/g adsorption by *A. niger* under optimized conditions and sorption efficiency was noticed to be 100%. Biosorption process was observed to be endothermic. On the basis of FTIR analysis, amino, methylene, hydroxyl, and phosphorous groups were involved in binding of chromium to fungal biomass.

Taboski et al. (2005) evaluated the toxicity level of Cadmium (Cd) and lead (Pb) to two fungal species *Corollospora lacera* and *Monodictys pelagica* isolated from the marine environment by exploring their growth rate and biomass. Biosorption of metals was also checked. Growth rate of fungi was not affected by lead, though, high cadmium concentration reduced the growth rate of fungi, particularly, *M. pelagica*. About 93% of extracellular lead segregation by *C. lacera* was observed. *M. Pelagica* accumulated about 60 mg/g Cd and about 6 mg/gPb. About 7 mg/g Cd and up to 250 mg/g Pb was accumulated by *C. lacera*.

Khambhaty et al. (2009) studied dead fungal biomass of four marine *Aspergillus* species for Hg(II) biosorption and noticed *Aspergillus niger* as the most efficient Hg (II) biosorbent. Dead biomass of *A. niger* showed 40.53 mg/g Hg(II) removal under optimized conditions. Assessment of possible cell-metal ion interaction disclosed involvement of hydroxyl(–OH) and amino (NH<sub>2</sub>) groups present on the cell surface in Hg(II) biosorption.

El-Kassas and El-Taher (2009) isolated hexavalent chromium (Cr(VI)) tolerant strain of *Trichoderma viride* from water samples of the Mediterranean Sea. The fungus could remove 4.66 mg/g Cr(VI). On the basis of transmission electron microscopic (TEM) analysis, it was observed that accumulation of chromium by the fungus did not affect its mycelial and conidial structures. Mendoza et al.(2010) studied that two marine fungal strains of *Dendryphiella salina* were observed to absorb 80–92% Hg<sup>2+</sup> from the liquid media. Strain Den32 had higher absorption

Fungal Biosorbent	Metal	Initial Metal Ion Concentration (mg/L)	Sorption capacity (mg/g)	References
Aspergillus Niger	Cu Pb Cr (VI)	100 100 50	15.6 34.6 6.6	Dursun et al. (2003)
Botrytis cinerea	Pb	350	107.1	Akar and Tunali (2005)
Phanerochaete chrysosporium	Cu Pb Zn	100 100 100	88.16 68.73 39.62	Iqbal and Edyvean (2004)
Pleurotus platypus	Ag	200	46.7	Das et al. (2010)
Rhizopus oryzae	Cu	100	34	Fu et al. (2012)

 Table 7.1
 Metal biosorption by marine fungal biosorbents (Ayangbenro and Babalola 2017)

efficiency than strain Den35. The study disclosed the potential application of both the strains for bioremediation of mercury, mainly through biosorption.

Vala and Upadhyay (2008) isolated arsenic tolerating *Aspergillus* sp. from coastal waters of Bhavnagar, Gulf of Khambhat, West coast of India, disclosed the fungus to tolerate supplied 100mg/L As (III) or As(V). Hydride generation atomic absorption spectrometric (HGAAS) analysis revealed higher removal of As (V) than As(III). Energy Dispersive X-ray spectroscopic (EDX) data further confirmed the presence of arsenic in fungal biomass.

Vala (2010) explored removal and tolerance of arsenic by *Aspergillus candidus* isolated from coastal waters of Bhavnagar, Gulf of Khambhat, West coast of India. The fungus showed tolerance for the trivalent and pentavalent forms of arsenic (25 and 50 mg/L). Maximum arsenic removal (mg/g) by the fungus was observed on third day. Vala (2010) also suggested that facultative marine fungus *A. candidus* was one of the most promising fungus for bioremediation of arsenic.

Vala (2010) and Vala et al. (2011) reported that *Aspergillus flavus* and *A. niger*, facultative marine fungi, have tolerance and removal capability for arsenic. Vala (2010) has reviewed *A. niger* as potential biosorbent. This perception was supported by marine-derived fungus *A. niger*. Vala and Patel (2011) explained that heat-killed biomass of marine-derived *A. niger was* studied for its As(III) biosorption capacity, it was noted to remove more than 90% of provided As(III) concentrations. Highest biosorption was found108.083 mg/g at the concentration 600 mg/L. (Table 7.1 depicts the sorption capacity of fungi for various metal ions).

Vala and Sutariya (2012) explored the amount of arsenic tolerance and removal efficacy of two facultative marine fungi *A. flavus* and *Rhizopus* sp. Upon exposure to 25 mg/L and 50 mg/L sodium arsenite (As (III)), both the fungi showed arsenic tolerance and accumulation. A little better accumulation was observed by *Rhizopus* sp. Increase in accumulation was observed with increasing concentration representing higher complexation rates between arsenic and arsenic complexing group on the fungal biomass.

Yeasts from the marine environment have been less studied for heavy metal removal. Strains of *Yarrowia lipolytica* have been reported as potential hexavalent chromium remediators by several workers (Rao et al. 2013; Imandi et al. 2014). Likewise, marine yeast *Rhodotorula rubra* has been exploited for arsenic metabolism (Cullen and Reimer 1989; Maher and Butler 1988). Though, arsenic remediation by marine yeasts has not been attended much attention in the recent past (Vala and Dave 2017). Abe et al. (2001) isolated thirteen yeast strains from deep-sea sediment samples of Japan Trench. Among them, *Cryptococcus* sp. was observed to have the maximum tolerance for  $Cu^{2+}$ . The authors also suggested the importance of enzyme superoxide dismutase (SOD) to resist high  $Cu^{2+}$  stress.

Deep-sea psychrotolerant yeast isolates *Cryptococcus* sp., when grown in presence of various concentrations of heavy metal salts viz.  $CdCl_2$ ,  $CuSO_4$ , Pb  $(CH_3COO)_2$ , and  $ZnSO_4$ , demonstrated remarkable growth in the presence of 100 mg/lmetal concentrations. Tolerance to these metals showed by the isolate was comparatively higher than other deep-sea and terrestrial yeasts. Modification in the cell morphology was observed in presence of heavy metals. The yeast can remove 30–90% of the provided heavy metals. The authors recommended the *Cryptococcus* sp. as a potential candidate for bioremediation of heavy metal-contaminated sites. The authors postulated the metal-tolerant property and characteristics of the yeast for the contribution to its ecological role and adaptations in extreme environments (Singh et al. 2013).

Oyetibo et al. (2015) isolated both resting and growing cells of mercury-resistant *Yarrowia* spp. from estuarine sediments polluted with mercury. The resting cells of yeast strain were recommended to be applicable as a reusable bioadsorbent, whereas the growing cells were recommended to be more suitable as efficient mercury bioreduction and volatilization agent.

Srivastava and Thakur (2006) reported efficiency of Aspergillus sp. for the removal of chromium in tannery wastewater. 85% chromium can be removed at 6 pH in a bioreactor by using synthetic medium, compared to 65% removal from the effluent. Lakkireddy and Kues (2017) studiedCoprinopsis atramentaria for its ability to accumulate 76% cadmium at concentration 1 mg/L and 94.7% of lead at concentration 800 mg/L. Study of Park et al. (2005) suggested that dead fungal biomass of A. niger, Rhizopus oryzae, Saccharomyces cerevisiae, and Penicilliumchrysogenum can be used to convert toxic metal Cr (VI) into less toxic or non-toxic Cr (III). It has been reported that catalase enzyme provides heavy metal tolerance capacity to fungi such as lead, copper, zinc, cadmium, etc. It has been observed A. niger, Rhizopus, and Penicillium fungi produce high amount catalase in the presence of heavy metals such as  $Pb^{2+}$ ,  $Cu^{2+}$  (Thippeswamy et al. 2014). Aspergillus foetidus has capacity to tolerate lead (Pb) concentration up to 200 mg/ L and can produce antioxidative enzymes including catalase for detoxifying  $H_2O_2$ and malondialdehyde. Aspergillus spp. Have oxidative stress tolerance for heavy metals like zinc and Copper. (Chakraborty et al. 2013; Mitra et al. 2014; Deshmukh et al. 2016).

Luna et al. (2016) stated that *Candida sphaerica* can produce biosurfactants with the removal of 95%, 90%, and 79% for Fe, Zn, and Pb, respectively. According to

Mulligan et al. (2001) biosurfactants have been widely used in recent years because of their low toxicity, biodegradability, and diversity. Surfactin, rhamnolipid, and sophorolipid can be used for the removal of copper and zinc. A single wash of 0.5% rhamnolipid can remove 65% copper and 18% zinc, while 4% sophorolipid can remove 25% copper and 60% zinc. Chatterjee et al. (2012) reported that *Hansenula polymorpha, S. cerevisiae, Yarrowia lipolytica, Rhodotorula pilimanae, Pichia guilliermondii*, and *Rhodotorula mucilage* can be used to convert toxic Cr (VI) to less toxic Cr (III).

Over the past few years, many bioremediation technologies have been applied all over the world to solve the problem of contaminated environment. Many research and review articles on these technologies for bioremediating heavy metals are available (Khan et al. 2004). Though, there are several gaps in the understanding of heavy metals bioremediation specifically because of the great complexity of soil chemistry. Therefore, expansive and site-specific research is still required to bring out the optimum performance from the technologies of fungal remediation.

# 7.3.1 Mechanisms of Mycoremediation for the Removal of Heavy Metals

Mycoremediation of heavy metals involves interaction between fungi and metal. Bioremediation process includes adsorption, precipitation, oxidation, reductions, and complexation reactions. The chemical reactions between microorganisms and metals can be categorized into six different processes: intracellular accumulation, cell wall-associated metals, extracellular mobilization or immobilization of metals, metal siderophore interactions, extracellular polymer-metals interaction with transformation and volatilization of metals (Davies and Bennett 1983; Siddiquee et al. 2015).

Gadd (2007) demonstrated that Fungi can use three possible strategies for toxic metal removal: (1) Active metal bioaccumulation in fungal cell and storage in vacuoles and/or passive metals bioabsorption on fungal wall; (2) Metalmobilization/transformation/immobilization in the external environments, due to metabolites and secondary organic acids production; (3) metal exclusion.

Gadd (2007) also mentioned that fungi can restrict entry of toxic metal into cells by these three mechanisms: (1) reduced metal uptake and/or increased metal efflux; (2) metal immobilization, e.g., cell wall adsorption, extracellular precipitation of secondary neoformed minerals (e.g., oxalates); (3) extracellular metal sequestration by, e.g., exopolysaccharides and other extracellular metabolites. Five different mechanisms for the heavy metal removal in fungi are mentioned below; (Fig. 7.3 depicts the mechanisms for the removal of heavy metals).

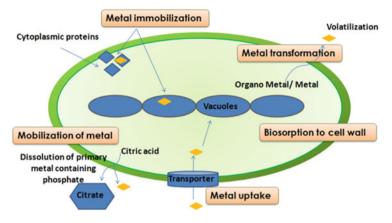


Fig. 7.3 Mechanisms of mycoremediation for the removal of heavy metals (modified from Siddiquee et al. 2015)

#### 7.3.1.1 Mobilization of Metals

Mobilization of metals by fungi takes place due to the production and secretion of fungal products like citric acid, a metal ions chelator and oxalic acid that can interact with metal ions to form insoluble oxalate, which can be resulted from the dissolution of primary metals containing phosphate. These organic acids produced by fungi can increase the metal solubility by acidification and formation of metal-complex structure (Siddiquee et al. 2015).

#### 7.3.1.2 Biosorption to Cell Wall

Fungal cell wall is the protective layer and barrier that controls uptake of toxic metals into the cell and the first cellular components that interact with metal. Heavy metal affects fungal growth and metabolism results in uptake of metals through chemisorption processes (Kapoor and Viraraghavan 1997), which includes adsorption coupled reduction process, ion exchange, precipitation, crystallization, and electrostatic interaction (Pundir et al. 2016). *Aspergillus niger* strains have been found better in biosorption capabilities of heavy metals such as Cu<sup>2+</sup>, Zn<sup>2+</sup> and Ni<sup>+2</sup> at 4 to 6 pH (Siddiquee et al. 2015).

#### 7.3.1.3 Metal Uptake and Translocation through Cell Membrane

Transporters are located on the cell wall of fungi and they are responsible to uptake essential metals. Carriers may consist of all the metabolically-coupled and H<sup>+</sup> gradient-driven transporter system (Siddiquee et al. 2015). Transportation of heavy metals into the cell from the extracellular environment using active or passive

transport mechanism through the cell membrane requires for the removal of heavy metal ions from the environment. Transportation system requires energy for the removal of heavy metals from the aqueous solution (Veglio and Beolchini 1997).

#### 7.3.1.4 Intracellular Metal Immobilization

Intracellular metal immobilization includes two processes that are vacuoles compartmentation and complexation by cytoplasmic protein, called metallothioneins and phytochelatins (Siddiquee et al. 2015). Fungal vacuole plays important roles in molecular degradation, storage of metabolites, regulation of cytosolic concentrations of metal ions and detoxifies potentially toxic metal ions. Metal-tolerant fungi can survive due to their abilities of intracellular chelation, for example, metallothioneins, phytochelatins, and metal sequestration within vacuoles (Liu and Culotta 1999). Metallothioneins is a metal-binding protein that can modulate the intracellular concentrations and bind both the essential metals such as Cu and Zn and inessential metals such as Cd.

#### 7.3.1.5 Metal Transformations

In fungi, biotransformation of metal occurs through chemical reactions such as oxidation, reduction, methylation, and dealkylation. These reactions convert metal ion into non or less toxic form. Chemisorption involves bond formation in chemical group (hydroxyl, amine, phosphoryl, thiol, etc.) present on fungal cell wall or on the surface and substrate to be adsorbed. Chemisorption excludes dependency on metabolic reaction within fungal cell (Bhainsa and D'Souza 2009) and forms strong bonding than ion exchange (Sheoran and Sheoran 2006). Metals may transfer to other parts of the fungi mycelium and plant symbionts by cytosplasmic vesicles and vacuoles. Condensation of heavy metal concentration in the absence of water molecules known as precipitation that helps in removal of contaminants in bulk amount (Gibert et al. 2005; Siddiquee et al. 2015).

## 7.4 Dye Degradation

Dyes are synthetic chemicals and recalcitrant in nature. More than 1,00,000 commercial dyes including acidic, basic, reactive, azo, and anthraquinone-based dyes are produced every year (Campos et al. 2001). Synthetic dyes are widely used in textile dyeing, color photography, paper printing, food, pharmaceutical, cosmetic, and leather industries. Among various industries, the textile dying industries discharge large amount of wastewater effluent after dyeing process. More than  $7 \times 10^5$  metric tons of dyes are produced worldwide yearly (Supaka et al. 2004). The amount of dyes that does not bind to the fibers, enters into wastewater during textile processing (Rai et al. 2005). It has been estimated that 2,80,000 tons of textile dyes are discharged in textile industrial effluents every year worldwide (Jin et al. 2007). Many dyes are visible in water at concentration as low as 1 mg/L (Sandhya 2010). Synthetic dyes can cause environmental pollution and serious health-risk factors due to large-scale production and extensive application (Forgacs et al. 2004).

Based on the chemical structure of the chromophoric group, dyes are classified as azo, triphenylmethane, anthraquinone, polymeric, and heterocyclic dyes. The versatile triphenylmethane and azo dyes account for most textile dyes (Yang et al. 2009). Azo dyes are characterized by the presence of one or more azo bonds [-N=N-] with aromatic ring. Different substitutions on aromatic nucleus give structurally different and versatile group of compounds which makes them recalcitrant and xenobiotic compound (Khan et al. 2013; Jain et al. 2012). Many dyes contain known carcinogens such as benzidine and other aromatic carcinogens (Singh 2006b).

In aquatic environment, dyes can interfere with photosynthetic activities of aquatic flora, diffusion of gases and badly affect food source of aquatic organisms and are of human health concern also. Dye forms thin layer over the surface of a water and thus decreases the amount of dissolved oxygen in the water, therefore adversely affects the aquatic flora and fauna. Dye-containing effluent increases biochemical oxygen demand of the contaminated water (Ciullini et al. 2008; Annuar et al. 2009; Ali 2010). Thus, nowadays degradation of dye is major point of concern.

Due to complex chemical nature, most of the synthetic dyes are highly resistant to degradation (Lin et al. 2010). Physical and chemical treatment methods such as precipitation, coagulation, adsorption, flocculation, flotation, electrochemical destruction, and mineralization and decolorization process have some disadvantages such as cost, time, and release of residues. All these techniques are minimizing the toxicity level but not neutralizing the toxicity. To replace these techniques, biodegradation can be used to completely degrade the dyes (Pandey et al. 2007).

Dye-contaminated industrial effluent is usually treated by physico-chemical processes include membrane filtration, precipitation, ion exchange, flocculation, flotation, ozonation, electro flotation, irradiation, and adsorption using activated carbon or by using bacteria, fungi, algae, plant biomass or other biological material (Robinson et al. 2001). Both living as well as dead cells are used for biosorption. Biodegradation is the most efficient method to remove dyes from industrial effluent and is energy-dependent process that involves the breakdown of dye into various byproducts by action of various enzymes such as laccase, azo reductase, peroxidase, and hydrogenase (Fu and Viraraghavan 2001).

Decolorization of the dye occurs when the chromophoric center of the dye is cleaved (Kaushik and Malik 2009). In biosorption process, the original structure of the dye remains intact and not degraded into fragments. Biosorption plays important role in the decolorization of dye by living fungi (Fu and Viraraghavan 2001). Several microorganisms, including bacteria, fungi, yeasts, and algae, can decolorize and completely mineralize many azo dyes under certain environmental conditions (Pandey et al. 2007). Both live as well as dead fungal biomasses can be utilized to remove dyes from the contaminated ecosystem.

## 7.4.1 Types of Toxic Dyes

During the manufacture and processing of textiles many different chemical reagents, such as acids, bases, water softeners, salts, and organic solvents dyes are utilized. From the 12 classes of chromogenic groups, azo dyes are largest group of synthetic colorants and the most common synthetic dyes released into environment (Zhao and Hardin 2007) followed by the anthraquinone type. They are widely used in the textile, food, pharmaceutical, cosmetics, plastics, paint, ink, photographic, and paper industries. Different types of dyes include azo, direct, acidic, basic and anthraquinone etc., are mentioned below with its structure and molecular weight in Table 7.2. (Pande et al. 2019).

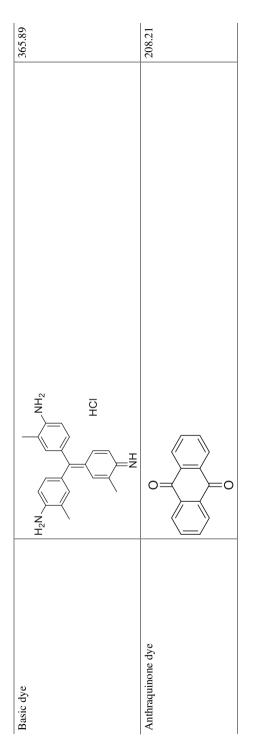
## 7.4.2 Dye Decolorization and Degradation by Marine Fungi

Marine-derived fungi, due to their adaptability to extreme conditions are better suitable in treatment of colored effluents than their counterparts in the terrestrial environment (Raghukumar 2004; Bonugli-Santos et al. 2015; Vala and Dave 2017). Fungi growing under marine conditions have adapted to grow under saline and alkaline conditions since the pH of seawater ranges from 7.5 to 8.2. *Alternaria tenuissima* (El Aty et al. 2017), *Cerrena unicolor* (D'Souza-Ticlo et al. 2009), *Aspergillus niger* (Lu et al. 2016; Joshi et al. 2012), *Flavodon flavus, Penicillium janthinellum* (Wang et al. 2015), *Peniophora* sp. (Bonugli-Santos et al. 2015), *Tinctoporellus* sp. (CBMAI 1061), *Marasmiellus* sp. (CBMAI 1062), and *Peniophora* sp. (MF 6), *Penicillium* sp. (MF 49), and *Cladosporium* sp. (Torres et al. 2011) are some examples of potential dye degrading fungi.

It has been reported that marine-derived fungi have potential for the decolorization of textile effluents and synthetic dyes such as Congo red, Brilliant green and RBBR (Raghukumar 2004, Raghukumar et al. 2008; D'Souza et al. 2006). According to Arun et al. (2008) the lignolytic extracellular enzymes produced by filamentous fungi have great relevance in bioremediation of toxic dyes. Bartlett (1971) illustrated that Some dyes are used as indicators for production of lignolytic enzymes and also play a very important role in bioremediation of lignin-based derivatives in colored industrial pollutants such as paper and pulp mills, textile mills, tanneries, and molasses-based distilleries.

Baccar et al. (2011) explained that White rot fungi such as *Trametes versicolor*, *Ganoderma lucidum*, and *Irpex lacteus* were evaluated for decolorization of Tannery Dye Black Dycem TTO and suggested adsorption and biodegradation as a key mechanism for removal of dye. Aksu et al. (2007) analyzed that *Trichoderma versicolor* biomass can be utilized for biosorption of Remazol Black B reactive dye. Laccase produced from Marine fungi can decolourize and mineralize high concentrations of pollutants (Vishwanath et al. 2014). *Myceliopthora thermophila* 

Table 7.2 Chemical structures of toxic dy	Table 7.2       Chemical structures of toxic dyes used in the textile industry (modified from Pande et al. 2019)	
Types of dyes	Structure	M.Wt.
Azo dye	HO	248.28
Direct yellow 4	HO N N N N N N N N N N N N N N N N N N N	624.55
Direct blue 98	SO <sub>3</sub> Na N H N SO <sub>3</sub> Na H O H N N SO <sub>3</sub> Na N H O H N SO <sub>3</sub> Na N H O H N N N H O H N N N N H O N N N N	928.79
Acid dye	HO N <sup>2</sup> N <sup>3</sup> N <sup>3</sup> N <sup>3</sup> N <sup>3</sup>	400.38



(*Ascomycetes*) have capacity for decolourization of flexographic inks in presence of mediators (Fillat et al. 2012; Deshmukh et al. 2016).

Young and Yu (1997) stated that Binding of dyes to the fungal hyphae, physical adsorption and enzymatic degradation by extracellular and intracellular enzymes are major mechanisms for the dye degradation (Young and Yu 1997). White rot fungi produce lignin peroxidase, manganese peroxidase and laccase that degrades many aromatic compounds due to their non-specific enzyme systems (Robinson et al. 2001; Madhavi et al. 2007). The predominantly reported enzymes for dye degradation are azoreductase, laccases, lignin peroxidase, manganese peroxidase, and hydroxylases. Azoreductase and Laccase have been shown to degenerate azo dyes (Rodrigue et al. 1999).

Chivukula and Renganathan (1995) stated that laccase enzymes can degrade the azo dye through a non-specific free radical mechanism to form phenolic compounds and prevent the formation of toxic aromatic amines. Manganese peroxidase has been reported as the main enzyme involved in dye decolorization by fungus *Phanerochaete chrysosporium* (Chagas and Durrant 2001). In fungus *Bjerkandera adusta*, lignin peroxidase has been reported as important enzyme in dye degradation (Robinson et al. 2001).

Dwivedi and Singh Tomar (2018) explained that *A.allhabadii* and *A. sulphureus* have higher decolorization capacity up to 95.13% and 93.01%, while *A. niger* has little lesser 83% decolorization capacity. Namdhari et al. (2012) explained that decolorization of azo and anthraquinonic dyes can be achieved by brown rot fungi such as *Coprinus micaceus, Fomtopsispinicola,* and *Gloeophyllum odoratum.* Saranraj et al. (2010) isolated *Aserpgillus niger, Aspergillus flavus, Aspergillus fumigatus, Trichoderma viride, Fusarium oxysporum, Penicillium chrysogenum* and Mucor sp. that are responsible for the degradation of a wide range of textile dyes.

Huanga et al. (2016) modified *Aspergillus versicolor* by using cetyl trimethyl ammonium bromide (CTAB) to enhance the fungal biosorption of Reactive Black 5 at various physiochemical conditions. Basidiomycetes fungi have been reported to decolourize dye by adsorption to the mycelial surface and further metabolic breakdown by both batch mode and continuous mode. *Schizophyllum commune* has found to be more efficient than *Lenzites eximia* for the treatment of azo dyes and textile dye industry effluent, (Selvam and Shanmuga Priya 2012). Yesilada (1995) analyzed that *Coriolus versicolour* and *Funalia trogii*are responsible for decolorization of crystal violet dye. Versatile peroxidase and lignin peroxidase have ability to oxidize non-phenolic aromatic compounds, reactive Black B dye and low redox potential was observed as seen from oxidation of phenolic substrates (Karigar and Rao 2011; Deshmukh et al. 2016).

Ollikka et al. (1993) described that isozymes of lignin peroxidase found in *Phanerochaete chrysosporium* has capability for decolourization of synthetic dye. *Phanerochaetechrysosporium* has been observed to degrade many dyes such as polymeric dyes, azo dyes, heterocyclic dyes, and crystal violet dyes. The fungus *P. Chrysosporium* can aerobically degrade three azo dyes includes congo red, orange II, and tropaeolin (Cripps et al. 1990).

Bonugli-Santos et al. (2015) studied that the ascomycetes and basidiomycetes can decolorize 30 to 60% of azo dye-containing effluent and 33 to 80% decolorization of mixture of 8 reactive dyes under saline conditions. Bucher et al. (2004) illustrated that decolorization of azure B is possible due to the production of ligninolytic peroxidase by fungi Rhizophila marina, Bathyascus grandisporus, Verruculina enalia, and Cryptovalsa halosarceicola. It has been found that Penicillium citrinum CBMAI 853 is the most efficient fungus that decolorizes RBBR (100%) after 12 days, A. sulphurous CBMAI 849 (95%), Cladosporium cladosporioides CBMAI 857 (93%), and Trichoderma sp. CBMAI 852 (89%) (Da Silva et al. 2008). Molitoris et al. (2000) isolated filamentous halophilic fungi Gymnoscella marismortui from the Dead Sea which is responsible for the decolorization of synthetic dye belonging to 4 different groups. Lalitha et al. (2011) explained that marine Aspergillus flavus has capacity for the bioremediation of synthetic, color photographic and paper mill dyes and can remove 80% and 90% synthetic dyes and 100% of color. It has been observed that sponge-derived basidiomycetes fungi have ability to decolorize textile dyes in solid medium under both saline as well as non-saline condition (Bonugli-Santos et al. 2012; Vala et al. 2018).

Raghukumar et al. (2008) explained that whole cell immobilization of marinederived fungi *Penicillium janthinellum* P1 and *Pestalotiopsis* sp. J63 showed the decolorization of Azure B dye. 70% decolorization of MSW in five days has been observed when marine-derived fungus NIOCC #312 is Immobilized on polyurethane foam (PUF) cubes. It has been seen that *Basidiomycetes* fungus, *Flavodon flavus* can decolorize synthetic dyes such as Congo red, Remazol brilliant blue R, Poly-B, and Poly-R. This fungus efficiently decolorized pigments in the molasses spent wash and could also reduce the total phenolic and COD up to 50% and toxicity completely. Verma et al. (2012) described that rapid decolorization and detoxification of anthraquinone dye Reactive Blue 4 can be achieved by enzymatic oxidation and sorption of degraded products on marine-derived fungal biomass. *Saagaromyces ratnagiriensis*, a non-white rot obligate marine ascomycete fungus has capability to decolorize effluent of paper mill (Sarma 2018).

#### 7.5 **Biomass Valorization**

Rapid exploration of Earth's resources has been steadily increased, giving rise to depletion of resources and rapid generation of waste product (Ferreira 2015). Nowadays, the best way to reduce the waste generation in large amount is their application for the production of value-added products. Valorization is the approach that facilitates sustainable development by value-added products from the waste (Kumari et al. 2018). Waste valorization is the process of converting waste materials into more useful products such as chemicals, reusable materials and fuels (Arancon et al. 2013).

Fungi are heterotrophic and obtain sustenance by hydrolyzing complex material and convert into simple form by taking up and utilizing substance for their biosynthesis and energy production (Hanson 2008). Filamentous fungi exist in a myriad of environments and have capacity to process complex and diverse substrates include starch or lignocellulosic polymers such as cellulose, hemicellulose, and lignin (Maity 2015). The biomass and byproducts produced by fungi during waste treatment are better valorized than bacteria. Fungi provide valuable enzymes as well as proteins. Several value-added products such as biofuels and biochemicals are produced by industrial cultivation of fungi using industrial waste as substrates.

It has been reported that processing of waste from dairy, sugarcane, tanning, oil, cotton, bioethanol, agro, marine, and poultry industries can be utilized as an attractive alternative source of low-cost organics and nutrients to valorize waste into fungal products with associated waste treatment. (Ali et al. 2020; Mahari et al. 2020: Gaur et al. 2020: Patel et al. 2017: Koutra et al. 2018). Compared to conventional physico-chemical processes, biological processes by using microorganisms including bacteria, fungi, and yeasts are offers a promising technique to produce biofuel while decolorizing recalcitrant synthetic dyes and lignin (Ali et al. 2019, 2020; Kiayia et al. 2019). Waste produced from the agro-industrial could be used as a sugar-based carbon source that can be either used alone or supplemented with various expensive nutrients like yeast extract for the production value-added products such as biodiesel, bioplastic, and exopolysaccharides at laboratory scale and pilot scale. Several value-added products that have been produced from wastes include biofuels like bioethanol and biohydrogen, short-chain organic acids, building-blocks, including 2, 3-butanediol, 1, 3-propanediol, and succinic acid, polymers like bioplastics, i.e., polyhydroxyalkanoates (Koutinas et al. 2014). The major waste generated in paper pulp industry is cellulose-based fibers that can be further treated for the production of useful products like fabric and paper.

Palmqvist and Hahn-Hägerdal (2000) explained that waste generated in pulp and paper industry is spent sulphite liquor (SSL) that can be used for the fabrication of phenolic compounds mainly aromatics syringic, gallic, and vanillic acids. According to Alexandri et al. (2016) the SSL can also be utilized as a raw material for the production of single-cell protein, bioethanol, bioplastics, bacterial cellulose and other valuable products. Mukherjee et al. (2015) stated that food waste can be product utilized for the production of another value-added called hydroxymethylfurfural (HMF), which could be utilized as the precursor of medicines, polymers, resins, solvents, and biofuels.

Similarly, lignocellulosic waste biomass has been used for the production of phytosterols, polypropylene, acrylic acid and esters (Bardhan et al. 2015). The main enzymes identified for lignin degradation include lignin peroxidase (LiP), manganese peroxidase (MnP), and the copper-containing phenoloxidase known as laccase. These ligninolytic enzymes have already been demonstrated utility in the food industry, pulp and paper industry, textile industry, and as biocatalysts (Jaqueline et al. 2010). Studies on utilization of lignin and/or lignin-like dyes by oleaginous yeasts hold much promise for achieving overall efficiency and sustainable utilization of lignocellulosic biomass and textile azo dyes for biofuel production (Ali et al. 2021).

White rot fungi, especially *Phanerochaete*, *Trametes*, *Bjerkandera*, and *Pleurotus* genera have ability to produce several lignocellulolytic extracellular enzymes. In general, the conversion of lignocellulosic biomass includes a pretreatment step for removal of protective lignin seal surrounding structural polysaccharides, followed by enzymatic hydrolysis and subsequent fermentation of released soluble sugars. Thus, the reducing sugars from hydrolysis of cellulose and hemicellulose fractions could be metabolized by other microorganisms producing value-added compounds such as alcohols, flavonoids, organic acids, and phenolics (Sánchez 2009; Mateo and Maicas 2015).

According to the study of pandey et al. (2015) *Aspergillus* spp. is involved in the production of many value-added products including enzymes such as amylase, protease, lipase, phytase, lactase, and catalase. *Trichoderma* spp. can be used for production of cellulose and xylanase. Moreover, *Aspergillus* spp. are responsible for a major fraction of commercial production of organic acids including citric acid, gluconic acid, and itaconic acid and they are also potential sources of malic and oxalic acid. Chitosan is used for production of superabsorbents can be obtained via hydrolysis of chitin from the cell walls of *Aspergillus* spp. and these ascomycetes can be used for production of keratinase hydrolysates (Pandey et al. 2015; Zamani 2010).

*Monascus* spp. have been important sources of pigments for the food industry and together with *Aspergillus* spp., *Fusarium* spp. and *Neurospora* spp. have been a source of different human food products (Ferreira 2015). However, unicellular ascomycetes, that is, yeasts such as *Saccharomyces* spp., *Pichia* spp., and *Yarrowia* spp. have also been reported to be potential sources of organic acids (such as a-ketoglutaric acid, lactic acid, malic acid and pyruvic acid), polysaccharides such as glucan, proteins like collagen, polyunsaturated fatty acids, sterols (e.g., squalene) and lipids (e.g., ceramides). Marine fungi can potentially play an important role as a bio catalyst in waste biorefineries due to their ability to produce enzymes that can break down these recalcitrant structures. By using filamentous ascomycetes, their biomass, normally rich in proteins and lipids, can represent another value-added product of the biorefinery (Ferreira 2015; Ferreira et al. 2016).

## 7.6 Conclusions and Future Prospectives

Fungi are considered as natural decomposers which can significantly reduce and degrade various recalcitrant, persistent, and toxic pollutants like hydrocarbons, heavy metals, and dyes. Most of the studies show the role of various extracellular ligninolytic enzymes and cytochrome 450 in the degradation of these pollutants. However, in most cases, the underlying mechanism of the mycoremediation of these harmful pollutants is elusive and needs further research. Mycoremediation can be augmented by adding carbon sources at polluted sites and providing optimum condition to increase degradation process. Naturally present community of microbes acts in concert with the fungi to decompose the harmful contaminants. White rot

fungi are extremely effective in decomposing toxic aromatic pollutants, heavy metals and dyes etc. Further studies could be helpful in understanding the mechanism and optimizing the process of mycoremediation. Benefit is offered that land that is contaminated and unfit for agriculture could be both restored and made to yield a nutritious food crop. Biomass valorization is the process which can convert waste materials into more useful products such as chemicals, reusable materials and fuels. This chapter will help to expand our understanding for the fungi from marine environment as potential candidates for biomass valorization and mycoremediation of hazardous pollutants that would be important for economical, ecological, and legal reasons as well.

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