

Highly Efficient Photocatalytic Remediation of Low Molecular Weight Polycyclic Aromatic Hydrocarbons (LMWPAHs) in Contaminated Soils



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Abstract

Soil contamination is a prevailing issue in the world and persistent in nature causing detrimental effects on human and environmental health. In this regard a study was conducted to identify the remedial effects of photodynamic treatment on contaminated soils of two most polluted and important sites of Saudi Arabia AL-Jubail Industrial City as affected by oil industry and Mayasn as affected by forest fires. In this research, the effect of light treatment on soils with different concentrations of Low Molecular Weight Polycyclic Aromatic Hydrocarbons (LMWPAHs) compounds like Naphthalene, Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene and Anthracene were studied. Photo catalysis was applied by using ultraviolet (UV) rays at two different wavelengths (254nm & 306nm) while soil was exposed to UV rays for 0, 2, 4, 6, 8, 10 and 12 hours with two decontaminators i.e., 1.0% of TiO₂ and 1.0% ZnO. The Extraction of LMWPAHs was done by using the QuEChERS method and the determination was done using a Quadruple Gas Chromatograph Mass Spectrometer (GCMSMS/TQD). The results revealed that more PAHs were present in soils from forest fires as compared to petroleum polluted soils. Moreover, ZnO was significantly affected in decontaminating the soils as compared to TiO₂. The concentration of Naphthalene, Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene and Anthracene at 2 hours was 20.12, 23.11, 21.22, 19.11, 21.34 and 21.3ppb under 256nm and was decreased to 1.61, 3.33, 4.03, 3.21, 4.18 and 4.55ppb at 12hrs exposure treatment respectively. The same initial concentrations were reduced as 1.40, 3.01, 3.85, 1.39, 2.76 and 2.82ppb at 12hrs under the high wavelength (306nm). It is recommended that exposure to UV rays under wavelength of 306nm can render more effective results in combination of ZnO for reducing di- and tri-cyclic PAHs in different polluted soils.

Keywords: Soil pollution; Remediation; UV light; Photo-catalysis; Contamination; Decontamination

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are chemical compounds containing benzene rings, many laying in the category of carcinogens, also persistent organic pollutants (POPs). Now it becomes a global concern because of their mutating and carcinogenic effects. Also linked to heart disease, cancer and mental illness. List of 16 environmental compounds certified by the US Environmental Protection Agency (USEPA) PAHs molecules are key to human and animal health problems. The PAHs are non-degradable compounds which remains in the soil matrix for a long time [1]. They can cause severe damage to human and animal population in the area where their release occurred and no control strategies adopted by the authorities. Overall, the ecosystem of that area may disturb and become a threat to the life of flora and fauna [2,3]. Therefore, effective, low-cost and robust methods to decontaminate soils are needed, which do not further stress the environment or endanger human health.

Several technologies are present for the remediation of PAHs from the soil and some are emerging in these days like advanced oxidative processes (OAPs), during which the pollutant is modified with regard to its distribution, reactivity and residence time in environment which ultimately leads to structural changes. The process follows a series of chemical reactions as a result of hydroxyl radicals (*OH) formation. The OH radicals are highly reactive thus they create conditions to attack various organic compounds. Among the POAs, heterogeneous photo catalysis uses a semiconductor acting as a catalyst to generate hydroxyl radicals. Researchers are putting their efforts in soil decontamination studies, for example, photo catalytic degradation of PAHs under UV light in the presence of some semiconductor material (TiO₂ and ZnO). These can be used alone or in combination with conventional methods. Zhang et al. [4] investigated the degradation of different PAHs under controlled temperature with the usage of TiO₂. The

results explored that catalyst TiO_2 enhanced the degradation of PYRE, BaP and PHE and their half-lives were reduced at 0.5%. Similarly, the degradation rates were also dependant on the UV irradiation wavelengths revealing that different UV wavelengths can affect the degradation of PAHs. Another study reported the effect of ZnO and TiO_2 (photo catalyst) with $\text{Na}_2\text{S}_2\text{O}_8$ as oxidant under the natural light conditions. Both semiconductors degraded the studied PAHs (benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, fluoranthene, and indene(1,2,3-cd)pyrene. In this experiment, it was concluded that by application of tandem ZnO/ $\text{Na}_2\text{S}_2\text{O}_8$ an economical decontamination of groundwater can be done with regard to no biodegradable pollutants like PAHs [5].

Similar research on phenanthrene photocatalyzation on soil surface was studied under the effect of nanometre anatase TiO_2 at various concentrations of 0, 1, 2, 3 and 4wt. % and exposed to UV irradiation for 25hrs. It was revealed that phenanthrene degradation followed pseudo first-order kinetics and its half-life was reduced from 45.90 to 31.36hr. Moreover, the phenanthrene degradation is also dependant on H_2O_2 concentration, humic acid concentration and light intensity [6]. In view of the multiple dangers of these compounds, and their persistence /contamination of some soil's regions of the Kingdom of Saudi Arabia, this research was designed to study modern treatment techniques such as light treatment at different wavelengths with the help of semiconductors served as a catalyst. Several sources of polluted soils are identified in the regions of the Kingdom. The area selected for studies are of due importance and it is necessary to estimate the pollution level in such areas. Among them, AL-Jubail Industrial City, represents one of the most important oil production cities in the Kingdom and is one of the largest industrial city in the world. It is located in the Eastern Province of Saudi Arabia on the coast of the Arabic Gulf and the city contributes about 7% of the Country GDP. Finally, the soils of forest fires areas are also important to be studied for their contamination concentration in the Asir region. Such areas are danger for the population as forests in the Kingdom of Saudi Arabia covers 2.7 million hectares and most of the lands covered by forests are located on the Sarawat mountain range and the Hijaz highlands. Owing to the present status of the contaminated soils in the Kingdom of Saudi Arabia and prevalence of toxic PAHs, this study is designed and aimed to evaluate the impact of photo catalysis by using TiO_2 under different UV irradiation time period on the on Remediation of Low Molecular Weight Polycyclic Aromatic Hydrocarbons (LMWPAHs). This study will help in the design of low-cost decontamination strategies for the heavily polluted soils in the region.

Material and Methods

Sampling

The soil samples used in this study were obtained from two regions. The first region was oil-polluted area of AL-Jubail Industrial City, in which soils are polluted with oil residues,

and the second study sample was taken from forest fires area i.e., forests of the Asir region. The samples were collected from a depth of 0 to 30 cm, then homogenized and passed through a 2mm steel sieve after air-drying for 7 days and then were tagged and analysed for the study.

Standard material

Standard compounds and standard compounds numbered C13 were obtained from AccuStandards Company in the United States of America in pure or mixture form in order to make soil samples supported by some or all compounds in order to calibrate the devices, and to estimate the efficiency of extraction.

Processing methods

Photolysis treatment method

Soil samples from the two selected sites were estimated for their aromatic hydrocarbons contents and further treated as explained by EL-Saeid et al. [3] and similar samples will be taken from them. After that reinforcement was done with standard compounds of different PAHs with known concentrations (100 to 300ng/g by dissolving 0.1 to 0.3g of each PAHs in 1L of methanol, mix well with soil, and air dry to evaporate the solvent). After that, 10g of each soil type were weighed into Petri dishes of 9cm diameter. The experiment was laid out in three replications, all the petri dishes were exposed under wavelengths of 254nm and 306 nanometers of ultraviolet rays and the time was adjusted every 10 hours in a day. The distance between the lamps and soil samples was maintained as 15 cm and a specific intensity of ultraviolet rays was given. This process was repeated after adding some oxidants such as titanium oxide, iron oxides, zinc and potassium permanganate in specific proportions to accelerate the effect Ultraviolet light for photo treatment of PAHs.

Analysis of PAHs

Extraction of PAHs using the QuEChERS method

Extraction of the PAHs was done by weighing 10g of soil sample in a special 50ml tube. The distilled water (7ml) was added to homogenize the soil samples and tubes were shake with Vortex for 1 minute. After that, 10ml of acetonitrile solvent was added to each sample and shake for 3 minutes to extract the compounds. The processes were followed by adding 1g of magnesium sulphate and, 2g of sodium chloride respectively and shake immediately for 2 minutes. The samples were left to homogenize for 25 minutes, and then, subjected to centrifuge for 5 minutes at 3000 revolutions. 1.5ml of the prepared solution was transferred from the top of the tube, which was the solvent layer, to a 2ml tube for kitchers purification containing CUMPS18CT MgSO_4 , PSA, (C18 dSPE). After that, it was Shake for 1 minute, and subjected to centrifugation for 5 minutes at 5000 revolutions. 1ml of solvent was transferred into a Kitchers tube and passed through a $0.2\mu\text{m}$ filter directly to the analysis tube of a GCMSMSTQD gas chromatograph quadrant [7].

Determination of PAHs using a quadruple gas chromatograph mass spectrometer GCMSMS/TQD

A gas chromatograph with a mass spectrometer was used to detect the volatile organic compounds such as polycyclic aromatic hydrocarbons (PAHs). The ions were identified with a mass spectrometer detector in both systems (Scan mode) and single ion monitor (SIM) under specific operating conditions [8].

Calculation of the recovery percentage

A calibration chart was developed for each compound using samples supplemented with different concentrations of standard compounds after extraction, to calculate the recovery rate to ensure the accuracy of the methods of analysis and the repeatability of the results.

Quality standards for analytical methods

The following quality criteria were applied to ensure the accuracy of the results including: Linearity, (R2) should be equal to or greater than 0.990 and the maximum quantification (LoQ) should be $S/N > 10$. Use of standard materials and high purity solvents, washing of all instruments used (whether for digestion, standard solution or filtration) in 10% HNO₃ solution for 24 hours, dried and washed with distilled water. 3 replicates will also be taken for each sample of the studied samples to ensure the stability of the reading with taking control samples at all stages of sample analysis. To estimate the accuracy of the method, some samples were supplemented with the compounds to be tested to estimate the sensitivity of the methods used (minimum detection, recovery rate, repeatability). Also, the application of the quality

assurance and continuity test (QC/QA) when estimating PAHs compounds by chromatography, by following the method made [9].

Results and Discussion

The results from our study were significant with regard to the photodynamic treatments under catalyst treatments along with ultraviolet wavelength. Moreover, the exposure time affected the concentration of identified PAHs from our soil samples. The results revealed that soil sample collected from AL-Jubail industrial soil where petroleum pollution prevails, had high concentrations of Anthracene and Acenaphthene while less concentration of Fluorene was present. After addition of catalyst, the highest reduction rate of PAHs was observed in soils treated with ZnO followed by TiO₂. Under the ZnO treated soils, the concentration of PAHs declines with the increase in exposure time as shown in (Table 1 & 2). It is clear that concentration of Naphthalene (Figure 1-6), Acenaphthene (Figure 7-12), Acenaphthylene (Figure 13-18), Fluorene (Figure 19-24), Phenanthrene (Figure 25-30) and Anthracene (Figure 31-36) were 5.39, 5.77, 4.82, 3.55, 4.23, 6.11 when samples were exposed to 2hrs at 256nm of wavelengths and it was decreased as 0.99, 1.03, 1.08, 0.72, 1.08, 2.29 at 8hrs respectively. However, at 10 and 12hrs, their concentration remained very minute and was not detected. A more rapid decrease in concentration was observed when soil with ZnO was exposed to wavelength of 306nm. The minimum values were observed at 6hr exposure, and the amounts were non-detectable under 8 to 12hr treated ones.

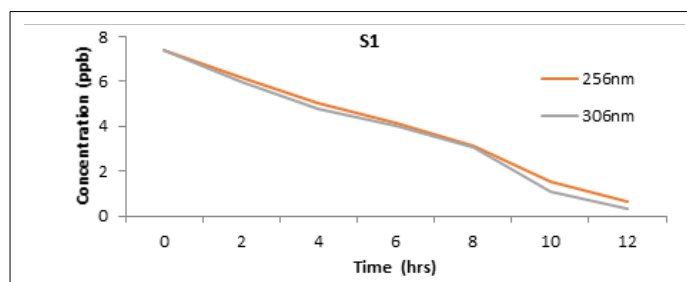


Figure 1: Degradation of Naphthalene with time (Jubail)

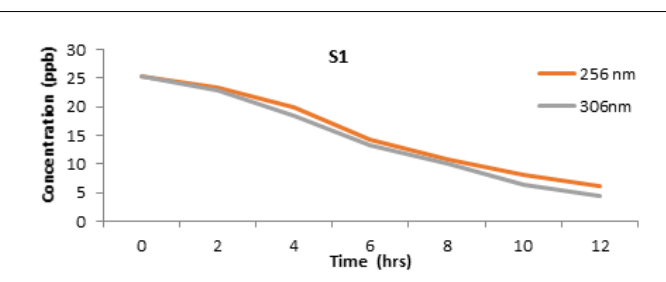


Figure 4: Degradation of Naphthalene with time (Maysan)

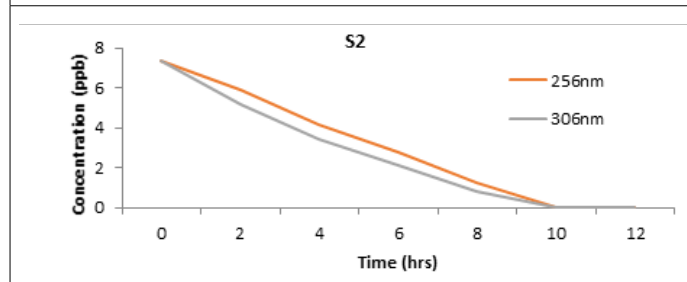


Figure 2: Degradation of Naphthalene with time (Jubail)

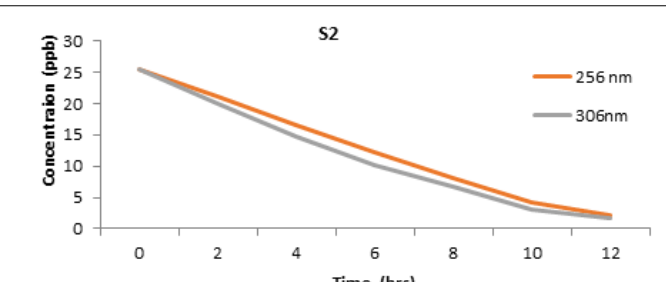
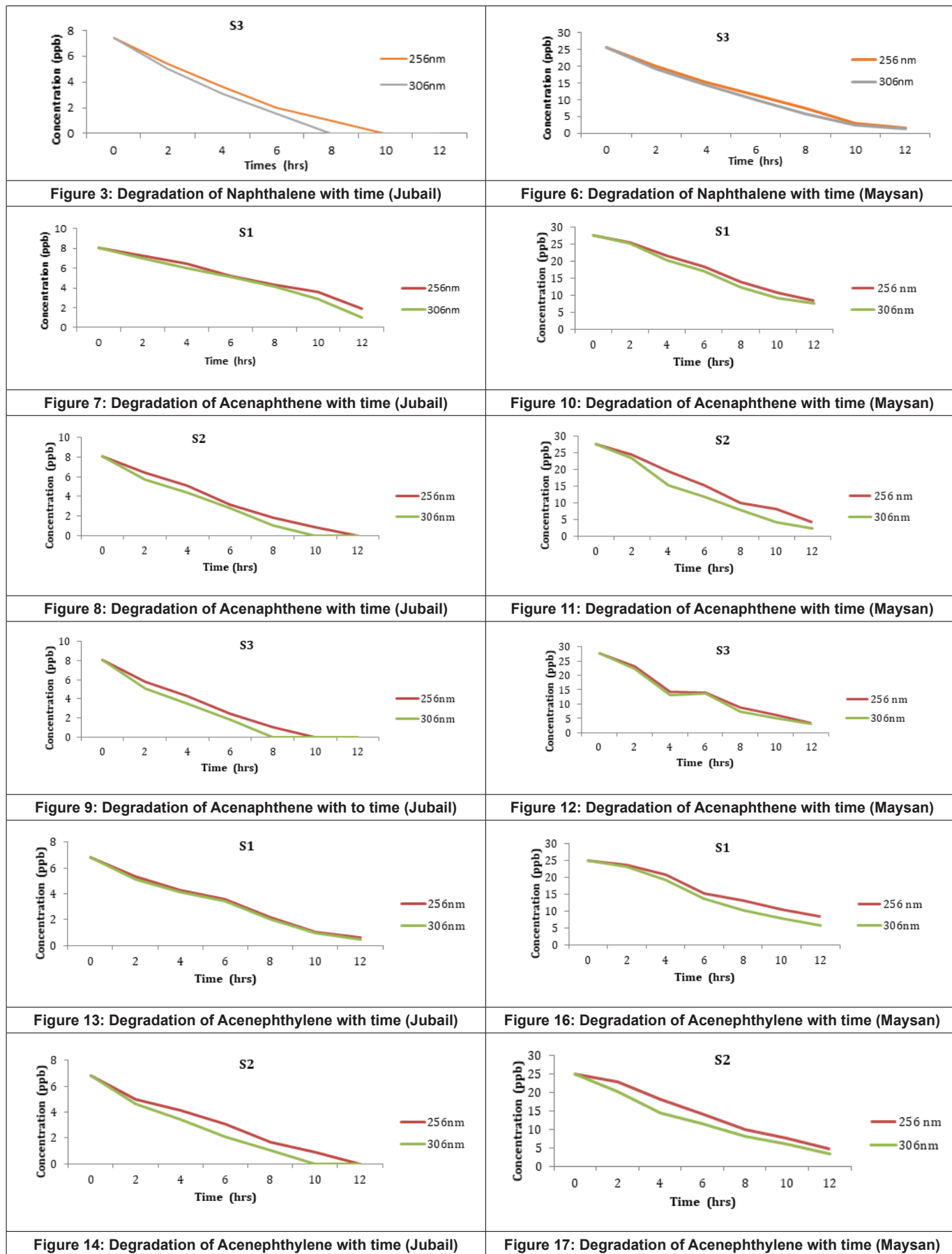
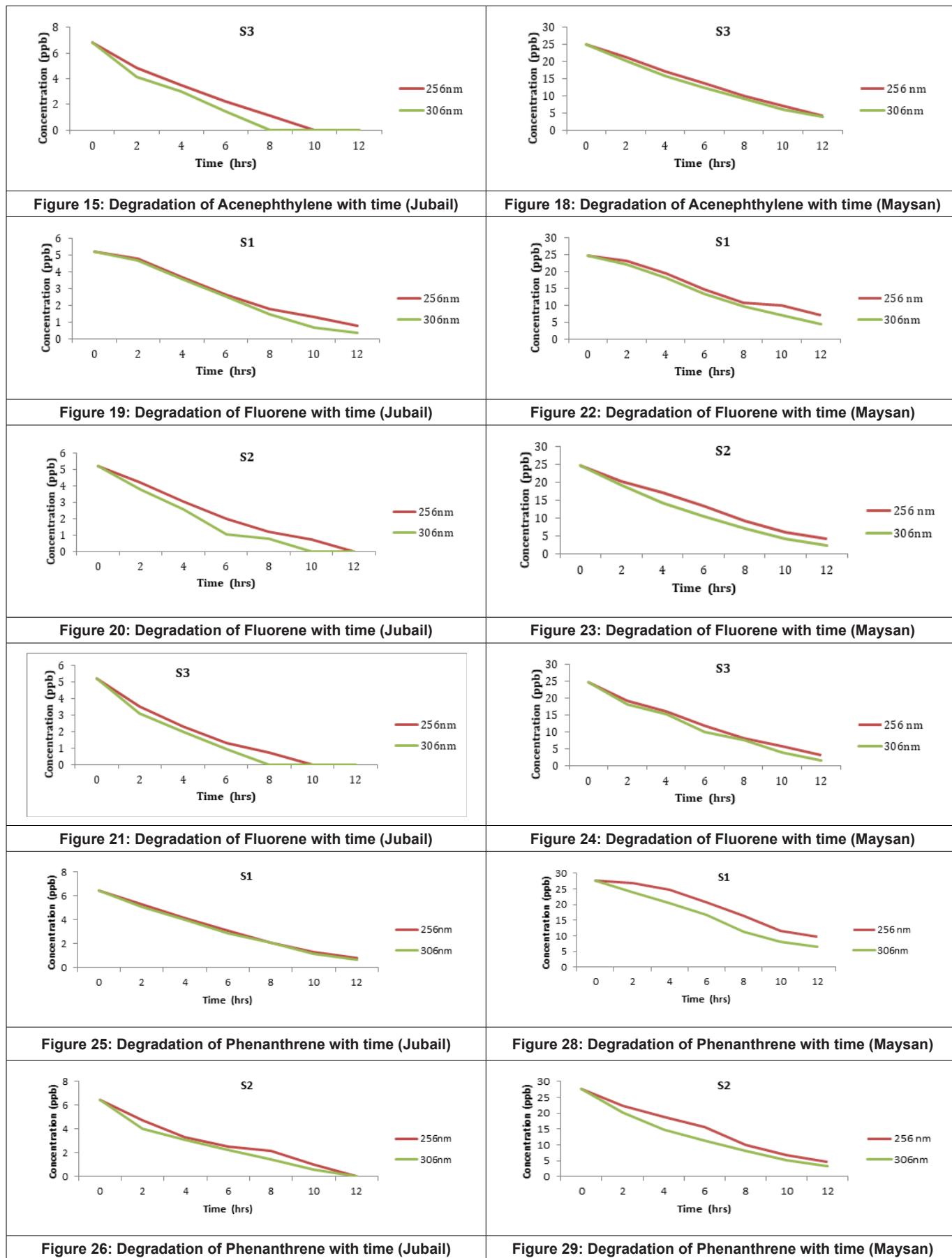


Figure 5: Degradation of Naphthalene with time (Maysan)





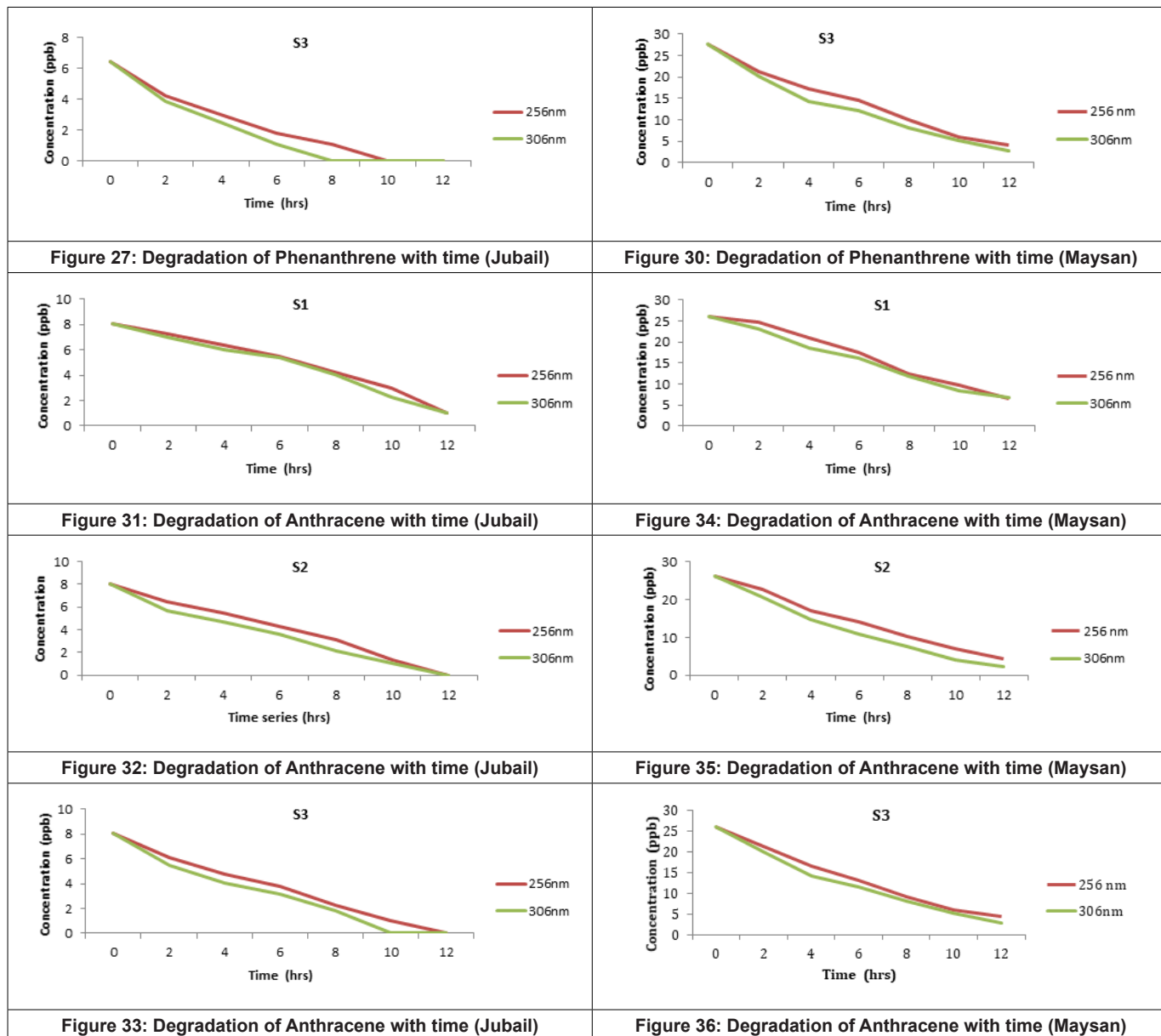


Figure 1-36:

As far as the soil with TiO_2 is concerned, it was less effective than ZnO treatment in reducing the concentrations of detected PAHs. It was found that concentration of Naphthalene (Figure 1-6), Acenaphthene (Figure 7-12), Acenaphthylene (Figure 13-18), Fluorene (Figure 19-24), Phenanthrene (Figure 25-30) and Anthracene (Figure 31-36) at 2hrs exposure under 256nm of wavelength were 5.89, 6.37, 5.01, 4.19, 4.73, 6.42 and reduced to 1.22, 1.83, 1.66, 1.22, 2.18, 3.09 respectively. In contrast to ZnO treatment detectable amounts were still present under the 10hrs treatment. The same trend was followed in 306nm treatment; however the concentration was accelerated as compared to 256nm wavelength. At 10hrs exposure the amounts become not detectable undetectable for all other PAHs apart from Phenanthrene and Anthracene. The detailed results are shown in Table 2.

The results from the forest fires sample studied revealed more amount of PAHs were detected in such soils as compared to those of petroleum polluted areas. The concentration of PAHs ranged from 24 to 28. The soil samples treated with ZnO and TiO_2 catalyst under different wavelengths and for various times revealed that all three of the factors were significant in affecting the concentrations of PAHs. The highest decrease in concentrations was observed in treated soils ZnO under 306nm wavelength treatment. The overall concentration was decreases with the increase in exposure time. The concentration of Naphthalene (Figure 1-6), Acenaphthene (Figure 7-12), Acenaphthylene (Figure 13-18), Fluorene (Figure 19-24), Phenanthrene (Figure 25-30) and Anthracene (Figure 31-36) at 2hrs were 20.12, 23.11, 21.22, 19.11, 21.34 and 21.33 under 256nm and was decreased to 1.61, 3.33, 4.03, 3.21, 4.18 and 4.55 at 12hrs exposure treatment respectively. The same initial

concentrations were reduced as 1.40, 3.01, 3.85, 1.39, 2.76 and 2.82 under 12hrs under the increased wavelength (306nm) exposure revealing that at highest wavelengths the PAHs concentrations

can reduced more rapidly. The results for TiO₂ were similar with regard to the decreasing trend with increase in exposure time as well as wavelength. The detailed results are shown in Table 1.

Table 1: Effect of photodynamic treatment on concentrations of Di- and tri-cyclic PAHs compounds in AL-Jubail industrial soils (petroleum pollution) using two wavelengths and TiO₂ and ZnO.

T	PAHs	256nm							306nm						
		0h	2h	4h	6h	8h	10h	12h	0h	2h	4h	6h	8h	10h	12h
S1	P1	7.38±1.32	6.21±1.12	5.06±1.05	4.12±1.00	3.14±0.95	1.52±0.45	0.65±0.32	7.38±1.32	6.02±1.15	4.76±1.07	4.00±1.00	3.04±0.99	1.12±0.52	0.32±0.12
	P2	8.04±1.77	7.22±1.22	6.44±1.09	5.23±1.01	4.28±0.97	3.62±0.56	1.87±0.21	8.04±1.77	7.01±1.13	6.02±1.11	5.10±0.97	4.11±0.99	2.92±0.43	0.98±0.20
	P3	6.78±2.06	5.33±2.00	4.26±1.88	3.55±1.54	2.14±1.09	1.01±0.92	0.64±0.21	6.78±2.06	5.11±1.34	4.12±1.09	3.44±0.78	2.01±0.52	1.00±0.21	0.45±0.10
	P4	5.23±1.22	4.81±1.22	3.66±1.02	2.61±0.94	1.77±0.89	1.32±0.44	0.77±0.21	5.23±1.22	4.71±1.01	3.56±0.84	2.51±0.56	1.44±0.33	0.67±0.16	0.35±0.07
	P5	6.44±1.33	5.33±1.23	4.18±1.03	3.12±0.89	2.10±0.78	1.34±0.32	0.78±0.21	6.44±1.33	5.11±1.00	4.00±0.86	2.92±0.62	2.11±0.33	1.15±0.10	0.67±0.15
	P6	8.08±2.11	7.22±1.67	6.39±1.32	5.51±0.99	4.23±0.76	3.01±0.32	1.02±0.11	8.08±2.11	7.00±1.23	6.01±0.88	5.35±0.62	4.03±0.31	2.27±0.33	1.01±0.32
S2	P1	7.38±1.32	5.89±1.33	4.16±1.05	2.76±0.76	1.22±0.65	ND	ND	7.38±1.32	5.17±1.01	3.46±0.89	2.11±0.45	0.81±0.12	ND	ND
	P2	8.04±1.77	6.37±1.23	5.04±1.10	3.18±0.87	1.83±0.52	0.82±0.22	ND	8.04±1.77	5.71±1.11	4.38±0.97	2.79±0.23	1.01±0.11	ND	ND
	P3	6.78±2.06	5.01±1.09	4.11±1.01	3.08±0.56	1.66±0.34	0.91±0.21	ND	6.78±2.06	4.66±1.54	3.41±0.78	2.11±0.54	1.03±0.13	ND	ND
	P4	5.23±1.22	4.19±1.02	3.04±0.99	2.02±0.23	1.22±0.11	0.72±0.03	ND	5.23±1.22	3.80±1.00	2.58±0.56	1.02±0.23	0.79±0.09	ND	ND
	P5	6.44±1.33	4.73±1.11	3.28±0.98	2.55±0.58	2.18±0.23	1.01±0.11	ND	6.44±1.33	4.03±0.99	3.10±0.56	2.21±0.18	1.45±0.11	0.63±0.05	ND
	P6	8.08±2.11	6.42±1.56	5.44±1.10	4.31±0.93	3.09±0.55	1.31±0.23	ND	8.08±2.11	5.63±0.96	4.74±0.23	3.61±0.11	2.11±0.05	1.00±0.10	ND
S3	P1	7.38±1.32	5.39±1.06	3.66±0.92	2.01±0.44	0.99±0.23	ND	ND	7.38±1.32	5.03±0.95	3.12±0.58	1.55±0.23	ND	ND	ND
	P2	8.04±1.77	5.77±1.29	4.27±1.01	2.45±0.43	1.03±0.11	ND	ND	8.04±1.77	5.12±0.87	3.47±0.44	1.85±0.21	ND	ND	ND
	P3	6.78±2.06	4.82±1.02	3.48±0.91	2.27±0.32	1.08±0.02	ND	ND	6.78±2.06	4.14±0.56	3.02±0.23	1.44±0.01	ND	ND	ND
	P4	5.23±1.22	3.55±1.10	2.29±0.92	1.32±0.22	0.72±0.01	ND	ND	5.23±1.22	3.12±0.23	2.00±0.10	0.93±0.01	ND	ND	ND
	P5	6.44±1.33	4.23±0.98	3.01±0.62	1.82±0.21	1.08±0.02	ND	ND	6.44±1.33	3.88±0.23	2.51±0.09	1.13±0.02	ND	ND	ND
	P6	8.08±2.11	6.11±1.67	4.74±1.22	3.81±0.97	2.29±0.23	1.01±0.05	ND	8.08±2.11	5.49±1.00	4.01±0.67	3.19±0.23	1.79±0.10	ND	ND

Values are means ± Standard error; T: Treatment; S1: soil without any treatment; S2: soil with TiO₂; S3: soil with ZnO; P1: Naphthalene; P2: Acenaphthene; P3: Acenaphthylene; P4: Fluorene; P5: Phenanthrene; P6: Anthracene.

In our results the photodegradation under the light was slow as compared to those with the catalysts. Similar results were presented by another study, they also claimed the slow reaction rates under sunlight as compared to photocatalyst and especially under the presence of ZnO. The final carryover rate for Fl and B[k]F were 23 to 67 % respectively in the study [5]. In previous studies addition of Nano particulate anatase (TiO₂) had been implemented under UV irradiation. Moreover, similar to our results, a profound effect of the photo catalytic reaction is present under light sources of different wavelengths in combination with the type of catalytic used. It also depends on the crystalline phase of catalytic, any modification of catalytic and anatase to rutile composition [10]. It is because, at different wavelengths the light intensity is a determinant of light absorbed by the semiconductor catalytic, ultimately the distributed light intensity determines the pollutant conversion rate and its efficiency [11]. A wide band gap is present in TiO₂ (3.2eV) that corresponds to UV radiation range. After the absorption of UV radiation, the reactions occurs under the influence of tiO₂ producing a paired of negatively charged electrons along with positively charges holes [12]. During the process several radicals are created [13].

Photo degradation results in the breakdown of benzene ring [14]. Evaporation is another factor that contributes to the PAHs removal. UV irradiation stimulates TiO and as result hydroxyl ions are created (OH) [15-17]. In addition, superoxide ionic radicals (O₂⁻) are produced during the reaction between available electrons and O₂ present in the environment. These both radicals (OH) and (O₂⁻) are highly reactive in nature and play the basic role in degradation of PAHs [13]. In our experiment radiation time, wavelength varied thus posing different affects. The removal time to reach the non-detectable amounts of most of the PAHs was 8-10hrs under both ZnO and TiO₂ treatments however, under control treatment; the complete removal of PAHs was not achieved even after 12hrs. Our results reveal that by increasing the exposure time the efficiency of the process also increases (Figure 1-36). It is because, at more time lapse, increased and higher UV light is radiated to the nanoparticles, release more hydroxyl radicals, photons thus enhancing the removal efficiency. Our results are also in accordance with previous ones that revealed the complete detoxification of PAHs (10mg/L) occurs through titanium dioxide (100mg/L) under 24hrs exposure [18].

Table 2: Effect of light treatment on concentrations of Di- and tri-cyclic PAHs compounds in Maysan soils (pollution due to forest fires) using two wavelengths and TiO₂ and ZnO catalysts

T	PAH	256nm							306nm						
		0h	2h	4h	6h	8h	10h	12h	0h	2h	4h	6h	8h	10h	12h
S1	P1	25.47±2.55	23.32±2.03	19.89±1.76	14.24±1.56	10.83±1.22	8.22±1.01	6.21±0.67	25.47±2.55	22.97±2.10	18.44±1.76	13.23±1.00	10.10±0.77	6.45±0.50	4.34±0.22
	P2	27.69±1.83	25.66±2.12	21.72±2.09	18.44±1.85	13.88±1.34	10.77±1.02	8.34±0.83	27.69±1.83	25.21±1.53	20.33±1.22	17.21±0.89	12.28±0.44	9.12±0.43	7.67±0.21
	P3	25.05±2.11	23.63±2.33	20.71±2.00	15.34±1.85	13.21±1.50	10.52±1.32	8.43±0.87	25.05±2.11	23.09±1.82	19.34±1.33	13.55±0.99	10.33±0.63	7.92±0.33	5.79±0.11
	P4	24.85±1.66	23.11±2.13	19.42±2.00	14.73±1.56	10.89±1.32	9.88±1.21	7.06±0.76	24.85±1.66	22.23±1.52	18.12±1.10	13.48±0.76	9.77±0.56	7.11±0.32	4.51±0.12
	P5	27.78±2.71	26.81±2.44	24.82±2.21	20.71±2.00	16.45±1.87	11.74±1.54	9.76±1.09	27.78±2.71	24.01±2.22	20.33±1.92	16.66±1.63	11.32±1.12	8.21±0.65	6.48±0.33
	P6	26.13±2.56	24.66±2.01	20.99±1.89	17.43±1.53	12.55±1.33	9.77±1.12	6.44±0.91	26.13±2.56	23.06±2.21	18.62±2.00	16.12±1.78	11.87±1.22	8.52±0.65	6.72±0.34
S2	P1	25.47±2.55	21.03±2.21	16.44±1.76	12.28±1.33	8.11±1.02	4.11±0.96	2.16±0.52	25.47±2.55	20.05±2.11	14.64±1.76	10.23±0.44	6.71±0.34	3.03±0.21	1.59±0.22
	P2	27.69±1.83	24.38±2.39	19.54±2.01	15.33±1.87	10.04±1.22	8.10±0.98	4.22±0.45	27.69±1.83	23.55±1.52	15.34±1.33	11.78±0.78	7.74±0.65	4.06±0.32	2.19±0.11
	P3	25.05±2.11	22.91±2.06	18.09±1.76	14.12±1.56	10.04±1.22	7.66±0.89	4.60±0.36	25.05±2.11	20.31±1.96	14.38±1.34	11.55±0.87	8.12±0.62	5.98±0.22	3.49±0.10
	P4	24.85±1.66	20.19±1.93	17.12±1.55	13.44±1.23	9.24±1.00	6.10±0.54	4.27±0.23	24.85±1.66	19.22±1.33	14.12±1.11	10.49±1.00	7.18±0.88	4.23±0.56	2.18±0.09
	P5	27.78±2.71	22.33±2.15	18.88±2.02	15.66±1.92	10.11±1.43	6.75±0.92	4.61±0.36	27.78±2.71	20.18±2.11	14.88±1.76	11.43±1.11	8.03±0.88	5.22±0.56	3.29±0.11
	P6	26.13±2.56	22.64±2.17	17.22±1.84	14.12±1.43	10.17±1.21	7.04±1.05	4.45±0.76	26.13±2.56	20.68±1.23	14.58±1.00	10.92±0.85	7.66±0.66	4.14±0.30	2.45±0.13
S3	P1	25.47±2.55	20.12±2.00	15.40±1.67	11.24±1.33	7.34±1.22	3.00±0.99	1.61±0.52	25.47±2.55	19.28±2.11	14.34±1.56	10.01±1.01	5.81±0.67	2.34±0.23	1.40±0.05
	P2	27.69±1.83	23.11±2.13	14.23±1.87	14.01±1.34	8.89±1.11	6.32±0.87	3.33±0.36	27.69±1.83	22.37±1.78	13.09±1.20	13.57±0.99	7.45±0.65	5.22±0.33	3.01±0.24
	P3	25.05±2.11	21.22±2.12	17.03±1.93	13.67±1.54	10.01±1.34	7.06±1.00	4.03±0.32	25.05±2.11	20.22±1.96	15.73±1.54	12.44±1.00	9.23±0.78	6.11±0.31	3.85±0.16
	P4	24.85±1.66	19.11±2.03	16.15±1.98	11.88±1.56	8.04±1.34	5.76±0.87	3.21±0.22	24.85±1.66	18.22±1.23	15.34±1.10	10.10±0.96	7.67±0.67	3.81±0.29	1.39±0.09
	P5	27.78±2.71	21.34±2.34	17.23±2.09	14.65±1.78	10.00±1.65	6.03±0.92	4.18±0.62	27.78±2.71	20.23±2.32	14.38±1.87	12.09±1.54	8.12±1.01	5.23±0.55	2.76±0.20
	P6	26.13±2.56	21.33±2.31	16.59±1.78	13.22±1.52	9.22±1.29	6.12±0.85	4.55±0.23	26.13±2.56	20.04±2.21	14.22±1.59	11.58±1.23	8.19±0.96	5.33±0.22	2.82±0.10

Values are means ± Standard error; T: Treatment; S1: soil without any treatment; S2: soil with TiO₂; S3: soil with ZnO; P1: Naphthalene; P2: Acenaphthene; P3: Acenaphthylene; P4: Fluorene; P5: Phenanthrene; P6: Anthracene.

Our results are in line with previous studies with regard to the efficiency of ZnO in de-contaminating the PAHs pollution. ZnO has wide band gap, has more energy, physical and chemical stability. Being easily available and low in cost ZnO has high oxidative capacity making it the perfect catalyst in polluted soils [19]. The ZnO is advantageous as it absorbs a larger fraction of UV rays as compared to TiO hence it is more used in photo catalytic degradation under the light [20]. ZnO powder has more quantum efficiency in comparison to TiO₂ [20]. Hariharan [21] stated that ZnO is more efficient in photocatalyst but it is important to determine the catalytic chemistry, life time, regeneration and deactivation of the semiconductor before implementing it any environmental photo catalysis system [22].

Conclusion

The soil is a complex matrix containing a mixture of particles and many pollutants, hence when exposed to high energy UV rays, an alteration or variation may occur in the composition of soil. During the exposure process, PAHs can be converted to less toxic components. With the addition of TiO₂ and ZnO radicals are formed which play the main role in breaking down the benzene rings of PAHs. It was found that ZnO application resulted in increased removal of studied pollutants. TiO₂ also resulted in de

contamination of soils but it follows a slow process, hence it is recommended not to use high-cost semi-conductors like TiO₂ for removal of PAHs when low cost ZnO semiconductors are available.

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