International Journal of Innovation and Applied Studies
ISSN 2028-9324 Vol. 3 No. 4 Aug. 2013, pp. 879-892
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http://www.issr-journals.org/ijias/

The effect of soil pH on photo-catalytic oxidation of polycyclic aromatic hydrocarbons (PAHs)

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ABSTRACT: The environmental fate of polycyclic aromatic hydrocarbons (PAH) is a significant issue, raising interest in its clean up using remediation. However, the physical, chemical, and biological properties of soils can drastically influence degradation of pollutants. The effect of soil pH on degradation of PAHs with a view to modify soil pH to enhance the degradation of PAH's was studied. The degradation rate of key model PAHs was monitored in topsoil modified to a range of pH 4 to 9 at half pH intervals. Photo-oxidation of PAHs in presence of catalyst under UV light at two different wavelengths was studied. The degradation of PAHs during photo-oxidation was carried out at varying soil pH, whilst the degradation rate of individual PAH was monitored using HPLC. Photo-degradation of PAHs at 375 nm showed higher rate of degradation compared at 254 nm. Higher degradation was observed at pH 6.5, whilst in general, acidic soil had greater photo-degradation rates than basic pH of soil. pH 7.5 and pH 8 had slowest photo-degradation. Phenanthrene at both the wavelengths had highest degradation rate and pyrene had slowest degradation rate. Therefore, photo-catalysis can be used as alternative process to eliminate PAHs by manipulating soil pH to enhance remediation.

KEYWORDS: Photo-catalytic oxidation, polycyclic aromatic hydrocarbons, phenanthrene, pyrene.

1 INTRODUCTION

In the natural environment, PAHs undergo an important reaction called photolysis [10], [11]. Photocatalysis (also called photolysis) is a process which uses catalysts such as Titanium dioxide (TiO_2) which facilitates photoreaction in order to degrade the toxic compound. TiO_2 a photo-catalyst is a chemical compound that, in presence of various wavelengths of UV light becomes highly reactive. TiO_2 induced photo-catalytic degradation of a variety of organic substrates is gaining attention due to its potential to degrade PAHs, specifically the PAHs in the environment [13].

Photo-catalytic oxidation (PCO) of PAHs occurs either in solution or in solid phase and also when catalyst is adsorbed onto solid substances. However, recently it has been investigated that photo-catalytic degradation of PAHs may occur in aqueous TiO_2 suspensions [13]. It has been found that when aromatic compounds are exposed to UV light, partially oxidized intermediates of the aromatic compounds are produced which are more susceptible to degradation than their parent compounds. Because of this property of aromatic compounds, photo-degradation has been recommended as an early stage strategy for biodegradation [9]. Photo-degradation of PAHs in the presence of a catalytic solution is considered as an oxidative process which has been further augmented in the presence of photo-inducers. The polarity of the solvent is directly proportional to the rate of the degradation process hence, the higher the polarity of the solvent, the faster the degradation process.

Thus, PAH photo-decomposition initiated by photo-ionization results in the production of PAH radical cations and hydrated electrons which further destroy PAH in the presence of water [15], [16]. PCO, one of the many advanced oxidation processes, relies on the generation of $\bullet OH$ by photo-catalysts (e.g. titanium dioxide semiconductor, TiO_2) to trigger oxidative

Corresponding Author: Rakesh M. Pawar (rakesh.pawar29@gmail.com) degradation [17]. TiO_2, a semiconductor can be used in photo-catalysis when exposed to ultraviolet (UV) light irradiation, due to its ability to transfer electrons and promote oxidation or reduction which plays a vital role in photo-catalysis [17].

A number of studies on the adsorption of PAHs on silica, alumina and other surfaces have been reported. However, the present work focuses on the possible advantages of various photo-catalytic processes using TiO_2 for the degradation of PAHs present in soil.

However, very few studies have investigated the photo-catalytic degradation of PAHs on soil surfaces using TiO_2 as the catalyst under UV irradiation. Investigating photo-catalytic degradation using a catalyst under varying abiotic conditions particularly soil pH, to enhance the degradation process is one of the objectives of this particular study.

2 MATERIALS AND METHODS

2.1 CHEMICALS

The test PAHs, namely phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU) (Sigma) and pyrene (PYR) (Fluka) were used throughout the experiment. Acetonitrile (HPLC grade), n-hexane (Fisher Scientific, UK). Particles of TiO_2 (Sigma Aldrich), UK.

2.2 STANDARD CURVE FOR PHOTO-CATALYTIC OXIDATION

2.2.1 PAHS STANDARD SOLUTION

A standard curve was made using the different concentrations in ppm of each PAH. 100 mg of each of these individual PAHs were dissolved in 1000 ml of acetonitrile to make 100 ppm of standard stock solutions which were further diluted to produce a standard curve for HPLC analysis. Carbazole (Sigma Aldrich) was used as the internal standard.

2.3 PHOTO-CATALYTIC DEGRADATION OF PAHS

See figure 1 for a schematic representation of the experimental design.

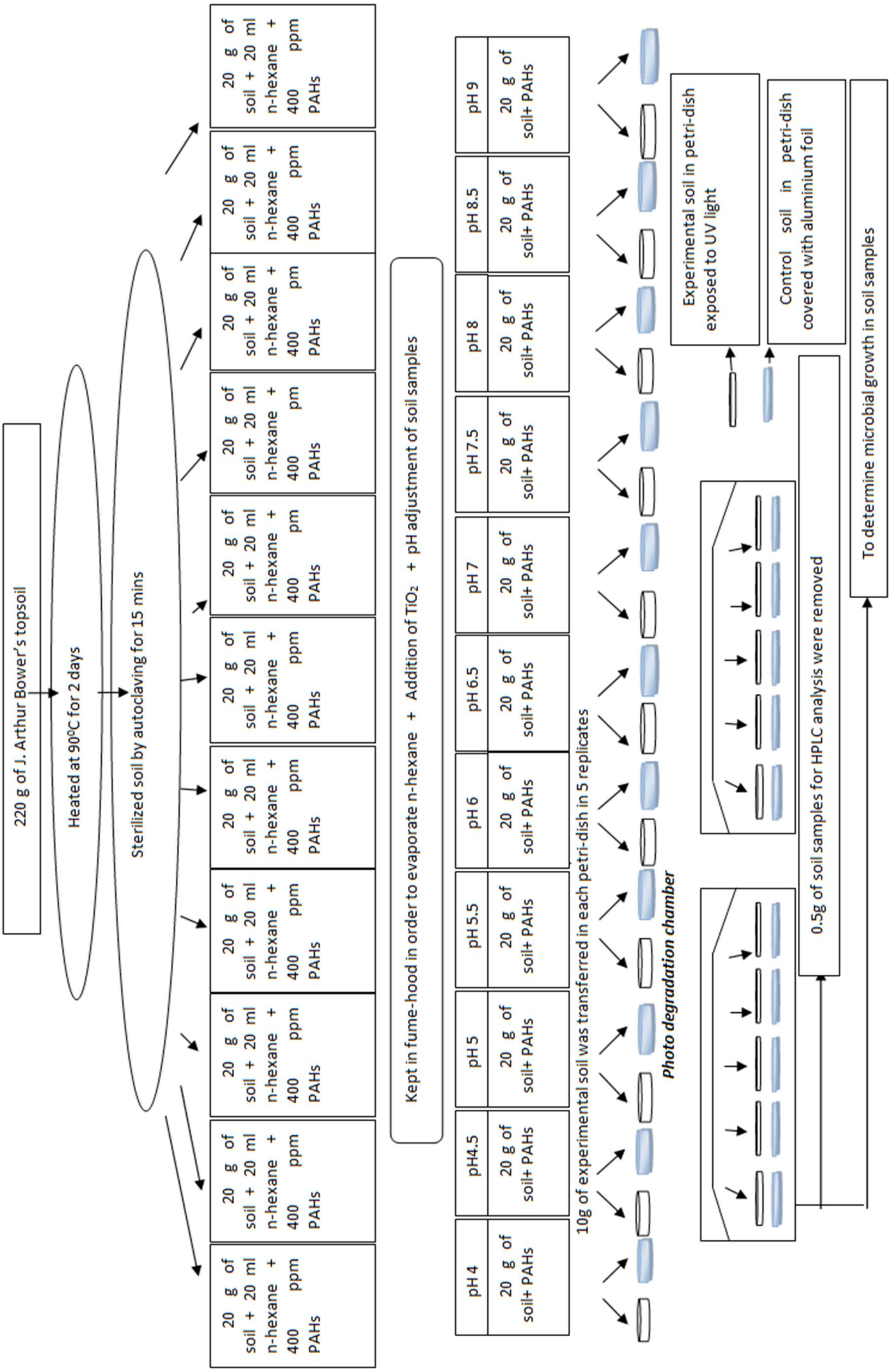

Fig. 1. Schematic representation of experimental design

2.4 PHOTO DEGRADATION CHAMBER

Photo degradation studies were performed in a chamber as shown in figure 1. The UV irradiation intensity was 1041_Wcm^{-2}. The UV lamps (Phillips ATLD 20W, Model UVA, UVB and UVC) were set at wavelengths of 254, and 375 nm. 90 mm plastic petri dishes containing the experimental soil samples were placed under the UV light for photo irradiation. The distance between the lamps and soil samples was 120 mm. Temperature within the chamber was maintained at 20^{0}C throughout all the experiments.

2.5 DISSOLUTION OF PAH COMPOUNDS AND TiO_2 AS CATALYST IN J. ARTHUR BOWER'S TOPSOIL

20 mg of each PAH was added to 20 ml of n-hexane in 500 ml sterile conical flask and used to contaminate 20 g of J. Arthur Bower's topsoil giving a final concentration of 100 ppm and 2% aqueous TiO_2 (Sigma Aldrich) was added. The weight of the pots containing J. Arthur Bower's topsoil was measured to confirmation evaporation of n-hexane.

2.6 MONITORING PH AND MOISTURE CONTENT OF THE EXPERIMENTAL SOIL

40 g of soil was transferred to seven different pots in order to monitor the pH of the soil along with PAH. Furthermore, deionised water was added to maintain a 30% moisture content of the soil and the pH was adjusted as half interval. From the eleven different pots containing soil of each pH treatment, 20 g of soil was transferred into five petri-dishes resulting in 5 replicates. All replicates were maintained at 20^{0}C in UV light chamber throughout the experiment. Treated samples from the Petri-dish were removed at 0, 24, 48, 72, 96, 120 hours respectively.

2.7 SAMPLES FOR HPLC ANALYSIS AND PAH EXTRACTION

0.5 g of treated sample, from the 5 replicates of petri-dishes was transferred into 1.5 ml Eppendorf tubes. PAHs were extracted in the eppendorf containing 200 ppm carbazole as an internal standard to 0.5 g of soil before analysis by HPLC. Samples were mixed well using round vortex mixer fitted with multi sample holder which holds a total of 12 samples (Sigma Aldrich) for 5 minutes and extract was filtered using sterile mill pore filter (HPLC grade) prior to HPLC analysis.

2.8 STATISTICAL ANALYSIS

Data obtained from experiments were used for statistical analysis. The final graphed values are represented as mean SD (Standard deviation). Statistical analysis was carried out performing calculations, analyzing and visualizing data in SPSS Statistic 16.0 version. Least significant difference and Tukeys HSD between two different wavelengths was calculated using variance post hoc test in SPSS analysis. And all the graphs were plotted in Microsoft office Excel 2007.

3 RESULTS

3.1 HPLC ANALYSIS OF PAH

To study the effect of abiotic factors particularly soil pH on the rate of photo-degradation, HPLC analysis was employed.

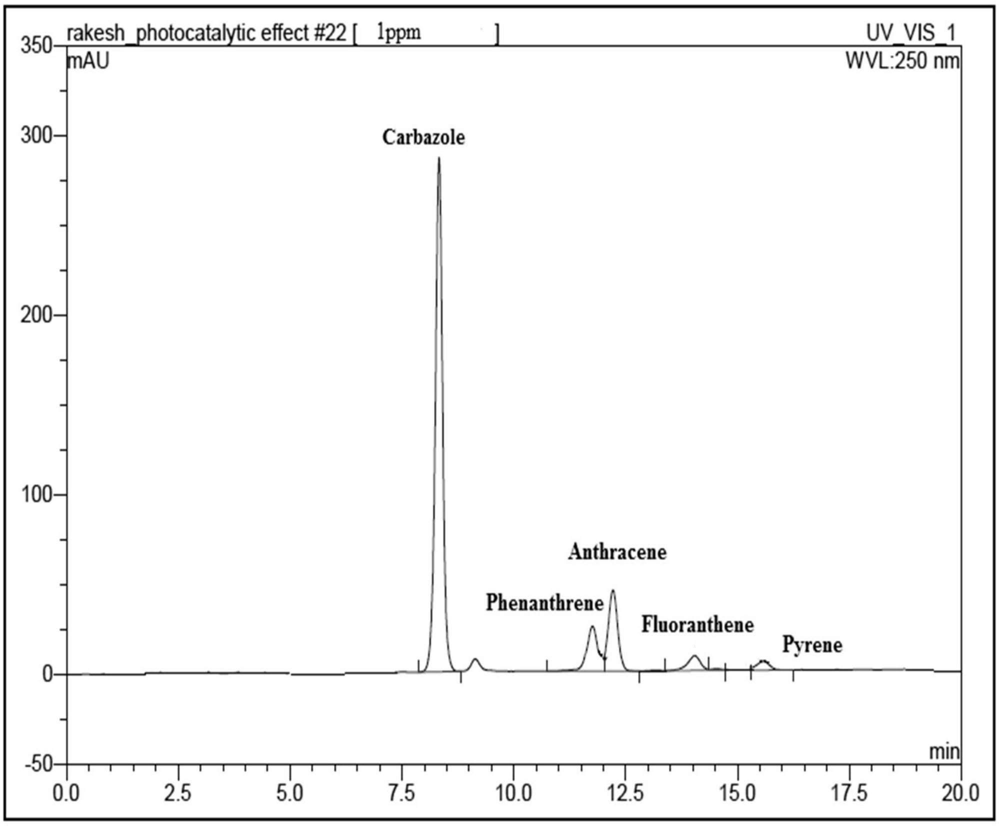

Fig. 2. Standard Chromatogram for HPLC analysis of four PAHs (concentration 1 ppm) and carbazole (20 ppm) with peak height against time

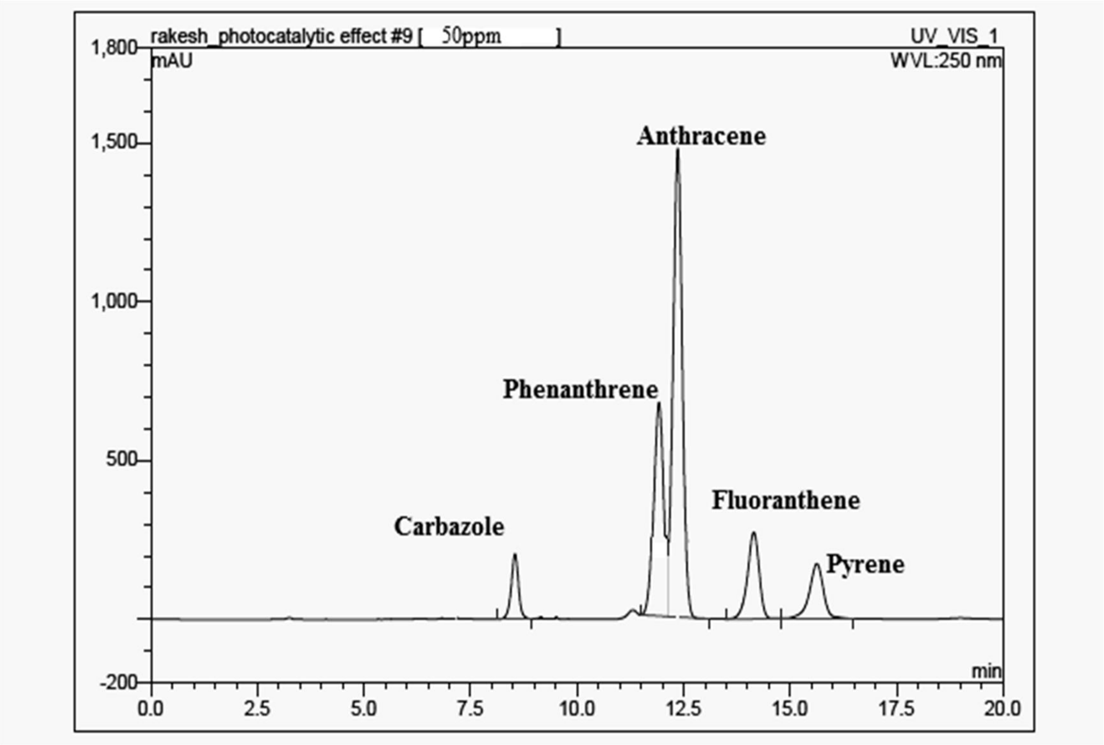

Fig. 3. Standard chromatogram for HPLC analysis of four PAHs (concentration 50 ppm) and carbazole (20 ppm) with peak height against time

Figures 2 and 3 show HPLC standards for 1 ppm and 50 ppm concentration of the four different PAHs dissolved in acetonitrile. The four PAHs present in the contaminated soil were also extracted using acetonitrile. Carbazole was the internal standard representing the first peak in both chromatograms at 20 ppm with a retention time of 8min. In figure 2 carbazole peak area was 300 mAU/min; similarly the peak area in figure 3 was 300 mAU/min with no difference in retention time. Therefore, constant results were found for carbazole. Phenanthrene follows carbazole with a retention time of 11 min and peak area of 30 mAU/min for 1 ppm and 700 mAU/min for 50 ppm. Anthracene is the third peak and second PAH to elute with a retention time of 12.5 mins. Anthracene, and phenanthrene peaks merge in both chromatograms before reaching the x axis. The split peak facility of the chromeleon software was implemented to statistically attribute peak area to these two PAHs. Anthracene at 1 ppm resulted in a peak area of 50 mAU/min and 1500 mAU/min for 50 ppm. The fourth peak and third PAH to elute was fluoranthene at 13 mins with a peak area of 20 mAU/min for 1 ppm and peak area of 300 mAU/min for 50ppm with no differences seen in retention time. The final PAH to elute was pyrene with a peak area of 10 mAU/min for the 1 ppm concentration whereas the peak area for pyrene in 50 ppm concentration was 200 mAU/min.

3.2 STANDARD GRAPH FOR POLYCYCLIC AROMATIC HYDROCARBONS

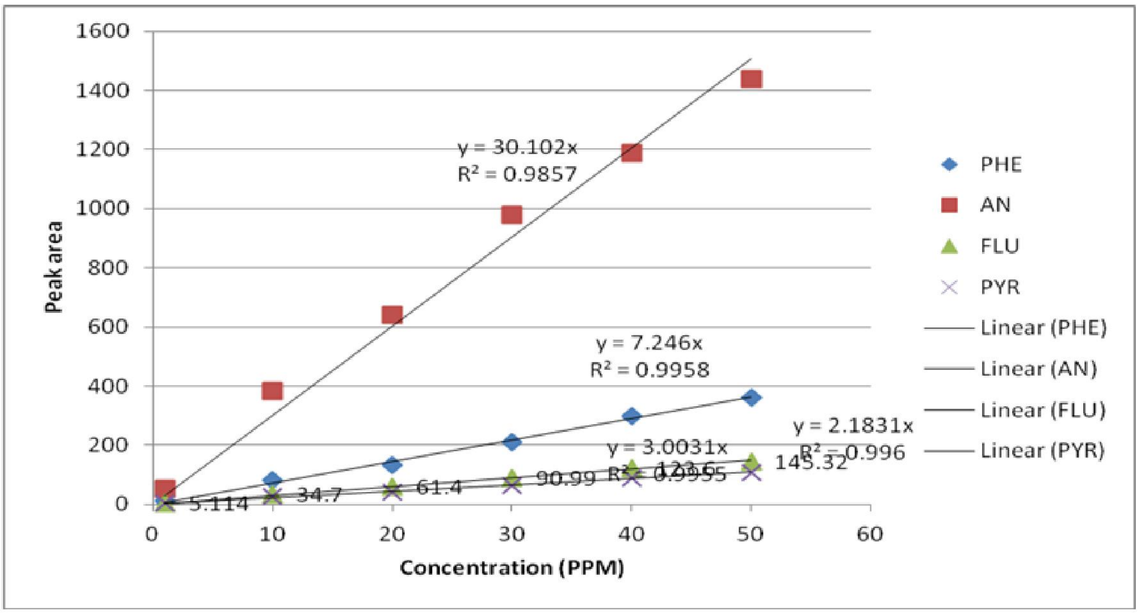

Fig. 4. HPLC standard curve of four PAH showing peak area against concentration. PAH used and their symbol abbreviations are (PHE) Phenanthrene; (AN) Anthracene; (FLU) Fluoranthene; (PYR) Pyrene

The peak areas obtained from running standards of the four PAHs at 1 ppm, 10 ppm, 20 ppm, 30 ppm, 40 ppm, 50 ppm were used to plot standard curves of peak area against the PAH concentration (figure 4). The chromeleon software was used to calculate a linear regression for each PAH (figure 4.). All PAH have r^2 (regression coefficient) values above 0.97 whilst the slope was estimated and displayed as Y values. The r^2value was 0.987 for phenanthrene, 0.978 for fluoranthene, 0.979 for pyrene and r^2 values for anthracene was 0.983 respectively. The Y value was around 35x for anthracene, 14x for phenanthrene, whilst fluoranthene and pyrene were much lower at 6.42x and 4.08x respectively.

In order to have a full evaluation of the extraction efficiency of the four PAHs, 100 ppm of each individual PAH was added to J. Arthur Bower's topsoil and extracted with acetonitrile. The re-extraction efficiency of the four PAHs obtained from these samples ranged from 52.81 to 74.69 % (table 1).

Table 1. Extraction efficiency of four PAHs from J. Arthur Bowers topsoil

PAH used	Amount of PAH added (ppm)	% efficiency for experimental values
Phenanthrene	100	74.69
Anthracene	100	68.42
Fluoranthene	100	64.98
Pyrene	100	52.81

3.3 DEGRADATION OF POLYCYCLIC AROMATIC HYDROCARBONS OVER TIME

Figures 5 to 12 exhibit the degradation curves obtained for the four different PAH in treated soil samples at varying pH under UV irradiation at 254 nm and 375 nm. PAH remaining is displayed as a percentage of the HPLC quantification results obtained after re-extraction at time 0. The control at both wavelengths exhibited little degradation figure (5 to 12 A) in contrast to the samples exposed to UV light figure (5 to 12 B). Greater degradation was more evident at 375 nm (figure 5 B to 9 B) than 254 nm (figure 10 to 12) for all PAHs with a significance value of $P<0.05$ obtained (Post hoc test including LSD and Tukey's test). Phenanthrene showed the highest degradation followed by anthracene, pyrene and fluoranthene. At 375 nm phenanthrene was 80-85% degraded and around 60- 65% degraded at 254 nm. The photo-catalytic degradation rate of anthracene was slower than phenanthrene whilst its degradation rate generally increased at acidic pH with most rapid rate evident at pH 6.5. At 375 nm anthracene was 75-80% degraded and at wavelength 254 nm degradation was 65-70%. Fluoranthene followed after anthracene was 70% degraded at 375 nm and 65% at 254 nm. Around 65% degradation was observed for pyrene at 375 nm and 60% degradation observed at 254 nm.

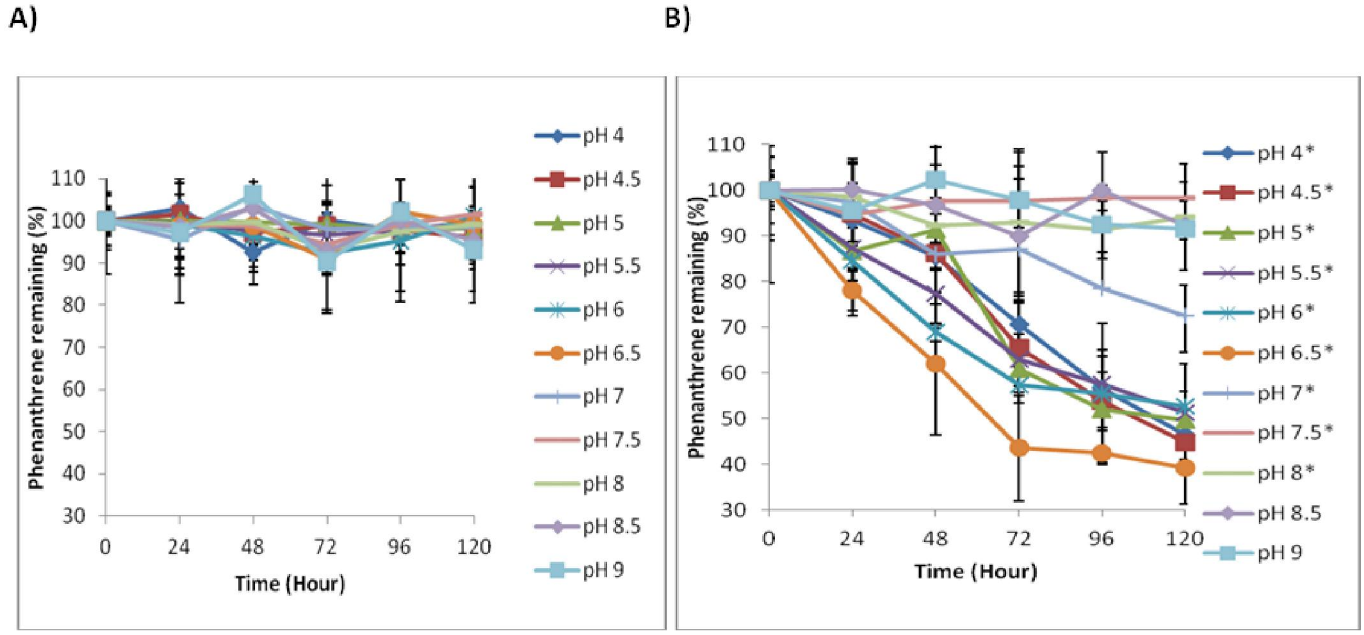

Fig. 5. Percentage phenanthrene remaining in J. Arthur Bower's topsoil at different pH over time during exposure to UV light at 375 nm in the presence of TiO_2

A): Percentage phenanthrene remaining in control samples not exposed to UV light. B): Percentage phenanthrene remaining in experimental sample exposed to UV light at 375 nm. *$P<0.05$ indicates significant difference between control and experimental sample.

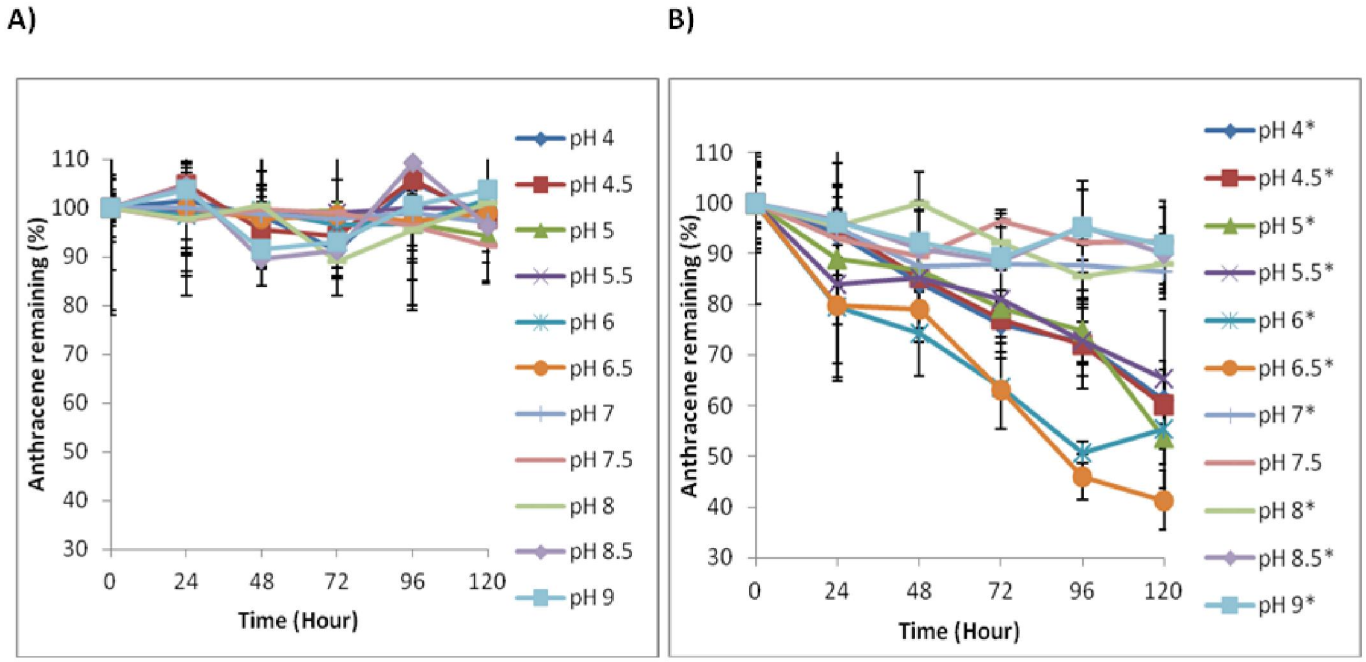

Fig. 6. Percentage anthracene remaining in J. Arthur Bower's topsoil at different pH over time during exposure to UV light at 375 nm in the presence of TiO_2

A): Percentage anthracene remaining in control samples not exposed to UV light. B): Percentage anthracene remaining in experimental sample exposed to UV light at 375 nm. *P<0.05 indicates significant difference between control and experimental sample.

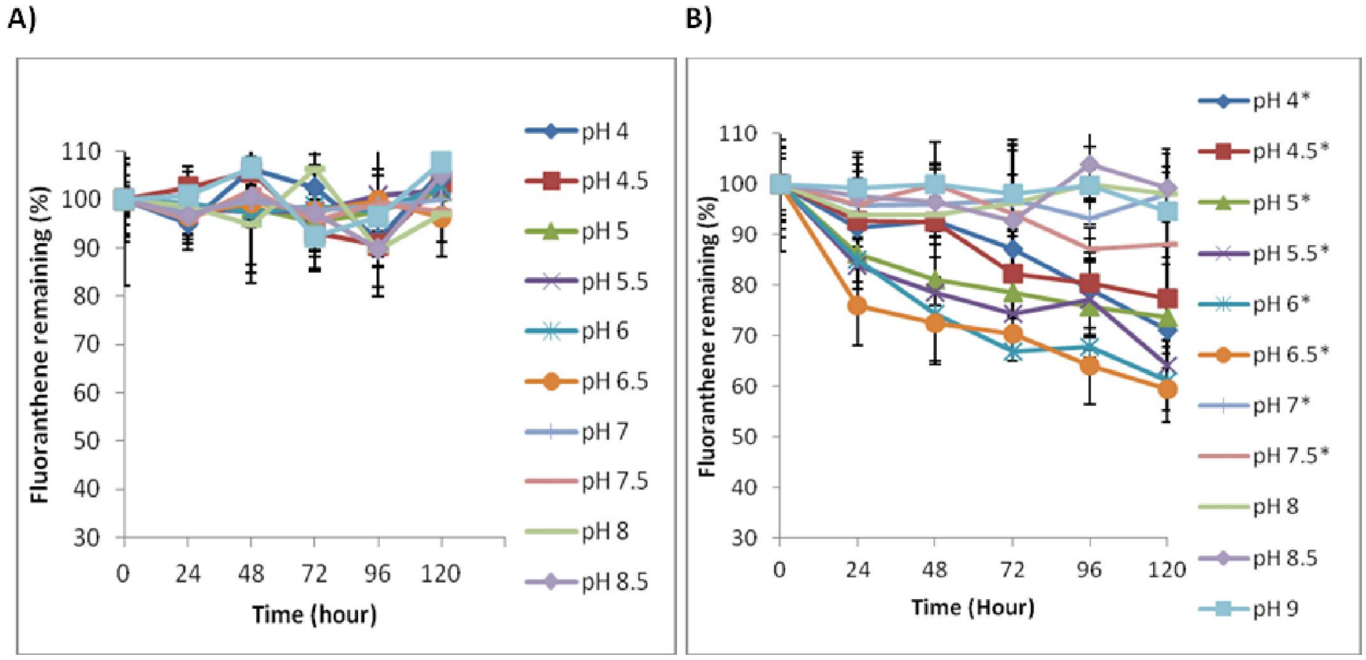

Fig. 7. Percentage fluoranthene remaining in J. Arthur Bower's topsoil at different pH over time exposure to UV light at 375 nm in the presence of TiO_2

A): Percentage fluoranthene remaining in control samples not exposed to UV light. B): Percentage fluroanthene remaining in experimental sample exposed to UV light at 375 nm. *P<0.05 indicates significant difference between control and experimental sample.

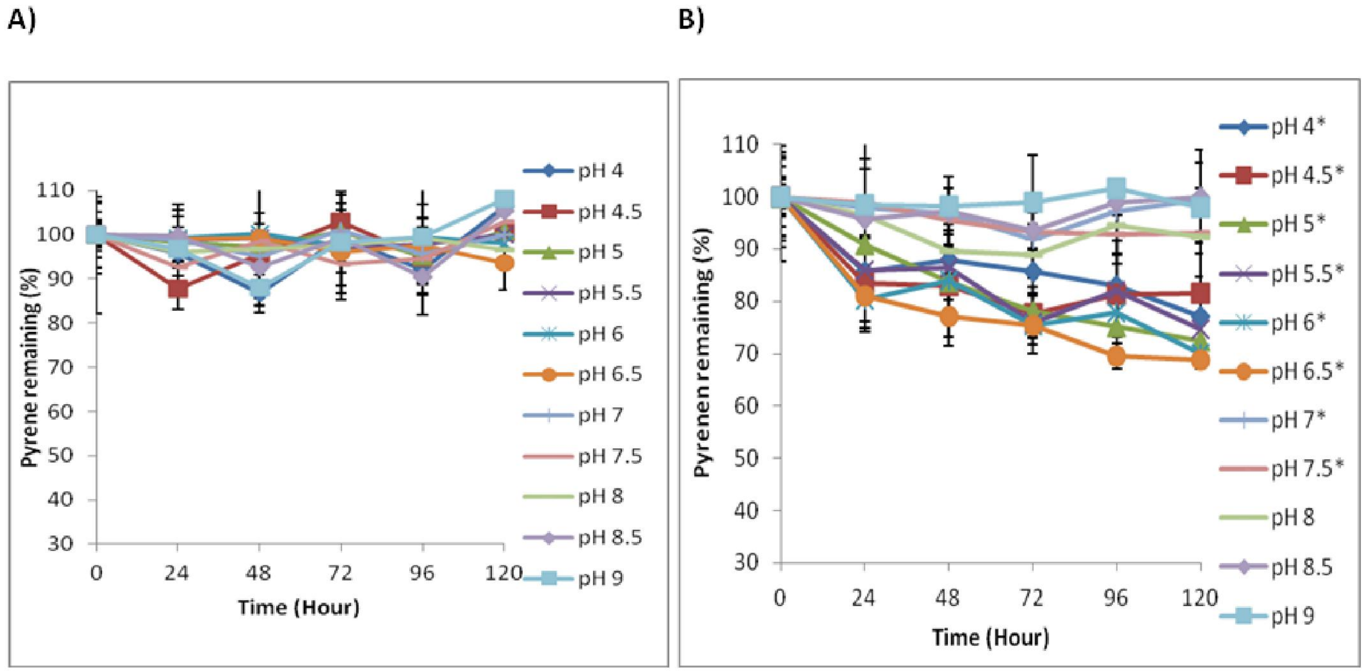

Fig. 8. Percentage pyrene remaining in J. Arthur Bower's topsoil at different pH over time during exposure to UV light at 375 nm in the presence of TiO_2

A): Percentage pyrene remaining in control samples not exposed to UV light. B): Percentage pyrene remaining in experimental sample exposed to UV light at 375 nm. *P<0.05 indicates significant difference between control and experimental sample.

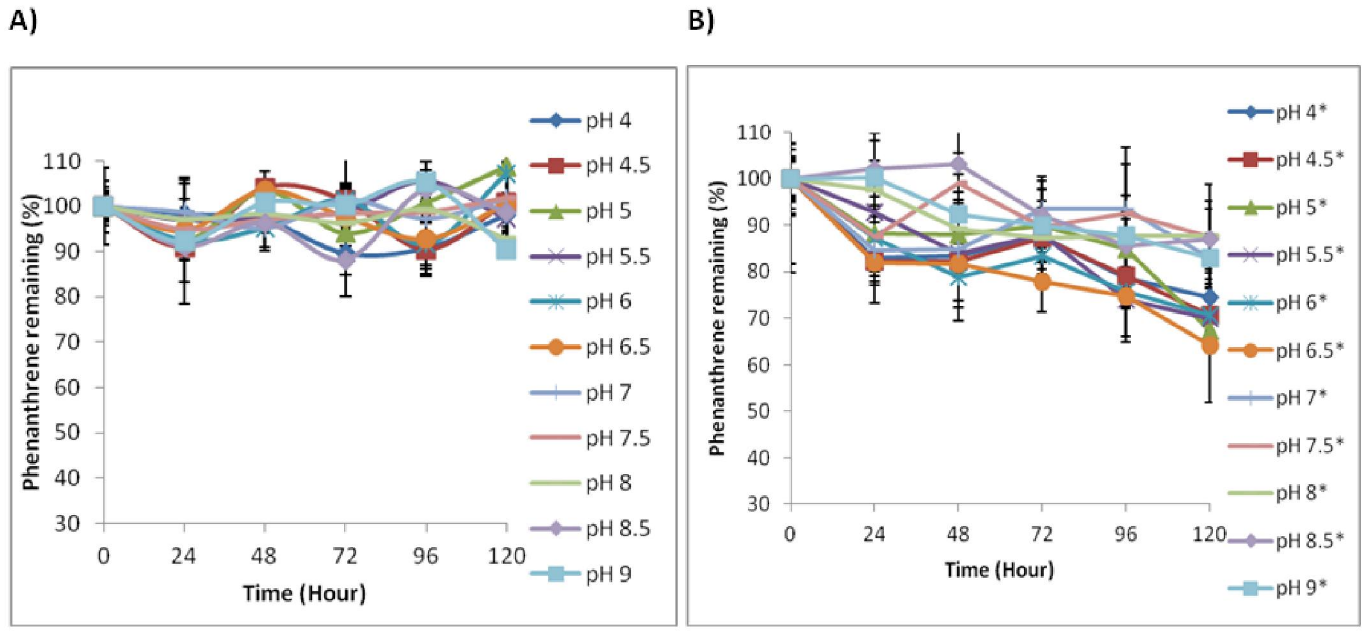

Fig. 9. Percentage phenanthrene remaining in J. Arthur Bower's topsoil at different pH over time during exposure to UV ligh at 254 nm in the presence of TiO_2

A): Percentage phenantherene remaining in control samples not exposed to UV light. B): Percentage phenanthereneremaining in experimental sample exposed to UV light at 254 nm. *P<0.05 indicates significant difference between control and experimental sample.

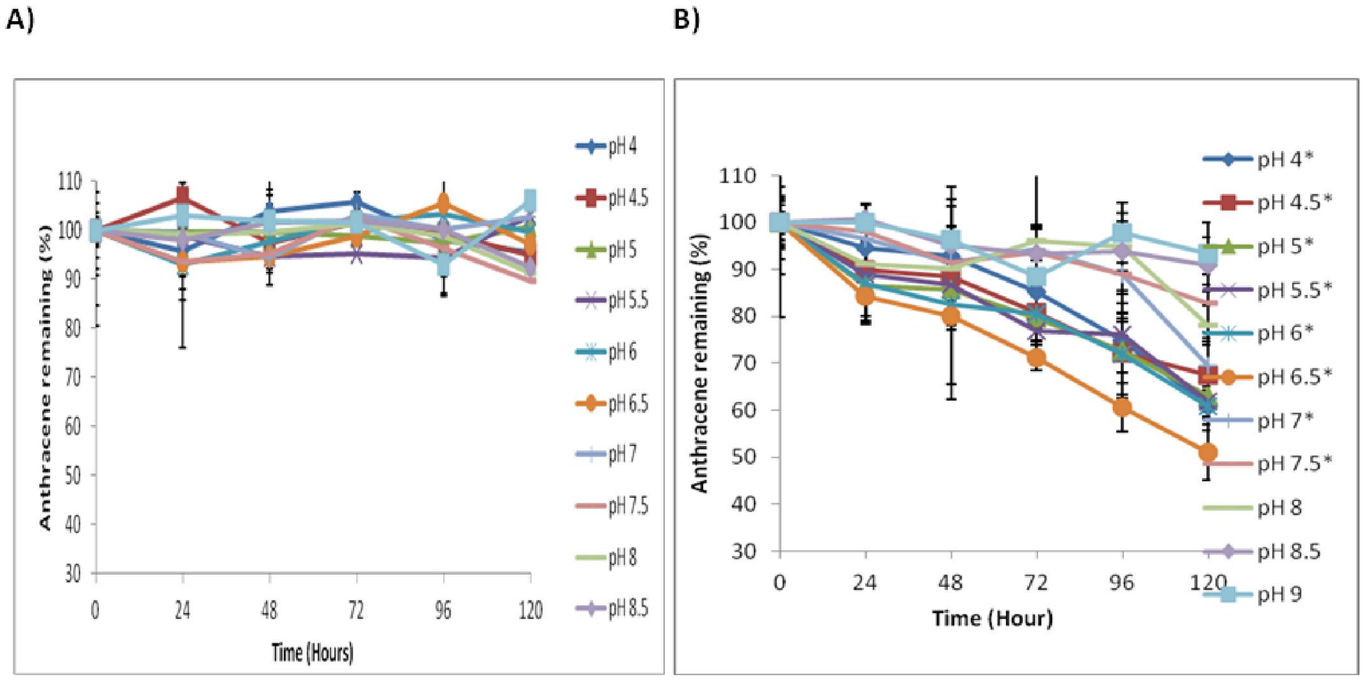

Fig. 10. Percentage anthracene remaining in J. Arthur Bower's topsoil at different pH over time during exposure to UV light 254 nm in the presence of TiO_2

A): Percentage anthracene remaining in 254nm control samples not exposed to UV light. B): Percentage anthracene remaining in experimental sample exposed to UV light at 254 nm. *P<0.05 indicates significant difference between control and experimental sample.

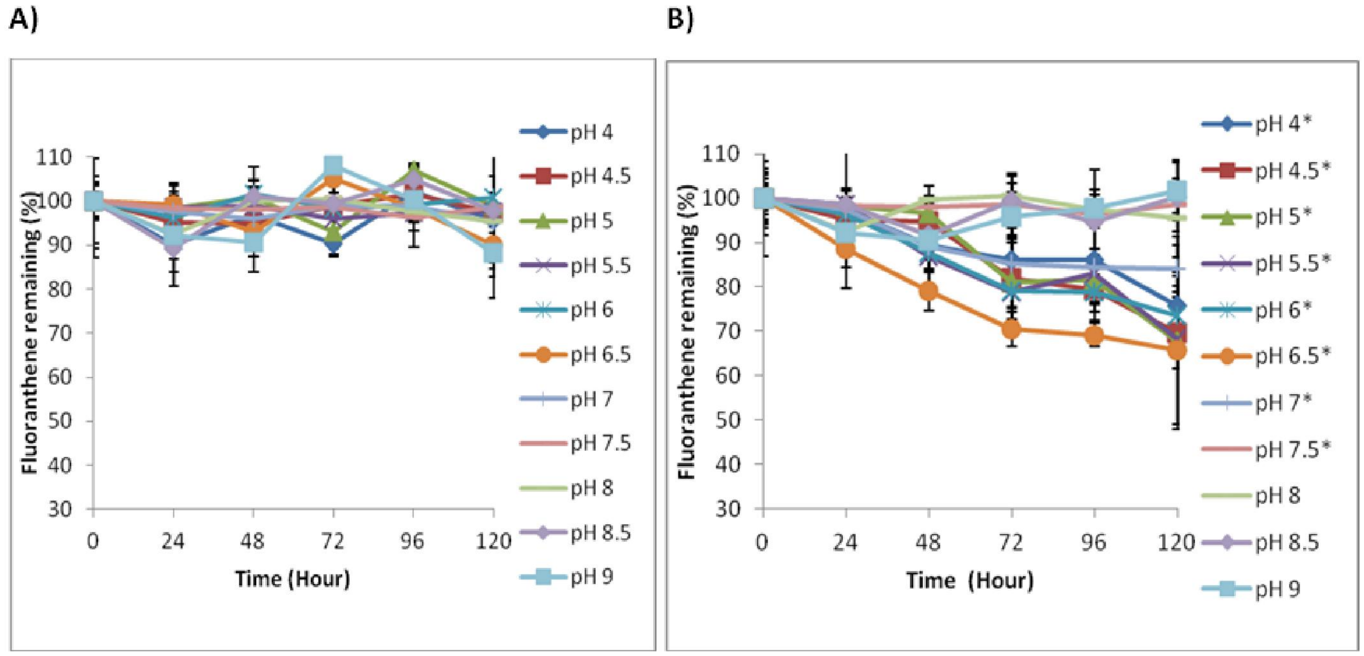

Fig. 11. Percentage fluoranthene remaining in J. Arthur Bower's topsoil at different pH over time during exposure to UV light 254 nm in the presence of TiO_2

A): Percentage fluoranthene remaining in control samples not exposed to UV light. B): Percentage fluoranthene remaining in experimental sample exposed to UV light at 254 nm. *P<0.05 indicates significant difference between control and experimental sample.

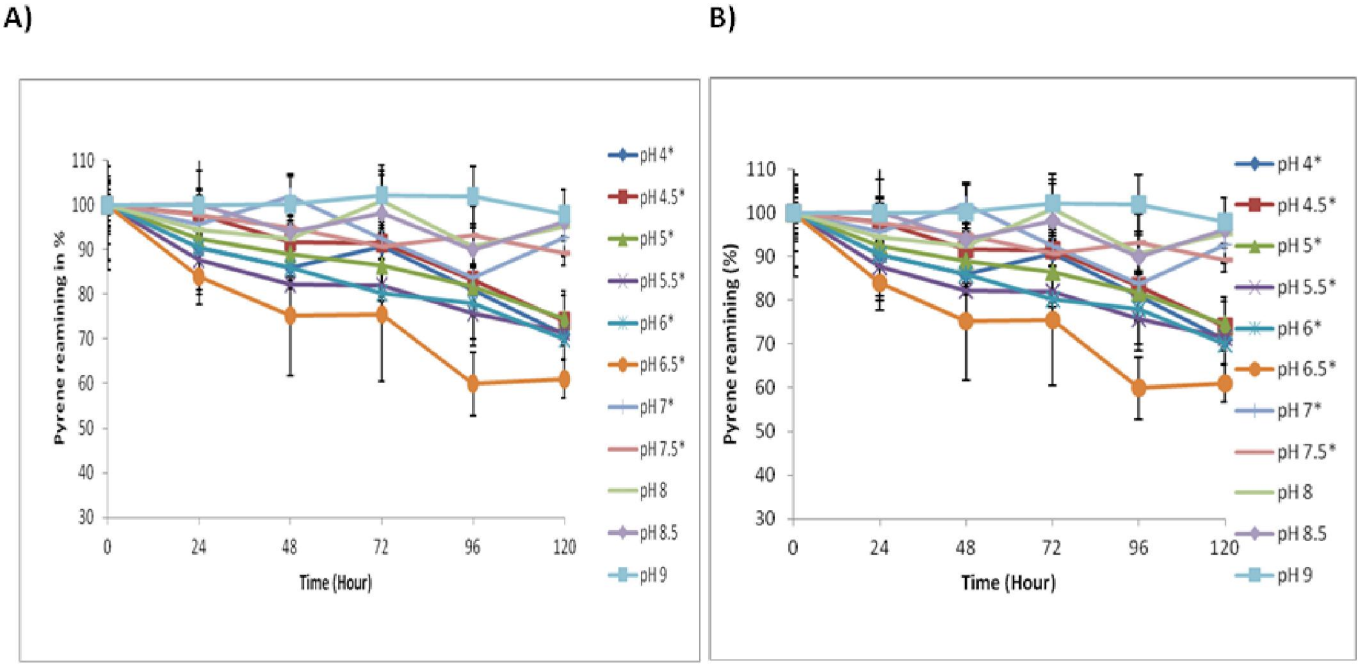

Fig. 12. Percentage pyrene remaining in J. Arthur Bower's topsoil at different pH over time during exposure to UV light at 254 nm in the presence of TiO_2

A): Percentage pyrene remaining in control samples not exposed to UV light. B): Percentage pyrene remaining in experimental sample exposed to UV light at 254 nm. *P<0.05 indicates significant difference between control and experimental sample.

Degradation rate was studied using HPLC for each PAH by calculating the remaining percentage of individual PAH. Phenanthrene, anthracene, fluoranthene and pyrene percentage were constant in all controls with very low degradation rates observed not exposed to UV irradiation. Greater degradation was observed at 375 nm compared to 254 nm with significance $P<0.05$. Time 0, was plotted at 100% in order to show the remaining percentage of individual PAHs in soil pH.

It was demonstrated in this study that photo catalytic degradation rates were greater in acidic soil pH (pH 5.0, 5.5, 6.0, 6.5) when compared to alkaline soil pH (7.5, 8.0, 8.5, and 9.0) and neutral soil pH (7.0) for each of individual phenanthrene, anthracene, flouranthene and pyrene. In figure 5-12 B, pH 6.5 exhibits greater degradation rate followed by pH 5.5, pH 6.0, pH 5.0, pH 4.5 and pH 4. However, at alkaline soil pH lower degradation rates were evident. Among alkaline soil pH greater degradation was measured in pH 7.5 followed by pH 8.5, pH 8.0 and pH 9.0.

Thus, UV irradiation by two different wavelengths in experimental soil in the presence of TiO_2 resulted in greater degradation at soil pH<6.5, whereas lower degradation resulted under alkaline conditions pH>6.5.

In general, results obtained during photo-catalytic degradation exhibited high influence on soil pH with highest rate of degradation obtained for low-molecular weight (LMW) PAH (phenanthrene and anthracene) when compared to high molecular weight PAH (fluoranthene and pyrene).

4 DISCUSSION

4.1 STANDARD CHROMATOGRAMS FOR HPLC

Standard curves were prepared using the HPLC analysis. Carbazole was used at the same concentration (20 ppm) in all experiments as an internal standard to monitor reproducibility of results. Concentrations of PAHs used for standard curves were 1 ppm, 10 ppm, 20 ppm, 30 ppm, 40 ppm, 50 ppm respectively; as the concentration in experimental samples would not reach levels above 50 ppm and the lower limit of detection is in the region of 1 ppm.

The peaks appearing on the chromatogram were observed based on the number of rings and molecular weights of the PAHs. The order of peaks was phenanthrene followed by anthracene, fluoranthene and at last pyrene. The peak of phenanthrene and anthracene appear to be merged in the chromatogram (section 3.1 in figure 2 & 3). The split peak facility of the chromeleon software was implemented to separate the peaks of the two PAHs (phenanthrene and anthracene) and was reproducible with standard PAH solutions. Anthracene resulted strong signals and appeared with larger peaks due to the linearity of the molecule as UV detection is greater for linear molecules [7].

Phenanthrene and anthracene are three ring compounds with molecular weight of 178.23 and appear before fluoranthene and pyrene (molecular weight 202.26) [5]. Although, anthracene and phenanthrene are stereoisomers, anthracene is a linear molecule while phenanthrene is non-linear, resulting in an anthracene being more hydrophobic and thus eluting from the column a little slower in the 90:10 acetonitrile: deionised water mobile phase. Peak area of anthracene at a particular retention time gives better symmetry to the molecule which consequently leads to less solubility in extraction solution. Therefore, in general anthracene is expected to degrade slower than phenanthrene followed by fluoranthene and then by pyrene based on their solubility/ hydrophobicity and molecule size [12].

In addition to this, phenanthrene has low molecular weight and is a three ring compound with high solvent solubility [7]. Whereas, fluoranthene and pyrene have lower solvent solubility [5]. Pyrene is a fused four ring compound with very low extractability. The low solvent extractability of pyrene might be due to its high hydrophobicity (sorption partition coefficient log K_{oc}: 4.88; water solubility= 0.13 mg l^{-1}) [7].

4.2 STANDARD CURVE

With respect to chromatogram obtained in the results displayed in figure 2 & 3, a standard curve was constructed to study the PAHs peak area in the standard solution based on their retention time. A linear standard curve (figure 4) was produced for each PAH with the regression coefficient of 0.97 for phenanthrene, 0.97 for fluoranthene, 0.97 for pyrene and 0.98 for anthracene. The value of the regression coefficient obtained for each calibration curve shows that the correlation between relative peak area and concentration was linear and reproducible within selected concentration range. The Y value representing linear regression equation for phenanthrene was 14.32x and for anthracene was 35.12x, whilst for fluoranthene and pyrene the values were much lower at 6.42x and 4.08x respectively. Thus, the data obtained from standard chromatogram were reliable and accurate (figure 4).

4.3 EXTRACTION EFFICIENCY

Contaminated J. Arthur Bower topsoil was used to examine the extraction efficiency (table 1) of the PAHs using HPLC analysis. All four PAHs were extracted with the greatest extraction rate found for phenanthrene. The total PAH recovered was phenanthrene 74.69%, anthracene 68.42%, fluoranthene 64.98%, and pyrene 52.81%. The extraction efficiency of phenanthrene was highest and of pyrene was the lowest. Reference [1] has suggested different extraction efficiency might be due to the poor contact of solvent and soil. PAHs with high-molecular weight may have stronger adsorption and formation of non-extractable residues especially within a complex substrate such as soil [12]. Recovery obtained for phenanthrene and pyrene was consequentially different. In general, relative recovery rates obtained for each PAH were as expected as the molecular weights of phenanthrene and anthracene are the same and for fluoranthene and pyrene are the same. However water solubility and molecular structures are different with greater linearity for anthracene and pyrene resulting in reduced solubility compared to phenanthrene and fluoranthene respectively [12]. Phenanthrene and anthracene are three ring compounds with molecular weight of 178.23 and fluoranthene and pyrene are four ring structures (molecular weight 202.26) [5]. Recovery rates obtained for each individual PAH correlates with the number of aromatic rings and molecular weight of the PAHs.

4.4 PHOTO-CATALYTIC DEGRADATION

Soil pH is considered as an important parameter due to amphoteric nature of most semiconductor oxides. The surface-charged particles present in the soil in presence of catalyst are influenced by the photo-semiconductor particles [8]. Therefore, the effect of pH on rate of photo catalytic degradation needs to be considered.

UV irradiation accelerated the photo degradation of phenanthrene, anthracene, fluoranthene and pyrene in this study. Some studies suggest that naphthalene, acenaphthene, anthracene, fluoranthene all undergo efficient photo-catalytic degradation by TiO_2 [2], [13]. Studies reported in [6] indicated that when TiO_2 is irradiated with light energy greater than its band gap energy (3.2eV), induction (b) and electron (e^-) and valence band holes (h^+) are generated. Thus, organic compounds reduces or react with electron acceptors such as O_2, reducing it to superoxide radical anion $O_2^{\bullet -}$ with the help of the photo-generated electrons. The H_2O molecules which are photo-generated holes are adsorbed to OH^- radicals at the surface of TiO_2

[6]. On the basis of adsorption of H_2O molecules photo-catalytic processes using TiO_2 could be an effective photo catalytic detoxification method for PAH contaminated soil.

This study demonstrated that photo-catalytic degradation rates were higher in acidic soil and lower in alkaline soil than in neutral soil for phenanthrene, anthracene, fluoranthene and pyrene. This is supported by the work reported in [17] suggests that H^+ was favorable for high molecular weight PAH degradation using TiO_2 under UV light, however the same study also suggested that OH^- made low molecular weight PAHs (example: phenanthrene) become more degradable. Similar results for PAH photo-catalytic degradation was found by reference [3].

Moreover, the lack of degradation at high pH is supported by the work in reference [17] who reported that in pesticide contaminated soil, “raising soil pH by adding $Ca (OH)_2$ did not significantly alter the photo-catalytic degradation of Diuron when compared to the soil that received no lime.”

In this study, higher degradation rates were obtained of phenanthrene and lower degradation rates of pyrene. Similar results were indicated exhibiting high molar absorptivity and disappearance quantum yield for phenanthrene and pyrene as suggested by reference [6]. The most efficient degradation of PAHs in various contaminated sites is recorded with UV irradiation in presence of the catalyst, TiO_2 [14]. In these studies, photo-catalytic oxidation degradation was carried out at varying soil pH at 375 nm and 254 nm respectively. The control (soil samples with TiO_2 not exposed to UV light) at both wavelengths exhibited little degradation (figure 5 A to 12 A) in comparison to the samples exposed to UV light (figure 5 B to 12 B). During photo-catalytic degradation, 375 nm resulted in greater degradation of each individual PAH compared to 254 nm. Phenanthrene had the highest degradation followed by anthracene, pyrene and last fluoranthene at 375 nm. Phenanthrene exhibited 65% of degradation after five days and 60- 65% was degraded at 254 nm.

The photo catalytic degradation rate of anthracene was slower than phenanthrene whilst its degradation rate generally increased with acidic pH with most rapid rate evident at pH 6.5. At 375 nm anthracene exhibited 55-60% degradation and at 254 nm degradation was 55-60%. Degradation of fluoranthene followed after anthracene exhibiting 60% degradation at 375 nm and 45% at 254 nm. Around 45-50% degradation rate was observed for pyrene at 375 nm and 45% degradation observed at 254 nm.

5 CONCLUSION

For photo-catalytic oxidation, it was observed that soil pH 6.5 gave the fastest rate of photo catalytic degradation in comparison to all other pH. The second greatest rate of degradation was found at pH 6.0. Acid pH resulted in higher degradation rates compared to alkaline pH of soil. Comparatively acidic pH from 4 to pH 6.5 exhibited greater degradation as OH^- and OOH^- radicals which plays important role are highly generated, whilst little degradation was evident at neutral and alkaline pH 7.0 to pH 9.0 where, OH^- and OOH^- radicals might be less. Similarly, [4] reported consistently greater degradation of phenol in acidic soil pH during investigating photo-catalytic oxidation. However, the current investigation suggests soil pH is an important parameter that needs to be monitored in order to control the degradation as high pH led to low photo-catalytic degradation rates.

ACKNOWLEDGMENT

This project was performed in University of Hertfordshire, department of biotechnology, Hatfield, Hertfordshire, UK. I take this opportunity to thanks all my family members and lab colleagues Dr. Zohreh Korasanizadeh, Dr. Arjomand Gharghani and all who have encouraged and supported me throughout my PhD for their valuable help.

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