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Photocatalytic degradation of polycyclic aromatic hydrocarbons on soil surfaces using TiO₂ under UV light

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Abstract

The photocatalytic degradation of phenanthrene (PHE), pyrene (PYRE) and benzo[*a*]pyrene (BaP) on soil surfaces in the presence of TiO₂ using ultraviolet (UV) light source was investigated in a photo chamber, in which the temperature was maintained 30 °C. The effects of various factors, namely TiO₂, soil pH, humic acid, and UV wavelength, on the degradation performance of polycyclic aromatic hydrocarbons (PAHs) were studied. The results show that photocatalytic degradation of PAHs follows the pseudo-first-order kinetics. Catalyst TiO₂ accelerated the photodegradation of PHE, PYRE and BaP significantly, with their half-lives being reduced from 533.15 to 130.77 h, 630.09 to 192.53 h and 363.22 to 103.26 h, respectively, when the TiO₂ content was 0.5%. In acidic or alkaline conditions, the photocatalytic degradation rates of the PAHs were greater than those in neutral conditions. Humic acid significantly enhanced the PAH photocatalytic degradation by sensitizing radicals capable of oxidizing PAHs. Photocatalytic degradation rates of PYRE and BaP on soil surfaces with 2% TiO₂ were different at UV irradiation wavelengths of 254, 310 and 365 nm, respectively. The synergistic effect of UV irradiation and TiO₂ catalysis was efficient for degradation of PAHs in contaminated soil. © 2008 Elsevier B.V. All rights reserved.

Keywords: Photocatalysis; Polycyclic aromatic hydrocarbons (PAHs); Soil; TiO₂; Ultraviolet (UV)

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants that are ubiquitous in the environment. They are considered as hazardous pollutants due to their toxicity, mutagenicity and carcinogenicity, and are classified as compounds with significant human health risk [1]. In industrial countries, anthropogenic activities are principal source of PAHs in soil [2,3]. Hundreds of thousands of gallons of used motor oil containing PAHs are disposed of improperly each year into soil [4]. This has prompted an intensive search for effective environmental remediation processes to "clean up" contaminated sites to some predetermined concentration level.

Recently photocatalytic processes involving TiO_2 semiconductor particles under ultraviolet (UV) light irradiation have shown the potential advantages to be used in several cases [5–10]. Solid TiO_2 (in the crystalline form of anatase) is a semi-

0304-3894/\$ - see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2008.01.119 conductor that under UV irradiation can promote an electron (e^-) from the valence band (VB) to the conduction band (CB), leaving a positive hole (h^+) at the site where the electron was originally captured. When appropriate scavengers are present, oxidation/reductions can take place.

Heterogeneous photocatalysis of organic pollutants using TiO₂ under UV-irradiation and/or solar light has demonstrated successful performance in various remediation systems of polluted soil. The addition of small amounts of TiO₂ (0.5, 1, 2 and 3 wt.%) enhanced the photodegradation of p,p'-DDT on soil surfaces significantly, and soil pH, photon flux and humic substances affected the photocatalytic degradation [11,12]. The photocatalytic treatment using TiO₂ combined with solar light was very efficient in the destruction of pesticide Diuron in the top 4 cm of contaminated soil, and the degradation rate was markedly dependent on the irradiation intensity [13]. The contaminated soils containing atrazine, 2-chlorophenol, 2,7dichlorodibenzodioxin were mixed with TiO2 and exposed to simulated solar radiation. The organic contaminants were destroyed in a relatively short time [14,15]. Polychlorinated biphenyls (PCBs) in soil can be effectively photodegraded

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in a dispersion containing anionic fluorinated surfactant and TiO_2 [16]. These studies show that photocatalytic processes are effective to decontaminate soils containing dangerous organic chemicals.

The photodegradation of PAHs in water catalyzed by TiO₂ has been extensively studied in the past few years. Catalyst TiO2 can efficiently photocatalyze the oxidation of PAHs, such as anthracene, fluorene and naphthalene, using artificial or sunlight radiation sources [17]. Phenanthrene with poor aqueous solubility was able to be easily degraded after pre-adsorbed on TiO₂ in an aqueous dispersion under UV irradiation. The pH of the dispersion and Ph/TiO2 value had little effect on the photooxidation rate of phenanthrene catalyzed by TiO₂ [18]. In fact, PAH compounds exist as a mixture of multi-ring structures (i.e. 2through 6-membered ring PAHs). These compounds were intentionally photocatalyzed as a mixture, more representative of the way these compounds had encountered in actual field remediation processes. Ireland et al. [4] investigated the photocatalytic degradation of a mixture of 16 PAHs in aqueous suspensions of high surface area TiO₂ illuminated with ultraviolet light. In order to enhance TiO₂ utilization rate, García-Martínez et al. [19] reported the photocatalytic degradation of naphthalene in water using TiO₂, supported on glass Raschig rings as catalyst. Pal and Sharon [20] studied the photocatalytic degradation of saturated aqueous solution of naphthalene and anthracene over thin films of porous TiO₂ particles on glass substrate.

However, there are few studies investigating the photocatalytic degradation of PAHs on soil surfaces using TiO_2 as the catalyst under UV irradiation.

The present paper focuses on the possible usefulness of heterogeneous photocatalytic processes using TiO_2 for the degradation of PAHs present in soil. Phenanthrene (PHE), pyrene (PYRE) and benzo[*a*]pyrene (BaP) were chosen as representative compounds for PAHs. Furthermore, the main influencing factors, such as photocatalyst concentration, soil pH, humic acid (HA) and wavelength of UV irradiation, were taken into consideration.

2. Materials and methods

2.1. Chemicals

The test PAHs, namely PHE, PYRE, and BaP, were purchased from Fluka, Germany, and were used without further purification. Methanol (HPLC grade) was purchased from Shandong Yuwang Company, China. Hexane and dichloromethane were purchased from Tianjin Concord Technical Company, China. Particles of TiO₂ were purchased from Degussa (P25, anatase, surface area $\sim 50 \text{ m}^2 \text{ g}^{-1}$, mean diameter 20 nm). Humic acid was purchased from Tianjin Jinke Company, China.

2.2. Experimental soil

Surface soil sample (top 10 cm) was collected from the Ecological Station of the Shenyang, Institute of Applied Ecology, Chinese Academy of Sciences. After being air-dried, the soil

Table 1

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Characteristics of	the experimental soil

pН	TOC (%)	Texture	Texture (%)		Bulk density $(g cm^{-3})$
		Sand	Silt	Clay	
6.8	1.78	21.4	46.5	32.1	2.53

sample was passed through a 1 mm sieve. To prepare a sterile soil, the sieved soil was autoclaved at 121 °C for 30 min twice, and stored in dark before use. The characteristics of the soil are presented in Table 1.

The soil samples were spiked with methanol solutions of PHE, PYRE and BaP, respectively, mixed thoroughly and then air-dried for the evaporation of methanol. The concentrations of PHE, PYRE, BaP were calculated to be 40 mg kg^{-1} in the soil, respectively.

The catalyst load was made by adding desired amount of TiO_2 to the PAH spiked soil, followed by shaking for 30 min in a 500 ml closed stainless steel reactor.

To study the influence of soil pH, the pH of PAH contaminated soil sample was adjusted to 4.2 or 9.7 using NaOH or H_2SO_4 , and TiO_2 addition amount was 2%.

Effects of humic acid on PAH degradation were also examined. One hundred grams of HA was dissolved in 0.1 M NaOH solution, diluted with 1000 ml distilled water as storage solution. Different dosages of HA storage solution were added to PAH contaminated soil samples. The additive concentrations of HA in the soil samples were 5, 10, 20 and 40 mg kg⁻¹, respectively. After being air-dried, the soil samples were mixed with 2 wt.% TiO₂.

2.3. Photodegradation chamber

Photodegradation studies were performed in a chamber as shown in Fig. 1. In parallel, two arrays of nine UV lamps were fixed in the top and middle of the chamber, respectively, with a distance of 60 mm between two lamps in the same array. The distance between the lamps and soil samples was 150 mm. The UV irradiation intensity was 1071 μ W cm⁻². The UV lamps (Phillips ATLD 20 W, Model UVA, UVB and UVC) can be changed for wavelength variation, and available wavelengths in the experiment were 254, 310 and 365 nm, respectively. Petri dishes containing the experimental soil samples were placed on the shelves for photo irradiation. Temperature within the chamber can be adjusted through refrigerator, heater and fans in the chamber. Chamber temperature was 30 °C throughout all the experiments.

2.4. Photocatalytic degradation experiments

In the photocatalytic degradation experiments, 5 g of soil sample was evenly spread on the Petri dishes at three replicates. Light proof Petri dishes containing also 5 g of soil sample were set as control for the measurement of non photocatalyzed PAHs loss throughout all the experiments. Effect of TiO_2 amount, soil pH, humic acid and wavelength on the photocatalytic degrada-





Fig. 1. Schematic experimental device and chamber photo for photodegradation of PAHs on soil surfaces.

tions of PAHs were examined by varying TiO_2 addition, pH, HA and wavelength. Detail conditions are shown in Table 2. Soil samples were taken at 24, 48, 72, 96 and 120 h from the dishes exposed to UV light.

Table 2 Experiment design for photocatalytic degradation of PAHs on the surfaces of contaminated soil

Experiment 1 Effect of TiO ₂	TiO ₂ treatment (wt.%): 0.5, 1, 2, 3 Other conditions: pH 6.8; HA was not added; UV wavelength (nm) 254
Experiment 2 Effect of pH	pH treatment: 4.2, 6.8, 9.7. Other conditions: TiO ₂ (wt.%) 2; HA was not added; UV wavelength (nm): 254
Experiment 3 Effect of humic acid	HA treatment (mg/kg): 5, 10, 20, 40 Other conditions: TiO ₂ (wt.%) 2; pH 6.8; UV wavelength (nm) 254
Experiment 4 Effect of wavelength	Wavelength (nm) treatment: 254, 310, 365 Other conditions: TiO ₂ (wt.%) 2; pH 6.8; HA was not added

2.5. Soil extraction and HPLC analysis

Concentrations of PHE, PYRE and BaP in the irradiated and non-irradiated samples were obtained by the following method. Soil samples were transferred into 100 ml Teflon tubes, and mixed with dichloromethane (1 g of soil: 5 ml of dichloromethane). Each sample was extracted for 2 h in an ultrasonic bath, in which the water temperature was lower than $40 \,^{\circ}$ C. The mixture was then centrifuged at 4000 rpm for 5 min to separate the supernatant from the soil. An aliquot of 0.5 ml of extract was passed through a glass column containing 1 g of silica gel wetted with hexane. The extract was eluted with 1 and then 2 ml of hexane: dichloromethane (50:50, v/v) in turn. The eluate was completely dried under the gentle stream of nitrogen. The solid residue was re-dissolved in 1 ml of methanol for HPLC analysis. Quantification of PAHs in methanol solutions was done by an HPLC (Hewlett-Packard 1090-IISeries) with a diode array detector. The mobile phase used was methanol: water (85:15, v/v) at a flow rate of 0.8 ml min⁻¹, and the detector wavelengths were 250 (PHE), 241 (PYRE) and 295 nm (BaP), respectively. Injection volume was 10 µl. Recoveries of the PAHs were examined by using the soil samples spiked with 10, 20, 40, and 80 mg/kg of individual PAHs, respectively, average extraction recoveries of PHE, PYRE and BaP under the given conditions were higher than 92%. Three replicates were performed for analysis.

3. Results and discussion

3.1. Effect of the photocatalyst concentration

It was assumed that PAHs could be degraded by direct UV irradiation, therefore, it should be examined to what extent the PHE, PYRE and BaP were 'photolyzed' if no catalyst was used. Experiments were first carried out on the PAH photodegradation on soil surfaces by UV without catalyst for this purpose. To determine the effect of the catalyst concentration, experiments were carried out by varying the amount of catalyst from 0.5 to 3 wt.%.

Experimental results indicated that photocatalytic degradation of PAHs fitted the pseudo-first-order kinetics. The pseudo-first-order kinetics form is:

$$\ln \frac{C_0}{C} = kt \tag{1}$$

where C_0 and C are the PAHs concentration at times zero and t, respectively, and k is the rate constant. Pseudo-first-order degradation rate constants were determined by regression analysis. Half-lives $t_{1/2}$ were calculated using Eq. (2) which was derived from Eq. (1) by replacing C with $C_0/2$:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k} \tag{2}$$

Kinetics parameters for the photocatalytic degradation of PAHs are listed in Table 3.

At the absence of catalyst, the pseudo-first-order rate constants of PHE, PYRE and BaP were 1.3×10^{-3} , 1.1×10^{-3}

Table 3

Kinetic parameters of PAH photocatalytic degradation on soil surfaces at different catalyst concentrations under UV light

PAHs	Photo-reactive conditions	$k (1 \times 10^{-3} \mathrm{h}^{-1})$	<i>t</i> _{1/2} (h)	r^2
	Natural soil sample	1.3	533.2	0.92
PHE	TiO ₂ (0.5 wt.%)	5.3	130.8	0.93
	TiO ₂ (1 wt.%)	5.4	128.4	0.93
	TiO ₂ (2 wt.%)	6.0	115.5	0.93
	TiO ₂ (3 wt.%)	5.1	135.9	0.94
PYRE	Natural soil sample	1.1	630.1	0.94
	TiO ₂ (0.5 wt.%)	3.6	192.5	0.94
	TiO ₂ (1 wt.%)	3.7	187.3	0.96
	TiO ₂ (2 wt.%)	3.7	187.3	0.97
	TiO ₂ (3 wt.%)	3.6	192.5	0.94
BaP	Natural soil sample	1.9	363.2	0.91
	$TiO_2 (0.5 \text{ wt.}\%)$	6.7	103.3	0.96
	TiO ₂ (1 wt.%)	7.2	95.9	0.97
	TiO ₂ (2 wt.%)	7.8	89.3	0.96
	TiO ₂ (3 wt.%)	7.3	95.0	0.96

and $1.9 \times 10^{-3} h^{-1}$, respectively. When the content of TiO₂ was 0.5%, the pseudo-first-order rates of PHE, PYRE and BaP increased to 5.3×10^{-3} , 3.6×10^{-3} and $6.7 \times 10^{-3} h^{-1}$, respectively. It is clear that TiO₂ accelerated the photodegradation of PHE, PYRE and BaP remarkably. Some studies showed that naphthalene, acenaphthene, anthracene, fluorene were found to undergo efficient photocatalytic degradation by TiO₂ [17–20].

It is well established that induction band electrons (e^-) and valence band holes (h^+) are generated when TiO₂ is irradiated with light energy greater than its band gap energy (3.2 eV). The photo-generated electrons could reduce the organic compounds or react with electron acceptors such as O₂, reducing it to superoxide radical anion O₂•⁻. The photo-generated holes can oxidize either the molecule directly, or the OH⁻ ions and the H₂O molecules adsorbed at the TiO₂ surfaces, to •OH radicals. Together with other highly oxidant species (peroxide radicals), they are responsible for the TiO₂ photodegradation of the compounds [21]. On these bases photocatalytic processes using TiO₂ could be an effective chemical detoxification method for PAH contaminated soil.

However, it was interesting that the variation of TiO₂ concentration from 0.5 to 3% had no significant effect on the rates of PHE, PYRE and BaP degradation. One possible explanation is that even low load provided enough catalyst surface area to promote maximum rates of destruction. On the other hand, at higher loading levels, scattering by catalyst particles attenuated light absorption inside the reaction medium. By comparing photodegradation of individual PAHs at same catalyst load, we found that the BaP degradation was the fastest. This result is different from biodegradation, because biodegradation rate of BaP is always lower than those of PHE and PYRE. The contribution of photodegradation is especially important, because this process preferentially attacks the same "tertiary carbon atoms" that tend to block biodegradation [22]. High molecular weight PAHs, such as BaP, can readily absorb UV light energy and are thus easily subject to photolytic breakdown [23-25]. Catalyst load was determined to be 2% for all the subsequent experiments 2, 3 and 4.

3.2. Effect of soil pH on photocatalytic degradation

Because of the amphoteric behavior of most semiconductor oxides, an important parameter is the pH of the dispersions, which influences the surface-charge properties of the photocatalysts and thus governs the rate of reaction taking place on semiconductor particle surfaces [26]. Therefore, the effect of pH on the rate of photocatalytic degradation needs to be considered. Experiments were carried out at pH values of 4.2, 6.8 and 9.7, respectively. Fig. 2 shows the results of degradation of PAHs at various soil pH under UV irradiation.

The pseudo-first-order rates at pH of 4.2, 6.8 and 9.7 were 7.2×10^{-3} , 6.0×10^{-3} and $1.1 \times 10^{-2} h^{-1}$ for PHE, 1.4×10^{-2} , 3.7×10^{-3} and $8.1 \times 10^{-3} h^{-1}$ for PYRE, and 1.7×10^{-2} , 7.8×10^{-3} and $9.7 \times 10^{-3} h^{-1}$ for BaP, respectively, after photocatalytic degradation.

It is demonstrated in this study that photocatalytic degradation rates were greater in acidic soil or alkaline soil than in neutral soil for individual PHE, PYRE, and BaP. It should be noted that the highest PYRE and BaP photocatalytic degradation rates were obtained at acidic conditions, whereas PHE was the most significantly photocatalytic degraded at alkaline conditions. These PAHs have different structures, BaP and PYRE are 5-ring and 4-ring PAHs, whereas PHE is 3-ring PAH. The ring cleaverages of these PAHs with 3-5 rings were different under various pH. It is assumed that H⁺ was favorable for high molecular weight PAH degradation using TiO₂ under UV light, while OH⁻ made low molecular weight PAHs become more degradable. Similar results about PAH photocatalytic degradation were found by Fan et al. [27]. Moreover, Lehto et al. [28] also reported the effect of pH on the photodegradation rate of PAHs in dilute aqueous solutions. Their results showed that rate constants of pyrene, benz[a]anthracene, and dibenz[a,h]anthracene were higher at pH 5.6 than those at pH 7.6. The TiO₂ surface was positively charged in acidic media (pH < 6.8), whereas it was negatively charged under alkaline conditions (pH>6.8). Under acidic or alkaline conditions, more H⁺ or OH⁻ ions were produced in soil, and these ions were able to facilitate the photocatalytic reactions of PAHs. However, our results differ from other reports obtained from pesticide contaminated soil, in which soil pH rising by adding Ca(OH)₂ did not significantly alter the photocatalytic degradation of Diuron when compared to the soil that received no lime [13]. Quan et al. [12] demonstrated that p,p'-DDT photocatalytic degradation rate on soil surfaces increased with the increasing soil pH.

3.3. Effect of HA on photocatalytic degradation

Humic acids (HAs) are complex organic molecules produced by the decomposition of plant and animals remained in soil, they can either enhance [29–32] or inhibit photolysis [33–35]. The influence of HA on the photocatalytic degradation of PAHs in the presence of TiO₂ on soil surfaces was investigated herein. Effect of HA was examined by the experiments that were undertaken



Fig. 2. Effect of soil pH on photocatalytic degradation of PAHs on soil surfaces using TiO_2 under UV light.

using the same initial concentration of PAHs in the presence of TiO_2 and various concentrations of additive HA. The pseudofirst-order constants of photocatalytic degradation of individual PAHs corresponding to different dosages of the HA are presented in Table 4.

The pseudo-first-order rates of PHE, PYRE, and BaP without HA addition in the presence of TiO₂ (2 wt.%) were 6.0×10^{-3} , 3.7×10^{-3} and 7.8×10^{-3} h⁻¹, respectively (Table 4). Clearly, all HA treatments significantly increased the photocatalytic

Table 4

Effect of humic acid concentrations on photocatalytic degradation of PAHs on soil surfaces in the presence of TiO_2 under UV light

PAHs	Humic acid $(mg kg^{-1})$	$k ({\rm h}^{-1})$	$t_{1/2}$ (h)	r^2
	0	0.0060	115.5	0.93
PHE	5	0.0113	61.3	0.94
	10	0.0102	68.0	0.95
	20	0.0088	78.8	0.93
	40	0.0071	97.6	0.93
	0	0.0037	187.3	0.97
	5	0.0179	38.7	0.96
PYRE	10	0.0151	45.9	0.96
	20	0.0132	52.5	0.94
	40	0.0119	58.2	0.98
BaP	0	0.0078	89.3	0.96
	5	0.0236	29.4	0.96
	10	0.0212	32.7	0.96
	20	0.0194	35.7	0.98
	40	0.0180	38.5	0.98

degradation of PAHs on soil surfaces under UV light. When humic substances absorbed UV irradiation, the reactive oxygen intermediates were generated and, therefore, may attack chemicals in the environments and initiate their degradation [36,37]. On the other hand, the TiO₂ surface was charged with more H⁺ ions in acidic conditions. Both processes might contribute to the promoting effect of the HA on the photocatalytic degradation of PAHs.

As the concentration of HA increased from 5 to 40 mg kg⁻¹, the pseudo-first-order rates of the PHE, PYRE and BaP decreased (Table 4) due to the shielding effect of HA, which protested PAHs from incident radiation, thus retarded the photodegradation. With the compound concentration increasing, the attenuation (absorption) of incident light by non-target substances should be a critical factor that influenced the photodegradation rate.

3.4. Effect of irradiation wavelength on photocatalytic degradation

Effect of different wavelengths of UV irradiation on photocatalytic degradation of PYRE and BaP was studied under three different conditions: UV irradiation in the presence of TiO₂ at 254, 310 and 365 nm, respectively (Table 2). Fig. 3 shows that the influence of wavelengths on photocatalysis was significant. Photodegradation rates of BaP in the presence of TiO_2 followed the order of 254 nm irradiation > 310 nm irradiation > 365 nm irradiation (Fig. 3). The pseudo-first-order rate constants were 7.8×10^{-3} , 6.1×10^{-3} and 5.0×10^{-3} h⁻¹ corresponding to the wavelengths of 254, 310 and 365 nm, respectively. It can be seen that BaP photocatalytic degradation decreased with the wavelength increasing. These results are consistent with the reports by Han et al. [38] and Zertal et al. [39]. The degrees of photocatalytic degradation of BaP at different wavelengths were due to two possible reasons. One was that the shorter the wavelength was, the higher the energy illumination was. The other should be ascribed to



Fig. 3. Effect of wavelength on photocatalytic degradation of BaP and PYRE on soil surfaces with 2 wt.% TiO₂.

that changes in wavelength altered the BaP binding affinity [40].

The photodegradation rates of PYRE in the presence of TiO₂ followed the order of 310 nm irradiation > 365 nm irradiation > 254 nm irradiation (Fig. 3). The pseudo-first-order rate constants were 5.6×10^{-3} , 4.8×10^{-3} and 3.7×10^{-3} h⁻¹ corresponding to the wavelengths of 310, 365 and 254 nm, respectively. The experiment results are coinciding with the results obtained by Akyol and Bayramoglu [41]. Photocatal-ysis of a chemical is greatly influenced by the characteristic of catalyst and the extent of spectral match between its absorption spectrum and the emission spectrum of the light source. A good spectral match between them will always result in fast photocatalytic degradation. Ultraviolet irradiation at 310 nm matched the PYRE absorption peak wavelength and thus resulted in good photocatalytic degradation of PYRE.

4. Conclusions

The photocatalytic degradation of PHE, PYRE, and BaP on soil surfaces under UV light irradiation followed pseudo-first-order kinetics. Photodegradation of PHE, PYRE and BaP was accelerated by TiO_2 significantly. Variation of TiO_2 concentration from 0.5 to 3 wt.% did not significantly affect PAH photodegradation.

Soil pH influenced photocatalytic degradation of PAHs. The highest PYRE and BaP photocatalytic degradation rates were obtained at acidic conditions, whereas PHE was the most significantly photocatalytic degraded at alkaline conditions.

Photocatalytic degradation of PAHs initiated by the UV irradiation will be enhanced in the presence of HA. This effect relatively decreased as the concentration of HA increased from 5 to 40 mg kg^{-1} .

Photocatalytic degradation rates of PAHs were different under distinct wavelengths of UV irradiation. Photocatalytic degradation rates of BaP in the presence of TiO₂ followed the order of 254 nm irradiation > 310 nm irradiation > 365 nm irradiation. Whereas those of PYRE followed the order of 310 nm irradiation > 365 nm irradiation > 254 nm irradiation.

The synergic effect of UV irradiation and TiO_2 catalyst led to the most efficient degradation of PAHs in contaminated soil. Meanwhile, some important parameters (such as soil pH, catalyst loads, irradiation condition, etc.) needed to be monitored in order to control the degradation. Catalytic technique with TiO_2 under UV light will be far attractive in remediation of surface soils contaminated with persistent organic pollutants.

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