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Fungal Degradation of Polycyclic Aromatic Hydrocarbons

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are two or more rings of benzene fused with both natural and anthropogenic sources. PAHs are to a large degree distributed contaminants of environmental that have detrimental biological effects, carcinogenicity toxicity, and mutagenicity. Because of their ubiquitous occurrence, bioaccumulation potential, recalcitrance and carcinogenic activity, the PAHs have compiled significant environmental concern. The PAHs may undergo volatilization, photolysis, adsorption, and chemical degradation. The microbial degradation is the main degradation process, numerous of fungi metabolize PAHs by using enzymes that include laccase, lignin and manganese peroxidase, as wall as cytochrome P450 and epoxide hydrolase. The enzymes of fungi implicated in the PAHs degradation, the fungal lignolytic enzymes are laccase, lignin and manganese peroxidase, those fungi extracellular and stimulate radical formation through oxidation to destabilize bonds in a molecule.In this review explains the biodegradation potential of ligninolytic and non-ligninolytic fungi to PAHs and also shows known conversion pathways.

Key words: *Fungi, Polycyclic Aromatic Hydrocarbons, Biodegradation , Metabolize, Enzymes*

Highlights

- *The enzymes of fungi involved in the PAHs degradation*
- *The microbial degradation can be considered as a key element to PAHs remediation*

INTRODUCTION

Microbial degradation is a viable technique for bioremediation of organic contaminants. It has long been known that microorganisms environmental contaminants of degrade in diverse matrices and environments. In process of bioremediation uses the metabolic diversity of microorganisms to degrade hazardous contaminants. The technique of bioremediation is intended to convert organic contaminants into non-harmful metabolites or mineralization of pollutants to water and carbon dioxide[1,2]. Effective remedial technology requires that microorganisms be able to adapt quickly to the effective utilizes of contaminants of interest in a given situation within a reasonable time.

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Numerous factors affect microorganisms to utlize contaminants as substrates or co-metabolize them. For understanding the pathways of catabolic and responsible enzymes is an effective way to identify significant factors for effective cleaning of contaminants. Studies have been conducted to understand the biological treatment of the environmental contaminants such as Polycyclic aromatic hydrocarbons (PAHs), which are among the most widespread and persistent environmental contaminants. PAHs are consist of two or more intensive aromatic rings of carbon and hydrogen atoms; rings are connected together in angular and linear arrangements. Due to their large negative resonance energy, they chemically stable at ambient temperature, because of their hydrophobic structures, and almost highly lipophilic or completely insoluble in water[3]. Low molecular weight (LMW) PAHs such as naphthalene, that two six-membered rings; fluorine, acenaphthene acenaphthylene and biphenylene, thta two six-membered rings and a four- or five-membered ring; and anthracene and phenanthrene, that three six-membered rings. High molecular weight (HMW) PAHs such as, pyrene, chrysene, benz[a], anthracene and fluoranthene, that four rings; benzo[a]pyrene, benzo[e]pyrene perylene, and dibenz[a,h], anthracene having five rings; and the others having six or more rings, Table 1. Despite, PAHs are present in petroleum and coal, the main modern source to PAHs is the incomplete combustion of organic matter from sources e.g., cars, coal fired power plants, forest fires and home heating furnaces[4]. PAHs are produced when petroleum products, coal, wood, old tires, urban solid wastes are burned. Also, other PAHs sources include oil refineries, steel mills, coke ovens, aluminum plants coal and gasification plants. spills of crude oil from drilling, pipelines and supertankers that deposit huge amounts of PAHs on the ocean and soil. PAHs are occur as colorless, white and pale yellow solids, low solubility into water, high boiling and melting points and lower vapor pressure as shown in Table.1. In an increase of molecular weight, their solubility in the water and vapor pressure decreases, while melting and boiling point both increases[5]. PAHs fate in the environment includes adsorption on soil particles, chemical oxidation, volatilization, photo-oxidation and leaching[6]. Those compounds are tough to degrade in the natural matrices and also their persistence increases much with their molecular weight. Moreover , PAHs represent a significant concern because of their widespread existence in environment, their potential to accumulate, and their resistance towards biodegradation and their carcinogenic and mutagenic impacts that occur by breathable air containing PAHs in the workplace, or through coming in contact with water, air, soil nearby hazardous waste sites or via drinking polluted milk or water etc.[7]. Potential treatments have performed to restrain further economic consequences and deterioration of water and soil quality. The process of bioremediation promise to deliver long lasting with low cost solutions to degradation of PAHs. Possible treatments have performed to prevent further economic consequences and degradation of water and soil quality. Biodegradation of petroleum hydrocarbons was done via bacteria, fungi and alga[8,10]. According to the results of numerous researchers over the years, the fungi protrude as a powerful choice to PAHs degradation. Fungi have characteristics over bacteria because their ability to grow into a large spectrum of substrates and meanwhile, they produce intracellular and extracellular enzymes, which can break through the contaminated soil and remove the petroleum hydrocarbons[11]. Therefore, many factors must to be taken into consideration due to affect their in the rate of PAHs biodegradation includes oxygen, temperature, accessibility for nutrients, and optimum conditions of enzyme like pH, cellular transport properties, chemical structure for compound and chemical partitioning into growth medium[12]. The rates of PAHs biodegradation are highly related to conditions of the environmental for the activity of enzyme and also to the growth of fungal. Biodegradation is a very broad field and

encompass the use of a wide range of microbial to break down chemical bonds. In fact, fungus is implicated in three main types of hydrocarbon metabolism, each with its distinct characteristic. Partial transformation reactions, complete degradation of hydrocarbons in the presence of second compatible substrate and independent use of hydrocarbons as a carbon source to energy .the present review is focused on fungal metabolize pathways of some polycyclic aromatic contaminants under aerobic conditions of culture.

2. PAHs Toxicity

PAHs are widespread contaminants, some of which have found to be genotoxic, cytotoxic, carcinogenic, or ecotoxic by studies carried out in vitro and also in vivo in animals, aquatic microorganisms, plants and humans. In contaminated air, PAHs are abundant in volatile particulate fractions and organic[13]. Photochemical reactions may change dramatically to carcinogenic nitro-PAHs or to endoproxides of the PAH and the radicals that are quickly converted to the quinones. Surface runoff water contains fluoranthene, pyrene and phenanthrene, and other PAHs emerging from wear and tear on vehicles and road. Many of those related areas are often associated with particles[2]. Soils along highway margins are contaminated from PAHs from exhaust, road tar, motor fuels, and street dust. These compounds may be related to organic molecules, silt or other fine particles in surface soils, or may absorb dissolved organic matter and filter into the soils.[14]. Some LMW PAHs are very toxic for aquatic organisms; and also several HMW PAHs are teratogenic and carcinogenic to mammals and also a mutagenic to bacteria. The germination of spore is prevented by phenanthrene in some fungi, The irradiation of the light of the PAHs that are in contact with the DNA may stimulate the cleavage of one strand of DNA, formation of DNA-PAH adducts, or oxidation of guanine to the 8-hydroxyguanine[2]. When the HMW PAHs are adsorbed to particulate matter in water sediments or soil, they are bioconverted a slowly. They also can be oxidized, however, via cytochrome P450 monooxygenases in the liver of mammalian. The products are ordinarily water soluble compounds that are excreted, But little of the metabolites probably be genotoxic compounds that form adducts with DNA[15]. Studies with animals have shown the ability of many other PAHs to cause cancer. The exposed of workers to industrial processes that released PAHs have also been exposed to high bladder cancer and lung cancer, and some PAHs have anti-estrogenic or weak estrogenic impacts[16]. Dibenz[a,h],anthracene was showed to cause skin tumors to mice, and also benzo[a]pyrene was proved to be more carcinogenic. Other studies have found that mammalian carcinogens are ultimately derived from benzo[a]pyrene, a stereoisomer of benzo[a]pyrene-7,8-diol-9,10-epoxide, and are produced by a series of enzymatic reactions induced by monoxygenases and epoxide Hydrolysis[15].

3. PAHs Metabolism by microbial

Bacteria are a type of microorganism actively participated in the organic pollutants degradation into polluted sites. A lots of bacterial species are known in the PAHs degrade. Most of which, representing efficiency of biodegradation, are isolated from polluted sediments or soil. Benzo[a]pyrene is one of the most carcinogenic and also toxic in PAH-petrochemical waste, researchs have found that bacteria able to degrade Benzo[a]pyrene when grown into it as sole carbon source in aqueous culture experiments[17]. *Sphingomonas paucimobilis* strain EPA 505 found a 5% decrease in Benzo[a]pyrene concentration within 168 h of incubation period[18]. Aitken *et al.*[19] reported that the 11 strains isolated from a different polluted sites (refinery oil, motor oil and wood treatment) was with great efficiency to degrade of Benzo[a]pyrene. A huge diversity of bacteria that are capable to oxidise Benzo[a]pyrene includes *Pseudomonas*, *Bacillus*, *Agrobacterium*, *Burkholderia* and *Sphingomonas* species[20]. Benzo[a]pyrene has reported to be degraded via another bacteria including Mycobacterium, *Rhodococcus* sp and mixed culture of Flavobacterium and

Pseudomonas species[19]. *Pseudomonas aerugino*sa isolated from a stream heavily contaminated by a petroleum refinery, which was showed to be actively growing over high phenanthrene dosages and complete removal of the pollutant at 30 days of incubation[21]. Romero et al.[21],reported that the phenanthrene degradation using microorganisms isolated from a polluted current, both *Pseudomonas aeruginosa* and *Rhodotorula glutinis* were the prevailing microorganisms using phenanthrene. Other studies performed to decontamination of contaminated soil in PAHs using a mixed microbial culture of the bacteria from the genera Klebsiella and Acenitobacter exhibited that after 6 months a great decline by 98% from PAH content took place. Several bacteria that have isolated and that utilizing a naphthalene as a energy and sole source of carbon are belong to the genera *Rhodococcus, Pseudomonas, Sphingomonas, Streptomyces, Ralstonia, Polaromonas, Alcaligenes, Burkholderia* and *Mycobacterium*[22]. Mycobacterium has most widely studied to degrading pyrene in culture to using it as a single carbon source[23]. Some fungi are known to have the ability to degradation of persistent pollutants. The degradation of lignolitic fungi has been studied intensively over the past few years, because of the irregular structure of lignin, lynolytic fungi produce extracellular enzymes in the privacy of the substrate low, making them suitable to degradation of various compounds. The system of lignolytic consists from three major enzyme groups including lignin peroxidase, phenoloxidases (lacases, tyrosinases), manganese dependent peroxidase, and H2O2-producing enzymes. The researches using purified enzymes found that lignolytic enzymes are capable for degrade PAHs[24]. Lignolytic enzymes execute a one electron radical oxidation, producing cation radicals from pollutants after then followed by quinines appearance. Clemente *et al.*[25], reported that the degradation of PAH by 13 deuteromycete ligninolytic fungal strains, shown that the degradation rate differs with the difference of lignolytic enzymes. Higher naphthalene degradation by 69% was shown via the strain 984 with Mn-peroxidase activity, for the strain 870 by 17% observing lignin peroxidase and laccase activities. Phenanthrene degradation by 12% was found in strain 870 having Mn-peroxidase and laccase activities. A high level of anthracene degradation (65%) was showed by the strain 710[25]. LMW PAHs (2-3 rings) were showed to be degraded more widely via *Trichocladium canadense Aspergillus sp.,* and *Fusarium oxysporum.* While HMW PAHs (4-7rings), the optimum degradation has showd via *Aspergillus* sp., *Trichocladium canadense*., *Achremonium* sp and *Verticillium* sp. These studies have observed that fungi have a significant efficiency to degrade a wide range of PAHs with low-oxygen conditions. The system of monooxygenase cytochrome P450 also generate epoxies that are implicated in degradation. Epoxides can be hydrolyzed to vicinal dihydrodiols or they may be rearranged into hydroxyl derivatives. Cajthaml *et al.*[26], studied the pathway for degradation of anthracene and phenanthrene using lignolytic fungus. Both bacteria and fungi metabolize a wide range of PAHs, but the main pathways used by each group are various, see Fig.1. Metabolism of PAHs by aerobic bacteria is usually started by dioxygenases, that incorporate atoms of O2 in to PAH to configure one or more isomeric cis-dihydrodiol metabolites.

Bacterial dioxygenases are enzyme systems of multi component ; for example , naphthalene dioxygenase comprises of a ferredoxin, a ferredoxin reductase and the terminal iron-sulfur protein with small β and large α subunits. The cis-dihydrodiols are decreased by dihydrodiol dehydrogenases to configure a dihydroxylated aromatic intermediates (catechols), that can serve as substrates to *ortho* and *meta* ring-fission dioxygenases[27]. The ring cleavage products are aslo metabolized for tricarboxylic acid cycle intermediates and finally to CO_2. Tongpim and Pickard[28], reported that the *Mycobacterium* spp. and *Streptomyces* produce monooxygenases, which can oxidize PAHs to trans-dihydrodiols. The trans-dihydrodiols are

encountered often among the metabolites resulted by fungi. Generally, aerobic microorganisms degrade LMW PAHs more faster than HMW PAHs. There are at four possible reasons make the degrade PAHs of HMW more slowly than PAHs of LMW: lower water solubility, insufficient ability to stimulate degradative enzymes, slower uptake into the cells and lower energy yield to growth[29]. If HMW PAHs are supplied as an energy carbon source, available energy from the start reactions may not be satisfactory for growth. Thus , other carbon source is normally added to supply the conditions to a co-metabolism. Due to the toxicity and persistence of HMW PAHs into the environment, numerous laboratories have tested a broader phylogenetic spectrum of microorganisms to the possible to degrade them[30,31].

4. PAHs Metabolism by Fungi

The Efficient PAHs biodegradation by a fungi and another microorganisms has reported intensively in the last few years[32]. The ligninolytic fungi (a group that secrete enzymes to breakdown a lignin in wood) and non-ligninolytic fungi (a group that do not secrete those enzymes) involved to the degradation of PAHs are listed in Table.2. Most of the main groups of non-ligninolytic fungi are ascomycetes, zygomycetes, hyphomycetes, and also others, include degraders of PAH. The *Aspergillus* species, *Cunninghamella*, and *Penicillium* the initial PAH transformation includes oxidation via the O2 cytochrome and P450 monooxygenase to form the water and an arene oxide. The arene oxide unsteady intermediate either is hydrated via the epoxide hydrolase to the trans-dihydrodiol Or re-arranged nonenzymatically to configure a phenol. PAH trans-dihydrodiols and phenols could be methylated or transformed to sulfates, glucuronides, xylosides or glucosides[33]. The metabolites of PAHs using nonligninolytic fungi are mostly same to those configured by mammalian stage I and phase II reactions , despite the existence of variances in the regio- and stereoselectivity of a participating enzymes[34]. Some fungi implement more wide metabolism to the PAHs that lead to rings cleavage and production of CO2. WRF is a big group belong to ligninolytic, wood-degrading basidiomycetes which includes species of *Pleurotus*, Trametes and *Phanerochaete* might induce a cytochrome P450 that functions in the initial PAHs oxidation. *Phanerochaete chrysosporium* has three cytochrome P450 genes CYP63 (A1, A2 and A3) could encode enzymes implicated to oxidation of low and HMW PAHs[35]. The CYP63 genes expression is depends on the cultural conditions, nutrients and the substrates used as inducer. Moreover, white rot fungi (WRF) can secrete extracellular ligninolytic enzymes, which are lignin peroxidases, laccases and manganese peroxidasesthat are also probable to be implicated. Those enzymes generally degrade components of wood but also oxidize PAHs to transient PAH diphenols, that are easily autoxidized to the quinones.

Lignin peroxidase with of H2O2, oxidizes PAHs by oxidation possibilities $\leq$ 7.55 eV[36], the Manganese peroxidase can be oxidizes the PAHs through means of the Mn-dependent unsaturated lipids peroxidation[37]. The laccase, a copper-containing enzyme, oxidizes PAHs with mediator compounds existence, includes aniline, phenol, 4-hydroxybenzyl alcohol, 4-hydroxybenzoic acid, methionine, cysteine/reduced glutathione[38]. Lignin is consdred a heterogeneous, HMW polymer from phenylpropane subunits along with β-aryl ether, carbon-carbon, and another kindso f connectors. Due to the lignin has chemical likeness with PAHs and some another environmental contaminants, ligninolytic fungi have considered promising candidates for tested the deterioration degradation of PAH[39]. The PAHs degradation by ligninolytic fungi probably implicate intracellular enzymes, including an epoxide hydrolase and cytochrome P450 monooxygenase[40]. When the *Phanerochaete chrysosporium* grown in the high-nitrogen medium, metabolizes phenanthrene to many metabolites, such as phenanthrene trans-9S,10S-dihydrodiol, the

similar enantiomer as that configured thru mammals, when grown in a low concentration of nitrogen culture medium, metabolizes phenanthrene instead to phenanthrene 9,10-quinone, with following cleavage of ring at the C-9 and the C-10 positions to configure 2,2 0-diphenic acid and ultimately CO2, Fig. 2.[41]. Therefore, at least two pathways of metabolic for PAHs coexist in *Phanerochaete chrysosporium*; first leads to trans-dihydrodiols, second to the quinones and other products of oxidation. A *Pleurotus ostreatus* is belong to a ligninolytic fungus, it can metabolize and mineralize anthracene, pyrene, fluorene and phenanthrene, when grown in both high and low nitrogen culture medium. The pathways suggested for the PAHs metabolism by *Pleurotus ostreatus* refer that it metabolizes them in a highly regio- and stereoselective manner[42]. The pathway of *Pleurotus ostreatus* is the same as to that in *Phanerochaete chrysosporium* different only in stereoselectivity and the production of laccase as an alternative of LiP[42]. Moreover, two major types of fungal PAHs metabolism; those are mediated by both non-ligninolytic and ligninolytic fungi. Most of non-ligninolytic fungi can not grow on wood, and then they have no need to produce the lignin peroxidase enzymes like in the ligninolytic fungi.

4. 1. Non-ligninolytic fungi

The initial step of PAHs metabolism via non-ligninolytic fungi is to oxidise the PAH in a cytochrome P450 monoxygenase enzyme stimulated reaction to configure an arene oxide[43]. This pathway is same to the mammalian PAHs metabolism. In comparison for aromatic compound oxidation via dioxygenase enzymes to configure cisdihydrodiols, the monoxygenase enzyme involves just one oxygen atom onto the compound to configure an arene oxide. this is hydrated by an epoxide-hydrolase catalysed reaction to configure a transdihydrodiol[44]. Moreover, phenol derivatives could resulted from arene oxides via the non-enzymatic re-arrangement of compound, that can act as substrates to subsequent methylation or sulfation, or conjugation with glucuronic acid xylose, or glucose. Despite most of non-ligninolytic fungi are not able to complete PAHs mineralisation, those conjugates PAH are mostly less toxic and much soluble than their respective orginal compounds. Pothuluri et al.[45] reported that the fluoranthene degradation by using the species of non-ligninolytic fungal *Cunninghamella elegans*, the metabolites 3-fluoranthene-β-glucopyranoside, 3-(8-hydroxy-fluoranthene)-β-glucopyranoside, fluoranthene trans-2,3-dihydrodiol and also 8-hydroxy-fluoranthene-trans-2,3-dihydrodiol showed no mutagenic impacts to a mouse liver homogenate fraction, and 9- hydroxy-fluoranthene-trans-2,3-dihydrodiol was considerably lower toxic than fluoranthene. *Aspergillus niger, Chrysosporium pannorum and Cunninghamella elegans* are instance of non-ligninolytic fungi that use a cytochrome P450 monoxygenase enzyme-mediated oxidative route for degradation of PAH. An instance the cytochrome P450-mediated oxidation pathway of phenanthrene is detailed in the Fig 2,steps 1 to 4 of .

4.2. Ligninolytic fungi

WRF are a major group from fungi that secrete ligninolytic enzymes that implicated in the lignin oxidation with extant in wood and another organic material. Ligninolytic enzymes include two classes; those being laccases and peroxidases. Those enzymes are produced extracellularly, and oxidise organic substance by a non-specific radical based reaction. A two major kinds of peroxidase enzyme depending on their reducing kind of substrate, manganese peroxidase (MnP) and lignin peroxidase (LP), those enzymes are able to oxidising the PAHs[46]. Laccases, that are phenol oxidase enzymes, are also able of oxidizing PAHs. In ligninolytic conditions, WRF can oxidise PAHs via generating free radicals (i.e., hydroxyl free radicals) via the donation of one electron, that oxidises the ring of PAH[43]. This generates a selection of PAH-quinones and acids instead dihydrodiols, llustrated in, Fig. 3, steps 5 and 6 . There is considerable interest for use the ligninolytic

fungi for degrade PAHs, Since they have a low substrate specificity and are therefore capable to degrade even the most compounds recalcitrant. Degradation researches of the ligninolytic fungi have reported that PAHs probably degraded by a incorporation of epoxide hydrolases, cytochrome P450 monooxygenases and ligninolytic enzymes, which can lead in the complete mineralisation of the compound[47]. Degradation experiments of HMW PAHs includes benzo[a]pyrene and pyrene using ligninolytic fungi (*Pleurotus ostreatus* and *Phanerochaete chrysosporium*) referred that a combination of non-ligninolytic and ligninolytic enzymes probably the key to the complete mineralisation of those recalcitrant compounds[47]. Substantial studies has focused in the possibility of this group of fungi to remediate materials of PAH-polluted. In bioremediation field that used ligninolytic fungi to remediate polluted soils by PAH and sediments have found mixed results. Canet et al.[48]proved that four WRF species was used to degrade a coal-tar-polluted soil, in this study, the soil was supplemented with straw (as a substrate for the ligninolytic fungi). Moreover , the indigenous soil microorganisms were successful in PAHs degradation than the introduced fungal species. Andersson and Lundstedt[49], reported that the WRF and brown-rot fungi (*Antrodia vaillantii* and *Pleurotus ostreatus*) were used to degrade a high range of PAHs.

5. Fungal metabolism of LMW PAHs

Naphthalene was used as a model hydrocarbon compound to examine the ability of microbial to degrade PAHs due it is the simplest and the most soluble PAH. Naphthalene metabolized by *Cunninghamella bainieri* and many other fungi[50]. A cytochrome P450 monooxygenase at first produces a transient naphthalene 1,2-epoxide, that is immediately converted further to metabolites which include the trans-1,2-dihydrodiol, 1- and 2-naphthols, 4-hydroxy-1-tetralone, 1,2- and 1,4-naphthoquinones, and sulfate and also glucuronide conjugates. Yogambal and Karegoudar[51], reported that the *Aspergillus niger* has been metabolized the naphthalene by gentisic acid. Biphenylene can be oxidized by using the laccase of WRF (*Coriolopsis gallica*) in the ABTS presence, and via the LiP of *Phanerochaete chrysosporium*[52]. *Cunninghamella elegans* metabolized acenaphthene to the 1-acenaphthenol, 1,5-dihydroxyacenaphthene, cis- and then to trans-1,2-dihydroxyacenaphthenes, 1-acenaphthenone, 6-hydroxy-1-acenaphthenone, and after to 1,2-acenaphthenedione[53]. *Cunninghamella elegans* oxidized the fluorine to form 9-fluorenol, 9-fluorenone, and to the 2-hydroxy-9-fluorenone[54]. Other fungi incudes *Cryphonectria parasitica, Ceriporiopsis subvermispora Bjerkandera adusta, Drechslera spicifera, Sporormiella australis, Aspergillus terreus, Embellisia annulata, Colletotrichum dematium, Cunninghamella blakesleeana, and Cunninghamella echinulata* also can create the 9-fluorenol and 9-fluorenone when oxidized the fluorine[55]. The laccases of *Coriolopsis gallica* and *Trametes versicolor* oxidize the fluorine to 9-fluorenone in the existence HBT mediator[38]. *Cunninghamella elegans* can be oxidized Phenanthrene to form the trans-1,2-, 3,4-, and 9,10- dihydrodiols, glucosides of the 1-, 2-, 3-, 4-, and then to 9-phenanthrols, and 6-sulfates, *Syncephalastrum racemosum* also can oxidized it to the trans-3,4- and 9,10-dihydrodiols, 4-phenanthrols, 5-sulfates, and a glucuronide Fig. 2.[56]. The process appears to have been initiated by the cytochrome P450 which is also implicated in steroid hydroxylation. *Aspergillus niger* metabolized the phenanthrene to form he trans-9,10-dihydrodiol, the 1- and 2-phenanthrols, 1-methoxyphenanthrene, and to a glucuronide, three sulfates, and protocatechuic acid[57].*Penicillium* spp., *Cyclothyrium* sp., *Mucor ramosissimus*, *Aspergillus terreus* and various other fungi are able to degraded the Phenanthrene[58]. phenanthrene metabolizes by *Phanerochaete chrysosporium* using a cytochrome P450, configuring the trans-9,10- and 3,4-dihydrodiols, 9-, 3-, and then to 4-phenanthrols, and a glucoside conjugate[59], *Cunninghamella elegans* oxidized anthracene to the trans-1,2-dihydrodiol, 1-anthrol, and

then to 1-anthryl sulfate, a cytochrome P450 seems implicated in the initial oxidation[60].

Aspergillus terreus, *Rhodotorula glutin*, *Ulocladium chartarum*, *Mucor ramosissimus*, *Cyclothyrium sp*., is also able to degraded anthracene[58]. The anthracene cleavage by *Aspergillus niger* led to producing a gentisic acid[51]. The anthracene metabolize by WRF using laccase, LiP or MnP, oxidizes of anthracene by *Phanerochaete chrysosporium* to 9,10-anthraquinone, then acid is the ring cleavage product[61]. The crude MnP of *Nematoloma frowardii* oxidizes anthracene to the CO2, particularly in the reduced glutathione presence[62]. The degrades of anthracene by *Irpex lacteus* produces anthraquinone, 1- and 2-hydroxyanthraquinones, anthrone, and hydroxyanthrone, 2-(2 0-hydroxybenzoyl) benzoic acid, and then to phthalic acid, 2-(hydroxymethyl) benzoic acid, and then dimethylphthalic acid[63].

6. Fungal metabolism of HMW PAHs

Cunninghamella elegans and other fungi can be transformed the fluoranthene to difference metabolites that such as the trans-2,3-dihydrodiol, 9-hydroxy- and also 8-hydroxy-trans-2,3-dihydrodiols, 3-hydroxyfluoranthene, and the 2- glucosides[64]. There are many fungi metabolize fluoranthene includes *Absidia cylindrospora*, *Absidia fusca*, *Penicillium* sp., *Flammulina velutipes*, *Marasmiellus* sp., *Laetiporus sulphureus*, *Trametes versicolor*,*Pleurotus ostreatus*, *Agrocybe praecox*, *Daedalea quercina*, *Bjerkandera adusta*, and others[65,67]. The MnP produced by *Nematoloma frowardii* mineralizes the fluoranthene in the existence of reduced glutathione[62]. The laccase of *Trametes versicolor* able to oxidizes fluoranthene, particularly in the presence of HBT[68]. Pyrene by fungus *Cunninghamella elegans* transformed to 1-hydroxypyrene, the 1,6- and 1,8-quinones, and to the glucoside conjugates, see Fig. 3[69]. *Mucor racemosus* var. *Gliocladium virens*, sphaerosporus, *Trichoderma harzianum*, *Scopulariopsis brumptii*, *Penicillium simplicissimum*, *Penicillium janthinellum*, *Penicillium ochrochloron* and *Coniothyrium fuckelii* are degrade pyrene[70]. The metabolizes of pyrene by *Aspergillus niger* is to 1-hydroxypyrene, 2-quinones, 2- diols, 1-methoxypyrene, 1-pyrenyl sulfate, and to the 1-hydroxy-8-pyrenyl sulfate[71]. *Aspergillus terreus* oxidizes pyrene to 1-pyrenyl sulfate by cytochrome P450 monooxygenation and sulfate conjugation reactions[72]. LiP of *Phanerochaete chrysosporium* is metabolizes pyrene to one or more quinones and finally to CO2[58,73]. *Nematoloma frowardii* produces an LiP that oxidizes pyrene at a rate which is improved with presence of veratryl Alcohol, while the MnP produced from the same strain is also oxidizes and mineralizes pyrene, particularly in the presence of reduced glutathione[73]. *Trametes versicolor* laccase can oxidizes pyrene, with the addition of HBT[68]. Growth of *Rhodotorula glutinis* and *Fusarium solani*, isolated from contaminated sediments, and for four various *Penicillium* spp. and *Trichoderma harzianum*, isolated from soil at a formergasworks site on pyrene as a energy and single carbon source has been reported[74]. *Cunninghamella elegans* is oxidized Benz[a],anthracene to the trans- 8,9-, 10,11-, and 3,4-dihydrodiols and also the 3,4-diol-1,2-epoxides[75]. The laccase produces by *Trametes versicolor* oxidizes benz[a], anthracene; oxidation is improved with HBT[76]. Passarini et al.[77],reported that the *Aspergillus sclerotiorum* CBMAI 849 exhibited the better execution with regard to pyrene degradation and benzo[a], pyrene, and also *Mucor racemosus* CBMAI 847 was capable to metabolize pyrene and benzo[a]pyrene, the hydroxylation mechanism was mediated by the cytochrome P-450 monooxygenase. Machín-Ramírez et al.[78], found that the use of *Aspergillus niger*, *Penicillium Trichoderm harzianum* has high effective to benzo[a], pyrene degradation. Verdin et al.[79], isolated fungi have been a greater ablity to degrade benzo[a], pyrene includes *Trichoderma viride* and *Fusarium solani* convert different amounts of benzo[a],pyrene in liquid state.

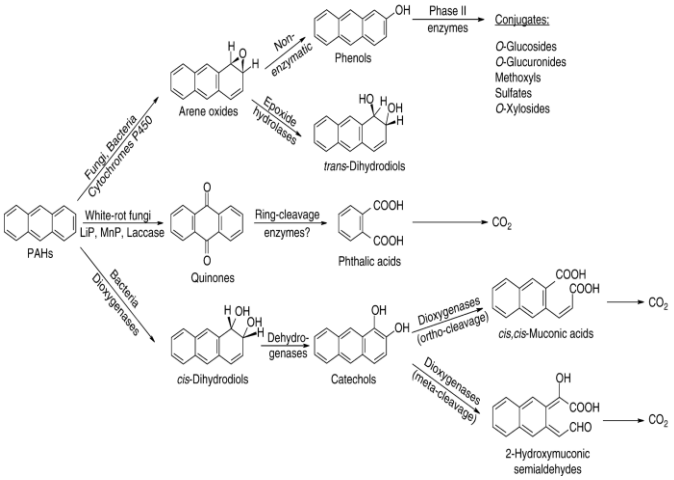


Fig. 1: Three main pathways for the metabolism of PAHs by fungi and bacteria [80]

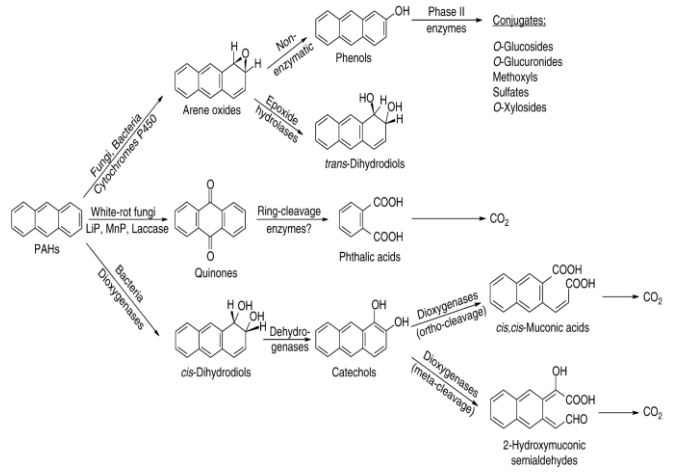


Fig. 2: Pathways for the metabolism of phenanthrene by various fungi[81,82]

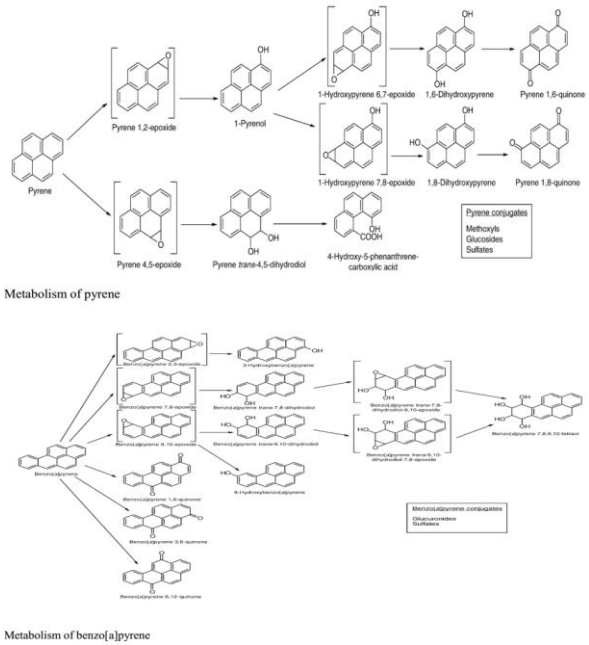


Fig. 3: Pathways for the metabolism of pyrene and benzo[a]pyrene by various fungi [81]

Table 1: Physical -chemical characteristics of PAHs

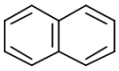
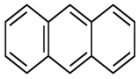
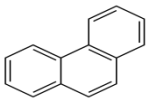
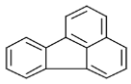
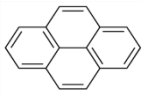
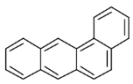
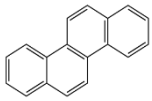
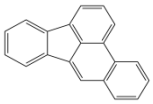
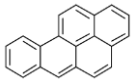
Compound	Formula	Mol. wt. (g/mol)	CAS registry No.	Boiling point (°C)	Melting point (°C)	Aqueous solubility (mg/l)	Structure
Naphthalene	$C_{10}H8$	128	91-20-3	218	80.2	30	
Anthracene	C14H10	178	120-12-7	340	216.4	0.015	
Phenanthrene	C14H10	178	85-01-8	339 -340	100.5	0.25	
Fluoranthene	C16H10	202	206-44-0	375 -393	108.8	0.12 -0.18	
Pyrene	C16H10	202	129-00-0	360 -404	393	0.0057	
Benz[a]anthracene	C18H12	228	56-55-3	438	162	0.0038	
Chrysene	C18H12	228	205-99-2	448	254	Insoluble	
Benzo[b]fluoranthene	C20H12	252	205-99-2	168	168.3	Insoluble	
Benz[a]pyrene	C20H12	252	50-32-8	495	179	0.0038	

Table 2: Polycyclic aromatic hydrocarbons oxidized by different species of fungi

Fungi	Compound	References
Trichoderma harzianum	Naphthalene	Mollea, Bosco [81]
Phanerochaete chrysosporium		Mollea, Bosco [81]
Cunninghamellaelegans		Cerniglia, Hebert [82]
Aspergillus niger		Cerniglia, Hebert [82]
Cunninghamella bainieri		Ferris, Fasco [48]
Cunninghamella elegans	Anthracene	Cerniglia [83]
Pleurotus ostreatus		Schützendübel, Majcherczyk [84]
Aspergillus fumigatus		Ye, Yin [85]
Phanerochaete chrysosporium		Juan, Jun [86]
Cunninghamella elegans	Phenanthrene	Romero, Cazau [19]
Aspergillus niger		Hammel, Kalyanaraman [34]
Phanerochaete chrysosporium		Sack, Hofrichter [87]
Pleurotus ostreatus		Bezalel, Hadar [40]
Cunninghamella elegans	Fluoranthene	Pothuluri, Freeman [52]
Penicillium sp		Pointing [30]
Pleurotus ostreatus		Pozdnyakova, Rodakiewicz-Nowak [88]
Aspergillus niger	Pyrene	Sack [63]
Cunninghamella elegans		Cerniglia, Mahaffey [89]
Pleurotus ostreatus		Sack, Heinze [65]
Candida krusei	Benzo[a]anthracene	MacGillivray and Shiaris [90]
Cunninghamella elegans		Cerniglia and Yang [91]
Phanerochaete chrysosporium		Bogan, Schoenike [92]
Aspergillus ochraceus	Benzo[a]pyrene	Passarini, Rodrigues [75]
Cunninghamella elegans		Cerniglia, Mahaffey [89]
Trametes versicolor		Collins, Kotterman [93]
Trichoderma viride		Machín-Ramírez, Morales [76]
Mucor sp		Dan, Li [94]
Fusarium solani		Fayeulle, Veignie [95]
Cunninghamella elegans	Chrysene	Pothuluri, Selby [96]
Penicillum janthinellum		Boonchan, Britz [97]

CONCLUSION

Several fungi from various groups are capable to metabolize LMW and HMW PAHs. Since most fungi cannot benefit PAHs as single carbon sources, culture media most of which provided with nutrients as a co-metabolism. The fungal transformation of PAHs involves different enzymatic pathways that count on upon the growth conditions and species.The enzymes include laccase, MnP, LiP, epoxide hydrolase and cytochrome P450. The ligninolytic fungi that produce laccase LiPand MnP show a much possible than most non-ligninolytic fungi for PAHs degrade because of the broad specificity of those extracellular enzymes, whose participation in the PAHs metabolism. The metabolize PAHs of ligninolytic fungi by free radical-mediated reactions to hydroxylated intermediates and PAH quinones, that probably degraded further by ring fission. The epoxide hydrolase and cytochrome P450 in ligninolytic fungi also play a significant role in the initial hydroxylation of PAHs. Based on a current review, it can be concluded that microbial degradation could be considered as a key element of the cleaning strategy to PAHs remediation.

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Disclosure statement

No potential conflict of interest was reported by the authors

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