International Journal of Advance Research in Science and Engineering
Vol. No.6, Issue No. 09 , September 2017
www.ijarse.com
IJARSE
ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346

Polycyclic Aromatic Hydrocarbons as Environmental Pollutants: A review

Ranjan[1], Masood F.[1], Singh H. P.[1], Batish D. R.[2]

[1]*Department of Environment Studies, Panjab University, Chandigarh, (India)*

[2]*Department of Botany, Panjab University, Chandigarh, (India)*

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) represent a group of persisting and prevalent environmental pollutants that are harmful to the environment and humans due to their toxic, mutagenic and carcinogenic potential. The emission of PAHs into the environment has increased with the increase in demand for petroleum products. The incomplete combustion of organic products such as coal, fuel oil, fire wood etc. remains an important contributor to emission of PAHs; the other sources being forest fires, motor vehicles, volcanoes, refineries and many more. Degradation of PAHs with chemical, photooxidative and biodegradative methods helps to reduce their harmful effects on the environment. Relevant literature has reported biodegradation to be the most cost-effective and environment-friendly method. This review presents the current information regarding the sources, bioaccumulation, health hazards and degradation techniques of PAHs.

***Keywords** – Bioaccumulation, Biodegradation, Carcinogenesis, Polycyclic aromatic hydrocarbons.*

I. INTRODUCTION

One of the most persistent, prevalent and potent environmental pollutants are the polycyclic aromatic hydrocarbons (PAH). The fused ring aromatic organic compounds are generated by anthropogenic as well as natural sources. The benzene rings can be fused in linear, angular or cluster arrangements [1, 2, 3]. These are colourless, white or pale yellow solid [4]. Natural sources include coal, coal tar, asphalt, few trees and grasses etc and incomplete burning of all these compounds acts as anthropogenic source of PAHs [5]. Even ill ventilated kitchens can lead to built of PAH in the surroundings. The varied structure and toxicity can have deleterious effects on environment and humans. These effects are mostly biological i.e. mutations, carcinogenicity and a high level of toxicity [6, 7, 8]. Hence its presence in the environment and exposure to humans is of great concern. With variations in the number of fused aromatic rings the physical and chemical properties of PAH change. Usually these well known pollutants can be found in soil, air and water. They differ in their transport, distribution and fate in the environment [3]. They do not degrade quickly and persist in nature for a long period of time. In this residing period, wind distributes the pollutants over a large area in a global manner [9, 5].

These hydrophobic pervading compounds consist of carbon and hydrogen only. In spite of having many PAH compounds, data lays emphasis only on a limited number of these. On the basis of their toxicity and abundance, 16 PAH compounds have been included in the US Environmental Protection Agency‘s list of priority pollutants to be monitored in the effluents of industry [10, 11]: 1) Naphthalene ($C_{10}H_8$), 2) Phenanthrene ($C_{14}H_{10}$), 3) Anthracene ($C_{14}H_{10}$), 4) Fluoranthene ($C_{16}H_{10}$), 5) Pyrene ($C_{16}H_{10}$), 6) Chrysene ($C_{18}H_{12}$), 7) Benzo (a)anthracene ($C_{18}H_{12}$), 8) Benzo (b)fluoranthene ($C_{20}H_{12}$), 9) Benzo (k)fluoranthene ($C_{20}H_{12}$), 10) Benzo (e)pyrene ($C_{20}H_{12}$), 11) Benzo (a)pyrene ($C_{20}H_{12}$), 12) Perylene ($C_{20}H_{12}$), 13) Benzo (ghi)perylene

(C22H12), 14) Dibenzo (ah)anthracene (C22H14), 15) Indeno(cd)pyrene (C22H12), 16) Coronene (C24H12). As the number of benzene rings increases so does the molecular weight of the compound. As the molecular weight of these pollutants increases their reactivity, volatility and aqueous solubility decrease [3]. PAH with six fused aromatic rings are said to be "small' PAHs, whereas those containing more than six aromatic compounds are called "large'' PAHs [4].

PAHs are very stable thermally and are resistant to degradation. These aromatic compounds have high melting and boiling points. PAHs with lower molecular weight are generally water soluble and with each additional ring the hydrophobicity and aqueous insolubility increases. These compounds have low vapour pressure [12]. Due to their lipophilic nature these pollutants are quite soluble in organic solvents. Owing to peculiar UV absorbance spectrum of each isomer of PAH and unique UV spectrum of each ring structure the identification becomes easy. These aromatic pollutants are light sensitive, corrosion resistant, heat stable and can exert physiological actions [13]. PAHs are important constituents of crude oil, creosote, asphalt and coal tar. These are mainly used in pharmaceutical industries in the manufacturing of pesticides, certain dyes, and pigments also in agrochemical production. These persistent pollutants are used in construction of roads and roofs. Furthermore, specific refined products of certain PAHs, are used in electronics, functional plastics and liquid crystals [4].

II. SOURCE

This ubiquitous group of compounds are widely distributed in the environment mainly in and around areas where bush burning for agricultural farming is commonly practiced, as also in petroleum exploration and refining operations [14]. Origin of these pollutants can be natural like grasses, forest fires, soil, sediments, leakage of petroleum, eruption of volcanoes and many more. The anthropogenic sources are even more unaccountable. It varies from a cigarette smoke to incinerators. Usually the human generated sources include incomplete combustion of organic materials, fuel combustion, exhaust from automobiles and aeroplanes. High concentrations are reported to be found near coal gasification sites and tar oil distillation plants [3, 15]. At times even discharge from industries and accidental release of raw and refined products can lead to the build up of PAH in the environment. Emissions from coal combustion for power generation are predominant in emerging countries. Air pollution by PAHs in industrialized nations mainly occurs from small combustion units in households. Sediments from urban waterways have an "urban background" signature from a variety of nonpoint sources of PAHs which may confound the interpretation of point sources of PAHs to these waterways [11]. Common point sources of PAHs include direct and indirect discharges from petroleum terminals, shipyards, aluminium smelting, manufactured gas production plants, tar distillation plants, rail yards, loading/unloading facilities, and spilled or seeped petroleum or coal or oil derived tars and their associated distillation products [16].

The sources are broadly divided into three categories i.e. Pyrogenic, petrogenic and biological. Resembling to the name of the source pyrogenic, PAHs generated during pyrolysis belong to this category. During combustion; destruction, distillation or cracking of heavy organic compounds into lighter hydrocarbon chains under very high temperature (350°C to even greater than 1200 °C) and absence or low concentration of oxygen. These are done intentionally, hence are voluntary processes. The other pyrogenic sources, which lead to the formation of PAHs, are unintentional or involuntary include incomplete combustion of motor fuels in vehicles, improper combustion of wood in forest fires and fireplaces, and incomplete combustion of fuel oil in heating systems [4].

PAHs can even be released at low temperature (100°C to 150 °C) in the process of aromatisation but it is a slow process and produces high concentrations of alkylated PAHs.

Petrogenic sources involve formation of PAHs during crude oil maturation or similar processes. Due to the dependence of human beings on petroleum products these sources are wide spread. PAHs are found on petroleum products and can be released in the transportation, storage and use of crude oil and its products. Most common sources of petrogenic PAHs include marine and freshwater oil spills, underground and above ground storage tank leaks, and the accumulation of vast numbers of small releases of gasoline, motor oil, and related substances associated with transportation [11, 17]. The third category of source of PAHs is not so well known. Few PAHs are produced biologically. For instance, they can be synthesized by certain plants and bacteria or formed during the degradation of vegetative matter [4].

III. EFFECTS ON HUMAN HEALTH

Apart from the environment, the PAHs are also attributed significant importance on account of their toxicity to humans. On exposure to PAHs, humans suffer from various consequences (Table 1). Such an exposure can occur through various portals of entry such as inhalation of polluted air or smoke (including cigarette smoking); ingestion of foods contaminated with PAHs from water, soil or air; and dermal contact through occupational exposure or otherwise [18]. The type and severity of toxicity that develops depends up on numerous factors such as the relative toxicity of the chemical, the degree or amount of exposure, the duration and route of exposure, the age and pre-existing health status [18]. For example, short-term exposure to PAHs has been reported to cause impairment in pulmonary function in asthmatics and increased risk of thrombotic events in patients with heart disease [18, 19].

Adverse effects due to short-term exposure	Adverse effects due to long-term exposure
• Nausea • Vomiting • Loose motions • Confusion • Eye irritation • Skin irritation	• Cataracts • Reduced immunity • Kidney damage • Liver damage ‘ • Haemolysis due to naphthalene • Breathing problems and asthma-like symptoms • Pulmonary abnormalities • Cancers – lung, skin, bladder, gastrointestinal tract

Table 1: Adverse effects on human health due to exposure to PAHs [20, 21, 22, 23, 24]

An important concern with PAHs is their ability to cause mutagenesis and carcinogenesis. Various PAHs have been identified and classified by the International Agency for Research on Cancer as carcinogens – benzo[a]pyrene has been included in Group A (carcinogenic to humans) while benz[a]anthracene, benzo[k]fluoranthene, benzo[b]fluoranthene, naphtahalene and chrysene are in Group 2B (Possibly carcinogenic to humans) (http://monographs.iarc.fr/ENG/Classification/). Owing to their highly lipophilic nature, the PAHs tend to accumulate in the human body, especially in the adipose tissue. Several studies have reported an increased risk of lung, skin, bladder and gastrointestinal cancers among populations exposed to PAHs [22].

The mutagenesis due to PAHs has been attributed to their electrophilic metabolites that interact covalently with DNA and form adducts leading to base pair substitutions and frameshift mutations [25, 26, 27, 28, 29, 30] Observational studies have also reported that exposure to high levels of PAH during pregnancy can lead to low birth weight, premature delivery, cardiac malformations, childhood asthma, lower IQ and increased behavioural problems in later life in the offspring [4, 31, 32, 33].

IV. BIOACCUMULATION

Bioaccumulation refers to accumulation of a substance in an organism. PAHs tend to accumulate in organisms on account of their lipophilic nature wherein they dissolve within the adipose tissue of the organisms [34]. Various investigations have documented a higher level of PAHs in plants following their administration that can be attributed to bioaccumulation [35, 36]. This may lead to an increased toxicity to the organism, though evidence for this is very limited. Moreover, PAHs also have the potential to undergo biomagnification as they get transferred in the food chain from lower organisms to higher [37]; a phenomenon also referred to as 'trophic transfer'.

V. DEGRADATION TECHNIQUES

The removal of PAHs from environment can be by degradation by various means. Based on the chemical and physical properties of PAHs the degradation can be chemical degradation, photooxidation, and biodegradation. Very few studies have reported degradation by photooxidation or chemical degradation. Most studies have examined biodegradation by various microorganisms such as *Ochrobactrum sp*., *Enterobactercloacae, Stenotrophomonas maltophilia* and many more [11].

5.1. Chemical degradation

PAHs being relatively stable and recalcitrant in soil are less easy to degrade than many other organic compounds. Upon addition of chemicals PAHs undergo chemical reaction but are transformed in to other polyaromatic hydrocarbons. Their aromaticity is conserved since a lot amount of energy is required to change an aromatic compound into a non aromatic compound [5]. Degradation of PAHs by chemicals depends on many factors like molecular weight, structure of the compound, its physical state, temperature and the strength of oxidizing agent. If the chemical oxidant is added in insufficient quantity, the PAH could be metabolically transferred into dead-end products which are resistant to further degradation [38]. This dead-end product could build-up in the environment and become a source for further contamination. The efficiency of chemical degradation of PAHs is limited by their low aqueous solubility and vapour pressure [39]. Nonetheless, surfactants have been reported to contain properties that overcome problems related to PAHs low aqueous solubility. Surfactants enhance the solubility of hydrophobic compounds [40]. Several studies have stressed the importance of surfactants to increase the solubility of PAHs by decreasing the interfacial surface tension between PAH and the soil/water interphase [5, 41].

Some researchers have reported negative or negligible effects of adding surfactants to soil substrate [42]. Possible reasons for this include the competition for substrate utilization and toxicity of the surfactants towards PAHs-degrading bacteria in the soil matrix [43]. Hence, PAHs-degradation process involving surfactant utilization need to be optimized for each of the factors influencing degradation including, surfactant type and concentration, PAH specificity as well as presence of host bacteria [44, 5]. Zhang et al. also reported that the synergistic effect of UV irradiation and TiO2 or ZnO catalysis was efficient for degradation of PAHs in contaminated soil [45, 46]. Iron oxides and oxalic acid can set up a photo-Fenton-like system without additional H2O2 in solid phase to enhance the photodegradation of pyrene under UV irradiation [47]. Also, sono-chemical degradation of PAHs using high frequency of ultrasound was also investigated [4, 48, 49].

5.2. Photooxidation

Photo oxidation or photolysis is said to be the process under which destruction of a compound occurs from reactions initiated by the absorption of light [50]. Such reactions take place when electrons in PAH compounds get excited due to absorption of light leading to unstable structural arrangement. Degradation of PAH is less when they are adsorbed on soil particles as compared to when they are in vapour or aqueous phase. The degradation effectiveness increases with increase in particle surface area. Also, photolysis reactions are also greater on light coloured particles, such as silica gel or alumina, than on darker particles, such as carbon black [4, 51].

Photolysis mainly depends on molecular weight and structure of the compound. Due to the bioavailability of compounds with low molecular weight and longer exposure time to sunlight, photolysis is more effective. Linear, 2-ring, and some clustered PAHs degrade rapidly under direct light. Angular PAHs (e.g., phenanthrene and dibenz(a,h)anthracene) are the slowest in degradation. This is mainly because they are the most structurally stable molecules [52]. Finally, PAH molecules, when they are adsorbed on fly ash particles, may get deposited inside the fly ash pore structure. When this occurs, the portion of the PAHs in the pore structure becomes shielded from sunlight which stops photolytic reactions from occurring [5, 53].

5.3. Biodegradation

Biodegradation is the promising technology for the treatment of contaminated soil, water or sediments contaminated with organic compounds. It involves complete mineralization of organic contaminants into carbon dioxide, water, inorganic compounds, and cell protein or transformation of complex organic contaminants to other simpler organic compounds by biological agents like microorganisms. The products of complete mineralization of the pollutant by biodegradation process include; CO2, H2O and cell biomass [54]. The optimization of biodegradation process involves many factors such as the existence of a microbial consortium capable of degrading the pollutant, the bioavailability of the contaminant to microbial attack and certain environmental factors (soil type, temperature, soil pH, oxygen level of soil, electron acceptor agents, nutrient content of soil) contributing to microbial growth [5, 54].

The rate of PAH degradation can be reduced if the bacteria involved in degrading PAHs find a chemical that is utilized 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 nonspecific. These non-specific enzymes can attach themselves to a number of different chemicals. If other chemicals are present that are more easily broken down, the enzyme will degrade those chemicals as its carbon source and the PAHs will persist [55].

Evidence have been accumulating to suggest that certain microorganisms namely; *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Torulopsis bombicola* could produce bioremediation surfactants such as surfactin, rhamolipid and sophorolipid capable of improving bioremediation by solubilising PAHs into the aqueous medium and enhance their bioavailability for degradation [5, 56, 57].

VI. CONCLUSION

Thus, PAHs represent a great concern to environment and human health due to their toxic nature. Of all the existing techniques of remediation, biodegradation remains the most cost effective and environment friendly. Moreover, combining two or more degradation techniques can prove to be more effective than individual methods. However, due to their recalcitrant nature, more research is required to determine better remediation techniques. Accumulation of PAHs by plants needs further study and microbes and plants can be used together for better remediation results. A thorough understanding of the source, physical and chemical properties and their effects is indispensable for this purpose. Public awareness regarding sources and health effects of PAHs needs attention on a global scale due to their potential for long range transport.

REFERENCES

[1] Cheung, P.Y. and Kinkle, B.K., Mycobacterium diversity and pyrene mineralization in petroleum-contaminated soils, *Applied and Environmental Microbiology*, *67(5*), 2001, 2222-2229.

[2] Cerniglia, C.E., Biodegradation of polycyclic aromatic hydrocarbons, *Biodegradation, 3(2-3),* 1992, 351-368.

[3] Seo, J.S., Keum, Y.S. and Li, Q.X., Bacterial degradation of aromatic compounds, *International journal of environmental research and public health*, *6(1),* 2009, 278-309.

[4] Abdel-Shafy, H.I. and Mansour, M.S., A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation, *Egyptian Journal of Petroleum*, *25*(1), 2016, 107-123.

[5] Ukiwe, L.N., Egereonu, U.U., Njoku, P.C., Nwoko, C.I. and Allinor, J.I., Polycyclic aromatic hydrocarbons degradation techniques: a review, *International Journal of Chemistry*, *5(4),* 2013, 43

[6] Johnsen, A.R. and Karlson, U., Diffuse PAH contamination of surface soils: environmental occurrence, bioavailability, and microbial degradation, *Applied Microbiology and Biotechnology*, *76(3)*, 2007, 533-543.

[7] Ramdine, G., Fichet, D., Louis, M. and Lemoine, S., Polycyclic aromatic hydrocarbons (PAHs) in surface sediment and oysters (Crassostrea rhizophorae) from mangrove of Guadeloupe: levels, bioavailability, and effects, *Ecotoxicology and environmental safety*, *79*, 2012, 80-89.

[8] Lyu, Y., Zheng, W., Zheng, T. and Tian, Y., Biodegradation of polycyclic aromatic hydrocarbons by Novosphingobium pentaromativorans US6-1, *PloS one*, *9(7),* 2014, p.e101438.

[9] Platt, H.M. and Mackie, P.R., Distribution and fate of aliphatic and aromatic hydrocarbons in Antarctic fauna and environment, *Helgoländer Meeresuntersuchungen*, *33(1),* 1980, 236.

[10] Rubailo, A.I. and Oberenko, A.V., Polycyclic aromatic hydrocarbons as priority pollutants, *J. Siberian Federal Univ. Chem.,1(4),* 2008, 344-354.

[11] Nikitha, T., Satyaprakash, M., Vani, S.S., Sadhana, B. and Padal, S.B., A Review on Polycyclic Aromatic Hydrocarbons: Their Transport, Fate and Biodegradation in the Environment, *Int. J. Curr. Microbiol. App. Sci*, *6(4),* 2017, 1627-1639.

[12] Masih, J., Masih, A., Kulshrestha, A., Singhvi, R. and Taneja, A., Characteristics of polycyclic aromatic hydrocarbons in indoor and outdoor atmosphere in the North central part of India, *Journal of hazardous materials*, *177(1),* 2010, 190-198.

[13] Akyüz, M. and Çabuk, H., Gas–particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey, *Science of the total environment*, *408(22)*, 2010, 5550-5558.

[14] Fetzer, J. C., *The chemistry and analysis of the large polycyclic aromatic hydrocarbon* (New York: Wiley Publishers, 2000)

[15] Capotorti, G., Digianvincenzo, P., Cesti, P., Bernardi, A. and Guglielmetti, G., Pyrene and benzo (a) pyrene metabolism by an Aspergillus terreus strain isolated from a polycylic aromatic hydrocarbons polluted soil, *Biodegradation*, *15(2)*, 2004, 79-85.

[16] Crane, J.L., Grosenheider, K. and Wilson, C.B., *Contamination of stormwater pond sediments by polycyclic aromatic hydrocarbons (PAHs) in Minnesota: The role of coal tar-based sealcoat products as a source of PAHs*, Minnesota Pollution Control Agency, 2010.

[17] Tolosa, I., Bayona, J.M. and Albaiges, J., Spatial and temporal distribution, fluxes, and budgets of organochlorinated compounds in Northwest Mediterranean sediments, *Environmental science & technology*, *29(10)*,1995, 2519-2527.

[18] ACGIH (American Conference of Governmental Industrial Hygienists), Polycyclic aromatic hydrocarbons (PAHs) biologic exposure indices (BEI) Cincinnati, OH: *American Conference of Governmental Industrial Hygienists*, 2005.

[19] Kim, K.H., Jahan, S.A., Kabir, E. and Brown, R.J.,A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects, *Environment international*, *60*, 2013, 71-80.

[20] Unwin, J., Cocker, J., Scobbie, E. and Chambers, H., An assessment of occupational exposure to polycyclic aromatic hydrocarbons in the UK, *Annals of Occupational Hygiene*, *50(4)*, 2006, 395-403.

[21] IPCS (International Programme on Chemical Safety), Polycyclic aromatic hydrocarbons, selected non-heterocyclic, 2010. <http://www.inchem.org/documents/ehc/ehc/ ehc202.htm>

[22] Bach, P.B., Kelley, M.J., Tate, R.C. and McCrory, D.C., Screening for lung cancer, *Chest*, *123(1)*, 2003, 72S-82S.

[23] Diggs, D.L., Huderson, A.C., Harris, K.L., Myers, J.N., Banks, L.D., Rekhadevi, P.V., Niaz, M.S. and Ramesh, A., Polycyclic aromatic hydrocarbons and digestive tract cancers: a perspective, *Journal of Environmental Science and Health, Part C*, *29*(4), 2011, 324-357

[24] Olsson, A.C., Fevotte, J., Fletcher, T., Cassidy, A., Mannetje, A.T., Zaridze, D., Szeszenia-Dabrowska, N., Rudnai, P., Lissowska, J., Fabianova, E. and Mates, D., Occupational exposure to polycyclic aromatic hydrocarbons and lung cancer risk: a multicenter study in Europe, *Occupational and environmental medicine*, *67(2)*, 2010, 98-103.

[25] Yang, H., Mazur-Melnyk, M., de Boer, J.G. and Glickman, B.W., A comparison of mutational specificity of mutations induced by S9-activated B [a] P and benzo [a] pyrene-7, 8-diol-9, 10-epoxide at the endogenous aprt gene in CHO cells, *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis*, *423(1)*, 1999, 23-32.

[26] Miller, M.L., Vasunia, K., Talaska, G., Andringa, A., de Boer, J. and Dixon, K., The tumor promoter TPA enhances benzo [a] pyrene and benzo [a] pyrene diolepoxide mutagenesis in Big Blue® mouse skin, *Environmental and molecular mutagenesis*, *35(4)*, 2000, 319-327.

[27] Wei, S.J.C., Chang, R.L., Merkler, K.A., Gwynne, M., Cui, X.X., Murthy, B., Huang, M.T., Xie, J.G., Lu, Y.P., Lou, Y.R. and Jerina, D.M., Dose dependent mutation profile in the c-Ha-ras protooncogene of skin tumors in mice initiated with benzo [a] pyrene, *Carcinogenesis*, *20(9),* 1999, 1689-1696.

[28] Prahalad, A.K., Ross, J.A., Nelson, G.B., Roop, B.C., King, L.C., Nesnow, S. and Mass, M.J., Dibenzo [a, l] pyrene-induced DNA adduction, tumorigenicity, and Ki-ras oncogene mutations in strain A/J mouse lung, *Carcinogenesis*, *18(10),* 1997, 1955-1963.

[29] Jung, K.H., Kim, J.K., Noh, J.H., Eun, J.W., Bae, H.J., Kim, M.G., Chang, Y.G., Shen, Q., Kim, S.J., Kwon, S.H. and Park, W.S., Characteristic molecular signature for the early detection and prediction of polycyclic aromatic hydrocarbons in rat liver, *Toxicology letters*, *216(1),* 2013, 1-8.

[30] IPCS, O.M.S., Environmental Health Criteria 202-Selected non-heterocyclic Polycyclic Aromatic Hydrocarbons, *World Health Organisation, International Programme on chemical Safety. http://www. inchem. org*, 1998, 179-179.

[31] Perera, F., Tang, D., Whyatt, R., Lederman, S.A. and Jedrychowski, W., DNA damage from polycyclic aromatic hydrocarbons measured by benzo [a] pyrene-DNA adducts in mothers and newborns from Northern Manhattan, the World Trade Center Area, Poland, and China, *Cancer Epidemiology and Prevention Biomarkers*, *14(3),* 2005, 709-714.

[32] Edwards, S.C., Jedrychowski, W., Butscher, M., Camann, D., Kieltyka, A., Mroz, E., Flak, E., Li, Z., Wang, S., Rauh, V. and Perera, F., Prenatal exposure to airborne polycyclic aromatic hydrocarbons and children’s intelligence at 5 years of age in a prospective cohort study in Poland, *Environmental health perspectives*, *118(9)*,2010, 1326.

[33] Abdel-Shafy, H.I., Al-Sulaiman, A.M. and Mansour, M.S., Anaerobic/aerobic treatment of greywater via UASB and MBR for unrestricted reuse, *Water Science and Technology*, *71(4),* 2015, 630-637.

[34] Stanković, D., Krstić, B. and Nikolić, N., Effect of traffic on the soil contamination with polycyclic aromatic hydrocarbons (PAHs), *Biotechnology & Biotechnological Equipment*, *22(2),* 2008,736-741.

[35] Zohair, A., Salim, A.B., Soyibo, A.A. and Beck, A.J., Residues of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides in organically-farmed vegetables, *Chemosphere*, *63(4),* 2006, 541-553.

[36] Khan, S., Aijun, L., Zhang, S., Hu, Q. and Zhu, Y.G., Accumulation of polycyclic aromatic hydrocarbons and heavy metals in lettuce grown in the soils contaminated with long-term wastewater irrigation, *Journal of Hazardous Materials*, *152(2),* 2008, 506-515.

[37] Aina, R., Palin, L. and Citterio, S., Molecular evidence for benzo [a] pyrene and naphthalene genotoxicity in Trifolium repens L, *Chemosphere*, *65(4),* 2006, 666-673.

[38] Freeman, H. M., & Harris, E. F., *Hazardous waste remediation: innovative treatment technologies* (Pennsylvania, USA: Technomic Publishing Company, 1995).

[39] Prak, D.J.L. and Pritchard, P.H., Solubilization of polycyclic aromatic hydrocarbon mixtures in micellar nonionic surfactant solutions, *Water Research*, *36(14),* 2002, 3463-3472.

[40] Boonchan, S., Britz, M.L. and Stanley, G.A., Surfactant- enhanced biodegradation of high molecular weight polycyclic aromatic hydrocarbons by Stenotrophomonas maltophilia, *Biotechnology and Bioengineering*, *59(4),* 1998, 482-494.

[41] Li, J.L. and Chen, B.H., Effect of nonionic surfactants on biodegradation of phenanthrene by a marine bacteria of Neptunomonas naphthovorans, *Journal of hazardous materials*, *162(1)*, 2009, 66-73.

[42] Laha, S. and Luthy, R.G., Effects of nonionic surfactants on the solubilization and mineralization of phenanthrene in soil–water systems, *Biotechnology and Bioengineering*, *40(11)*, 1992, 1367-1380.

[43] Liu, Y., Zhu, L. and Shen, X., Polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of Hangzhou, China, *Environmental science & technology*, *35(5)*, 2001, 840-844.

[44] Jin, D., Jiang, X., Jing, X. and Ou, Z., Effects of concentration, head group, and structure of surfactants on the degradation of phenanthrene, *Journal of Hazardous Materials*, *144(1)*, 2007, 215-221.

[45] Zhang, L., Li, P., Gong, Z. and Li, X., Photocatalytic degradation of polycyclic aromatic hydrocarbons on soil surfaces using TiO 2 under UV light, *Journal of Hazardous Materials*, *158(2)*, 2008, 478-484.

[46] Hassan SSM, El Azab WIM, Ali HR, Mansour MSM, The 18th International conference on petroleum, mineral resources and development, EPRI, Cairo, Egypt, 2015.

[47] Wang, Y., Liu, C.S., Li, F.B., Liu, C.P. and Liang, J.B., Photodegradation of polycyclic aromatic hydrocarbon pyrene by iron oxide in solid phase, *Journal of Hazardous Materials*, *162(2)*, 2009, 716-723.

[48] Wang, X.K., Chen, G.H. and Yao, Z.Y., Sonochemical degradation of polychlorinated biphenyls in aqueous solution, *Chinese Chemical Letters*, *14(2)*, 2003, 205-208.

[49] Manariotis, I.D., Karapanagioti, H.K. and Chrysikopoulos, C.V., Degradation of PAHs by high frequency ultrasound, *Water Research*, *45(8)*, 2011, 2587-2594.

[50] E. Stanley Manahan, *Environmental chemistry* (CRC Press Inc., 1994).

[51] Finlayson-Pitts, B.J. and Pitts, J.N., Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles, *Science*, *276(5315)*, 1997, 1045-1051.

[52] Korfmacher, W.A., Wehry, E.L., Mamantov, G. and Natusch, D.F.S., Resistance to photochemical decomposition of polycyclic aromatic hydrocarbons vapour-adsorbed on coal fly ash, *Environmental Science & Technology*, *14(9)*, 1980, 1094-1099.

[53] Niu, J., Sun, P. and Schramm, K.W., Photolysis of polycyclic aromatic hydrocarbons associated with fly ash particles under simulated sunlight irradiation, *Journal of Photochemistry and Photobiology A: Chemistry*, *186(1)*, 2007, 93-98.

[54] Gratia, E., Weekers, F., Margesin, R., D'Amico, S., Thonart, P. and Feller, G., Selection of a cold-adapted bacterium for bioremediation of wastewater at low temperatures, *Extremophiles*, *13(5)*, 2009, 763-768.

[55] Wang, C., Sun, H., Li, J., Li, Y. and Zhang, Q., Enzyme activities during degradation of polycyclic aromatic hydrocarbons by white rot fungus Phanerochaete chrysosporium in soils, *Chemosphere*, *77(6)*, 2009, 733-738.

[56] Cottin, N.C. and Merlin, G., Study of pyrene biodegradation capacity in two types of solid media, *Science of the total environment*, *380(1)*, 2007, 116-123.

[57] Kuyukina, M.S., Ivshina, I.B., Makarov, S.O., Litvinenko, L.V., Cunningham, C.J. and Philp, J.C., Effect of biosurfactants on crude oil desorption and mobilization in a soil system, *Environment international*, *31(2)*, 2005, 155-161.