Effect of pH in evaluating phosphate-dependent degradation of polycyclic aromatic hydrocarbons in contaminated soil leachate

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ABSTRACT

The effect of pH on the ability of sodium phosphate (Na_3PO_4) in degrading polycyclic aromatic hydrocarbons (PAHs) in contaminated soil was studied. Results obtained from Gas Chromatography/Mass Spectroscopy (GC/MS) analyses indicated that 23% of 2-methylnaphthalene was degraded as the overall highest polycyclic aromatic hydrocarbon at pH 2.0 using 2 g Na_3PO_4, while acenaphthene (1.7%) was the least overall degraded polycyclic aromatic hydrocarbon at pH 2.0 using 4 g Na_3PO_4 powder. An increase in PAHs degraded trend was observed using 4 g Na_3PO_4 as the pH was increased from 2.0 to 4.0.

Keywords: benzo(a)anthracene, concentration, contamination, fluorene, petrogenic, redox, sulphate.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) consist of fused aromatic rings and do not contain hetereoatoms or carry substituents [1]. PAHs contamination in soil sediment is a serious environmental issue due to its high toxicity, carcinogenicity, mutagenicity, and tetratogenicity [2]. As pollutants, they are of concern because some of these components are lipophylic; they mix more easily with oil. PAHs occur naturally in bituminous fossil fuels such as coal and crude oil deposits and in soil. Their sources could be pyrogenic, petrogenic or anthropogenic. Pyrogenic PAHs are suggested to be partially occluded in the soot matrix during in complete combustion processes [3]. Petrogenic sources are generated from petroleum products such as crankcase oil from vehicles, lubricating oil, asphalt as well as crude oil [4], while anthropogenic sources include road traffic, combustion of fossil fuels and forest fires [3]. Certain physical properties act against PAHs utilization or degradation. These properties include; their low aqueous solubility and high solid water distribution ratios [5]. Circumstances such as; presence of low molecular weight PAHs species, relatively recent polycyclic aromatic hydrocarbon (PAH) emission or deposition, moderate soil pH, presence of appropriate PAH degrading bacteria, and plants to facilitate decomposition by virtue of large root surface area or uptake affinity, influence the probability and rate of PAH degradation.

Evaluation of PAHs degradation in the environment is very difficult. PAHs fate under anaerobic conditions depends not only on substrate interactions and composition of microbial population but also on pH and redox conditions [6]. A study to evaluate PAHs removal during co-fermentation of sewage sludge and organic fraction of municipal solid waste under nitrate and sulphate reducing conditions revealed that redox conditions had effect on PAHs fates [2]. Some authors have noted stimulation of PAHs degradation rate under sulphate reducing conditions compared to methane digestion [7], while others have not observed significant PAHs concentration decrease in the environment [8]. Ambrosoli *et al.* [9] suggested that under denitrifying conditions, PAHs could be biodegraded both through

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fermentative and respiratory metabolism. However, it has been demonstrated that compared to aerobic degradation, PAHs removal in anaerobic environment is considered to be slower [10]. A recent study on aerobic degradation of PAHs in municipal and petrochemical active sludge to assess the potential for bio-treating PAHs in contaminated sludge has revealed the order of degradation rate in municipal sludge under anaerobic condition to be phenanthrene>pyrene>anthracene>fluorene>acenaphthene, while in petrochemical sludge, the order was acenaphthene>fluorine>phenanthrene>anthracene>pyrene. It was noted by the study that no significant differences were found in PAHs degradation rates within a pH range of 6.0-8.0, but a delay in PAHs degradation was noted at pH 9.0 in both sludge types [11]. Another study, nevertheless, has shown that as a chemical oxidant, Fenton's reagent has observed efficacy in destroying of PAHs (ie., naphthalene, fluorene, phenanthrene, anthracene, pyrene, chrysene, and benzo(a)pyrene) in model soil samples [12]. Titania thin film annular photocatalytic reactors have also been used successfully to degrade PAHs in dilute water streams [13]. However, a follow-up study by Chang *et al.* [6] to investigate the anaerobic degradation potential of PAHs in river sediments taken from sites of long-term pollution revealed that when mixtures of soil, river sediments and PAHs (individual or combined) were amended with nutrients and batch incubated, a high-to-low degradation rate for mixture soil types was observed but faster individual PAHs degradation rates were also observed in cultures containing a mixture of PAH substrates compared to the presence of a single substrate. The addition of electron donors such as acetate, lactate, and pyruvate have been shown to enhance PAHs degradation under methanogenic and sulphate-reducing conditions [7]. Rothermich *et al.* [14] also demonstrated that (^{14}C) labeled PAHs could be oxidized to (^{14}CO$_2$) in anoxic, PAH-contaminated marine harbor sediments in which sulphate-reduction is the terminal electron accepting process. These studies have demonstrated for the first time that degradation by anaerobic microorganisms can significantly impact in-situ pools of PAHs in petroleum-contaminated anoxic, sulphate-reducing harbor sediments.

Depending on the environmental compartment in which organic compounds are present (e.g., soil) they can undergo slow changes resulting from different chemical or biological processes. Phosphate has been documented to enhance degradation pathways of organic pollutants [15]. The biodegradation of PAHs has been observed under both aerobic and anaerobic conditions and the rate of degradation also has been shown to be enhanced by physical/chemical pretreatment of contaminated soils using phosphates [16]. Effect of additional carbon source, inorganic nitrogen (N) and phosphorus (P), temperature variations on PAHs degradation have been investigated by several authors including Leys *et al*. [17] and Xiangchun *et al.* [18]. In this regard, certain microorganisms have been reported to promote degradation of PAHs especially when phosphorus is added as fertilizer to the soil [19]. In further studies, Johnson and Scow [20], noted that addition of N and P to soil can help to evaluate the response of phenanthrene degradation. The present study, however, notes that studies relating to the time and conditions given for PAHs in soil to degrade under different conditions of pH and other salts are rare.

The purpose of this study was to investigate the effect of pH in evaluating phosphate-dependent degradation of PAHs in contaminated soil leachate.

MATERIALS AND METHODS

The soil sample used in this experiment was obtained from the commercial bus park of the Federal University of Technology, Owerri, Nigeria. Soil pre-treatment include sieving to select particle size of 10 mm and air dried for 48 hrs [21]. Obtaining this particle size is important to facilitate contact between soil and contaminant as well as organic solvent used for extraction. The soil sample was dried in an autoclave (Ac 064) for 30 mins at 105 $^{\circ}$C. About 5 kg of the dried soil sample was placed into a 25 L plastic bucket previously washed and rinsed with deionised water. About 500 g of the dried soil sample was also separately weighed and placed in a 1 L beaker. This sample in the 1 L beaker was used for the control experiment.

About 5 L of waste automobile engine oil was poured into the soil sample in the 25 L plastic bucket. It has been previously reported that waste automobile engine oil contain 2-6 ring PAH compounds [22],[23]. The mixture was triturated for 10 mins and 5 L of n-hexane solution was added to the triturated mixture and further trituration was performed for another 10 mins. About 10 L of distilled water was then added to the mixture and the content was stirred for a further 10 mins and allowed to stand for 2 hrs. The supernatant was decanted and filtered through Whatman No. 42 filter papers. About 9 L of the filtrate was recovered to serve as the stock solution.

To 100 ml of the stock solution in a 250 ml beaker was added 2 g of Na$_3$PO$_4$ powder. The mixture was stirred for 2 mins and the pH of the mixture was adjusted to 2.0 using 1 M NaOH/HCl as appropriate and filtered. The filtrate

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was then transferred into a 500 ml separatory funnel and 500 ml of n-hexane solution was further added. The mixture was shaken for 2 mins with periodic venting to release excess pressure. The organic layer was allowed to separate from the water phase and collected through a funnel containing solvent-moistened filter paper containing anhydrous sodium sulphate into a 1 L Erlenmeyer flask. The solvent was evaporated on a water bath at 110 ^{o}C to 10 ml and concentrated with a stream of nitrogen gas to 2 ml.

PAHs concentration in the extract was determined using Gas Chromatography/Mass Spectroscopy (GC/MS), Shimadzu QP2010 GCMS, Japan, at flow rate 1.18 ml/min with a helium carrier gas, column oven temperature was ramped at 80 to 280 ^{o}C at 5 ^{o}C/min with 5 min holding time, then to 300 ^{o}C at 10 ^{o}C/min with 10 min holding time. HP5MS column (30m x 0.25μm x 0.25 mm ID) was used. Three replicate sample treatments were processed and mean PAHs concentration was obtained.

The above procedure was repeated at pH 4.0. However, the procedure was also repeated at pH 2.0 and 4.0 using 2 g and 4 g Na_3PO_4 .

The control sample was also processed as in above at pH 2.0 without addition of Na_3PO_4.

Physicochemical characteristics of the soil substrate included the following tests; pH, organic matter, trace elements, temperature, bulk density, and soil texture. Analyses of physicochemical properties were performed according to methods described in USAID [24]. The values are shown in **Table 2.**

Statistical analysis
Data are given as arithmetic mean and standard deviation. The *F*-test was used to estimate significant difference in mean PAHs concentration between pH levels.

RESULTS AND DISCUSSION

Table 1 show values of priority of PAHs in µg/g of soil extract at pH 2.0 and 4.0 using 2 and 4 g Na_3PO_4. It was observed that 23% of 2-methylnaphthalene was the overall degraded PAH at pH 2.0 using 2 g Na_3PO_4. However, 0.3% of acenapthrene was degraded as the least PAH at pH 4.0 using 2 g of Na_3PO_4. It was also noted that except for naphthalene and 2-methylnaphthalene, there was an increase trend in PAHs degradation in acenaphthylene, acenaphthrene, fluorine, phenanthrene, anthracene, fluoranthene and pyrene as the pH was exceeded from 2.0 to 4.0 using 2 g Na_3PO_4. Moreover, using 4 g Na_3PO_4, it was observed that 9.3% phenanthrene was degraded as the highest PAH at pH 4.0, while acenaphthrene (2.0%) was the least degraded PAH at same pH level. Nevertheless, 1.7% acenaphthrene was the least PAH degraded at pH 2.0, while phenanthrene (6.7%) was the highest degraded PAH at pH 2.0. An increase in trend of PAHs degradation was also noted using 4 g Na_3PO_4 for all nine PAHs examined as the pH was increases from 2.0 to 4.0. A notable fact was established with naphthalene and 2-methyl naphthalene degradation when Na_3PO_4 mass was increased from 2 to 4 g. In this regard, for pH 2.0, naphthalene degradation reduced four-fold as Na_3PO_4 mass was increased from 2 to 4 g a fact that was replicated with 2-methyl naphthalene. However, for pH 4.0, as Na_3PO_4 mass was increased from 2 to 4 g, naphthalene and 2-methyl naphthalene degradation double. Nevertheless, **Table 1** also show *F*-test values at pH 2.0 and 4.0 for 2 and 4 g Na_3PO_4. In accordance with tabulated values, it was found that there was no significant difference in PAHs degradation between the two pH levels for both Na_3PO_4 mass since these values were tested at 8 and 8 degree of freedom and P < 0.05.

The increasing rate of population, agricultural burning, industrialization, burning of fossil fuels etc. has significantly contributed to extensive soil contamination over the past decades. Different measures have been taken in improving the fertility of these contaminated soils. Among these measures include; soil washing, incineration, thermal desorption and landfilling [25]. However, various organic contaminant, primarily petroleum hydrocarbons, aromatic hydrocarbons, PAHs, chloroaromatics and nitroaromatics etc. are easily controlled by chemical treatment. Potassium permanganate, widely used in water treatment, has been shown to have applicability in reducing PAH contamination in groundwater and soils when the substance was investigated under the influence of two factors (weight ratio $KMnO_4$/PAH and reaction time). Three factorial designs were performed and batch experiments were run to study the degradation of phenanthrene and pyrene on soils spiked with the contaminant at different concentrations. The study revealed that treatment with potassium permanganate significantly reduced PAH concentration, but pyrene was more recalcitrant than phenanthrene [26]. Fenton's reagent has also been shown to oxidize organic

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contaminants. Certain operating parameters such as pH, reaction time, UV irradiation, hydrogen peroxide concentration and Fe (II) amendment were investigated for their effect on process efficiency for soil highly contaminated by PAHs. For phenanthrene, it was reported that oxidation done with soil contaminated at 700 mg/kg was reduced to about 40 mg/kg of the contaminant using Fenton's reagent. The most important factor responsible for this degradation was the reaction time, followed at a certain distance by UV irradiation, Fe (II) H_2O_2 concentration and pH. The study further revealed the feasibility of photo-Fenton-like oxidation for the treatment of soil highly contaminated with PAHs and the relative importance of the process variables [27]. Another method of chemical treatment to degrade PAH is a combination of anaerobic digestion and ozonation investigated by Martínez *et al.* [28]. It was demonstrated that ozonation of anaerobically digested sludge improved the PAH removal rate by about 61%. An additional enhancement (up to 81%) of PAH removal rate was obtained by addition of hydrogen peroxide during ozonation. It was also reported that high degradation rate of PAH was obtained when surfactant were added to the combination of anaerobic digestion and ozonation. It has been documented that researchers disagree markedly on the effect of pH and redox condition on PAHs degradation [2].

Table 1: Values of PAHs in µg/g of soil leachate using 2 and 4 g Na₃PO₄ at pH 2.0 and 4.0

PAHs	2 g Na₃PO₄		4 g Na₃PO₄		Control
	pH 2.0[(i)]	pH 4.0[(ii)]	pH 2.0[(iii)]	pH 4.0[(iv)]	
	Mean (µg/g) ± SD	Mean (µg/g) ± SD	Mean (µg/g) ± SD	Mean (µg/g) ± SD	Mean (µg/g) ± SD
Naphthalene	30.123 ± 0.5	23.121 ± 0.3	6.774 ± 0.0	10.208 ± 0.1	143.9 ± 0.1
2-methyl naphthalene	22.343 ± 0.2	21.316 ± 0.3	5.629 ± 0.2	8.571 ± 0.1	96.41 ± 1.2
Acenaphthylene	0.286 ± 0.1	0.291 ± 0.1	0.255 ± 0.5	0.324 ± 0.1	12.98 ± 1.2
Acenaphthrene	0.204 ± 0.1	0.283 ± 1.1	0.185 ± 0.1	0.215 ± 0.1	10.66 ± 0.1
Fluorene	0.397 ± 1.1	0.423 ± 1.2	0.308 ± 0.3	0.412 ± 0.3	6.937 ± 0.3
Phenanthrene	0.883 ± 0.3	0.967 ± 0.1	0.399 ± 0.2	0.558± 0.2	5.993 ± 1.1
Anthracene	0.111 ± 0.2	0.102 ± 0.5	0.166 ± 0.2	0.184± 1.1	6.728 ± 1.4
Fluoranthrene	0.156 ± 0.4	0.143 ± 0.4	0.188 ± 0.4	0.202±1.0	3.625 ± 1.4
Pyrene	0.195 ± 0.1	0.230 ± 0.1	0.189 ± 0.3	0.210±1.0	4.921 ± 0.6
F-test i and ii = 1.80; iii and iv = 3.30					

Table 2: Physicochemical characteristics of soil sample

S/N	Parameters	Values
1	pH	5.91
2	Organic matter (%)	0.55
3	Mg^{2+} (mg/100g)	19.17
4	K^+ (mg/100g)	0.07
5	Ca^{2+} mg/100g)	17.06
6	Temperature (^{o}C)	29.0
7	Bulk density (g/cm^3)	1.50
8	Soil texture (mm)	10

CONCLUSION

There was no statistical significant difference in PAHs degradation between the two pH levels (2.0 and 4.0) as well as for both Na₃PO₄ mass. The present study has highlighted the fact that pH affect the mechanism of redox conditions when PAHs degradation is desired. The study would also encourage more research in other aspects (such as reaction time and redox chemicals) relating to the influence of pH on redox potential's degradation of PAHs in contamination system.

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