

# Combined Chemical and Water Hyacinth (*Eichhornia crassipes*) Treatment of PAHs Contaminated Soil

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## Abstract

The ability of chemicals sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), sodium nitrate ( $\text{NaNO}_3$ ), and sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) together with water hyacinth (*Eichhornia crassipes*) to decontaminate polluted soil leachate was investigated. Results obtained from analysis using gas chromatography – flame ionization detector (GC/FID) indicated that using 4 g  $\text{NaNO}_3$  with *E. crassipes*, 99.4% of acenaphthrene (pH 2.0) was the overall highest degraded PAH while 90.4% (pH 4.0) of acenaphthrene was the overall least degraded PAH using  $\text{Na}_2\text{SO}_4$  with *E. crassipes*. Applying  $\text{Na}_3\text{PO}_4$  with *E. crassipes* was observed to be the most efficient and effective protocol for PAHs degradation at all pH (2.0, 4.0, 6.0) levels studied in-as-much-as pH 6.0 was also noted as the best pH overall for the contaminant removal, most especially when applied using  $\text{Na}_3\text{PO}_4$  plus *E. crassipes*.

**Keywords:** compounds, degradation, environment, leachate, plants, pyrene, remediation, sorption

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the main classes of contaminants in the terrestrial environment. The presence of PAHs in the environment at higher concentrations is an object of human civilization. High levels of PAHs have been found in meat cooked at high temperatures such as grilling or barbecuing, and in smoked fish [1]. PAHs mix more easily with oil than water. They may be classified according to molecular weights into low or high molecular weight compounds. The high molecular weight PAHs (those with four or more benzene rings) are prone to irreversible sorption, while low molecular weight PAHs (those with two or three benzene rings) are more likely to be directly taken up by roots. Low molecular weight PAHs are relatively water soluble, but PAHs containing four or more rings are quite hydrophobic and insoluble. Evaluation of PAHs degradation in the environment is extremely difficult. Some

researchers have observed stimulation of PAHs degradation rate under sulphate reducing conditions [2]. Ambrosoli et al. noted that biodegradation of PAHs could proceed both through fermentative and respiratory metabolism [3]. In a related study [4] suggested that PAHs could also be degraded and thus be removed from anaerobic system though removal of PAHs from this system appear to be slower than in aerobic degradation. It has been suggested that PAHs are remarkably degraded at pH range of 6.0-8.0 using chemicals [5],[6]. A related study has shown that chemical oxidant such as Fenton's reagent has observed efficacy in destroying PAHs in soil samples [7]. Lin and Valsaraj investigated titanium thin film photocatalytic reactors as possible means to degrade PAHs in dilute water streams [8]. Several studies have concluded that depending on the environment (air, water, soil) in which organic compounds are present, these compounds may undergo slow changes as a result of various chemical processes. For instance phosphate has been shown to enhance degradation pathways of

PAHs in soil substrate [9],[5]. Degradation of PAHs has also been observed under both aerobic and anaerobic conditions by physical/chemical pretreatment of contaminated soil using phosphorus [10]. Effect of additional carbon source, inorganic nitrogen (N), phosphorus (P) and temperature variations on PAHs degradation have been reported by several authors including [11],[12]. When phosphorus was added to sample soil as fertilizer, degradation of PAHs was reported to occur [13]. Further studies have noted that addition of N and P to soil degrades phenanthrene and it was revealed that some PAHs could be degraded anaerobically if nitrate is available as electron acceptor [14],[15],[16]. Fe (III) and Mn (IV) reduction have been reported to be the dominant process of degradation of most PAHs [17]. Recent developments have demonstrated that PAHs are rapidly mineralized to CO<sub>2</sub> and H<sub>2</sub>O using sulphate reduction process [18].

Other chemicals such as surfactants have been shown to be useful for bioremediation of sites polluted with PAHs in overcoming problems associated with low PAHs solubility since surfactants are reported to enhance solubility of hydrophobic compounds [19]. Surfactants increase the solubility of PAHs by decreasing the interfacial surface tension between PAHs and soil/water interphase [20]. Zhou and Zhu observed that the efficiency of surfactants in enhancing desorption of PAHs show strong dependence on the soil composition, surfactant structure as well as PAHs properties [21].

Plant use in detoxifying organic pollutants such as PAHs from contaminated system has been studied by several authors including [22]. Not all plants species are able to tolerate and effectively enhance remediation of hydrocarbons from the soil. Variation in plant morphology, physiology and microbial interaction in the plant rhizosphere are important factors to consider in selecting plants species for PAHs detoxification [23]. Monocotyledons plants such as grasses which has highly branched fibrous roots and can cover a large surface area have seen more interest in this area of research [24]. Research has shown that various grasses and leguminous plants are potential candidates for plant uptake of PAHs [25]. Recently published data has revealed that the tall

fescue grass (*Festuca arundinacea*) and switch grass (*Panicum virgatum*) degrade pyrene appreciably [26]. Other studies involving pyrene degradation have been reported by [27],[28]. These studies indicated that the presence of vegetation such as corn (*Zea mays*), alfalfa (*Medicago sativa*) and rape seed oil (*Brassica napus*) enhanced the adsorption of phenanthrene and pyrene from contaminated soils. Ryegrass (*Lolium perenne*) has also been successfully tested for its ability to germinate, grow and decontaminate PAHs in soil [29]. More recent published findings by [30] noted that naphthalene was significantly adsorbed while pyrene was least adsorbed by water hyacinth (*Eichhornia crassipes*). Ukiwe et al. also observed about 5% adsorption of naphthalene by *E. crassipes* in about 7 days in non microbial aided treatment of PAHs contaminated soil [31]. Nor [32] demonstrated that *E. crassipes* has tremendous capability to adsorb hydrocarbons as well as heavy metals simultaneously. However, [33] examined the ability of *E. crassipes* to adsorb organo-pesticides and noted that the plant was able to significantly adsorb organo-pesticide such as dicofol in about 7 days of treatment of the contaminated streams.

In the present study, combined chemical and phytodegradation process in degrading PAHs from contaminated soil substrate using Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, and Na<sub>3</sub>PO<sub>4</sub> each with *E. crassipes* was examined at various pH ranges.

## 2. Experimentals

### 2.1 Preparation of Stock Solution

The soil sample used in this experiment was obtained from the commercial bus park of the Federal University of Technology, Owerri, Nigeria in April, 2011, while the *E. crassipes* plant also used in the present experiment was harvested from Enyioha farms in Imerienwe, Ngor Okpala LGA, Nigeria, in March, 2012 and identified by Dr C.E. Ihejirika, of the Department of Environmental Technology, Federal University of Technology, Owerri, Nigeria. The plant specimen number was given as EVS 00100029. Stratification sampling method was used to select the sample site, while random sampling was then applied within each stratification sub-groups to improve

representativeness of the sample. Soil pre-treatment included sieving to select particle size of 10 mm and air dried for 48 hrs [34]. Obtaining this particle size was important to facilitate contact between soil and contaminant as well as organic solvent to be used for extraction.

The soil sample was autoclaved for 1hr at 110°C. About 5 kg of the dried soil sample was placed into a 25 L plastic bucket previously washed and rinsed with deionized water. About 5 L of waste engine oil was measured and poured into the 25 L plastic bucket and the entire mixture was mixed thoroughly. An amount equaling 500 g of the mixed soil sample was separately weighed and placed in a 2 L beaker. This sample in the 2 L beaker was used for the control experiment. It has been reported that waste engine oil contain appreciable amount of PAHs [35],[36]. About 5 L of n-hexane was further added to the triturated mixture and further trituration performed for another 10 mins. About 10 L of distilled water was then added to the mixture and the entire content stirred for another 10 mins and allowed to stand for 2 hrs. The supernatant was decanted and filtered through white cheese cloth and then through Whatman No. 42 filter papers. About 10 L of this filtrate was reserved to serve as the stock solution.

### 2.2 Combined experiment

The choice of *E. crassipes* for this experiment is based on the following desirable criteria;

- 1) Dense aggressive and fibrous root system for maximum surface area to trap hydrophobic contaminants [37].
- 2) Dense coverage of contaminated site [38].
- 3) High hydrocarbon tolerance [39].
- 4) Ability to tolerate low nutrient availability [40].

About three *E. crassipes* plants were potted in three 2 L plastic sample holder vessels previously washed and rinsed with distilled water. The potted plants were prepared and placed in the Project Laboratory of the Department of Chemistry, Federal University of Technology, Owerri, Nigeria. To each of the three potted plants was added 500 ml of distilled water, 4 g of  $\text{Na}_2\text{SO}_4$  salt and 500 ml each of the stock solution and the mixture triturated for 5 mins and the pH of the mixture in the three potted plants maintained each at 2.0, 4.0, 6.0 respectively using 1M NaOH/HCl as appropriate. These pH levels were maintained for two weeks. After this period, the resultant

substance in each of the three potted plants was separately placed in six 500 ml beakers and 50 ml each of n-hexane solution was poured separately into the three beakers. The mixtures were separately triturated for 10 mins and filtered separately through clean cheese cloth and Whatman No. 42 filter papers into another three 500 ml beakers. The filtrates were then concentrated to 2 ml in a water bath at 40 °C. A Hewlett-Packard GC 6890 series 11 was used to determine the concentration of PAHs (naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthrene, fluorene, phenanthrene, anthracene, fluoranthrene and pyrene) remaining in the mixture using an FID and a Hewlett-Packard HP-5 column (length, 10 m; inner diameter (ID), 0.25 mm; film thickness, 0.25  $\mu\text{m}$ ). Methylene chloride was used for column preparation. The carrier gas was helium at a pressure of 7.5 lb/inch and a flow rate of 2.5 ml/min. The temperature program was as follows: 40 °C for 3 min, 40 °C /min to 300 °C, hold for 10 min. The injector and detector temperature were 290 and 300 °C respectively. Samples of 2  $\mu\text{l}$  were injected in splitless mode for 1 min. Three replicate treatments each in each of the three beakers were processed and the mean PAHs concentration determined separately. Ukiwe et al. in a previous related study had noted that the *E. crassipes* plant used in the present experiment contained none of the PAHs under study [31]. The above process was repeated separately using 4 g  $\text{NaNO}_3$  and  $\text{Na}_3\text{PO}_4$  salts each.

### 2.3 Control experiment

About 100 ml of the stock solution was measured into a 250 ml beaker. The mixture was stirred for 5 mins and the pH of the mixture adjusted to 2.0 using 1M NaOH/HCl as appropriate. The mixture was then transferred into a separatory funnel and 50 ml of n-hexane added and the funnel agitated for 3 mins with intermittent venting of pressure. The organic layer was separated from the water phase and collected through a funnel containing solvent-moistened anhydrous  $\text{Na}_2\text{SO}_4$  filter paper

into a 250 ml Erlenmeyer flask. The solvent was evaporated on a water-bath at 110 °C to 10 ml and concentrated with a stream of nitrogen gas to 5 ml.

PAHs concentration in the extract was determined using a Gas Chromatography/Mass Spectroscopy (GC/MS),(Shimadzu QP 2010 GCMS), for the following priority PAHs [41]; naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthrene, fluorene, phenanthrene, anthracene, fluoranthrene and pyrene. Three replicate treatments were processed and the mean PAHs concentration obtained.

#### 2.4 Statistical Analysis

Data is presented as arithmetic mean and standard deviation. The one-way Analysis of Variance (ANOVA) was employed to determine the difference in PAHs concentration between pH levels. The *F-test* was used to estimate significant difference in mean PAHs concentration between pH levels.

Percentage concentration of PAHs degradation was obtained using the following formulae

$$(Y - X / Y) \times 100$$

Y = Control.

X = Concentration of PAHs observed at pH levels.

### 3. Results and Discussion

#### 3.1 Results

Table 1: Values of PAHs in µg/g of experiment of Na<sub>2</sub>SO<sub>4</sub> and *E. crassipes*

PAHs	pH 2.0 <sup>(i)</sup>	pH 4.0 <sup>(ii)</sup>	pH 6.0 <sup>(iii)</sup>	Control
	Mean (µg/g) ±SD	Mean (µg/g) ± SD	Mean (µg/g) ± SD	Mean (µg/g) ± SD
Naphthalene	6.139 ± 0.3	2.114 ± 0.1	1.127 ± 0.1	143.900 ± 0.1
2-methyl naphthalene	6.418 ± 0.3	0.605 ± 0.2	1.153 ± 0.1	96.410 ± 1.2
Acenaphthylene	1.061 ± 0.1	1.175 ± 0.2	0.150 ± 0.0	12.980 ± 1.2
Acenaphthrene	0.104 ± 0.0	1.066 ± 0.0	0.062 ± 0.0	10.660 ± 0.1
Fluorene	0.112 ± 0.0	0.147 ± 0.0	0.213 ± 0.0	6.937 ± 0.3
Phenanthrene	0.143 ± 0.0	0.750 ± 0.0	0.008 ± 0.0	5.993 ± 1.1
Anthracene	0.091 ± 0.0	0.621 ± 0.0	0.301 ± 0.0	6.728 ± 1.4
Fluoranthrene	0.110 ± 0.1	0.012 ± 0.0	0.045 ± 0.0	3.625 ± 1.4
Pyrene	0.133 ± 0.0	0.006 ± 0.0	0.225 ± 0.0	4.921 ± 0.6

*F*-test i and ii = 1.60; Not significantly different [standard deviation of nth (8) samples; n = 8 and 8] at p < 0.05

Table 2: Values of PAHs in  $\mu\text{g/g}$  of experiment of  $\text{NaNO}_3$  and *E. crassipes*

PAHs	pH 2.0 <sup>(i)</sup>	pH 4.0 <sup>(ii)</sup>	pH 6.0 <sup>(iii)</sup>	Control
	Mean ( $\mu\text{g/g}$ ) $\pm$ SD	Mean ( $\mu\text{g/g}$ ) $\pm$ SD	Mean ( $\mu\text{g/g}$ ) $\pm$ SD	Mean ( $\mu\text{g/g}$ ) $\pm$ SD
Naphthalene	4.349 $\pm$ 0.3	7.881 $\pm$ 0.5	10.038 $\pm$ 0.7	143.900 $\pm$ 0.1
2-methyl naphthalene	3.832 $\pm$ 0.1	8.735 $\pm$ 0.5	8.027 $\pm$ 0.3	96.410 $\pm$ 1.2
Acenaphthylene	0.066 $\pm$ 0.0	0.113 $\pm$ 0.1	0.122 $\pm$ 0.1	12.980 $\pm$ 1.2
Acenaphthrene	0.109 $\pm$ 0.1	0.075 $\pm$ 0.0	0.194 $\pm$ 0.1	10.660 $\pm$ 0.1
Fluorene	0.068 $\pm$ 0.0	0.124 $\pm$ 0.1	0.175 $\pm$ 0.2	6.937 $\pm$ 0.3
Phenanthrene	0.429 $\pm$ 0.1	0.348 $\pm$ 0.1	0.474 $\pm$ 0.2	5.993 $\pm$ 1.1
Anthracene	0.038 $\pm$ 0.0	0.051 $\pm$ 0.0	0.086 $\pm$ 0.0	6.728 $\pm$ 1.4
Fluoranthrene	0.071 $\pm$ 0.0	0.076 $\pm$ 0.0	0.097 $\pm$ 0.0	3.625 $\pm$ 1.4
Pyrene	0.064 $\pm$ 0.0	0.083 $\pm$ 0.0	0.071 $\pm$ 0.0	4.921 $\pm$ 0.6

F-test i and ii = 2.16; Not significantly different [standard deviation of nth (8) samples; n = 8 and 8] at  $p < 0.05$

Table 3: Values of PAHs in  $\mu\text{g/g}$  of experiment of  $\text{Na}_3\text{PO}_4$  and *E. crassipes*

PAHs	pH 2.0 <sup>(i)</sup>	pH 4.0 <sup>(ii)</sup>	pH 6.0 <sup>(iii)</sup>	Control
	Mean ( $\mu\text{g/g}$ ) $\pm$ SD	Mean ( $\mu\text{g/g}$ ) $\pm$ SD	Mean ( $\mu\text{g/g}$ ) $\pm$ SD	Mean ( $\mu\text{g/g}$ ) $\pm$ SD
Naphthalene	2.117 $\pm$ 0.5	3.435 $\pm$ 0.1	2.730 $\pm$ 0.2	143.900 $\pm$ 0.1
2-methyl naphthalene	1.878 $\pm$ 0.3	2.521 $\pm$ 0.1	2.406 $\pm$ 0.1	96.410 $\pm$ 1.2
Acenaphthylene	0.182 $\pm$ 0.0	0.115 $\pm$ 0.1	0.117 $\pm$ 0.1	12.980 $\pm$ 1.2
Acenaphthrene	0.054 $\pm$ 0.0	0.071 $\pm$ 0.0	0.064 $\pm$ 0.0	10.660 $\pm$ 0.1
Fluorene	0.068 $\pm$ 0.1	0.137 $\pm$ 0.0	0.117 $\pm$ 0.1	6.937 $\pm$ 0.3
Phenanthrene	0.129 $\pm$ 0.2	0.181 $\pm$ 0.0	0.188 $\pm$ 0.2	5.993 $\pm$ 1.1
Anthracene	0.042 $\pm$ 0.2	0.158 $\pm$ 0.1	0.059 $\pm$ 0.0	6.728 $\pm$ 1.4
Fluoranthrene	0.056 $\pm$ 0.0	0.061 $\pm$ 0.0	0.071 $\pm$ 0.0	3.625 $\pm$ 1.4
Pyrene	0.061 $\pm$ 0.0	0.071 $\pm$ 0.0	0.060 $\pm$ 0.0	4.921 $\pm$ 0.6

F-test i and ii = 2.75; Not significantly different [standard deviation of nth (8) samples; n = 8 and 8] at  $p < 0.05$

### 3.2 Discussion

**Table 1 – 3** show values of concentration ( $\mu\text{g/g}$ ) of PAHs using 4 g  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$  and  $\text{Na}_3\text{PO}_4$  salts each with *E. crassipes* at pH 2.0, 4.0 and 6.0. In **Table 1**, it was observed that using 4 g  $\text{Na}_2\text{SO}_4$  with *E. crassipes*, 99.3% of 2-methyl naphthalene was noted as the highest degraded PAH (pH 2.0), while acenaphthrene 90.0% (pH 4.0) was the least degraded PAH. It was however recognized that using  $\text{Na}_2\text{SO}_4$  salt, pH 6.0 was observed as the most effective pH for PAHs noticed as degradation since it led to degradation rates of all PAHs beyond 95%. No trend in PAHs degradation was noticed as pH increased from 2.0 to 6.0. **Table 2** also show values

of PAHs degradation of soil leachate using 4 g  $\text{NaNO}_3$  with *E. crassipes* at the above mentioned pH ranges. Acenaphthrene (99.4%, pH 2.0) was the most degraded PAH as 2-methyl naphthalene (90.0%, pH 4.0) was regarded as the least degraded PAH. Overall degradation of PAHs was highest at pH 6.0 using 4 g  $\text{NaNO}_3$  with *E. crassipes*. However, applying the same amount of  $\text{Na}_3\text{PO}_4$  salt together with *E. crassipes*, about 99.4% of acenaphthrene (pH 2.0) was the highest PAH degraded, while 2-methyl naphthalene (97.3%, pH 4.0) was the least degraded PAH, **Table 3**. As the pH was ascended from 2.0 to 6.0, overall PAHs degradation ranged between 97.3 to 99.4% using  $\text{Na}_3\text{PO}_4$  salt together with *E. crassipes*. This experimental protocol was demonstrated as the

best method for amongst three methods applied to degrade PAHs from the soil leachate. In-as-much-as it was revealed that pH 6.0 was the overall best pH for the contaminant degradation, the three and above rings PAHs were significantly degraded more than the two rings PAH.

Studies on combined degradation experiments have been limited to chemical pre-oxidation and bioremediation [42], anaerobic digestion and ozonation [43], biodegradation and modified Fenton reaction [44], biological, chemical and electrochemical treatment [45], Fenton reagent versus ozonation [46]. Evaluation of the effect of combined vegetation establishment with chemicals in degradation of PAHs has been demonstrated by several researchers. Combination of fescue (*Lolium arundinacum*) and ryegrass (*Lolium multiflorum*) mixture with fertilizer to degrade two rings PAHs such as naphthalene, while non-fertilized mixture of bermudagrass (*Cynodon dactylon*) and *L. arundinacum* has been reported to degrade more of three rings PAHs including phenanthrene, anthracene and dibenzothiophenes [47]. Chouychai et al. revealed that pyrene and phenanthrene were significantly biodegraded in acidic soil [48]. In his contribution, Cheema et al. noted that pyrene and phenanthrene were also degraded in soils spiked with fertilizer in single and combined plants cultivation [28]. Pan et al. extensively documented the ability of *B. napus* in degrading PAHs [49]. The study concluded that using *B. napus* in humic acid environment, total content of PAHs decreased by almost half their original value in 31 to 61 days, though some differences in PAHs degradation was observed between PAHs with 2-3 rings and those with four or more rings. Two and three rings PAHs except phenanthrene showed continuous decrease rate of degradation, while phenanthrene and four or more rings PAHs showed increased degradation only in about 46 days. Very few recognized studies have come to light in the development of combined chemical and phytodegradation process in degrading PAHs. However, recent advances in combined degradation research have been documented in pressure and assisted ozonation [50], integrated treatment using soil washing, ozonation and biological treatment [51], oxidation using ozone in the presence of sand [52], combined treatment using sequence extraction with surfactant-electrochemical degradation [53], anaerobic digestion with recirculation of ozonated digestion sludge [54], and anaerobic digestion

using ozone pre-treatment [55]. These findings tend to support the already general held belief that studies relating to combine PAHs degradation using plants especially *E. crassipes* and chemicals are rare [31].

#### 4. Conclusion

Combined chemical and phytodegradation experiment using 4 g Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub> and Na<sub>3</sub>PO<sub>4</sub> salts each with *E. crassipes* at pH 2.0, 4.0 and 6.0 was studied. It was revealed that acenaphthrene was regarded as the most degraded PAH overall while 2-methyl naphthalene was the least degraded PAH. No trend in PAHs degradation was observed as the pH was increased from 2.0, to 6.0. However, applying Na<sub>3</sub>PO<sub>4</sub> salts with *E. crassipes* to degrade PAHs was shown to be the most effective protocol in total PAHs degradation.

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