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Sources, Fate and Degradation of Polycyclic Aromatic Hydrocarbons in the Environment

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ABSTRACT

This review is dealing with the human exposure, sources, fate, health effects and possible ways to eliminate the hazardous effects of polycyclic aromatic hydrocarbons (PAHs) from the environment. PAHs are compounds produced as a result of day to day activities that have heaped up in the environment majorly as a result of anthropogenic activities such as the burning of fossil fuels, coal gasification, liquefying plants, and natural activities such as burning in the open, oil spillage, seepage of petroleum and volcanic activities. They are organic contaminants and they have a great resistant to deterioration and can also persist in the environment for a long time causing unfavourable environmental effects, some of the unfavourable environmental effects caused by these pollutants are identified as carcinogenic, mutagenic and teratogenic. The interest researchers have in solving these environmental problems has given rise to various researches over the years some of which include the possible ways to eliminate the pollutant from the natural environment. Remediation is an inspiring option to remove PAHs completely from the environment or convert them to compounds that are less harmful. There are diver methods through which the pollutants can be completely eliminated from the natural environment and each method has its own mode of operation and advantages. This review gives various methods such as chemical degradation; photolysis degradation; biodegradation and chemical adsorption degradation through which PAHs can be removed without possible side effects, the review also focuses on the sources, fate of PAHs, human exposure, health effect and its degradation among others.

Keywords: Pollution; polyaromatic hdrocarbons; organic compounds; environment; degredation.

INTRODUCTION

PAHs are class of organic compounds that are often colourless, pale yellow, or white solids. PAHs are class of chemicals that are present everywhere with several hundreds of chemically related compounds, they can exist for many years in the environment with many structures and diverse harmful consequences. They have exhibit various harmful health effects on human system through various actions (Abdel-Shaffy *et al*., 2016). They are organic pollutants produce by natural sources, anthropogenic sources and mainly when there is an incomplete burning of fuels in liquid and solid states (Gemma, 2006). PAHs are formed as a result of the combustion of fossil fuels, hydrocarbons, peptides, and carbohydrates. PAHs can be distributed through various means but the common one is through atmospheric long-range transport and it is so because they are usually engrossed onto particulate matter from the source of combustion (Ou, 2000). There are various sources of PAHs, which include power generation, burning of incinerators, emissions from motor cycles, industrial processes, oil spillage, forest fires and smoke from cigarette (Ou, 2000) these sources can either be in gaseous phase or solid phases. PAHs that have 2 or more aromatic rings usually exist in the gaseous phase and those with 4 or more aromatic rings are mostly classified as the particulate phase (Li *et al.,* 2009). Polycyclic Aromatic Hydrocarbons (PAHs) as pollutants generated mainly via natural and anthropogenic sources, are very prevalent pollutant of both the aquatic and terrestrial ecosystems, and their existence is attributed to petrogenic and pyrogenic sources and these sources has waxed a long time ago (Jonsen *et al.,* 2005). Their persistence biologically and chemically in the environment is as a result of some formations which occur from cloudy packs of electrons on the two sides of the ring (Jonsen *et al.,* 2005). High molecular weight PAHs containing more than four benzene rings are the main cause of the dangers been done to the environment and human health (EPA, 1984) while the lower molecular weight PAHs such as naphthalene are known to have health effects that could be potentially hazardous and also though are comparatively mild (Klaasen, 2001). The harmful effects of both the high and low molecular weight PAH has given rise to a keen interest of researchers and also a cause to study more mainly due to their environmental effects (Ravindra *et al.,* 2008).

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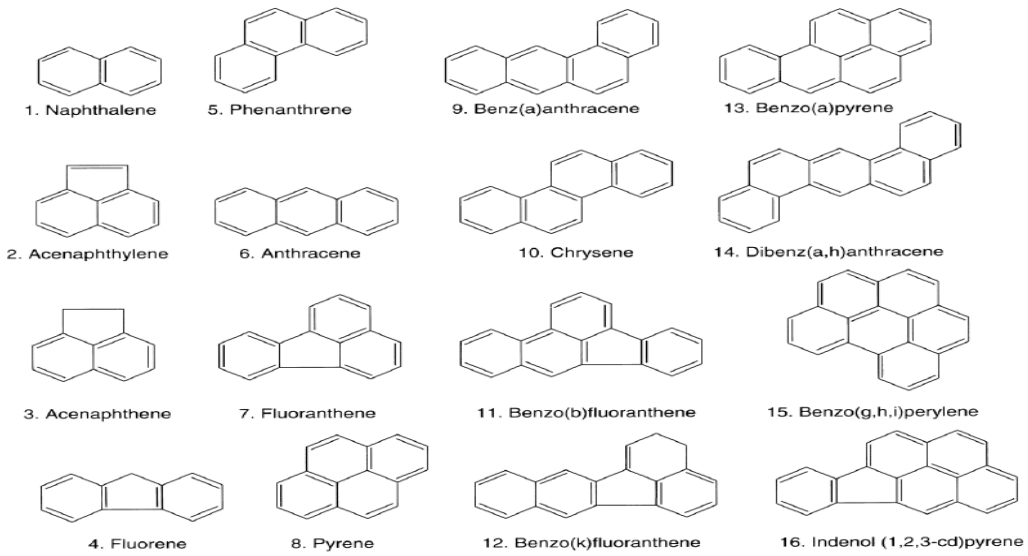

Fig 1. The molecular structure of the 16 major PAHs (Adapted from Marcé *et al.,* 2000).

Remediation is an encouraging option to completely eliminate PAHs from the environment and also convert them to other compounds that are less harmful. Various methods can be used for the complete elimination of PAHs and each of this methods has its own mode of operation and useful conditions. Physical processes such as volatilization, leaching, chemical and photo oxidation are effective in lowering the level of PAHs in the environment (Heitkamp *et al.,* 1988; Okoro *et al.*, 2019) but these physical processes are only applicable in aquatic environment. However, the interest over the environmental persistency, inclination and occurrence of other contaminations of metals and PAHs in the environment has increased, since these chemicals have been shown to be dangerous to living organism.

SOURCES OF PAHs

PAHs are being gotten from various sources, which can either be through influence of human activities or naturally. Natural sources of PAH emission are mainly as a result of volcanic eruption, oil seeps from crude oil reservoirs, bush burning and erosion of sediments of ages while the anthropogenic sources of PAHs are formed mainly as a result of thermal alteration, incomplete burning of organic matters, combustion of fossil fuels, and industrial waste water (Zahra and Reza, 2017). The three main ways through which PAHs are being released to the environment are petrogenic, pyrogenic, and biological means. PAHs that are released during crude oil processing and other similar reactions are referred to as petrogenic. Petrogenic PAHs are formed mostly by petroleum products and they are the most common sources of PAHs due to the various modes of transportation being used widely, storage of crude oil and its products in the environment, the major sources of petrogenic PAHs are oil spills from marine and freshwaters, tank leaks from petroleum products stored underneath the ground and above the ground, the retention of various numbers of discharge of gasoline, motor oil, and other substances that are associated with transportation. (Hussein *et al.,* 2016; Tolosa et al., 1996). PAHs that are formed during pyrolysis are known as pyrogenic PAHs. Pyrolysis is the breakdown of organic material at high temperatures (350^{o}C to >1200^{o}C) in the absence of oxygen. Common examples of pyrogenic sources of PAHs that occur naturally in the environment are the destructive distillation of coal into coke and coal tar plus the thermal cracking of petroleum by-products into lighter hydrocarbons. The processes of pyrolysis that leads to the formation of PAHs are the incomplete combustion of fuels in vehicles and trailers, incomplete burning of wood in forest, and so many others (Abdel-Shaffy *et al.,* 2015). Biologically produced PAHs are formed by various biological activities some of which include the synthesis of some plants and bacteria and the degradation of plants (Hussein *et al.,* 2016).

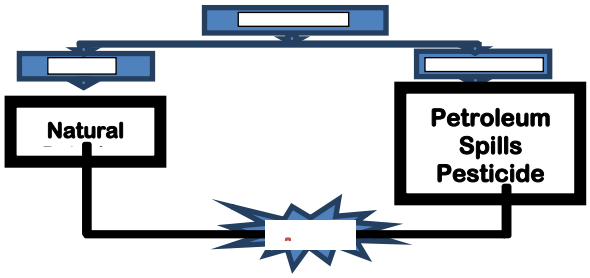

Fig. 2 Various sources of PAHs from the environment (Adapted from Abdel Shaffy *et al.,* 2016).

Fates of PAHS in the Environment

PAHs are been transported over a long distance in the environment without degrading significantly and this is because they are very prevalent in the environment. PAHs are sparsely dissolved in water and have a strong affinity for sediment, soil, and biota. PAH are adsorbed to particulate matter when found in air and water which makes them strongly attached to the atmosphere. Also PAHs can be washed by rain when absorbed by plants, or deposited into soil as a result of plant decay (Eisler, 1987). PAHs can be removed from the environment by biodegradation or photodegradation processes, the rates of reduction of PAHs varies and the process decreases with increasing numbers of aromatic rings (Igwe and Ukaogo, 2015). PAHs are strongly attached to the organic fraction of soils and sediments. Also the leaching of PAHs from the surface of the soil to the groundwater is assumed to be insignificant although it has been reported that small detectable concentrations can be obtained from the groundwater. Polycyclic aromatic hydrocarbons can be washed away from either soil or soils surface primarily by volatilization, these processes depend on several physical factors such as temperature, soil texture and previous contamination (Wild, 1991).

Human Exposure oo PAHs

There are various ways through which human can be exposed to PAHs in the general population, some of the common ones is breathing indoor and ambient air, smoking of cigarettes, eating food contaminated with PAHs (ACGIH, 2005). Smoke and fumes from tobacco companies contains various types of PAHs, such as benzo(a)pyrene, and many more PAHs which are suspected to be carcinogenic. From findings it has been discovered that some farm produce, such as lentils and wheat, may produce PAHs naturally or absorb them to itself through water or air medium. Water consists of small amounts of PAHs, they enter water directly from industrial effluents, remains from oil spillage, burning of bushes, forest, and biological activities. PAHs also get into the soil, primarily from airborne fallout (Ciecierska and Obiedzin, 2013). People have been exposed to PAHs on daily basis especially those that carry out their daily activities in environments that are highly filled with contaminants from PAHs. The common routes of exposure to PAHs are through ingestion of contaminated plant materials, inhaling contaminated air, and skin contact (Wang *et al.,* 2012 ; Armstrong *et al.,* 2004; Ravindra *et al.,* 2008).

Health Effects of PAHs

Human beings are being exposed to PAHs on a regular basis. This exposure has been linked with the high risk of cancerous cell development in various organs of the human body, such as the lungs, breast, hand and legs, and skin (including the scrotum), depending on the mode through which an individual is been exposed and the form of PAH an individual is exposed to (IARC, 2006). The future effects of PAHs have given rise to a great concern for the level of these pollutants in the environment, the higher the level of these compounds the greater their effects. The common health effects of these compounds are mutagenic and carcinogenic. The health effect has been classified into two, as indicated below:

Short -Term Health Effects

Short -term or acute is the form of health effects which rely mainly on the period of time it takes human being to be exposed to PAHs, the pathway through which an individual has been exposed (routes) and the amounts of PAHs an individual is exposed to (ACGIH, 2005). Anthracene and naphthalene are common examples of PAHs that have direct impact on skin. Benzo(a)pyrene and anthracene are skin sensitizers, i.e. cause a sensitive reaction in human and animal skin (IPCS, 2010). There are diverse factors that can also disturb human health, some of these factors are, pre-occurring health status, immune system and age of individual. Workers and individuals exposed to high concentration of contaminants containing PAHs have suffered various health conditions such as nausea, irritation of the eyes, vomiting, and confusion (Unwin *et al.,* 2005).

Chronic Health Effects

Chronic health effect can take a long period of time, this effect may cause cataracts, kidney damage, decreased immune function, jaundice, lung function abnormalities and asthma-like symptoms, (Band *et al.,* 2002) reported that contact of these contaminant with human skin directly may cause redness and various skin problems. Naphthalene is a common example of PAH and it is the major cause of the depletion of red blood cells if ingested or inhaled in high quantity. If an individual is opened to PAHs, the harmful effects that will occur mainly depend on the way of exposure, the routes of exposure and the concentration of the PAHs (Diggs *et al.,* 2011).

Methods of Remediating PAHS from the Environment

Remediation which is also known as reclamation is the procedure through which organic effluence are reduced by controlled conditions to a non toxic state The main aim of remediation is to eliminate pollutants from the immediate environment and transform the pollutants to a less damaging product. There are various ways through which PAHs can be degraded in the natural environment; some of

which include: Biological decomposition, Phytodegradation and chemical degradation (Nadarajah *et al.,* 2002). There are several ways through which the remediation methods affects each PAHs owing to their different varying structures and properties

Chemical Degradation

Chemical oxidation of PAHs is of little significance when talking about PAH depletion process under most conditions. The rates at which PAH is been oxidized depend on several properties of the system. During chemical oxidation which could be natural or as treatment processes, the structure and molecular weight of the pollutant, the temperature, its physical form and the intensity of the oxidizing agent all influence the outcome (Abdel-Shafy and Mansour, 2013). Abdel-Shafy and Mansour (2013) showed that the chemical and physical treatments have the tendency of removing PAHs in a large proportion from surface water. Fluoranthene was detected in high concentrations in the soil because fluoranthene was the most consistent of all the PAHs tested for oxidation by ozone (Alebic–Juretic *et al.,* 1990). It was also reported that the mutual effect of UV irradiation and TiO_2 catalysis was exact for depletion of PAHs in polluted soil (Zhang *et al.,* 2008; Hassan *et al.,* 2015).

Photolysis Degradation

Photolysis is defined as the decomposition of a compound by application of light; it is also known as photodissociation or photodecompostion. (Stanley, 1994). Photolytic reactions occur when light emitted by PAHs excites the electrons within the molecules which creates a structural arrangement that is liable to various physical and chemical processe (Schwarzenbach *et al.,* 1993). Biodegradation reactions can be likened to photolysis reactions involving PAHs. Small photo-degradation may occur when PAHs are attached to particles in the atmosphere or soil giving rise to a more active reactions with increasing particle surface area. These reactions are also more on brightly colored fragments such as silica gel or alumina, than on dark particles, such as soot. Photolysis degradation reactions depend mainly on the structure of the PAH that is being depleted. Photolysis is more efficient for compounds with low molecular weight, such as naphthalene, this is because they are more bioavailable and can be exposed to sunlight for a long period of time. Finally, Other methods of PAH depletion appears less frequently in the scientific books and literature than degradation.

PAH Biodegradation

This study is based on aerobic and anaerobic depletion which has been described recently under some denitrifying conditions (Haritash, 2009; Peng *et al.,*2008). PAHs become biologically available when they are in the dissolved phase or in the vapour phase so that bacteria can deplete any given PAH. must be readily available for absorption by the bacteria (Cerniglia, 2008; Dandie *et al.,* 2004; Fredslund *et al.,* 2008). PAHs that are sorbed onto soil particles are not easily depleted by bacteria, this is because the PAHs are separated from the enzymes that are used by bacteria to break them down (Hatzinger and Martin, 1995; Kim *et al.,* 2007; Rappert *et al.,* 2006; Archana, 2008).. Hatzinger and Martin (Hatzinger and Martin, 2005) explained that fresh C-14 labelled phenanthrene and chrysene are removed rapidly. Furthermore phenanthrene and chrysene that had been exposed to soil for a long period of time are removed slowly. The important factor in the PAHs bioavailability is their solubility character. The solubility of PAHs in aqueous state is strongly dependent on each of their molecular weights (Thorsen *et al.,* 2004). PAH depletion also can be influenced by competitive inhibition. Likewise, the rate of PAH depletion can be reduced if the bacteria used in depleting PAHs find a chemical that has been used more easily as a food source. Competitive inhibition occurs when the active sites of enzymes used by bacteria to break down PAHs as a carbon source are not specific. (Teng *et al.,* 2010).

Chemical Adsorption Degradation

Adsorption is among the most viable options used for depletion due to its high removal efficiency (Eckenfelder, 2000). It has various advantages, one of which includes is the fact that the persistent compounds are removed, rather than being broken down to potentially dangerous metabolites that may be produced by oxidation and reduction processes (Valderrama *et al.,* 2007). Although activated carbon is widely adjudged to be the most effective and widely used adsorbent in the adsorption treatment of wastewater containing PAHs, other adsorbents have reportedly been studied for the removal of PAHs from the environment for example zeolite (Chang *et al.,* 2004); organoclays (Dentel *et al.,* 1998); other organic-free hydrophilic minerals like silica, alumina and talc (Su *et al.,* 2006; Vidal *et al.,* 2011); solid residue from agricultural activities like ash waste, and pine bark (Li *et al.,* 2010).

CONCLUSION

PAHs are part of the classes of compounds classified as polycyclic organic matters (POM). Common examples of daily activities that lead to the discharge of PAHs to the natural environment are the use of oil, gas, coal and wood in energy production, indoor smoking, heating and bush burning. PAHs are being discharged in the atmosphere in gaseous or particulate phases and

they are settled by wet and dry deposition. The existence of PAHs in crops, plants and food is due to effluents resulting from manufacturing industries, daily activities such as drying, roasting, deposits from the air on the surface of plants, and smoking. Also, the presence of PAHs in foods and consumables results in health risk to the human and infants. Most of the compounds are classified as carcinogenic and they consist of a major class of chemical carcinogens present in the environment. Eliminating PAHs from the environment is a very hard task. Therefore, it is very essential to have a deep understanding of the mechanism of the various remediation processes. Some of the methods considered to remove PAHs from the substrates in this review are said to be most efficient, cost effective and environmentally friendly. Phytodegradation is one of the efficient, effective and environmentally friendly method and this is because it is a green degradation method that is mindful of the environment therefore reducing the harm being done to the natural environment and secondly, no dead-end products are produced to initiate further contamination of the environment.

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Conflict of Interest
The authors state that no conflicts of interest exist in respect to publishing this review article.

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