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BIODEGRADATION OF PETROCHEMICALS: A POTENT WEAPON FOR THE CLEANUP OF ENVIRONMENT

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ABSTRACT

The extensive use of petrochemicals all around the world has been taking place with the increasing urbanization of the mankind. Accidental releases of petrochemicals are of particular concern in the environment because they are Xenobiotic as well as recalcitrant. Petroleum Hydrocarbons particularly are having disastrous and catastrophic consequences, not only on the human beings but also on other biotic components of the ecosystem. Currently there are two possible ways for the remediation of petroleum-contaminated system, either physicochemical or biological methods. The physicochemical methods are very expensive especially when the amount of contaminants is very large; also it is not that very effective. Bioremediation is very propitious technology as it very economic as well as leads to complete degradation of the Petrochemicals and the end products are absolutely non-toxic. This paper furnishes a review on the nuisance caused by the petrochemical pollution and its degradation in the environment along with the perspective of understanding the degradation process under different ecosystems.

Keywords: *Petrochemicals, Xenobiotic, Recalcitrant, Bioremediation.*

INTRODUCTION

Petroleum-based products are a crucial source of energy for industries as well as day to day life. Seepage of crude oil generally occurs regularly during the exploration, production, refining, transport, and storage of petroleum and petroleum products. The amount of natural crude oil seepage was estimated to be 600,000 metric tons per year with a range of uncertainty of 200,000 metric tons per year [1]. Release of hydrocarbons into the environment whether accidentally or due to human activities is a main cause of water and soil pollution [2]. Soil contamination with hydrocarbons causes extensive damage of local system since accumulation of pollutants in animals and plant tissue may cause death or mutations [3]. The technology commonly used for the soil remediation includes mechanical, burying, evaporation, dispersion, and washing. The currently accepted disposal methods of incineration or burial in secure landfills (USEPA 2001; ITOPF 2006) can become prohibitively expensive when the amounts of contaminants are large. This often results in cleanup delays. While the contaminated soil continues to pollute groundwater resources if on land, and death of aquatic life if on waterways [4], thus necessitating speedy removal of the contaminants. However, these technologies are expensive and can lead to incomplete decomposition of contaminants. Claude U. Sable, in the year about 1946, recognised that many microorganisms have the ability to utilise hydrocarbons as the sole source of carbon and energy, and that such microorganisms are widely distributed in nature. He further recognised that the microbial utilisation of hydrocarbons was highly dependent on the chemical nature of the components within the petroleum mixture, and environmental determinants [5]. The biodegradation of oil pollutants is not a new concept as it has been intensively studied in controlled conditions [6] and in open field experiments [7], but it has acquired a new significance as an increasingly effective and potentially inexpensive cleanup technology. Its potential contribution as a countermeasure biotechnology for decontamination of oil polluted systems could be enormous. The initial interest was in the fate and persistence of pesticides in soils [8]. However, the field has expanded in recent years to encompass a wide variety of chemicals and a broad array of issues. Some technologies are being developed that markedly enhance microbial destruction or degradation of organic pollutants that otherwise would have persisted at the cleanup of many polluted groundwater and soils using the orthodox physical and chemical methods [9]. Biodegradation is a very broad field and involves uses of a wide range of microorganisms to break chemical bonds. It has been well reviewed, however, it is a very active field and new data are rapidly contributed to the literature. Bioremediation, which employs the biodegradative potentials of organisms or their attributes, is an effective technology that can be used to accomplish both effective detoxification and volume reduction. It is useful in the recovery of sites contaminated with oil and hazardous wastes [10]. Besides, bioremediation technology is believed to be non-invasive and relatively cost effective [11]. In some cases it may not require more than the addition of some degradation enhancers to the polluted system. It could end up being the most reliable and probably least expensive option for exploitation in solving some chemical pollution problems [12].

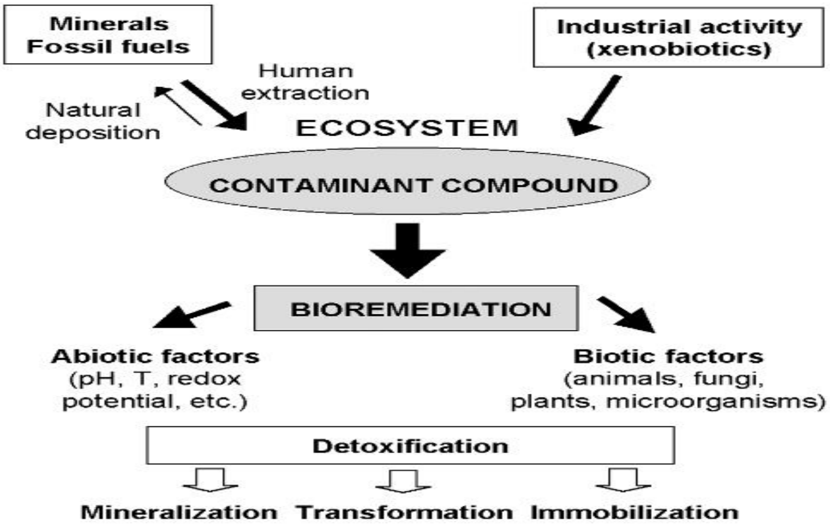

Fig 1 Main Origins for the pollution in the environment and the other parameters affecting the Biodegradation process.

Chemistry and Microbial degradation of varied petrochemicals and petro products:

Petroleum has been known for several years to occur in the surface seepage and was first obtained in pre- Christian times by the Chinese. The modern petroleum industry had its beginning in Romania and in a well-sunk in Pennsylvania by Colonel E. A. Drake in 1859 [13]. The principal early use of the product of the petroleum industry was for the replacement of expensive whale oil for lighting. Today, its consumption as a fuel and its dominance in the world market as a source of chemicals has diversified tremendously. Petroleum is defined as any mixture of natural gas, condensate, and crude oil. Crude oil which is a heterogeneous liquid consisting of hydrocarbons comprised almost entirely of the elements hydrogen and carbon in the ratio of about 2 hydrogen atoms to 1 carbon atom. It also contains elements such as nitrogen, sulphur and oxygen, all of which constitute less than 3% (v/v). Crude oils could be classified according to their respective distillation residues as paraffins, naphthenes or aromatics and based on the relative proportions of the heavy molecular weight constituents as light, medium or heavy. Also, the composition of crudes may vary with the location and age of an oil field, and may even be depth dependent within an individual well. About 85% of the components of all types of crude oil can be classified as either asphalt base, paraffin base or mixed base.

Physical properties and Occurrence of various Polyaromatic Hydrocarbons (PAHs):

The term PAH generally refers to hydrocarbons containing two or more fused benzene rings in linear, angular or clustered arrangements [14]. PAHs are hydrophobic compounds and their persistence in the environment is chiefly due to their low water solubility [15]. Generally, PAH solubility decreases and hydrophobicity increases with an increase in number of fused benzene rings. In addition, volatility decreases with an increasing number of fused rings [16]. The major source of PAHs is from the combustion of organic material [17]. PAHs are formed naturally during thermal geologic production and during burning of vegetation in forest and bushes [18]. PAHs and their alkyl homolog may also be derived from biogenic precursors during early digenesis [19]. However, anthropogenic sources, particularly from fuel combustion, pyrolytic processes, spillage of petroleum products, waste incinerators and domestic heaters [20], are significant sources of PAHs in the environment. In industrial countries, anthropogenic combustion activities are a principal source of PAHs in soils where they arise from atmospheric deposition. This had lead to an increase in soil PAH concentration over the last 100-150 years [21, 22]. The release of PAHs into the environment is wide- spread since these compounds are ubiquitous products of incomplete combustion. PAHs have been detected in a wide variety of environmental samples, including air [23], soil [24], sediments [25], water [26], oils, tars [27] and foodstuffs [28]. Industrial activities, such as processing, combustion and disposal of fossil fuels, are usually associated with the presence of PAHs at highly contaminated sites. PAH contamination on industrial sites is commonly associated with spills and leaks from storage tanks and with the conveyance, processing, use and disposal of these fuel/oil products [29]. PAHs are also a major constituent of creosote (approximately 85% PAH by weight) and Anthracene oil, which are commonly used pesticides for wood treatment [30]. As such, PAH contamination is frequently associated with wood treatment activities [31, 32]. PAHs may accumulate in high concentrations in terrestrial environments near coal gasification sites and tar oil distillation plants [33]. Major sources of PAHs are incomplete combustion of organic materials, gas production, wood treatment facilities, and waste incineration [34-37]. PAHs are formed naturally during thermal geologic reactions associated with fossil-fuel and mineral production, and during burning of vegetation in forest and bush fires [38, 39]. Anthropogenic sources, particularly fuel combustion, automobiles, spillage of petroleum products, and waste incinerators are significant sources of PAHs into the environment. Tobacco cigarette smoking is a significant source of PAH exposure to smokers and secondary smokers. PAHs generated during anthropogenic combustion activities are primarily transported via atmospheric deposition [40, 41]. Petroleum refining and transport activities are major contributors to localized loadings of PAHs into the environment. Such loadings may occur through discharge of industrial effluents and through accidental release of raw and refined products [42]. Heterocyclic compounds including dibenzothiophene and carbazole are components of creosote, crude oils, and shale oils and often co-exist in the environment with PAHs and other aromatic compounds [43]. Dibenzothiophene is a sulfur heterocyclic compound and is quite persistent in the environment. Little information about dibenzothiophene toxicity is available in the literature. Carbazole, a nitrogen heterocyclic, is carcinogenic and toxic [44]. Dibenzofuran and its substituted analogues are found in several woody plants as stress chemicals, so called phytoalexins [45]. However, most of the environmental concerns with dibenzofuran are related to its halogenated analogues, especially its chloro/bromo derivatives. Persistent organic pollutants (POPs) are among the most concerned environmental pollutants because they persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to the environment and human health. POPs are also referred to as persistent, bioaccumulative and toxic chemicals (PBTs). POPs include aldrin, brominated flame retardants, chlordane, DDT, dieldrin, endrin, mirex, organometallic compounds such as tributyltin, PAHs, heptachlor, hexachlorobenzene, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and toxaphene. PCDD/Fs are formed unintentionally from human activities. One of the main sources of PCDD/Fs is municipal waste incinerators [46]. PCDD/Fs formed are absorbed on the fly ash, and then enter into the environment. Therefore, the fly ash has been considered as a harmful waste causing environmental pollution. Yang *et al.* [47] suggested an efficient catalytic detoxification method for PCDD/Fs in fly ash. Alkyl PAHs (e.g., methylnaphthalene) have increasingly become an environmental concern. Because alkyl substitution causes a substantial decrease of water solubility, alkyl PAHs tend to be bioaccumulative. They are abundant in fossil fuels, crude oil and petroleum derived products. Boylan and Tripp [48] identified a large number of aromatic hydrocarbons (e.g., alkyl-benzenes and naphthalenes) in seawater extracts of several crude oils and kerosene. Alexander *et al.* [49] suggested that methylnaphthalenes may be useful indicators of thermal maturity of sedimentary organic matter. Methylnaphthalenes in a petroleum oil fraction can be used as active ingredient of repellent to control mosquitoes [50]. Alkylbenz[*a*]anthracene, especially 7, 12-dimethylbenz[*a*]anthracene, is a potent carcinogen in rodent skin and mammal cells [51].

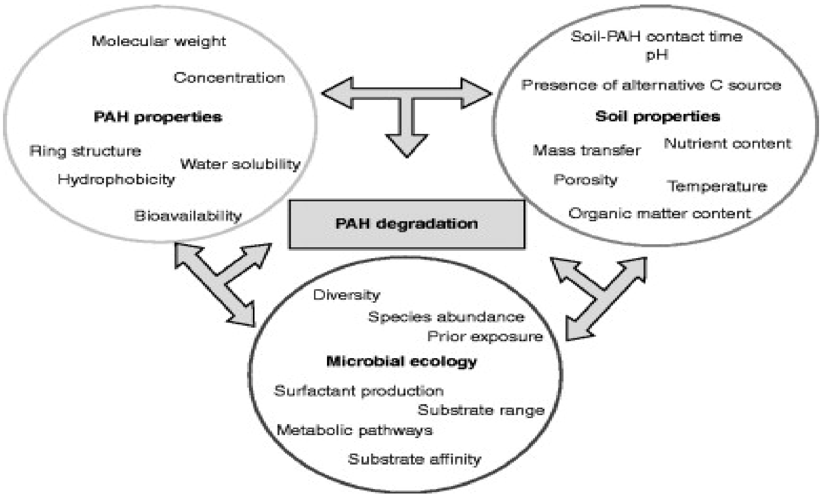

Figure 2 Parameters for PAH degradation

Degradation of Petrochemicals

Petroleum oil biodegradation by bacteria can occur under both oxic and anoxic conditions [52], albeit by the action of different consortia of organisms. In the subsurface, oil biodegradation occurs primarily under anoxic conditions, mediated by sulphate reducing bacteria [53] or other anaerobes using a variety of other electron acceptors as the oxidant. On a structural basis, the hydrocarbons in crude oil are classified as alkanes (*normal* or *iso*), cycloalkanes, and aromatics. Alkenes, which are the unsaturated analogs of alkanes, are rare in crude oil but occur in many refined petroleum products as a consequence of the cracking process. Increasing carbon numbers of alkanes (homology), variations in carbon. chain branching (*iso*-alkanes), ring condensations, and interclass combinations e.g., phenylalkanes, account for the high numbers of hydrocarbons that occur in crude oil. In addition, smaller amounts of oxygen – (phenols, naphthenic acids), nitrogen- (pyridine, pyrrole, indole), and sulfur- (alkylthiol, thiophene) containing compounds, collectively designated as “resins” and partially oxygenated, highly condensed asphaltic fraction occur also in crude but not in refined petroleum [54]. The inherent biodegradability of these individual components is a reflection of their chemical structure, but is also strongly influenced by the physical state and toxicity of the compounds. As an example, while *n*-alkanes as a structural group are the most biodegradable petroleum hydrocarbons, the C5 – C10 homologues have been shown to be inhibitory to the majority of hydrocarbon degraders. As solvents, these homologues tend to disrupt lipid membrane structures of microorganisms. Similarly, alkanes in the C20 – C40 range, often referred to as “waxes”, are hydrophobic solids at physiological temperatures. Apparently, it is this physical state that strongly influences their biodegradation [55]. Primary attack on intact hydrocarbons always requires the action of oxygenases and, therefore, requires the presence of free oxygen. In the case of alkanes, monooxygenase attack results in the production of alcohol. Most microorganisms attack alkanes terminally whereas some perform sub-terminal oxidation. Primary attack on intact hydrocarbons always requires the action of oxygenases and, therefore, requires the presence of free oxygen. In the case of alkanes, monooxygenase attack results in the production of alcohol. Most microorganisms attack alkanes terminally whereas some perform sub-terminal oxidation. The alcohol product is oxidised finally into an aldehyde and finally, to a fatty acid. The latter is degraded further by *beta*-oxidation. Extensive methyl branching interferes with the beta oxidation process and necessitates di terminal attack or other bypass mechanisms. Therefore, *n* alkanes are degraded more readily than iso-alkanes. Cycloalkanes are transformed by a not fully characterized oxidase system to a corresponding cyclic alcohol, which is dehydrated to ketone. Then, a mono oxygenase system lactonises the ring, which is subsequently opened by a lactone hydrolase. These two oxygenase systems usually never occur in the same organisms and hence, the frustrated attempts to isolate pure cultures that grow on cycloalkanes [56]. However, synergistic actions of microbial communities are capable of dealing with degradation of various cycloalkanes quite effectively.

CH3-(CH2) n-CH3
n-alkane
↓(1/2O2)
CH3-(CH2) n-CH2OH
Primary fatty alcohol
↓(-2H+)
CH3-(CH2) n-CHO
Fatty aldehyde
↓ (1/2O2)
CH3-(CH2) n-COOH
Mono carboxylic fatty acid
↓ (1/2O2)
HOCH2-(CH2) n-COOH
ω hydroxy fatty acid
↓ (- 2H+)
HOC-(CH2) n-COOH
ω aldehyde fatty acid
↓ (1/2O2)
HOOC-(CH2) n-COOH
Di carboxylic acid fatty acid

Figure 3 Pathway of diterminal alkane oxidation (Atlas 1984).

Degradation of Aromatic Hydrocarbons

Photosynthetic bacteria obtain energy from light and they degrade aromatic compounds anaerobically to form intermediary metabolites, such as acetyl-CoA, which are subsequently used in biosynthetic reactions (Fig. 4) [57]. Some aromatic compounds serve as electron acceptors rather than electron donors in bioremediation reactions. Thus, an important type of bioremediation is reductive dechlorination, in which bacteria remove chlorines from contaminants, such as chlorinated solvents and PCBs, by using these compounds as electron acceptors in dehalorespiration. Aerobic and anaerobic biodegradation of aromatic compounds have several common features. Structurally diverse compounds are degraded through many different peripheral pathways to a few intermediates that are further channeledvia a few central pathways to the central metabolism of the cell.

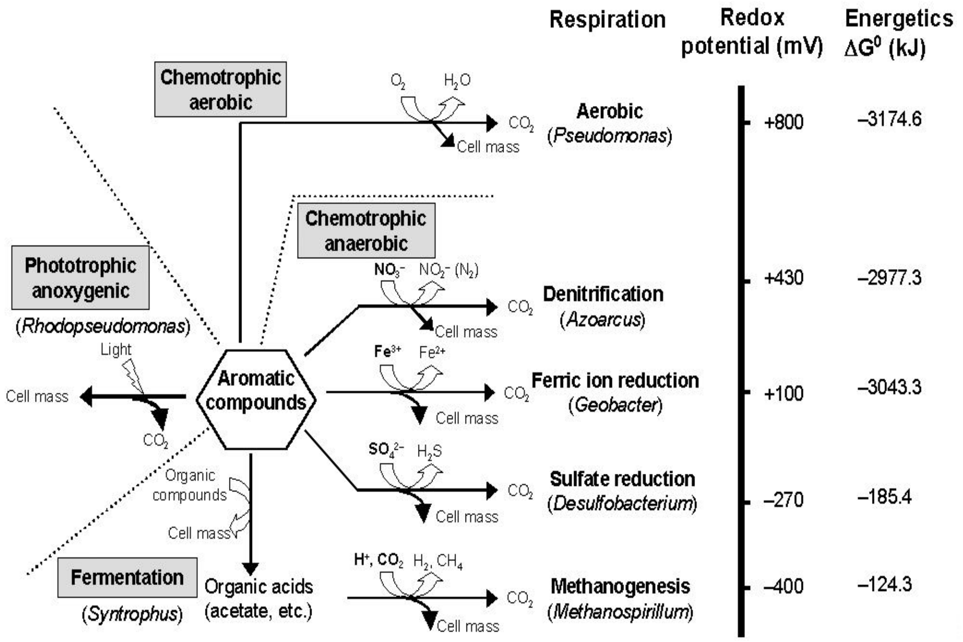

Fig 4 Microbial utilization of aromatic compounds.

In the aerobic catabolic funnel, most peripheral pathways involve oxygenation reactions carried out by monooxygenases and/or hydroxylating dioxygenases that generate dihydroxy aromatic compounds (catechol, protocatechuate, gentisate, homoprotocatechuate, homogentisate, hydroquinone, hydroxyquinol). These intermediate compounds are the substrates of ring-cleavage enzymes that use molecular oxygen to open the aromatic ring between the two hydroxyl groups (ortho cleavage, catalyzed by intradiol dioxygenases) or proximal to one of the two hydroxyl groups (meta cleavage, catalyzed by extradiol dioxygenases) [58]. Central pathways involve a series of reactions leading to the formation of Krebs cycle intermediates (central metabolism). In the anaerobic catabolism of aromatic compounds, the peripheral pathways converge to benzoyl-CoA (occasionallyto resorcinol and phloroglucinol), which becomes dearomatized by a specific multicomponent reductase that requires energy in the form of ATP [57].

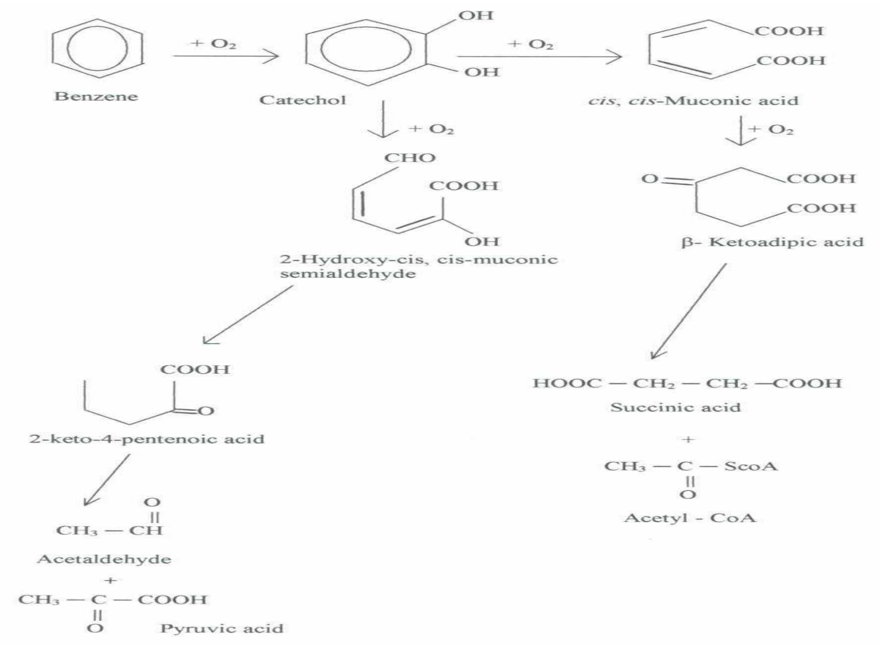

Figure 5 Microbial metabolism of the aromatic ring by *meta* or *ortho* cleavage as shown for benzene.

CONCLUSION

Petrochemicals are one of the most important pollutants causing pollution of Air, land as well as Water. There are some important ways which can be used to reduce this pollution but amongst all the methods that are existing right now microbial degradation of the petrochemicals is the best way that can be used to save our environment from the ill effects of these pollutants as this method is not expensive also does not has any other side effects on the environment.

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