International Journal of Research Publication and Reviews

Journal homepage: www.ijrpr.com ISSN 2582-7421

Biodegradation of Various PAHs Compound

[1]Avi Niranjan, [2]Sweta Patel

[1,2] Bhagwan Mahavir University, Surat.

DOI: https://doi.org/10.55248/gengpi.2022.3.8.19

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs), including Phenanthrene, are commonly found as pollutants in soils, estuarine, sediments, and terrestrial and other aquatic ecosystems. The Phenanthrene degrading bacterial degradation of Naphthalene, Anthracene, Fluoranthene, Benzo[a]pyrene were reviewed. Many bacteria have the potential and capability to degrade PAHs contaminated sites and are consequently recommended for bioremediation. The biodegradation ability can be evidenced by different methods like gas chromatography and flame ionization detector.

Keywords: Bacterial degradation; bioremediation; polycyclic aromatic hydrocarbons;

INTRODUCTION

Consuming almost 70% of the Earth's surface, the marine environment is one of the largest ecosystems on the planet. Due to changes in variables, including temperature, pH, salinity, currents, precipitation, and wind currents, it is the most adaptable habitat. Recent years have seen an increase in the contamination of the marine environment by various organic pollutants from various sources, including uncontrolled releases from industrial manufacturing and refining installations, discharge from effluent treatment plants, run-off from terrestrial sources, and oil spillages during transportation. (Head and Swannell, 1999)

Since benzene moieties have high thermodynamic stability and are hydrophobic, polycyclic aromatic hydrocarbons (PAHs) are common organic contaminants that remain in the environment (John et al., 2012; Dave et al., 2014). The elimination of polycyclic aromatic hydrocarbons (PAHs) from the environment has garnered much attention in recent years.

The angularity, water solubility, molecular weight of the PAHs, the nature of the location, and different legal and environmental restrictions frequently determine the best strategy for removing these PAHs from the soil, sediment, and aquifer. The excavation and removal of contaminated soil, landfilling, and incineration are the traditional techniques utilized for the remediation of polluted soils and sediments. These procedures are costly, and either on-site or off-site containment only moves or confines the pollutant without destroying it, demanding long-term monitoring.

Numerous studies on the breakdown of PAHs by microorganisms such as bacteria, fungus, and algae have been conducted over the past 20 years (Cerniglia, 1992). Common bacterial genera for PAH degradation include Bacillus, Beijerinckia, Mycobacterium, Pseudomonas, Sphingomonas, Serratia, and Rhodococcus (Haritash and Kaushik, 2009). Microorganisms are used in biodegradation to change or mineralize harmful substances, such as PAHs. Removing PAHs from the environment and cleaning contaminated areas have drawn attention to biodegradation. Because environmental conditions can vary greatly, microbes have unique traits that help them adapt to these adverse situations. Therefore, microorganisms isolated from the marine environment can use PAHs and other recalcitrant contaminants. The primary benefit of using these native microbial communities is that they may be employed in bioremediation experiments without undergoing any genetic modification. (Dash et al., 2013).

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a sizable and diverse class of organic pollutants that can develop naturally or as a result of human activity. Forest fires, oil seeps, volcanic eruptions, and tree exudates are examples of natural sources. Burning fossil fuels, coal tar, wood, trash, old lubricating oil, oil transportation, releases from petrochemical refineries burning municipal solid waste, and petroleum spills are all examples of anthropogenic sources of PAH (Haritash and Kaushik, 2009). Carbon and hydrogen atoms are present in PAHs, fused benzene rings arranged in linear, angular, and clustered patterns. However, heterocyclic aromatic compounds, frequently classed with the PAHs, can be created by substituting nitrogen, sulfur, and oxygen atoms in the benzene rings.

Additionally, alkyl-substituted PAHs are typically discovered in the environment with PAHs. Polycyclic aromatic compounds is a term that is occasionally used to refer to the entire class of PAHs and associated substances (PACs). Due to their toxicity, mutagenicity, carcinogenicity, and environmental persistence, PAHs have been extensively researched. As a result, the United States Environmental Protection Agency has classified several PAHs as priority pollutants (US EPA) (Kanaly and Harayama, 2000).

Structure of PAHs

A class of substances known as PAHs is made of carbon and hydrogen. A "bay region," a "K-region," and an "L-region" make up the majority of PAHs. Figure 1 shows the various areas of the structure of the example PAH molecule benz[a]anthracene.

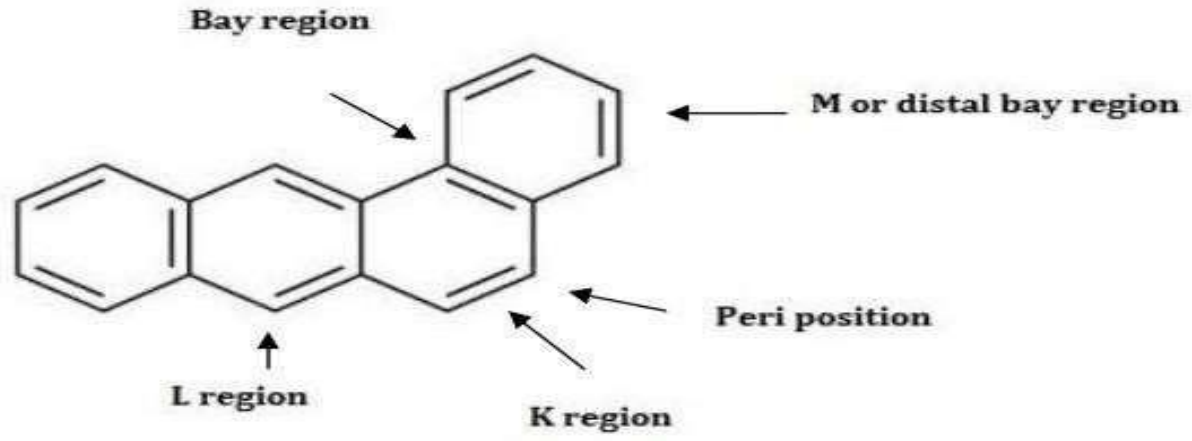


Figure 1. Regions related to biological activity in PAHs (Guillén and Sopelana, 2003).

The phenanthrene structure's internal, open bay region is a corner. The L-region is a pair of opposing anthracene point atoms, while the K-region is an exterior closed corner (Ramesh et al., 2011). These epoxides from the bay and K regions react chemically. Low molecular weight (LMW) PAHs are more soluble, volatile, and quickly destroyed. High molecular weight (HMW) PAHs, on the other hand, have a great ability to bind to soils and are hence less susceptible to microbial breakdown. High molecular weight PAHs compounds are highly hazardous to entire cells because they are hydrophobic in their solid state (Cerniglia, 1992). The size, number of aromatic rings, molecular topology, or the pattern of ring linking of a PAH molecule all affect its qualities. Figure 2 shows the chemical structures of the sixteen PAHs identified by the US EPA according to their abundance and toxicity (Kanaly and Harayama, 2000).

Source of PAHs

The incomplete combustion of organic molecules results in the formation of PAHs. Their emissions are caused by various combustion processes, including home, industrial, and agricultural. The incomplete combustion of organic materials is caused by both industrial and daily human activities, such as the processing of coal, the burning of wood, crude oil, and natural gas for heating, transportation, cooking, and smoking, or even by natural processes like carbonization (Ravindra et al. 2008). stated that, generally, there are five primary sources of PAH emissions: natural, home, mobile, industrial, and agricultural

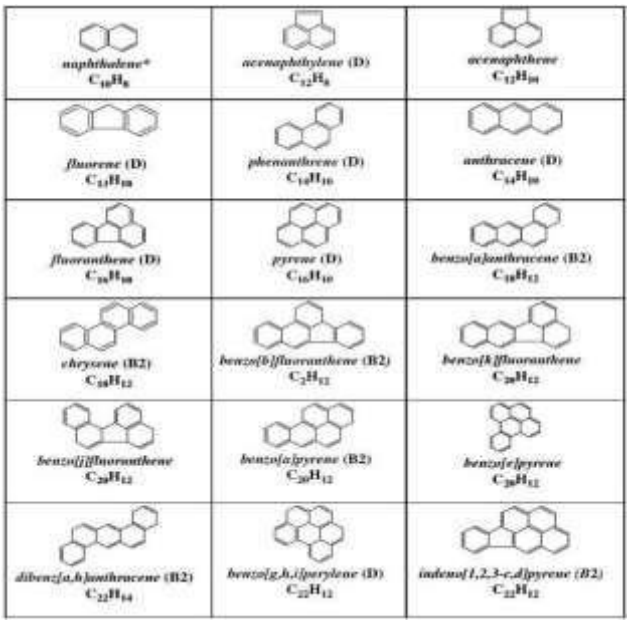


Figure 2. Structures of the 16 PAHs listed by the US EPA as priority pollutants; D (not listed as a human carcinogen); B2 (probable human carcinogen).

- Burning and pyrolysis of coal, oil, gas, trash, wood, or other organic materials are examples of domestic sources. The main source of PAHs in indoor environments is cigarette smoke. According to numerous studies, smoking homes often have higher indoor PAH levels than non-smoking homes.
- Urban areas, vehicles like aircraft, ships, cars, off-road vehicles, and machinery are all examples of mobile sources that emit PAHs. The heavy usage of diesel, coal, gasoline, oil and lubricating oil is also linked to PAH emissions.
- Urban areas, vehicles like aircraft, ships, cars, off-road vehicles, and machinery are all examples of mobile sources that emit PAHs. The heavy usage of diesel, coal, gasoline, oil and lubricating oil is also linked to PAH emissions.
- Open burning of biomass, a typical practice for getting rid of crop and forest leftovers, is one agricultural source of PAHs. However, burning agricultural waste is a source of PAHs in the atmosphere. The open burning of firewood and straw are examples of agricultural sources.
- Burning of forests, volcanic eruptions, and organic matter degradation are examples of natural sources. The amount of PAHs in the air is influenced by factors like wind, temperature, and humidity.

Physical and chemical properties of PAHs

The majority of the time, PAHs are colorless, white, or yellow solids with poor water solubility and high lipophilicity. They exhibit hydrophobic properties. The US EPA has classified 16 PAHs' physical and chemical properties without any derivatization as a priority for controlling pollution (Fig 2). The molecular weight of numerous aromatic rings as well as the ring's molecular configuration affect the chemical characteristics of specific PAHs. The hydrophobicity, lipophilicity, and electrothermal stability of PAHs increase with increasing molecule size and angularity, which contributes to their environmental persistence (Kanaly and Harayama, 2000; Loick et al., 2009). Some of the characteristics of PAHs, such as their octanol-water partition coefficient value (Kow) and vapor pressure, have a significant impact on how they are distributed in the environment. These characteristics also affect how bioaccumulative and bioavailable they are (Juhasz and Naidu, 2000). As PAH molecular size grows, the hydrophobicity of PAHs as stated in terms of Kow increases. While their liquid vapor pressure and aqueous solubility both drop with an increase in molecule size, their boiling temperatures both rise. Due to the substantial cloud of electrons on both sides of benzene ring configurations, PAHs display biological persistence. Consequently, they are better able to withstand nucleophilic attacks (Haritash and Kaushik, 2009).

Based on the number of benzene rings, PAHs can be split into two groups: low molecular weight (LMW) PAHs (two to three rings) and high molecular weight (HMW) PAHs (4 or more rings). In general, the ratio of the number of rings in a PAH molecule to its rate of degradation is inverse (Cerniglia, 1992). Because they may be broken down more quickly, LMW-PAHs like naphthalene, acenaphthene anthracene, and Phenanthrene are frequently used as model compounds to study how HMW-PAHs degrade. HMW-PAHs are more hazardous, persistent, mutagenic, and carcinogenic than LMW-PAHs.

Toxicity of PAHs

In a wide spectrum of biota, including microorganisms, plants, aquatic biota, amphibians, reptiles, birds, and terrestrial mammals, a variety of PAH-induced ecotoxicological consequences have been documented. Effects on survival, growth, metabolism, and tumor development have been observed.

i.e., cytotoxicity, genotoxicity, carcinogenicity, and developmental and reproductive toxicity. However, genotoxicity and carcinogenicity have been the main areas of interest in toxicological research on PAHs. The health of humans is negatively impacted by PAH poisoning. Benzo[a]pyrene is regarded by the US EPA as the most hazardous pollutant of all known PAHs due to its extremely high carcinogenic potential. It makes up a sizable portion of the smoke produced by cigarettes as well. Due to PAHs' extremely high lipid solubility, both humans and animals' digestive tracts absorb them quickly (Gibson and Subramanian, 1984).

In addition to their previously studied carcinogenic, mutagenic, and teratogenic effects, PAHs have also been revealed to have endocrine disruptive capabilities. The mutagenic properties of PAHs are what cause the development of tumors (Lee and Hosomi, 2001). Variable amounts of PAHs may be present in food, especially if it has been exposed to high temperatures. According to studies, cereals, oils, and fats, all contain PAHs. Additionally, they can be acquired by eating cooked meat and vegetables (Eriksson et al., 2003). Because soil-disseminated PAHs are harmful to human health and may enter the food chain, they are a significant source of contamination and a major environmental worry (Tao et al., 2006). Another important pathway for absorbing PAHs is through the skin, which accounts for 75% of all absorbed PAHs (namely pyrene). Due to the significant potential for biomagnifications in the food chain, PAH absorption rates are quick. According to Cerniglia (1992), "the toxicity of the PAH increases with the number of benzene rings." The LD50 values can be used to calculate the relative acute toxicity of PAHs (the lethal dose in 50 percent of the population tested).

Although PAHs have also been linked to cancer, they are not thought to be genotoxic until reactive epoxide and quinones activate mammalian enzymes. The enzyme cytochrome P 450 monooxygenase is primarily found in fungi, which oxidize the aromatic ring to produce genotoxic epoxide and diol-epoxide reactive intermediates (Harvey, 1996). These intermediates interact with DNA during oxidation to create covalent DNA adducts, which can result in the development of tumors (Bamforth and Singleton, 2005).

Microbial Degradation

A significant environmental destiny for both terrestrial and aquatic ecosystems is the microbial breakdown of PAHs. PAHs are converted into either organic or inorganic end products by microorganisms like bacteria and fungi. The rates of biodegradation of PAHs are highly variable and reliant on the

structure of the PAHs as well as the Physico-chemical characteristics of the soil and the types and amount of microorganisms that are present (Cerniglia, 1993).

The breakdown of PAHs may produce metabolites that are more hazardous than the original substance.

There are several papers on the microbial degradation of LMW PAHs, but there are few on the microbial degradation of HMW PAHs. The potential of new biological technologies for the cleanup of hazardous places is now being investigated. However, their effective use necessitates a deeper comprehension of the biochemical processes by which PAHs are broken down, both singly and in mixtures. There is a sizable body of literature that describes the breakdown of specific PAHs by bacteria that can use them as their only source of carbon and energy. These investigations have provided vital knowledge on the biodegradability of specific substances (Cerniglia, 1992; Juhasz and Naidu, 2000; Samanta et al., 2002). Numerous studies on aerobic bacteria for remediation techniques have been conducted.

Microbial degradation of PAHs

The aerobic metabolism of PAHs by microorganisms occurs through three fundamentally distinct processes (Figure 3). The oxidation of PAHs, followed by their disintegration into intermediates and CO2, is the foundation of these pathways.

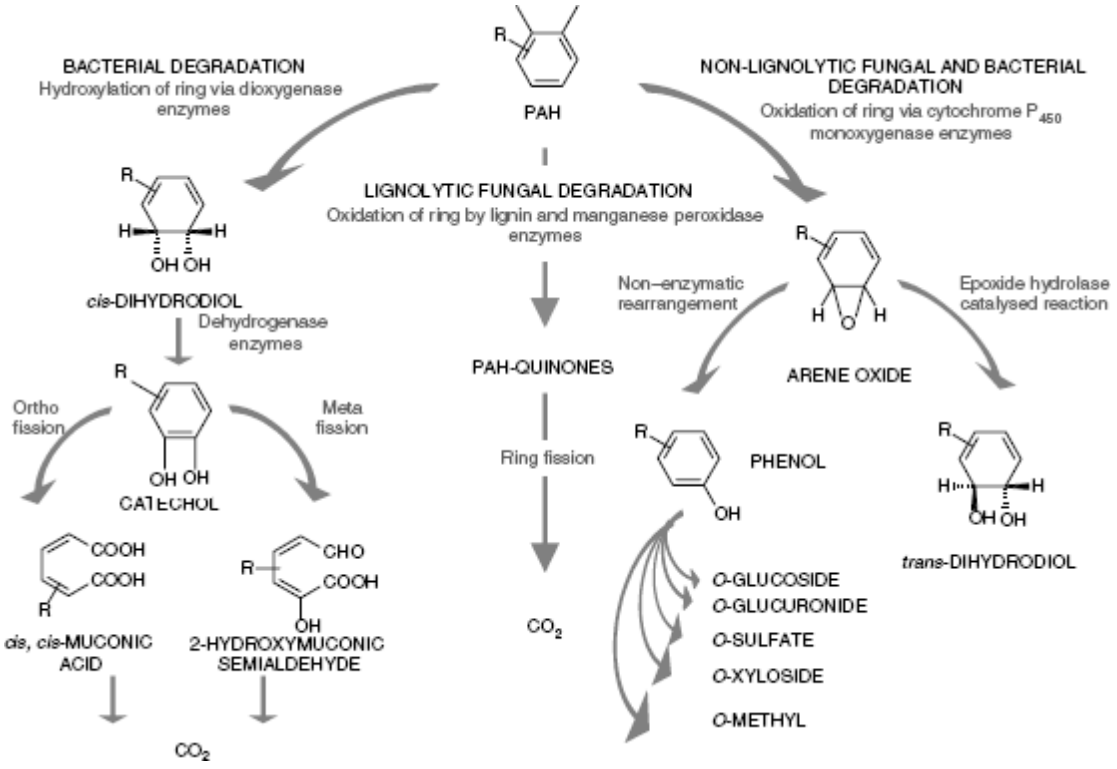


Figure 3. General pathway for the degradation of PAHs by bacteria and fungi (Bamforth and Singleton, 2005).

Bacterial metabolism of PAHs

Bacteria actively degrade organic contaminants from the contaminated site in the environment. Abiotic conditions at the contaminated site can be changed to speed up the natural processes of bacterial breakdown (Haritash and Kaushik, 2009). It has been discovered that bacteria can destroy PAHs through co-metabolism or metabolism (Chauhan et al., 2008). In general, the most prevalent bacterial genera examined for PAH degradation include Beijerinckia, Bacillus, Mycobacterium, Pseudomonas, Sphingomonas, Serratia, and Rhodococcus (Haritash and Kaushik, 2009).

Due to the stability of PAHs as reduced compounds, there are two main ways in which they can degrade: aerobically or anaerobically. The multicomponent dioxygenases that may catalyze the incorporation of both atoms of oxygen and two electrons from NADH to generate cis-dihydrodiol to start the bacterial aerobic breakdown of PAHs are often what starts the process. These multicomponent dioxygenases typically contain reductase, ferredoxin, and a third component made up of two proteins—large and small iron-sulfur protein—as well as ferredoxin (Labana et al., 2007). A hydroxylated intermediate is created by the subsequent dehydrogenation by dehydrogenase, which can then be further degraded via the ortho or meta ring cleavage route before entering the TCA cycle.

Monooxygenases are responsible for the other route of PAH breakdown. Trans dihydro diols are first produced in bacteria by monooxygenases, a slower process than dioxygenases. Similar to the bacterial aromatic ring dioxygenases, cytochrome P-450 monooxygenases are intricate multicomponent enzyme systems that are typically found in fungi. They typically have broad substrate specificities and are membrane-bound. The monooxygenase incorporates

one molecular oxygen atom into the PAH to create arene oxide, while the other atom is reduced to water. The resulting arene oxide passes through spontaneous isomerization to produce a phenol that can be coupled with glutathione, glucuronic acid, glucose, or sulfate. The creation of a trans-dihydrodiol, which is catalyzed by epoxide hydrolase, results from the enzymatic hydration of the arene oxide.

Factors Affecting the Degradation of PAHs

The bioremediation of PAHs is influenced by environmental parameters including temperature, oxygen, nutritional availability, salinity, water holding capacity, and pH. They also have an impact on the bacterial communities and the pace of deterioration (Bamforth and Singleton, 2005).

Temperature

Temperature is thought to have a significant impact on the breakdown of PAHs. The solubility of PAHs and temperature are inversely correlated. The degree of deterioration is influenced by seasonal temperature variations (Margesin and Schinner, 2001). According to Erickson, a temperature increase can hurt an organism's metabolic activity because an increase in temperature causes oxygen to become less soluble.

Oxygen

Anaerobic or aerobic conditions can be used to digest organic contaminants. For multicomponent enzyme systems like mono and dioxygenase enzymes, which carry out the initial reaction of PAH breakdown, oxygen is a limiting element. But the rate of PAH breakdown in denitrifying settings was similar to the rate of PAH degradation in aerobic circumstances (Mcnally et al., 1998). This shows that PAH-degrading microorganisms make up the majority of the in situ microbial population and that poor environmental conditions, rather than a lack of PAH-degrading microorganisms, were the main inhibitors of bioremediation.

Nutrient availability

Nutrients including nitrogen, phosphate, and potassium are needed for the growth and destruction of PAH-degrading bacteria. As a result, polluted site biostimulation is typically done to increase microbial activity. Only when the C: N ratio was high (25:1) did creosote bioremediation and optimal development occur, as opposed to when the ratio was low (5:1). (Atagana et al., 2003).

Bioavailability of PAHs

PAHs' limited bioavailability is a result of their hydrophobicity. The most important component in the bioremediation of PAHs is bioavailability, which influences both the pace and amount of PAH breakdown. Additionally, PAHs can quickly bind to the organic matter (humic and) and mineral surfaces (clays) in the soil matrix. The stronger the sorption of the PAH to the soil particle and the poorer the chemical and biological extractability are the longer the PAH stays in contact with the soil. This occurrence is referred to as PAH "aging." As a result, the persistence of organic pollutants (POPs) in the environment is correlated with the bioavailability of contaminants (Bamforth and Singleton, 2005).

Salinity

Salinity and the rate of PAH mineralization are both positively linked with the mineralization of PAHs in soil and sediment. According to reports, as the salinity of soil or sediment rises, the mineralization of PAHs declines (Leahy and Colwell, 1990).

Water holding capacity

According to Baker (1994), water holding capacity is "the quantity of the water remaining inside the soil ter gravity water has drained away" or the proportion of water that is saturated in the soil. One of the key elements influencing the pace of PAH gradation and mineralization is water activity. Generally speaking, for soil to function metabolically, it has to have at least 30 to 45 percent water. The availability of water content frequently restricts microbial metabolism. The kind of soil determines the ideal soil water content. Generally speaking, the soil moisture should be between 50 and 80 percent for optimum activity.

pH

Most PAHs-contaminated locations are not at the ideal pH for bioremediation. It's possible that the local microorganisms can't change PAHs in the acidic or alkaline environments that are most common. Therefore, adjusting the pH at these locations is a standard technique. Microbial activity also has an impact on soil acidity; fungi are reported to be more active in acidic pH levels, whilst bacteria are more active in neutral or alkaline pH levels. By maximizing pH conditions, PAH decomposition can be accelerated. The excessive pH of the soil has a detrimental effect on microbial communities capacity to break down hydrocarbons (Leahy and Colwell, 1990).

Metabolic Pathways for PAHs degradation

The following is a description of the metabolic routes for the degradation of 2, 3, 4, and 5 rings of PAHs.

Naphthalene

Due to its straightforward structure and high water solubility, naphtha, a 2-ring PAH, is one of the most researched PAHs. Therefore, it is quite simple to separate naphthalene-degrading microbes from the environment. Numerous bacterial strains, mostly from contaminated sediments, have been consistently discovered that can break down aromatic hydrocarbons. These bacteria are typically gram-negative and primarily belong to the genus Pseudomonas. Additionally, bacteria from the genera Mycobacterium, Corynebacterium, Aeromonas, Rhodococcus, Bacillus, Sphingomonas, and Pseudomonas have been found to possess biodegradative processes. According to studies, naphthalene is oxidized by bacteria by absorbing both oxygen atoms at the C-1 and C-2 positions to create cis-1,2 dihydroxy- 1,2 dihydroxy naphthalene.

The conversion of cis1,2 dihydroxy- 1,2 dihydroxy naphthalene to 1,2 dihydroxy naphthalene, which is mediated by naphthalene(+)-cis-dihydrodiol dehydrogenase and necessitates NAD+ as an electron acceptor, is the second stage in the bacterial oxidation of naphthalene. By the activity of dioxygenase, 1,2 dihydroxy naphthalene undergoes a series of events that ultimately result in the formation of pyruvate and salicylate. Salicylate hydroxylase, which can undergo ring fission by either ortho or meta cleavage depending on bacterial metabolism, oxidizes salicylate to catechol. The suggested Pseudomonas mechanism for naphthalene breakdown is shown. When Pseudomonas testosterone breaks down Phenanthrene, salicylate is changed to gentisic acid, which then goes through a ring fission process, according to Kiyohara and Nagao (1978).

The plasmid is where the gene for naphthalene catabolism is found, according to numerous researchers. Naphthalene can be broken down into three different plasmids: NAH7, NAL1, and pND. The plasmid NAH7 has received the most attention out of all of them. The structural genes for naphthalene catabolism are found in two operons of NAH7. The gene required for the conversion of naphthalene to salicylate can be found in one operon, while the gene for the conversion of salicylate to catechol can be found in another operon.

Anthracene

Anthracene with a three-ring structure is a linear tricyclic PAH that is abundantly present in the environment and frequently used as a model PAH for studies on degradation. Numerous bacteria, including Pseudomonas, Sphingomonas, Nocardia, Beijerinckia, Rhodococcus, and Mycobacterium, can mineralize anthracene. These species first oxidize the 1,2 position of anthracene to create cis-1,2 dihydroxy-1,2 dihydroxy anthracene, which is subsequently transformed to 1,2 dihydroxy anthracene by NAD+ dependent dihydrodiol dehydrogenase.

The next step involves the oxidation of 1,2 dihydroxy anthracene to the ring fission product cis-4-(2-hydroxynaphth-3-yl)-2-oxo butanoic acid, which is then changed into 2-hydroxynaphthoic acid. comparable to naphthalene, 2-hydroxynaphthoic acid experiences ring fission cleavage. Salicylate and catechol are created via the ring fission reaction with 2,3-dihydroxy naphthalene. Anthracene was also oxidized by Mycobacterium strain PYR-1 at sites C-9 and 10, producing the dead-end product anthraquinone.

Fluoranthene

A 4-ringed PAH found in the environment is fluoranthene. The mechanism used by the strains of Burkholderia, Pasteurella, Rhodococcus, Sphingomonas, Stenotrophomonas, and Mycobacterium to degrade fluoranthene is collectively depicted in the picture. Fluoranthene is typically degraded by bacteria via 1,2 or 7,8-deoxygenation, which produces cis-1,2 or cis-7,8 fluoranthene dihydrodiol, respectively. Dehydrogenation of these two dihydrodiols results in 1, 2, or 7, 8-dihydroxy fluoranthene, respectively. Through the meta-cleavage of 7,8-dihydroxy-fluoranthene, 2-hydroxyl-4-(2-oxo-2H-acenaphthylen-1-ylidene)-but-2-enoic acid, 2-hydroxymethyl-2H-acenaphthylen-1-one, and 2-oxoacenaphthene-1-carboxylic acid, 1-acenaphthene and 3-hydroxymethyl-3.

suggested that Mycobacterium sp. JS14 had four potential dimethoxy fluoranthenes and four potential beginning deoxygenation sites at the fluoranthene's 1, 2, 3, 7, 8, and 9 positions. Rehmann et al. (2001) reported the 2,3-deoxygenation of fluoranthene and discovered five metabolites, including cis-2,3-fluoranthene dihydrodiol, 9-carboxymethylene-9H-fluorene-1-carboxylic acid, cis1,9a-dihydroxy-1-hydrofluoric-9-one, 8-carboxylic acid, 4-hydroxybenzochromene-6.

Benzo[a]pyrene

One of the most potently carcinogenic PAHs is the 5-ring compound benzo(a)pyrene. Because benzo[a]pyrene is resistant to microbial degradation, it has a low aqueous solubility (0.0023 mg/L) and a high octanol/water partition coefficient (Log Kow, 6.06). Its low abundance in environmental samples restricts the ability of bacterial assemblages to break it down. There is currently a dearth of knowledge regarding the bacterial breakdown of PAHs with five or more rings. the mechanism by which microorganisms break down benzo(a)pyrene. Except for ring cleavage metabolites, Gibson et al. (1975) were the first to identify metabolites produced by Beijerinckia strain B1, such as cis-7,8 and 9,10-benzo[a]pyrene-dihydrodiol. Mycobacterium strain RJGII-135 was discovered to be able to convert benzo[a]pyrene into its original ring oxidation and ring cleavage metabolites by Schneider et al. in 1996. Benzo[a]pyrene cis-7,8-dihydrodiol, a ring-oxidation metabolite, and 4,5-chrysene dicarboxylic acid, a ring-cleavage metabolite, were both discovered (8-hydroxypyrene-7-yl) cis-4- or -2- oxobut-3-enoic acid (7- hydroxypyrene-8-yl) 2,8-dihydropyridine-7-carboxylic acid, also known as 2,8-dihydropyridine-8-carboxylic acid, and but-3-enoic acid. These metabolites show that the 4,5, 7, 8, and 9, 10 locations of benzo[a]pyrene are the sites of

the initial enzyme assault. Through meta cleavage, benzo[a]pyrene cis-7,8-dihydrodiol is further catabolized to 7,8-dihydropyran. cis-4-(7-hydroxypyrene-8-yl)-2-oxo but-3-enoic acid through -8-carboxylic acid. Through meta-cleavage, benzo[a]pyrene cis9,10-dihydrodiol degrades to 7,8-dihydropyridine. cis-4-(8-hydroxypyrene-7-yl)-2-oxo but-3-enoic acid through -7- carboxylic acid. Furthermore, 10-oxabenzo[def]chrysene Dehydration of benzo[a]pyrene cis-9,10-dihydrodiol yields cis-4-(8-hydroxypyrene-7-yl)- 2-oxo but-3-enoic acid, which is then meta-cleaved and given an aromatic ring closure. This compound is known as 9-one. By cleaving 4,5-dihydroxy benzo[a]pyrene orthogonally, 4-formylchrysene-5- carboxylic acid is converted to 4,5-Chrysene-dicarboxylic acid. Additionally, Moody reported on brand-new benzo[a]pyrene metabolism routes in Mycobacterium vanbaalenii PYR-1. The formation of benzo[a]pyrene cis and trans-11,12- dihydrodiol by the enzymes dioxygenase and monooxygenase at the 11, 12, and 13 locations of the molecule starts the new pathways. Through the use of hydroxymethoxy benzo[a]pyrene, benzo[a]pyrene cis-11,12-dihydrodiol is further transformed into dimethoxybenzo[a]pyrene. Cytochrome P-450 monooxygenase produces benzo[a]pyrene 11,12-epoxide, which is then hydrolyzed by epoxide hydrolase to produce benzo[a]pyrene trans-11,12-dihydrodiol. Recently, Rentz discovered two new metabolites produced by Sphingomonas yanoikuyae JAR02, pyrene-8-hydroxy-7-carboxylic acid and pyrene-7-hydroxy-8-carboxylic acid.

Bacterial consortium for degradation of PAHs

Well-known PAH-degraders include bacteria from the genera Sphingomonas, Burkholderia, Pseudomonas, Acinetobacter, Achromobacter Rhodococcus, and Mycobacterium. Both LMW and HMW PAHs have been reported to be mineralized by them. Although pure cultures of several PAH-degrading bacteria may easily utilize PAHs as a carbon source, using a consortium or mixed bacterial culture may increase degradation. Since bioremediation in naturally PAH-contaminated soils relies on the cooperative metabolic activities of mixed microbial populations, it is common that biodegradation using a pure strain does not accurately depict the behavior of microorganisms.

The fact that microbial consortia have a variety of metabolic capabilities that boost the effectiveness of the bioremediation process is a significant benefit of their use.

LMW and HMW PAHs are among the complex hydrocarbon mixes that are frequently found in contaminated environments.

It is unlikely that one strain would be able to break down all of these PAHs in a contaminated area. A consortium made up of many microorganisms can better accomplish this

including those that are capable of breaking down a variety of PAHs and others that can use partially broken-down byproducts that might be poisonous or antagonistic to some of the primary degraders.

Bioremediation

An option that provides the potential to eliminate hazardous contaminants through normal biological activity is bioremediation. The process of biologically degrading organic wastes to a harmless state or concentrations below the regulatory authorities' stated concentration limits is known as bioremediation. To decompose or detoxify pollutants harmful to human health and the environment, it uses naturally occurring bacteria, fungus, or plants. The microorganisms may be local to the contaminated site or they may have been isolated from another location and introduced there. Living things change contaminant chemicals through reactions that happen as part of their metabolic activities. Multiple species' activity frequently leads to the biodegradation of a chemical. Thermal and physical-chemical cleanup is more expensive than bioremediation approaches (Korda et al., 1997; Cho et al., 2000; RoblesGonzález et al., 2008).

Microbial enzymes as a tool for bioremediation of organic pollutants

Enzymes play a well-known part in the degradation of contaminants. It has been shown that various specialized microorganisms present in a contaminated environment, having the enzymatic potential for the breakdown of these chemicals, can change pollutants, particularly those that are stubborn. Complex metabolic pathways that gradually convert the substance into simpler molecules that can join the regular metabolic system are what give them their abilities. The existence of a particular enzyme that carries out the first, unusual chemical reaction necessary to make the pollutant accessible to subsequent enzymatic transformations is very typically what allows a pollutant to enter these metabolic pathways. The degradative enzyme may have bacterial, fungal, or plant origins. The breakdown of PAHs involves two main groups of enzymes, which are discussed below (Rao et al., 2014).

Oxidoreductases

Oxidoreductases are enzymes that assist different bacteria and fungi in detoxifying hazardous chemical substances. By carrying out the biochemical reaction mediated by these enzymes, in which an electron is transferred from the reduced substrate to a chemical molecule, microorganisms produce energy.

Oxidoreductases from fungi and some bacteria, such as ligninases, laccases, peroxidases, and tyrosinases, can change PAHs. These primarily fungal-derived enzymes can change phenols, including resistant chlorinated and nonchlorinated chemicals.

It is possible for the aromatic ring to be broken, as well as for unstable substrate cati radicals to develop and then undergo enzymatic transformation and polymerization. Tyrosinases and laccases are examples of phenoloxidases that need molecular oxygen to function, whereas horseradish peroxidase,

ligninases (LiP and MnP), and chloroperoxidases (CPO) need hydrogen peroxide. When MnP is involved, for instance, the reaction is dependent on the presence of other elements like divalent manganese (Rao et al., 2014).

Microbial oxygenases

The transfer of oxygen is carried out by oxygenases using FAD/NAD/NADPH as a cosubstrate. Based on the amount of oxygen needed for oxygenation, oxygenases are categorized into two categories: monooxygenases and dioxygenases. By making the compounds more soluble by incorporating O2 molecules, they play a crucial part in the breakdown of PAHs and other related chemical compounds, which causes the ring opening of PAHs. Figure 4 depicts the chemical reaction that the monooxygenase and dioxygenase enzymes carry out.

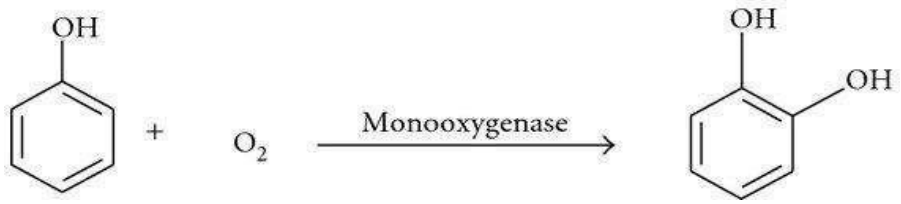
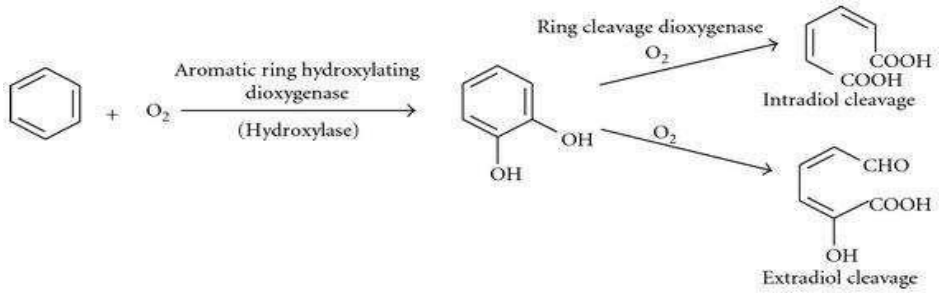


Figure 4. Degradation of the aromatic compounds by mono-, and dioxygenases (Que and Ho, 1996; Arora et al., 2009; Chandrakant and Shwetha, 2011).



Cytochrome P-450 enzymes and fungal oxidase are two more intriguing, adaptable biocatalysts. Hemoproteins known as cytochrome P-450 enzymes are capable of changing a wide variety of substrates and initiating several chemical processes, including the bioconversion of pollutants. They are widely present in all living things. Carbon hydroxylation, epoxidation, heteroatom oxygenation, dealkylation, aromatic hydroxylation, reduction, and dehalogenation are a few processes that cytochrome P-450 can catalyze. This enzyme family is extremely promising for biotechnological and environmental applications due to its extensive catalytic activity. However, due to their great complexity and frequently low catalytic performance, these catalysts have not been widely used in biotechnological or environmental applications.

An oxidative coupling reaction, which produces polymeric molecules with escalating complexity, is the primary reaction carried out by oxidative enzymes. Crosscoupling reactions can occur across substrates with various chemical makeups. Pollutants may also completely mineralize as well as oxidize comparatively inert substrates when more reactive molecules are present (Kobayashi and Higashimura, 2003).

CONCLUSION

There is a substantial likelihood that PAHs will have negative effects on marine sediments, according to estimates of their ecological risk and possible toxicity. The current study would unquestionably add value to the worldwide database by giving regulatory organizations new information to enhance environmental quality.

References

Al-Dhabi, N. A., Esmail, G. A., & Arasu, M. V. (2021). Effective degradation of tetracycline by manganese peroxidase producing Bacillus velezensis strain Al-Dhabi 140 from Saudi Arabia using fibrous-bed reactor. Chemosphere, 268, 128726.

Atagana, H. I., Haynes, R. J., & Wallis, F. M. (2003). Optimization of soil physical and chemical conditions for the bioremediation of creosote-contaminated soil. Biodegradation, 14(4), 297-307.

Bamforth, S. M., & Singleton, I. (2005). Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions. Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology, 80(7), 723-736.

Bispo, A., Jourdain, M. J., & Jauzein, M. (1999). Toxicity and genotoxicity of industrial soils polluted by polycyclic aromatic hydrocarbons (PAHs). Organic Geochemistry, 30(8), 947- 952.

Cerniglia, C. E., & Sutherland, J. B. (2006). Relative roles of bacteria and fungi in polycyclic aromatic hydrocarbon biodegradation and bioremediation of contaminated soils. Fungi in Biogeochemical Cycles. Cambridge University Press, Cambridge, 182-211.

Desai, S. A. (2017). Isolation and characterization of Laccase-producing bacteria from contaminated sites. Biosci Discov, 8, 567-573.

Dash, H. R., Mangwani, N., Chakraborty, J., Kumari, S., & Das, S. (2013). Marine bacteria: potential candidates for enhanced bioremediation. Applied microbiology and biotechnology, 97(2), 561-571.

Diggs, D. L., Hudson, A. C., Harris, K. L., Myers, J. N., Banks, L. D., Rekhadevi, P. V., ... & Ramesh, A. (2011). Polycyclic aromatic hydrocarbons and digestive tract cancers: a perspective. Journal of environmental science and health, part c, 29(4), 324-357.

Finette, B. A., Subramanian, V., & Gibson, D. T. (1984). Isolation and characterization of Pseudomonas putida PpF1 mutants defective in the toluene dioxygenase enzyme system. Journal of Bacteriology, 160(3), 1003-1009.

Head, I. M., & Swannell, R. P. (1999). Bioremediation of petroleum hydrocarbon contaminants in marine habitats. Current opinion in biotechnology, 10(3), 234-239.

Haritash, A. K., & Kaushik, C. P. (2009). Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. Journal of hazardous materials, 169(1-3), 1-15.

Juhasz, A. L., & Naidu, R. (2000). Bioremediation of high molecular weight polycyclic aromatic hydrocarbons: a review of the microbial degradation of benzo [a] pyrene. International biodeterioration & biodegradation, 45(1-2), 57-88.

Kanaly, R. A., & Harayama, S. (2000). Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. Journal of Bacteriology, 182(8), 2059-2067.

Labana, S., Kapur, M., Malik, D. K., Prakash, D., & Jain, R. K. (2007). Diversity, biodegradation, and bioremediation of polycyclic aromatic hydrocarbons. In Environmental bioremediation technologies (pp. 409-443). Springer, Berlin, Heidelberg

Lee, B. D., Iso, M., & Hosomi, M. (2001). Prediction of Fenton oxidation positions in polycyclic aromatic hydrocarbons by Frontier electron density. Chemosphere, 42(4), 431- 435.

Loick, N., Hobbs, P. J., Hale, M. D., & Jones, D. L. (2009). Bioremediation of poly-aromatic hydrocarbon (PAH)-contaminated soil by composting. Critical Reviews in Environmental Science and Technology, 39(4), 271-332.

Lu, M., Zeng, D. C., Liao, Y., & Tong, B. (2012). Distribution and characterization of organochlorine pesticides and polycyclic aromatic hydrocarbons in surface sediment from Poyang Lake, China. Science of the Total Environment, 433, 491-497.

Margesin, R., & Schinner, F. (2001). Biodegradation and bioremediation of hydrocarbons in extreme environments. Applied microbiology and biotechnology, 56(5), 650-663.

Ravindra, K., Sokhi, R., & Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors, and regulation. Atmospheric environment, 42(13), 2895-2921.

Robles-González, I. V. Bioremediation of an Agricultural Heavy Soil Polluted with Lindane: Comparison of Anaerobic and Aerobic Slurry Bioreactors.

Samanta, S. K., Chakraborti, A. K., & Jain, R. K. (1999). Degradation of Phenanthrene by different bacteria: evidence for novel transformation sequences involving the formation of 1- naphthol. Applied Microbiology and Biotechnology, 53(1), 98-107.

Shukla, S., & Padhiar, A. Isolation and screening of lignin peroxidase producing microorganism from different geographical locations of Andaman and Nicobar Island.

.Sukhdhane, K. S., Pandey, P. K., Ajima, M. N. O., Jayakumar, T., Vennila, A., & Raut, S. M. (2019). Isolation and characterization of phenanthrene-degrading bacteria from PAHs contaminated mangrove sediment of Thane Creek in Mumbai, India. Polycyclic Aromatic Compounds, 39(1), 73-83.

Shuttleworth, K. L., & Cerniglia, E. (1995). Environmental aspects of PAH biodegradation. Applied biochemistry and biotechnology, 54(1), 291-302.

Woyach, J. A., Furman, R. R., Liu, T. M., Ozer, H. G., Zapatka, M., Ruppert, A. S., ... & Byrd, J. C. (2014). Resistance mechanisms for Bruton's tyrosine kinase inhibitor ibrutinib. New England Journal of Medicine, 370(24), 2286-2294.

Zhao, B., Wang, H., Mao, X., & Li, R. (2009). A rapid screening method for bacteria degrading polycyclic aromatic hydrocarbons. Letters in applied microbiology, 49(3), 408- 410