Academic Journal of Science and Technology
ISSN: 2771-3032 | Vol. 3, No. 2, 2022

Progress in Research on Sources and Removal Methods of PAHs

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Abstract: The exploitation of natural resources and the rapid development of the economy have brought us great material wealth. The standard of living of the people has been renewed both materially and spiritually, but at the same time it has also caused excessive consumption of resources and the continuous deterioration of the ecological environment. Studies have shown that 70% to 90% of human cancers are caused by environmental carcinogens, or are closely related to environmental factors. Among environmental pollutants, the most difficult for human beings to deal with are substances that cannot be fully degraded by staying in the environment for a long time, cannot be degraded in living organisms and remain for a long time to poison them, can be transferred over long distances and are strongly toxic, and these problems have received widespread international attention.

Keywords: PAHs, Degradation, Pollution.

1. Hazards and Effects of Polycyclic Aromatic Hydrocarbons

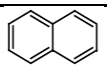
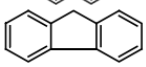
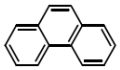
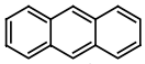
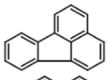
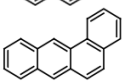
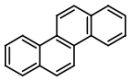
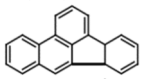
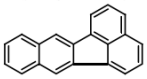
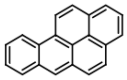
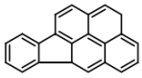
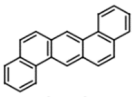
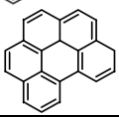
Polycyclic aromatic hydrocarbons (PAHs) [1] are typical persistent organic pollutants and are the first chemical carcinogens to be identified and studied [2]. They are widely distributed in the natural environment, including air, water, soil and sediment [3]. PAHs are one of the most abundant pollutants in the environment and low molecular weight hydrocarbons are relatively soluble in water, making them biodegradable. Being insoluble in water, they are less likely to be degraded by microorganisms, thus making them more persistent in the environment. Damage to DNA due to their toxic effects exerts a carcinogenic effect, not only interfering with the growth rate and reproduction of animals, but also increasing susceptibility to pathogens and damaging the immune system of animals and potential bioconcentration and high toxicity such as carcinogenicity, teratogenicity and mutagenicity [4-6], in addition to the accumulation of adsorbed PAHs and the formation of reservoirs of pollutants, producing the so-called In addition, the adsorbed PAHs accumulate and form a reservoir of pollutants, producing the so-called "chronic toxicity effect". The United States Environmental Protection Agency (USEPA) and the European Union (EU) have listed 16 PAHs as "priority pollutants" [7]. As a result, the environmental behaviour of PAHs and their remediation have been extensively studied over the past decades. Studies have shown that bioremediation is the most powerful means of removing PAH contamination from the environment because of its operability, low economic cost, low secondary contamination and complete remediation [8]. For example, fungi (e.g. white rot fungi) can completely degrade PAHs into CO2 and H2O with a large group of microorganisms using a ligninase system [9], and because of their special metabolic type and proprietary extracellular degradation properties, they have a highly efficient, broad-spectrum, low-consumption, and highly applicable biodegradation capacity for substances with unique degradation advantages for a variety of toxic, hazardous, and difficult-to-degrade pollutants [10].

2. Structure and Properties of Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons（PAHs）are organic compounds consisting of different numbers of benzene rings. According to the number of benzene rings, PAHs can be divided into low molecular weight (2-3 dumb rings) PAHs and high molecular weight (4 or more dumb rings) PAHs. Low molecular weight PAHs such as naphthalene, acenaphthene, fluorene and anthracene are relatively easy to degrade, while PAHs with 4 or more rings such as pyrene and benzo[a]pyrene are not easy to degrade.

PAHs crystals come in four colours: colourless, white, light yellow and dark. They are colourless, white, yellowish and dark. They are insoluble in water and readily soluble in organic solutions. At room temperature, pure PAHs compounds are solid and are generally characterised by high melting and boiling points, low vapour pressure and low water solubility [11]. When these highly hydrophobic pollutants enter the atmosphere, the vast majority of them will enter the soil or water column by way of deposition [12]. In 1976, the US EPA added 16 PAHs to the list of priority pollutants for control [7], whose physicochemical properties and structural formulae are shown in Table 1.

Table 1. Physicochemical property and structure of 16 PAHs

Name	Molecular formula	Molecular weight	Melting point (℃)	Boiling point (℃)	Solubility (g/L)	Structured
(Nap)	$C_{10}H_8$	121.18	81	218	3.1×10^{-2}	
(Acy)	$C_{12}H_8$	152.20	93	270	3.9×10^{-3}	
(Ace)	$C_{12}H_{10}$	154.21	96	278	3.5×10^{-3}	
(FI)	$C_{13}H_{10}$	166.22	116	280	1.9×10^{-4}	
(Phe)	$C_{14}H_{10}$	178.23	100	340	1.2×10^{-3}	
(An)	$C_{14}H_{10}$	178.22	217	342	4.3×10^{-5}	
(Flu)	$C_{16}H_{10}$	202.26	110	367	2.7×10^{-4}	
(Pyr)	$C_{16}H_{10}$	202.26	150	394	1.3×10^{-4}	
(BaA)	$C_{18}H_{12}$	228.30	162	435	1.4×10^{-4}	
(Chr)	$C_{11}H_{15}$	163.24	253	448	1.8×10^{-6}	
(BbF)	$C_{20}H_{12}$	252.00	167	481	$1.2\times10^{-}$	
(BKF)	$C_{20}H_{12}$	252.00	217	480	5.5×10^{-7}	
(BaP)	$C_{20}H_{12}$	252.32	179	475	3.8×10^{-6}	
(Inp)	$C_{22}H_{12}$	276.00	162	497	6.2×10^{-5}	
(DBA)	$C_{22}H_{14}$	278.35	262	535	1.2×10^{-3}	
(BgP)	$C_{22}H_{12}$	276.33	276	500	2.6×10^{-7}	

3. Sources and Hazards of Polycyclic Aromatic Hydrocarbons

The sources of PAHs in the environment generally fall into two main categories: natural sources and anthropogenic sources. natural sources of PAHs formation such as natural fires in areas such as forests and grasslands, volcanic eruptions etc. also produce PAHs, which together with biosynthetic PAHs make up the natural background value of PAHs in the environment. Synthesis by bacteria and algae: In the natural environment they can be synthesised by certain algae, plants and bacteria or have the ability to synthesise PAHs during the degradation of plant matter and they can produce PAHs within themselves during growth, including some that are carcinogenic. oil seeps, erosion of sedimentary rocks containing petroleum hydrocarbons and decomposition by plant growth. biosynthesis of PAHs can occur at at ambient temperature and pressure, but the amount of biosynthesized PAHs is generally small and can therefore remain relatively stable in the ecosystem in which they are found.

Anthropogenic sources of PAHs include: large point sources including incomplete combustion (e.g. incinerators and some industrial processes, factory waste emissions, combustion of various fuels). Smaller point sources are more diffuse (e.g. vehicle emissions, smoke from stoves, aeroplane exhaust, cigarette and cigar smoke, and barbecues). Other anthropogenic sources of PAHs include petroleum product spills, sewage sludge, and tar or creosote waste. the pattern of PAHs formation can be natural or anthropogenic, and Figure 1-1 illustrates this pattern of PAHs formation [13, 14]. Nevertheless, many PAHs have some commercial use. They are mainly used with pharmaceuticals, agricultural intermediates, photographic products, thermosetting plastics, lubricating materials and other chemical industries [15]. For example some PAHs are used: acenaphthene dilute to make pigments, dyes, plastics, pesticides and pharmaceuticals; anthracene is a diluent for wood preservatives and a maker of dyes and pigments; and fluoranthene is used to make agrochemicals, dyes and dye drugs. Fluorene makes pharmaceuticals, pigments, dyes, insecticides and thermosetting plastics; phenanthrene makes resins and

insecticides; pyrene makes pigments; and other PAHs besides roofing tar may be used in asphalt for road construction. In addition, specific refined PAHs products are used in the electronics sector, functional plastics and liquid crystals. It is worth mentioning that both natural and anthropogenic are considered to be the biggest contributors of PAHs to the environment [16].

PAHs can enter the human body in the environment by various routes, such as inhalation, dermal contact and ingestion. In addition, the bioconcentration of PAHs and the expansion of the food chain pose a significant risk to aquatic organisms and human health, with some damage to ecosystems [18]. In animals, carcinogenicity caused by benzo[k]fluoranthene is well documented, and in the International Agency for Research on Cancer [19], benzo[a]pyrene is the most studied carcinogen PAHs, which inhibits the conversion of monocytes into macrophages, thereby disrupting the human immune system, and is classified as a class 2B carcinogen by humans. In mammalian cells, it induces DNA binding, sister chromatid exchange, chromosomal aberrations, point mutations and transformation. When ingested in mammals, PAHs are rapidly absorbed into the gastrointestinal tract due to their high lipid solubility [20]. The rapid absorption of PAHs in humans has led to a significant potential for their biomagnification in the food chain. Short-term exposure to PAHs has also been shown to cause impaired lung function and impaired thrombogenic effects in asthmatics in people affected by coronary heart disease; long-term exposure to low levels of some PAHs has been identified as a major cause of cancer in experimental animals. PAHs have low solubility in water, they tend to attach to particles in air, water and sediment, and they accumulate in lipids (i.e. fats) that cannot metabolise benthic organisms.

The acute toxicity of PAHs exhibited by organisms is mainly caused by PAHs with less than or equal to 3 rings, while the toxicity of PAHs with more than 3 rings is mainly inherited by the offspring. PAHs that accumulate in the human body cannot be removed by their own metabolism, but can instead cause greater toxic effects. Therefore, in order to reduce its persecution of the environment and humans, we must take active and effective measures to remove PAHs from the environment, an issue that cannot be ignored

4. Removal Methods for Polycyclic Aromatic Hydrocarbons

The main methods for removing PAHs from the environment are physical, chemical and biological. Each of these processes affects individual PAHs in different ways. this is mainly due to the fact that each PAH has a unique structure and set of physical, chemical and biological properties. The removal of sites contaminated with PAHs using biological methods is the most promising technology, such as the complete mineralisation of organic pollutants by microorganisms into CO2, water, inorganic compounds or the conversion of complex organic compounds into simpler organic compounds.

The use of biological methods to remove PAHs is nowadays one of the main methods to remove PAHs due to its low economic cost, the ability to transform pollutants into low or non-toxic substances, low environmental hazard and high operability. The key to this remediation technology is the selection of microorganisms with high efficiency in degrading PAHs. There are many microorganisms in the environment that have the ability to degrade PAHs, and they usually adsorb contaminants to cell walls or cell surfaces (biosorption) through physical-chemical adsorption, resulting in the rapid disappearance of contaminants. Similarly to the case of phytoplankton and higher plants, contaminants then accumulate within cells through active uptake and are degraded through a series of enzymatic interactions. In recent years, scholars have conducted numerous studies related to the microbial remediation of PAHs, and hundreds of different species of PAHs-degrading bacteria have been isolated one after another from various environments, and at least 40 genera of microorganisms with PAHs degradation capabilities have been obtained, including a wide range of bacteria, fungi and algae (e.g. Table. 2).

Table 2. Microbial species degrading PAHs

Category	Degradable low ring PAHs	Degradable high ring PAHs	Degrades both low and high ring PAHs
Bacteria	*Sphingomonas* sp., *Beijerinckia* sp, *Nocardia* sp., *Micrococcus* sp.,	*Pseudomonas* sp., *Corynebacterium* sp.*Flavobacterium* sp., *Gordonia* sp.	*Aeromonas* sp. , *Bacillus* sp.. *Rhodococcus* sp., *Mycobacterium* sp.,
Fungi	*Cladosporium* sp． , *Phanerochaete chrysosporium*	*Penicillium funiculosum, Mucor*	*White Rot Fungi, Aspergillus, Fusarium*
Algae	*Nitzschia clostertum*	Chlorella vulgaris	*Selenastrum capricornutum*

Among the identified PAHs-degrading bacteria, Erythrobacter spp., Gordonella spp., Pseudomonas spp. and Bacillus spp. are more effective in the degradation of high molecular weight (tetracyclic or above) PAHs, and most of these microorganisms participate in the degradation of PAHs by secreting both dioxygenases and monooxygenases together. Pseudomonas aeruginosa genus DN1 obtained from petroleum-contaminated soil by Lu Wei et alwas able to grow with fluoranthene as the only carbon source and energy source.

Over 220 PAHs-degrading fungi have been identified, and more than 30 species have been used in the remediation of contaminated soils. White rot fungi are also common soil fungi that have been applied to soil environments early on due to their efficient PAHs degradation mechanism. Hou Xuemin et al used Aspergillus niger to degrade phenanthrene (98.6%) in simulated wastewater. Song Lichao et al obtained a strain of Penicillium spp. TJF1 from saline soil contaminated with PAHs from the Dagang oilfield in Tianjin that was able to use phenanthrene and pyrene as the sole carbon source. balachandran et al isolated Streptomycetaceae from which the removal of diesel, naphthalene and phenanthrene within 7 d (303 K) reached 98.25%, 99.14% and 17.5%.

To date, there have been many reports assessing the degradation capacity of microorganisms, including bacteria and fungi, while relatively little attention has been paid to microalgae.Cerniglia et al found that 18 microalgal species from different taxonomic groups, including cyanobacteria, diatoms and green, red and brown microalgae, were able to metabolise naphthalene (0.1%-2.4%). Agmenellum quadruplicatum PR-6 degraded 2.4% of phenanthrene and Lei et al. reported that six species of microalgae degraded 34% - 100% of pyrene at 0.1 mg/L within 7 days. In contrast, Anabaena flosaquae, Ankistrodesmus braunii, Chlamydomonas reinhardtii, Euglena gracilis, Ochromonas malhamensis and Scenedsemus acutus can also metabolise benzo[a]pyrene to varying degrees. This is because different species have different cell wall compositions, cell sizes and degradation mechanisms. Higher biomass provides more cell surface volume and enzymes, as well as adsorption, uptake and degradation of contaminants. If the biomass is too high, the cells will aggregate, resulting in a reduced effective adsorption area for metal adsorption. At very high cell densities, competition for resources and problems with self-shading and mixing can limit cell growth and the ability of cells to take up and degrade.

Acknowledgment

The project was supported by the projects of Land Engineering Construction Group of Shaanxi Provincial (DJNY2022-18).

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