

236. Methods for Treatment of PAH Contaminated Soils; Review and Comparison

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Abstract

To reduce environmental and human health risks of contaminated sites, having a comprehensive knowledge about polycyclic aromatic hydrocarbons (PAHs) removal processes is crucial. PAHs are contaminants which are highly recognized to pose threats to humans, animals and some plants, because of their toxic, carcinogenic, mutagenic, and teratogenic characteristics. They may also damage skin and eyesight of the people who are in touch with these pollutants. PAHs are hydrophobic and own two or more benzene rings, hence are resistant to structural degradation. In addition, higher molecular weights of these contaminants are more persistent in the environment. There are different techniques which have been developed to treat PAHs contaminated soil, namely: soil washing, chemical oxidation, electrokinetic remediation, and solidification/stabilization (S/S) are discussed and reviewed in this study. Moreover, effective parameters on such methods and their advantages and disadvantages are discussed. An exclusive method is not recognized to be efficient in all contaminated sites and site conditions affect our decision to select the most suited method for a given site. This selection criterion is based on our knowledge about methods, shortcomings and advantages which are all discussed.

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1. Introduction

In organic chemistry, hydrocarbons are divided into two classes: aromatic compounds and aliphatic compounds (non-aromatic compounds), as illustrated in Figure 1. Aromatics are a huge class of hydrocarbons including benzene and compounds with similar chemical behaviors, though they may differ widely in their appearances. PAHs are found in different levels of earth. Polycyclic aromatics with low molecular weight are mainly found in lower levels while heavier PAHs are available on surface of earth. PAHs are referred as a subcategory of HOCs - hydrophobic organic contaminants. They are highly recognized as a menace to environment and public health because of their carcinogenic, mutagenic, and teratogenic properties [1]–[4]. As one of the most widespread organic pollutants, contaminants are neutral, nonpolar molecules, formed by two or more benzene rings, with low hydrogen-to-carbon ratio, found in oil, coal and tar deposits and are also results of incomplete combustion of organic matter [5].

Major concerns of scientists are listed as EPA's priorities which include 16 PAHs, namely: acenaphthene, acenaphthylene, anthracene, naphthalene, benzo (a) pyrene, dibenz(a,h)anthracene, fluoranthene, phenanthrene, and pyrene etc. These pollutants that are listed by the Environmental Protection Agency are also among the 126 major pollutants and 5 of them are listed among the 25 hazardous substances found to be highly threatening to human health at the superfund sites [6]. Kim et al viewed treatment/removal of such materials - mainly with low water solubility and high octanol-water partition coefficient - as difficult [7]. Low permeability, moreover, hinders contaminants clean up [8]. Because of low solubility in water, PAHs are costly and time-consuming to be removed [1], [9], [10].

PAHs, though different in their physical and chemical characteristics, are generally recognized by their low volatility, low solubility in water, and lipophilicity, and are assessed by their octanol-water partition coefficient (K_{ow}). The coefficient specifies pollutant's fate. High K_{ow} indicates that the pollutant absorbs lipid, while low K_{ow} signifies a high level of solubility in water. About PAHs, those with lower molecular weight are more volatile, more soluble in water, more lipophilic [11]. Considering these

characteristics, their behavior in environment is predictable; Lighter PAHs are easier to be transferred or removed. Moreover, higher number of benzene rings makes them more resistant to be dissolved [12]. Thus having physical and chemical features, such as molecular weight, partition coefficient Log (K_{ow}), and numbers of aromatic rings, their characteristics and behavior are predicted and suited method of remediation is readily chosen. As an example, PAHs with low molecular weight are easier to be removed by bioremediation methods, compared with heavier PAHs [13], [14]. To become more accurate in description of chemical/physical features, PAHs with 2 or 3 aromatic ring are named as light PAHs and heavy PAHs are those with more rings. Log octanol-water coefficient higher than 5, shows an utterly hydrophobic PAH [15].

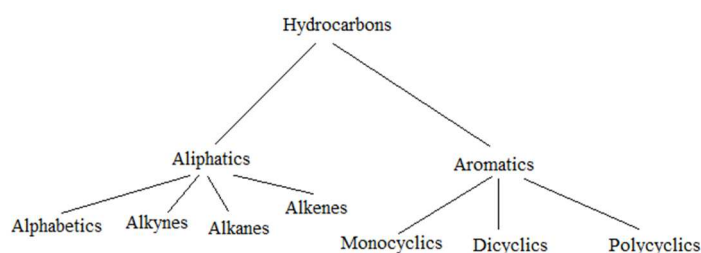


Fig. 1. Classification of hydrocarbons

Numerous methods are proposed for treatment of PAH polluted soils. Each and every one of the methods has its own superiority and shortcoming. First of all, a brief knowledge of each procedure is needed, and then advantages and disadvantages are evaluated. These methods, basically, are divided into physical, chemical, and biological categories.

This article studies PAHs' sources, their health effects and finally evaluates five treatment methods including soil washing/flushing, chemical oxidation, electrokinetic remediation and S/S; each method has been assessed and removal rates and affecting parameters are discussed. Advantages and defects of each method are also compared to others'. Employing two or more methods to reach better results is another approach which was also discussed.

2. Sources

One of the most stable forms of hydrocarbons, known as PAHs, are either originated from natural or anthropogenic sources and are mainly accumulated in soil [16]. Natural sources of their generation include: forest fires, oil seeps, and volcanic eruptions. Gasworks and chemical industries are considered as two basic PAH-generating activities [17]. According to Manahan (1999), anthropogenic processes including petroleum, incomplete combustion, and pyrolysis are also considered as sources of these pollutants. In a comprehensive approach, Ravindra et al. categorized the sources of PAH into five groups, namely: domestic, mobile, industrial, agricultural and natural [19].

PAHs are categorized into three groups, petrogenic, pyrogenic and natural, and it is possible to get information regarding where they can be traced back [20]. These compounds are migrated to the environment by evaporation, dispersion, dissolution, adsorption, etc. [21]–[24]. Petrogenic PAHs are petroleum products which are originated from crude oil including fuels, lubricants and other oil derivatives. Usually by accident, these contaminants leak out of underground storage tanks and pollute surface or ground water sources [25]. Petrogenic PAHs are listed as 16 EPA's priority pollutants [26].

Pyrogenic PAHs are usually generated by combustion of fuels and biomasses in high temperatures when there is not sufficient oxygen. Incomplete combustion, pyrolysis, cracking, destructive distillation are the main mechanisms for the generation of these pollutants [27]. Pyrogenic PAHs are often in solid shape and are found in aquatic environments [28]. During the last decades, one of the main sources of PAHs generation in metropolises, were power plants [29], [30]. Other sources include pollutants from aluminium smelt, industrial and agricultural runoff. These sources are also considered as origins of petrogenic and natural PAHs contaminants.

Natural PAHs are generated during organic matters chemical transformation in plants, planktons, microorganisms, fungi, and sediments etc. [26]. For instance, perylene is found in termite nests [31], [32]. Other PAHs such as benzo[b]fluoranthene, phenanthrene, and naphthalene may be generated by

vascular land plants and termite activities [33], [34]. Benzo[a]pyrene is generated by specific bacteria and plants. Generally, PAHs are generated by more than one exclusive source and numerous PAHs, such as perylene, may possibly be produced by anthropogenic sources.

3. Exposure/health effects

PAHs are mostly toxic, mutagenic, and carcinogenic [35]. Additionally, as a result of their high solubility in lipid they are not difficult to be absorbed in mammals organs [36].

PAHs pose threat to human health; nowadays many of them exist in food chain and may be swallowed by animals and humans. For instance, naphthalene is one of those pollutants which adhere to cells of liver, lung, and kidney. They may also affect skin and eyesight of the people who are in touch with these pollutants [36]. In some studies of indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)anthracene, benzo(a)pyrene, they have all been confirmed to be carcinogenic [37], [38].

Pyrene derivatives have also found to be slightly mutagenic [36]. Pyrene is a PAH with 4 dense rings and is hard to be eliminated [39]. Owing four cycles, the contaminant is difficult to be removed from the environment. Pyrene is not carcinogenic though contaminated sites need to be remediated because it is included in EPA 16 priorities, based on its destructive effects on human health, as the contaminant transforms into toxic benzopyrene [40].

Treatment techniques

3.1. Soil washing/flushing

Organic pollutants are isolated, separated and extracted by chemical and physical methods [17]. During the last two decades, this approach has been comprehensively studied [41]. Soil washing can be either ex-situ or in-situ (flushing). Soil washing or solvent extraction has been reviewed as a method in which land ecology disruption is insignificant [42]. As discussed in previous section, PAHs removal rate is not constant and depends on factors such as molecular weight which modifies the contaminants' solubility in extraction agent [43].

Toxicity, cost, and low efficiency in removing PAHs are factors motivating experts to further their experience in using alternative extraction agents or recycle surfactant solution [44]. Previous attempts to remediate PAH contaminated soils via solvent extraction technique are optimized by using alternative extraction agents (surfactants, biosurfactants etc.), which are capable of achieving higher rates of removal [45], [46]. Vegetable oil is introduced as an environmentally friendly alternative to remediate polluted soil cost-effectively [47].

Effects of solution pH on PAH removal rate was examined and it was concluded that soil washing efficiency is augmented in alkaline environment, especially for loamy soils. Salinity effect on clean up efficiency, moreover, was investigated. In loamy soils, decrease of removal efficiency was observed in saline solutions [46].

To achieve higher efficiency in persistent pollutant removal, the approach can be integrated with several other treatment methods. Song et al combined ultrasonic technology with soil washing and observed extremely positive influence of ultrasound technique on removal rate [48]. Integrated remediation of contaminated soil, using soil washing, ozonation and biological treatment methods, highly facilitated PAH removal and 90% reduction of PAHs was achieved [49].

Soil washing effluent can potentially contain materials which pose serious risks to the ecological health. Thus soil washing wastewater should be treated in a separate process [44]. López-Vizcaíno et al remediated a low-permeability PAH-polluted soil by washing method with efficiency of 90% and treated washing wastewater in a coagulation process [50].

3.2. Oxidation

Although there are some sorts of solutions which enhance solubility and contact area of PAHs and

decomposition bacteria, heavy PAHs are difficult to be completely remediated by biological approaches, thus chemical methods, which are faster and stronger, are deployed; methods which are not as sensitive as biologic methods, to sort or concentration of pollutants [13].

Oxidation methods are considered to be highly effective to lift limitations specifically in environments contaminated by recalcitrant PAHs. Conventional oxidations for environmental goals are ozone, hydrogen peroxide, permanganate, and persulfate.

Chemical oxidation is an on-situ, in-situ and off-situ treatment method. In in-situ procedure, chemical components are added to the soil directly. In On-situ mode, the soil is removed but processed in the site. Off-situ process needs soil to be transferred to somewhere outside of the site. Each mode has its own advantages and disadvantages. Economical point of view, ranks the modes as in-situ, on-situ, and off-situ. Off-situ mode provides higher efficiency because soil is processed in an isolated and controlled condition [51].

Oxidation is classified into three groups: using ozone reagent, using Fenton reagent and subcritical/supercritical oxidation.

3.2.1. Fenton's reagent

Most of oxidation studies concentrate on Fenton that is executed in-situ, on-situ, and off-situ, since 1980s [51].

During oxidation process, hydrogen peroxide (H₂O₂) and an iron salt transform into hydroxyl radicals or other high capacity irons. Hydroxyl radicals are unstable and can degrade organic materials in two ways: 1. Organic materials with hydrogen, lose it in the presence of hydroxyl radicals and hydroxyl radical transforms to water (H₂O); 2. Hydroxyl radical is added to organic material [1].

In some studies Fenton's reagents are employed to be combined with other methods. Venny et al. combined bioremediation with Fenton or a novel chelating agent (CA), investigating contaminated soil treatment [52].

3.2.2. Ozone

Remediation of soil by ozone is conducted in-situ, on-situ, and off-situ, in either horizontal or vertical wells. Gaseous or aqueous ozone may be used to oxidate PAHs, either by direct reaction or as hydroxyl radical [1], [51].

Gan has reported that Fenton's reagents are more capable to degrade PAHs. It has also been reported that for PAHs with low molecular weight, ozone has shown more efficacy [1].

3.2.3. Sub- and super-critical water

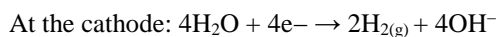
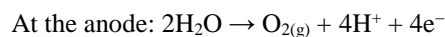
This method is limited to on-situ and off-situ processes. Characteristics of high temperature water are similar to organic solutions and it can oxidate the contained materials by its dissolved oxygen or other oxidants.

Pressurized hot water in critical condition occurs at $T_c = 374$ °C, $P_c = 221$ bar. Super- and sub-critical conditions are upper and lower that points, respectively. In that point, chemical and physical conditions are extremely changed and steam/liquid phase is not identifiable. Organic compounds and gases can be dissolved in super critical water and inorganic compounds are not dissolved. Considering type and state of liquid, diffusivity increases and dielectric constant and hydrogen bonds of water molecules decreases and dissolved compound is easily oxidated [53].

3.3. Electrokinetics

Electrokinetic remediation has not been hugely successful specially dealing with clayey soils [54]. Recently, nevertheless, researches has been focused on electrokinetic remediation of PAH contaminated sites containing clayey soil and mobilization enhancement of PAHs using surfactants [55]. James evaluated electro osmosis as one of the most applicable methods in soils with low permeability (lower than 10^{-9} m/s) to remove the contamination [56]. Electroremediation was primarily a method to remove

heavy metals and during years was recognized as an approach to remediate inorganic contamination. Nowadays, this method, solely or combined with other methods such as Fenton and bioremediation, has achieved reliable results in removal of PAHs. One of the advantages is its efficacy in soils with low hydraulic conductivity which is a severe challenge for most remediation methods. Decontamination using electricity is only on its early stages and needs further research to be comprehensively assessed [57]. As an in-situ method, electrokinetic remediation or electroremediation intensifies contaminants movement [58]. During electroremediation, water electrolysis happens as below [59]:



As the equations represent, acidic and alkali solutions are formed in anode and cathode, respectively; and electrical current drives substances in the solutions toward electrodes. The migration occurs in two forms: electromigration and electro-osmosis. In electromigration, ions move toward opposite charged electrodes, while electro-osmosis, is the motion of liquid across the soil. Fig. 2 depicts details of the process.

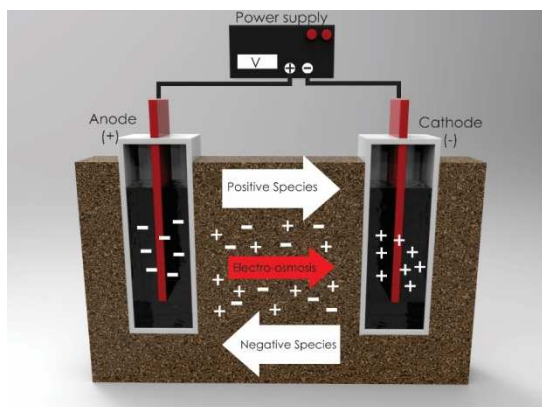


Fig. 2. Migration mechanisms in electroremediation process

Therefore, for organic matters with no charge, migration is done through electro-osmosis process. The next step is removal of soil pollutants accumulated in electrode chambers.

In some cases, due to insufficient solubility and low porosity, clean up efficiency is dropped considerably. Consequently, some changes should be applied to the environment and pollutant to facilitate the treatment procedure. For instance, agents are added to improve PAHs desorption through micellisation and tension reduction. The most commonly used solubilizing agents in electroremediation method include surfactants, co-solvents, and cyclodextrins [60].

Lima et al conducted experiments on Netherland's rivers. In the study, electro-osmosis was deployed to eliminate PAHs from clayey soil by using 0.01 M NaCl, solely and also combined with surfactant Tween 80. The surfactant is placed in anode plate vicinity. It was aimed to move surfactant through the soil from anode to cathode and increase its contact with PAHs. Using surfactants, PAHs moved with the liquid. They concluded, having lower molar mass and consequent higher solubility, naphthalene and acenaphthylene are transferred needing little effort, compared with no-surfactant mode. It was also found that time is not a main effective parameter on process efficacy [57]. Tab. 1 summarizes recent efforts to eliminate PAHs using electrokinetic method combined with other techniques.

3.4. Stabilization/solidification

From decades ago, it was predicted that future regulations may lead to severer restrictions on site selection for wastes disposal. Hence waste treatment by S/S technique was considered to become prominent [61]. EPA introduced S/S as a method by which waste handling and physical characteristics are improved and solubility or toxicity are curbed [62]. S/S is a well-established immobilization technique to mitigate destructive effects of leachate on ecological health. The method is particularly efficient for heavy metals but also suited to various types of wastes [63].