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# Photocatalytic degradation of phenanthrene and pyrene on soil surfaces in the presence of nanometer rutile $TiO_2$ under UV-irradiation

Dianbo Dong[a,b], Peijun Li[a,*], Xiaojun Li[a], Chengbin Xu[c], Dawei Gong[d],
Yinqiu Zhang[a,b], Qing Zhao[a,b], Peng Li[b,e]

[a] Institute of Applied Ecology, Chinese Academy of Sciences, Wenhua Road No.72, Shenyang 110016, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[c] School of Environmental Science, Liaoning University, Shenyang 110036, China
[d] Liaoning Provincial Center or Disease Control and Prevention, Shenyang 110005, China
[e] Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

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ABSTRACT

Photocatalytic degradation of phenanthrene and pyrene on soil surfaces in the presence of nanometer rutile $TiO_2$ was investigated. After being spiked with phenanthrene and pyrene, soil samples loaded with different dosages of nanometer rutile $TiO_2$ (0, 1, 2, 3, and 4 wt%) were exposed to UV-irradiation for 25 h. The results indicated that the photocatalytic degradation of phenanthrene and pyrene followed the pseudo-first-order kinetics. The catalyst dosage of 2 wt% was chosen as the optimal one for further studies. According to the half-life, the degradation rate of the phenanthrene and pyrene on soil surfaces was related to their absorption spectra in soil and oxidation-half-wave-potential. In addition, the degradation of phenanthrene and pyrene increased along with increasing $H_2O_2$, light intensity and humic acids. All results indicated that the photocatalytic method in the presence of nanometer rutile $TiO_2$ was an advisable choice for the treatments of PAHs polluted soil in the future.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a class of POPs, are widely distributed in the environment. Many of them are toxic and carcinogenic [1–5], and 16 PAHs are listed by the US Environmental Protection Agency (EPA) as priority pollutants [6,7]. These compounds may be produced by oil processing, accidental spilling, coal liquefaction and gasification, or organic oil seepage and surface run-off from forest/brush fires and natural geologic processes and are often found in contaminated soils [8,9]. In China, the backgrounds of PAHs in arable soils vary between 10 and 20 $\mu g\,kg^{-1}$, while the concentrations of PAHs have been found to be as high as $10^2$–$10^4$ $\mu g\,kg^{-1}$ in some contaminated areas [10], which may pose great threats to the agricultural food quality, human health, and ecological security. Thus great attentions have been paid to the remediation of the contaminated soils [11].

Heterogeneous photocatalysis of organic pollutants using $TiO_2$ under UV-irradiation and/or solar light has been successfully demonstrated in various systems for remediation of polluted soil. The addition of small amounts of $TiO_2$ enhanced the photodegradation of p,p′-DDT on soil surfaces significantly [12,13]. Photocatalytic treatment using $TiO_2$ combined with solar light was very efficient in the destruction of pesticide Diuron in the top 4 cm of contaminated soil [14]. The organic contaminants were destroyed in a relatively short time when the contaminated soil containing atrazine, 2-chlorophenol and 2,7-dichlorodibenzodioxin were mixed with $TiO_2$ and exposed to simulated solar radiation [15,16].

Photocatalytic degradation might be an efficient way to eliminate PAHs. It is extensively reported that PAHs can be photocatalytically degraded in pure solid phase such as silica, alumina, $Fe_2O_3$ [17–22] and liquid phase [23–25]. However, few studies investigated the photocatalytic degradation of PAHs on soil surfaces in the presence of nanometer rutile $TiO_2$.

In this paper, the result of the photocatalytic degradation of phenanthrene and pyrene on soil surfaces with the addition of nanometer rutile $TiO_2$ under UV-irradiation was presented and the possibility of heterogeneous photocatalysis using nanometer rutile $TiO_2$ in remediation of phenanthrene and pyrene contaminated soils was discussed. The main influencing factors, such as $H_2O_2$, the light intensity and the humic acids (HA) were taken into consideration.

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* Corresponding author. Tel.: +86 24 83970367; fax: +86 24 83970368.
*E-mail address:* lipeijun@iae.ac.cn (P. Li).

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**Table 1**
Physical properties of the experimental soil.

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

## 2. Materials and methods

### 2.1. Reagents and materials

Phenanthrene and pyrene were purchased from Fluka (Germany). Methanol (HPLC grade) was purchased from Shandong Yuwang Company (China). Hexane and dichloromethane (Analytical grade) were purchased from Tianjin Concord Technical Company (China). $NaN_3$ was purchased from Zhejang Hailan Chemical Co., Ltd. (China). Nanometer rutile $TiO_2$ (chemical purity) was obtained from the Hangzhou Wang Jing New Material Co., Ltd. (China). $H_2O_2$ (AR, 30% content) was purchased from Shenyang Chemistry Reagent Corporation (China). Humic acid was purchased from Tianjin Jinke Company (China).

Soil samples (0–10 cm) were collected from the Ecological Station of the Shenyang, Institute of Applied Ecology, Chinese Academy of Sciences. The soil samples were sterilized by soaking in $NaN_3$ solution for about 48 h and then dried in an oven at 105 °C. After drying, the soil samples were passed through a 1 mm sieve. The sieved soil samples were then stored in dark before use. The physical properties of the experimental soil samples were presented in Table 1. Mineral components of the experimental soil samples were analyzed by X-ray fluorescence (XRF) and the results were listed in Table 2.

For the individual experiments, the soil samples were treated with methanol solution of phenanthrene and pyrene, mixed thoroughly and then air-dried to evaporate the methanol. The concentration of phenanthrene and pyrene in the resulting soil samples was 40 $mg\,kg^{-1}$, respectively.

### 2.2. Photodegradation experiments

Photodegradation experiments were conducted in a chamber with UV lamps fixed at the top and separated by 60 mm as shown in Fig. 1. The UV lamps (Phillips ATLD 20W, Model UVA) had a wavelength of 253.7 nm. In all experiments, three replicates of 5.00 g of soil samples were evenly spread on Petri dishes and randomly located in the photodegradation chamber under the UV lamps. Light proof Petri dishes also containing 5.00 g of uniformly spread soil samples were used as controls for the measurement of non-photolytic phenanthrene and pyrene loss for all experimental treatments. Petri dishes containing soil samples were placed on the shelves for UV-irradiation. The height of the lamps above the soil samples was 100 mm. Temperature within the chamber was held constant at 25 °C using a heater and fans throughout all experiments. Soil samples were taken at 5 h intervals from the Petri dishes exposed to UV-light irradiation.

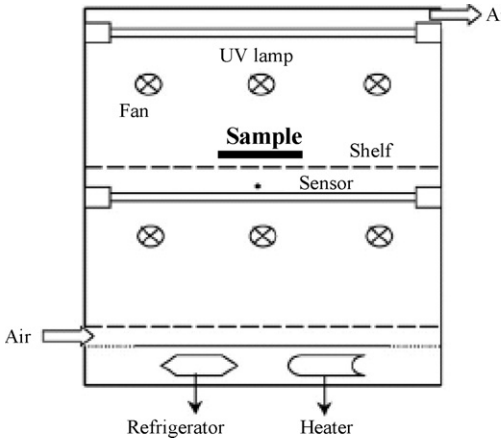

**Fig. 1.** Schematic experimental device for photocatalytic degradation of pyrene on soil surfaces.

Obtained soil samples were spiked with nanometer rutile $TiO_2$ powder in a similar way as the method described by Higarashi and Jardim [14]. The catalyst load was made by adding desired dosage of $TiO_2$ to the phenanthrene and pyrene spiked soil.

Effect of $H_2O_2$ on the photocatalytic degradation was investigated by loading the desired dosage of $H_2O_2$ to the soil samples in the presence of 2 wt% $TiO_2$.

The different number of UV lamps was adjusted accordingly to change the light intensity. Three different levels of light intensity were obtained corresponding to three different number of UV lamps, respectively.

Effect of HA on the degradation of phenanthrene and pyrene was also examined. Ten grams of HA was dissolved in 0.1 M NaOH solution, diluted with 1000 ml distilled water as storage solution. Different dosages of HA stock solution were added to contaminated soil samples to give concentrations of HA of 0, 10, 20, 30 and 40 $mg\,kg^{-1}$. After being air-dried, the soil samples were mixed with 2 wt% $TiO_2$.

### 2.3. PAHs extraction procedure

Concentrations of PAHs in the irradiated and non-irradiated soil samples were obtained by the following method: the soil samples were transferred into 100 ml Teflon tubes and mixed 20 ml dichloromethane. Each sample was extracted for 2 h in an ultrasonic bath in which the water temperature was lower than 35 °C. The mixtures were then centrifuged at 4000 rpm for 5 min to separate the supernatant from the soil samples. An aliquot of 0.5 ml of extraction was passed through a glass column containing 0.9 g of silica gel wetted with hexane. The extraction was eluted with 1 ml hexane:dichloromethane (1:1, v/v) four times. The eluate was completely dried under a gentle stream of nitrogen. The solid residue was re-dissolved in 1 ml of methanol for HPLC analysis.

**Table 2**
Main elements and components of the experimental soil.

| Element | Concentration ($mg\,kg^{-1}$) | Element | Concentration ($mg\,kg^{-1}$) | Component | Concentration (%) |
|---|---|---|---|---|---|
| As | 8.95 | Ni | 26.70 | $SiO_2$ | 68.22 |
| Ba | 676.65 | Mn | 577.70 | $Al_2O_3$ | 13.41 |
| Ce | 123.00 | Pb | 37.00 | $Fe_2O_3$ | 4.19 |
| Zn | 70.45 | Rb | 109.75 | MgO | 1.13 |
| Co | 11.70 | Sr | 189.75 | CaO | 1.16 |
| Cr | 67.65 | Th | 13.00 | $Na_2O$ | 1.78 |
| Cu | 36.70 | Ti | 4,459.40 | $K_2O$ | 2.43 |

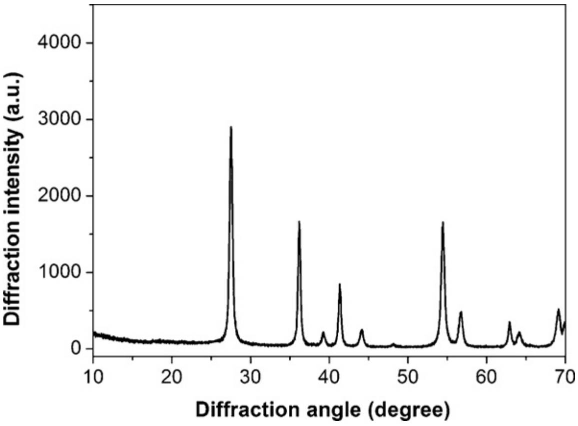

**Fig. 2.** X-ray diffractometer (XRD) pattern of nanometer rutile $TiO_2$ after calcination.

### *2.4. Analytical methods*

Quantification of PAHs in methanol solutions was conducted using an Agilent model 1200 HPLC with a variable wavelength detector set at 254 nm (Agilent Technologies, USA). The mobile phase used was methanol:water (90:10, v/v) at a flow rate of 0.7 ml $min^{-1}$. Injection volume was 10 μl. Three replicates were performed for analysis.

The crystalline of $TiO_2$ was determined by X-ray diffractometer (Rigaku, RINT2200, Japan). Transmission electron microscopy (TEM) which was operated using JEM 2010 electron microscope (JEOL company, Japan) at 200 kV.

## 3. Results and discussion

### *3.1. Characterization of nanometer rutile $TiO_2$ particles after calcination*

It is well known that there are three naturally occurring phases of titania: rutile, anatase and brookite. The photocatalytic activity of $TiO_2$ is related to their crystalline phase. In order to characterize the nanometer $TiO_2$ which was calcined at 450 °C, the crystalline phase of $TiO_2$ was determined by X-ray diffractometry (XRD), and transmission electron microscopy (TEM) was used to determine the size of the $TiO_2$ particles. Fig. 2 shows the XRD patterns over a scan range from 10° to 70° for a calcined sample. The XRD data for the sample matched the standard rutile pattern (peaks at 27.8). There were no diffraction peaks at 25° or 31°, indicating that samples were free of anatase and brookite $TiO_2$ [27,28]. Fig. 3 shows the TEM for a sample which indicates a crystal size of the sample of about 15–25 nm.

### *3.2. Effect of $TiO_2$ dosage*

The dosage of catalyst is an important parameter in photocatalytic degradation processes. To determine the optimal dosage of photocatalyst, various dosages of $TiO_2$ (0, 1, 2, 3 and 4 wt%) were used to investigate the photocatalytic activity of $TiO_2$ toward degrading the phenanthrene and pyrene on soil surfaces. Experimental results indicated that photocatalytic degradation of phenanthrene and pyrene fitted the pseudo-first-order kinetics.

The pseudo-first-order kinetics form is:

$$-\ln\frac{C_t}{C_0} = kt \tag{1}$$

where $C_0$ and $C_t$ are the phenanthrene and pyrene concentrations at time zero and $t$, respectively, and $k$ is the rate constant.

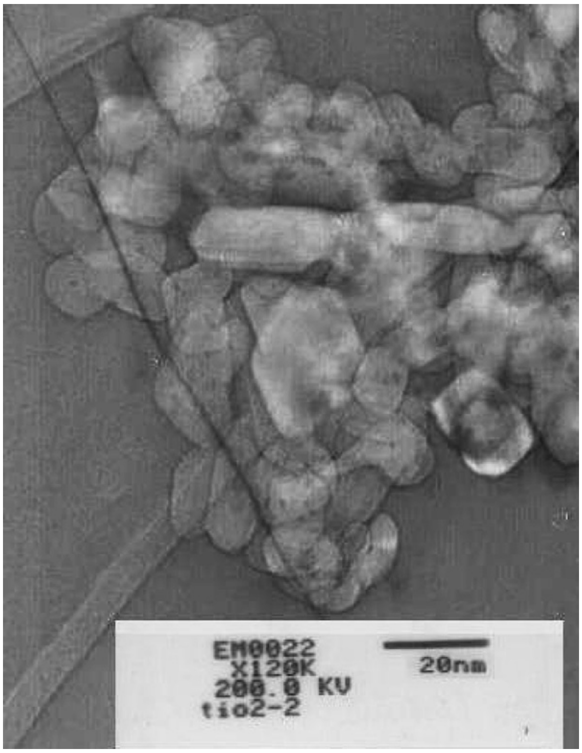

**Fig. 3.** Transmission electron microscopy (TEM) of nanometer rutile $TiO_2$ after calcination.

Half-life $t_{1/2}$ was calculated using Eq. (2) which was derived from Eq. (1) by replacing $C_t$ with $C_0/2$:

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

The pseudo-first-order rate constant ($k$) in the presence of 0, 1%, 2%, 3% and 4% $TiO_2$ in soil were listed in Table 3.

It was found that the rate constants of phenanthrene and pyrene in the absence of nanometer rutile $TiO_2$ were 0.0131 and 0.0151 $h^{-1}$, respectively. When nanometer rutile $TiO_2$ dosage increases from 1% to 2%, the rate constants of phenanthrene and pyrene increase from 0.0137 and 0.0162 $h^{-1}$ to 0.0147 and 0.0175 $h^{-1}$, respectively; however, further increase in $TiO_2$ dosage results in a slight decrease in the rate constants of phenanthrene and pyrene to 0.0139 and 0.0163 $h^{-1}$, respectively. This indicates that nanometer rutile $TiO_2$ is capable of promoting the degradation of PAHs on soil surfaces.

Many studies have demonstrated that the rates of photocatalytic degradation of organic pollutants on soil surfaces are strongly affected by the dosage of the $TiO_2$ used [31]. Adequate

**Table 3**
Kinetic parameters for the photocatalytic degradation of phenanthrene and pyrene on soil surfaces at different $TiO_2$ dosages.

| Compound | Catalyst dosage (wt%) | $k$ ($h^{-1}$) ± S.D. | $t_{1/2}$ (h) |
|---|---|---|---|
| Phenanthrene | 0 | 0.0131 ± 0.00014 | 52.90 |
| | 1 | 0.0137 ± 0.00007 | 50.59 |
| | 2 | 0.0147 ± 0.00035 | 47.15 |
| | 3 | 0.0142 ± 0.00021 | 48.81 |
| | 4 | 0.0139 ± 0.00017 | 49.86 |
| Pyrene | 0 | 0.0151 ± 0.00007 | 45.90 |
| | 1 | 0.0162 ± 0.00035 | 42.78 |
| | 2 | 0.0175 ± 0.00014 | 39.61 |
| | 3 | 0.017 ± 0.00021 | 40.77 |
| | 4 | 0.0163 ± 0.00007 | 42.52 |

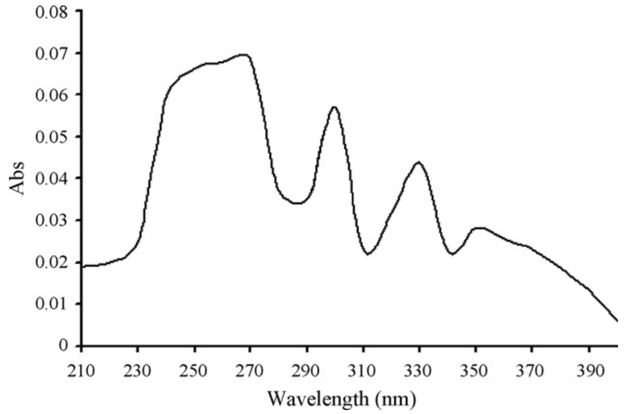

**Fig. 4.** The molar absorption spectrum of phenanthrene on soil surfaces.

dosage of nanometer rutile $TiO_2$ increases the generation rate of electron–hole pairs; thus, the formation of superoxide radical anion ($O_2^{\bullet-}$) for enhancing the photodegradation. However, an excess dosage of nanometer rutile $TiO_2$ decreases the light penetration via increasing the depth of soil and hence reduces photocatalytic rate. On the basis of the experiments discussed above, a catalyst dosage of 2% was chosen as the optimal one for further studies.

It is well established that the photodegradation of organic pollution on soil surfaces includes direct photolysis and photocatalytic oxidation [12]. As shown in Table 3, the results indicate that the photodegradation of pyrene is higher than phenanthrene. There are two reasons contributing to results: firstly, according to photochemical theory, the direct photolysis of phenanthrene and pyrene is highly dependent on their molar absorption spectra on soil surfaces, Xia et al. has reported the similar result in the liquid phase [26]. It can be seen in Figs. 4 and 5, that the phenanthrene absorption peaks have a fewer number than that of pyrene in the range of 253.7–400 nm. Hence, the more absorption peaks the pyrene molecules have, the more easily the pyrene molecules degrade. Secondly, the "oxidation-half-wave-potential" ($E_{1/2}$) illustrates the difficulty of photocatalytic oxidation of the PAHs. The lower $E_{1/2}$ is, the more easily PAHs can be oxidized. The oxidation-half-wave-potentials are 1.50 and 1.54 for phenanthrene and pyrene, respectively [29]. The obvious difference of $E_{1/2}$ does not exist between phenanthrene and pyrene. Therefore, the photocatalytic degradation of pyrene is slightly faster than that of phenanthrene on soil surfaces in the presence of the nanometer rutile $TiO_2$ according to their absorption spectra in soil and oxidation-half-wave-potential (Table 3).

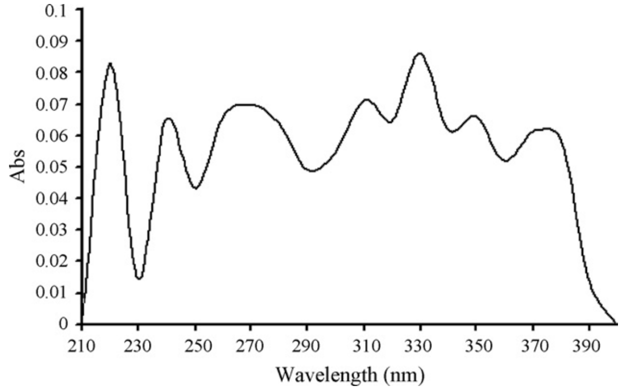

**Fig. 5.** The molar absorption spectrum of pyrene on soil surfaces.

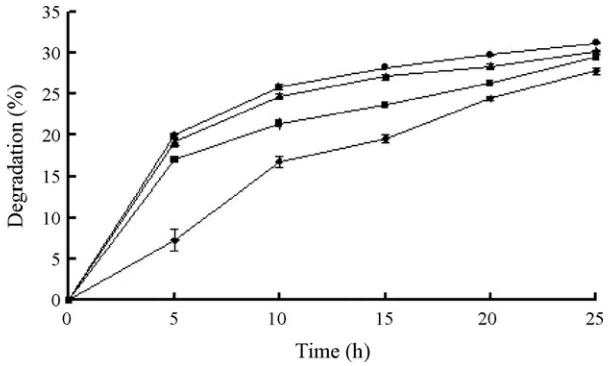

**Fig. 6.** Effect of $H_2O_2$ on phenanthrene degradation: (◆) 0%, (■) 10%, (▲) 20%, and (●) 30%.

### 3.3. *Effect of $H_2O_2$*

Hydrogen peroxide has been shown to accelerate the degradation of organic pollution, depending on its concentration and the nature of reductants [30]. The effect of $H_2O_2$ in the range of 0–30% (w/w) on the degradation of phenanthrene and pyrene was examined over 25 h. The results are shown in Figs. 6 and 7. The addition of $H_2O_2$ from 0% to 30% (w/w) leads to an increase in degradation of phenanthrene and pyrene from 27.54 ± 0.35% and 33.59 ± 0.64% to 32.49 ± 0.02% and 38.70 ± 0.05%, respectively. The da Rocha et al. [32] had reported that the degradations of phenanthrene were 36.43% for white light and 38.88% for black light and the degradations of pyrene were 52.17% for white light and 29.67% for black light in the presence of $H_2O_2$. Some factors such as the main components of experimental samples, the sample depths, the size of sample particle, the temperature within the chamber and the crystalline of $TiO_2$, etc. can influence the effect of photocatalytic degradation of PAHs. Hence, the photocatalytic degradation of PAHs in this research is different from that of Rocha et al.'s research. It is evident that the degradation of PAHs on soil surfaces increases with increasing $H_2O_2$ concentration. The observed enhancement by $H_2O_2$ of phenanthrene and pyrene degradation was due to both the increase of soil moisture and the oxidative effect of hydroxyl radicals formed from the $H_2O_2$.

The photodegradation of phenanthrene and pyrene could increase with increasing soil moisture. Hilarides et al. [33], Shelton and Parkin [34], Frank et al. [35] and Graebing et al. [36] have reported that the photodegradation of organic pollution could increase with increasing soil moisture. There are two probable reasons contributing to this. Firstly, the superoxide radical anion ($O_2^{\bullet-}$) and hole can react with water ($H_2O$) to produce hydroxyl radicals ($OH^{\bullet}$) which can enhance the degradation of phenanthrene and pyrene on soil surfaces. Secondly, there is a direct radiation

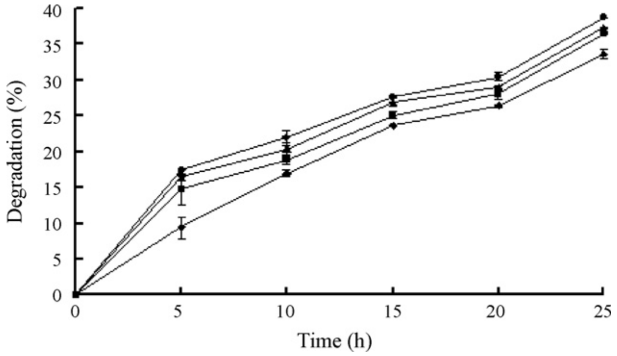

**Fig. 7.** Effect of $H_2O_2$ on pyrene degradation: (◆) 0%, (■) 10%, (▲) 20%, and (●) 30%.

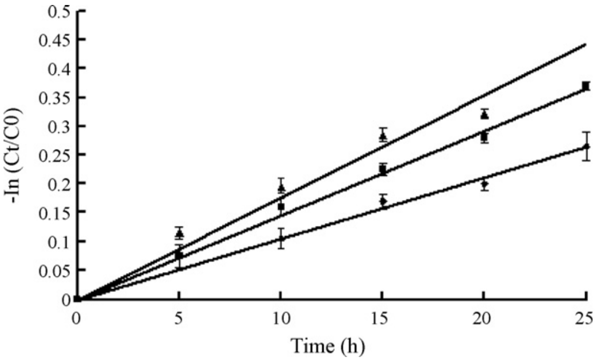

**Fig. 8.** Degradation kinetics of phenanthrene on soil surfaces under different light intensities: (◆) 119 $\mu$W/cm$^2$, (■) 238 $\mu$W/cm$^2$, and (▲) 357 $\mu$W/cm$^2$.

effect; water greatly increases the amount of radiation absorbed in the soil.

$H_2O_2$ could also increase the formation rate of hydroxyl radicals in two ways. Firstly, $H_2O_2$ could enhance the degradation by providing additional hydroxyl radicals through trapping of photogenerated electrons shown in Eq. (3) [37]. Secondly, the self-decomposition by illumination would also produce hydroxyl radicals shown in Eq. (4) [37,38].

$$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet \tag{3}$$

$$H_2O_2 + h\gamma \rightarrow 2OH^\bullet \tag{4}$$

### 3.4. *Effect of light intensity*

UV light intensity is an important factor in the process of photocatalytic degradation. The effect of the UV light intensity (119–357 $\mu$W/cm$^2$) on the degradation of phenanthrene and pyrene on soil surfaces was studied in the presence of $TiO_2$. It is found that all the reactions still follow the first-order kinetics (Figs. 8 and 9). The degradation rate constants with a light intensity of 119, 238 and 357 $\mu$W/cm$^2$ are 0.0106 ($R^2 = 0.9827$), 0.0147 ($R^2 = 0.9955$) and 0.0177 ($R^2 = 0.9639$) $h^{-1}$ for phenanthrene and 0.0126 ($R^2 = 0.9827$), 0.0175 ($R^2 = 0.9834$) and 0.0192 ($R^2 = 0.9745$) $h^{-1}$ for pyrene, respectively.

Apparently, UV light intensity has a positive effect on the rate of PAHs photodegradation. This phenomenon may be explained as following: under the higher light intensity, the enhancement was considerably higher because that the electron–hole formation is predominant and, hence, electron–hole recombination is negligible; however, at lower light intensity, electron–hole pair separation competes with recombination which in turn decreases the formation of free radicals, thereby, causing less effect on the degradation of the phenanthrene and pyrene on soil surfaces [39].

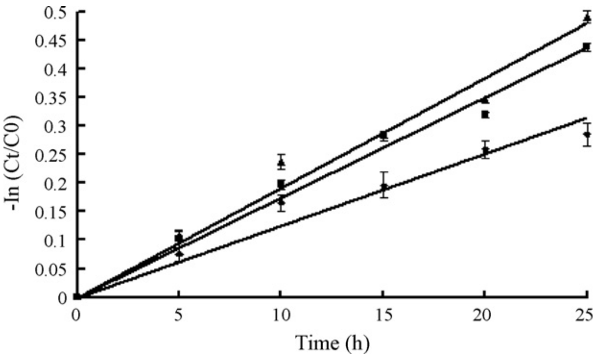

**Fig. 9.** Degradation kinetics of pyrene on soil surfaces under different light intensities: (◆) 119 $\mu$W/cm$^2$, (■) 238 $\mu$W/cm$^2$, and (▲) 357 $\mu$W/cm$^2$.

**Table 4**
Effect of humic acid on photocatalytic degradation of phenanthrene and pyrene on soil surfaces with 2% $TiO_2$.

| Compound | Humic acid (mg kg$^{-1}$) | $k$ (h$^{-1}$) ± S.D. | $t_{1/2}$ (h) |
|---|---|---|---|
| Phenanthrene | 0 | 0.0147 ± 0.00035 | 47.15 |
| | 10 | 0.0154 ± 0.00023 | 45.01 |
| | 20 | 0.0165 ± 0.00046 | 42.01 |
| | 30 | 0.017 ± 0.00037 | 40.77 |
| | 40 | 0.0173 ± 0.00009 | 40.06 |
| Pyrene | 0 | 0.0175 ± 0.00014 | 39.61 |
| | 10 | 0.0186 ± 0.00031 | 37.26 |
| | 20 | 0.019 ± 0.00024 | 36.48 |
| | 30 | 0.0192 ± 0.00025 | 36.10 |
| | 40 | 0.0195 ± 0.0008 | 35.54 |

### 3.5. *Effect of humic acids*

Humic acids are complex organic molecules produced by the decomposition of plant and animals remained in soil, they can either enhance [40–44] or inhibit photolysis [45,46]. The effect of humic acids on the photocatalytic degradation of phenanthrene and pyrene was studied when the concentration increased from 0 to 40 mg kg$^{-1}$. The pseudo-first-order rate constants were 0.0147, 0.0154, 0.0165, 0.017 and 0.0173 h$^{-1}$ for phenanthrene and 0.0175, 0.0186, 0.019, 0.0192 and 0.0195 h$^{-1}$ for pyrene, respectively, as listed in Table 4.

It can be seen from Table 4, humic acids have accelerating effects on the photocatalytic degradation of phenanthrene and pyrene in the presence of $TiO_2$. Humic acids can enhance the degradation of phenanthrene and pyrene in two ways. Firstly, Zepp and Schlotzhauer [47] have found that the photosensitized reactions can be sensitized by humic substances (HS) only when the pollutants with triplet state energies are less than 250 kJ mol$^{-1}$. Phenanthrene and pyrene with triplet state energies are less than 250 kJ mol$^{-1}$ [48], the absorption of light by HA can lead to rapid photosensitized reactions of phenanthrene and pyrene via energy transfer from molecules in its triplet state. Secondly, ultraviolet irradiation also induces a variety of photochemical changes in HA and leads to production of reactive oxygen species (e.g., singlet oxygen, free radicals) [49,50]. These reactive oxygen species could oxidize the phenanthrene and pyrene on soil surfaces.

## 4. Conclusions

The photocatalytic degradation of phenanthrene and pyrene on soil surfaces in the presence of nanometer rutile $TiO_2$ under UV-light irradiation followed pseudo-first-order kinetics. Photocatalytic degradation of phenanthrene and pyrene were enhanced by $TiO_2$ dosage from 0 to 4 wt%. A catalyst dosage of 2% was chosen as the optimal one. The degradation rate of the phenanthrene and pyrene on soil surfaces was related to their absorption spectra in soil and oxidation-half-wave-potential. The increases of the addition of $H_2O_2$, the concentration of HA and irradiation intensity sped up the photocatalytic degradation of phenanthrene and pyrene on soil surfaces in the presence of nanometer rutile $TiO_2$.

The obtained results demonstrate that the phenanthrene and pyrene on soil surfaces can be decomposed by the method of photocatalytic degradation in the presence of nanometer rutile $TiO_2$. Meanwhile, some important parameters (such as catalyst dosage, the addition of $H_2O_2$, the concentration of HA and light intensity, etc.) needed to be monitored in order to control the degradation.

## Acknowledgements

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## References

[1] A. Bjorseth, G. Lunde, A. Lindskog, Long-range transport of polycyclic aromatic hydrocarbons, Atmos. Environ. 13 (1979) 45–53.

[2] W.F. Günther, G.E. Jones, Two stage mineralization of phenanthrene by estuarine enrichment cultures, Appl. Environ. Microbiol. 54 (1988) 929–936.

[3] B. Gevao, K.C. Jones, T.J. Hamilton, Polycyclic aromatic hydrocarbon (PAH) deposition in a small rural lake Cumbria, UK, Sci. Total Environ. 215 (1998) 231–242.

[4] F. Haeseler, D. Blanchet, V. Druelle, P. Werner, J.P. Vandecasteele, Ecotoxicological assessment of soils of former manufactured gas plant sites: bioremediation potential and pollutant mobility, Environ. Sci. Technol. 24 (1999) 4379–4384.

[5] Y.Z. Gao, L.Z. Zhu, Plant uptake, accumulation and translocation of phenanthrene and pyrene in soils, Chemosphere 55 (2004) 1169–1178.

[6] M.A. Heitkamp, C.E. Cerniglia, Mineralization of polycyclic aromatic hydrocarbons by a bacterium isolated from sediment below an oil field, Appl. Environ. Microbiol. 54 (1988) 1612–1614.

[7] Y. Jian, L. Wan, P.F. Peter, H.T. Yu, Photomutagenicity of 16 polycyclic aromatic hydrocarbons from the US EPA priority pollutant list, Mutat. Res. 557 (2004) 99–108.

[8] D.J. Freeman, F.C.R. Cattell, Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons, Environ. Sci. Technol. 24 (1990) 1581–1585.

[9] F. Daniele, V. Ivano, C.G. Sun, E. Colin, C.M. Snape, E.F. Anthony, Source apportionment of polycyclic aromatic hydrocarbons in a coastal lagoon by molecular and isotopic characterization, Mar. Chem. 84 (2004) 123–135.

[10] X.H. Li, L.L. Ma, X.F. Liu, S. Fu, H.X. Cheng, X.B. Xu, Polycyclic aromatic hydrocarbon in urban soil from Beijing, China, J. Environ. Sci. 18 (2006) 944–950.

[11] A.M. Kipoponlou, E. Manoli, C. Samara, Bioconcentration of polycyclic aromatic hydrocarbons in vegetables grown in an industrial area, Environ. Pollut. 106 (1999) 369–380.

[12] X. Zhao, X. Quan, H.M. Zhao, S. Chen, J.W. Chen, Y.Z. Zhao, Different effects of humic substances on photodegradation of p,p′-DDT on soil surfaces in the presence of $TiO_2$ under UV and visible light, J. Photochem. Photobiol. A 167 (2004) 177–183.

[13] X. Quan, X. Zhao, H.M. Zhao, S. Chen, J.W. Chen, Y.Z. Zhao, Enhancement of p,p′-DDT photodegradation on soil surfaces using $TiO_2$ induced by UV-light, Chemosphere 60 (2005) 266–273.

[14] M.M. Higarashi, W.F. Jardim, Remediation of pesticide contaminated soil using $TiO_2$ mediated by solar light, Catal. Today 76 (2002) 201–207.

[15] E. Pelizzetti, V. Carlin, V. Maurino, C. Minero, M. Dolci, A. Marchesini, Degradation of atrazine in soil through induced photocatalytic processes, Soil Sci. 150 (1990) 523–526.

[16] E. Pelizzetti, C. Minero, V. Carlin, E. Borgarello, Photocatalytic soil decontamination, Chemosphere 25 (1992) 343–350.

[17] B. David, P. Boule, Phototransformation of hydrophobic pollutants in aqueous medium I––PAHs adsorbed on silica, Chemosphere 26 (1993) 1617–1630.

[18] C.A. Reyes, M.E. Sigman, R. Arce, J.T. Barbas, R. Dabestani, Photochemistry of acenaphthene at a silica gel/air interface, J. Photochem. Photobiol. A: Chem. 112 (1998) 277–283.

[19] C.A. Reyes, M. Medina, C.Z. Hernandez, M.Z. Cedeno, R. Arce, O. Rosario, D.M. Sterffenson, I.N. Ivanov, M. Sigman, R. Dabestani, Photochemistry of pyrene on unactivated and activated silica surfaces, Environ. Sci. Technol. 34 (2000) 415–421.

[20] S. Wen, J.C. Zhao, G. Sheng, J. Fu, P. Peng, Photocatalytic reactions of phenanthrene at $TiO_2$/water interfaces, Chemosphere 46 (2002) 871–877.

[21] S. Wen, J.C. Zhao, G. Sheng, J. Fu, P. Peng, Photocatalytic reactions of pyrene at $TiO_2$/water interfaces, Chemosphere 50 (2003) 111–119.

[22] Y. Wang, C.S. Liu, F.B. Li, C.P. Liu, J.B. Liang, Photodegradation of polycyclic aromatic hydrocarbon pyrene by iron oxide in solid phase, J. Hazard. Mater. 62 (2009) 716–723.

[23] J.C. Irland, B. Dávila, H. Moreno, S.K. Fink, S. Tassos, Heterogeneous photocatalytic decomposition of polyaromatic hydrocarbons over titanium dioxide, Chemosphere 30 (1995) 965–984.

[24] B. Pal, M. Sharon, Photodegradation of polyaromatic hydrocarbons over thin film of $TiO_2$ nanoparticles; a study of intermediate photoproducts, J. Mol. Catal. A: Chem. 160 (2000) 453–460.

[25] M.J. García-Martínez, L. Canoira, G. Blázquez, I. Da Riva, R. Alcántara, J.F. Llamas, Continuous photodegradation of naphthalene in water catalyzed by $TiO_2$ supported on glass Raschig rings, Chem. Eng. J. 110 (2005) 123–128.

[26] X.H. Xia, G.C. Li, Z.F. Yang, Y.M. Chen, G.H. Huang, Effects of fulvic acid concentration and origin on photodegradation of polycyclic aromatic hydrocarbons in aqueous solution: importance of active oxygen, Environ. Pollut. 157 (2009) 1352–1359.

[27] G.S. Li, L.P. Li, J. Boerio-Goates, B.F. Woodfield, High purity anatase $TiO_2$ nanocrystals: near room-temperature synthesis, grain growth kinetics, and surface hydration chemistry, J. Am. Chem. Soc. 127 (2005) 8659–8666.

[28] M. Pal, J. Garciá-Serrano, P. Santiago, U. Pal, Size-controlled synthesis of spherical $TiO_2$ nanoparticles: morphology, crystallization, and phase transition, J. Phys. Chem. C 111 (2007) 96–102.

[29] X.M. Pan, L.M. Chen, Y. Cheng, S.H. Qi, G.Y. Sheng, Photodegradation of PAHs in aerosols sorbed on quartz filters, J. Fudan Univ. (Nat. Sci.) 38 (1999) 119–122.

[30] C.M. So, M.Y. Cheng, J.C. Yu, P.K. Wong, Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation, Chemosphere 46 (2002) 905–912.

[31] D.B. Dong, P.J. Li, X.J. Li, Q. Zhao, Y.Q. Zhang, C.Y. Jia, P. Li, Investigation on the photocatalytic degradation of pyrene on soil surfaces using nanometer anatase $TiO_2$ under UV irradiation, J. Hazard. Mater. 174 (2010) 859–863.

[32] O.R.S. da Rocha, R.F. Dantas, M.M.M.B. Duarte, M.M.L. Duarte, V.L. da Silva, Oil sludge treatment by photocatalysis applying black and white light, Chem. Eng. J. (2009), doi:10.1016/j.cej.2009.10.050.

[33] R.J. Hilarides, K.A. Gray, J. Gurzetta, N. Cortellucci, C. Sommer, Radiolytic degradation of 2,3,7,8-TCDD in artificially contaminated soils, Environ. Sci. Technol. 28 (1994) 2249–2258.

[34] D.R. Shelton, T.B. Parkin, Effect of moisture on sorption and biodegradation of carbofuran in soil, J. Agric. Food Chem. 39 (1991) 2063–2068.

[35] M.P. Frank, P. Graebing, J.S. Chib, Effect of soil moisture and sample depth on pesticide photolysis, J. Agric. Food Chem. 50 (2002) 2607–2614.

[36] P. Graebing, M.P. Frank, J.S. Chib, Soil photolysis of herbicides in a moisture- and temperature-controlled environment, J. Agric. Food Chem. 51 (2003) 4331–4337.

[37] H.M. Coleman, V. Vimonses, G. Leslie, R. Amal, Degradation of 1,4-dioxane in water using $TiO_2$ based photocatalytic and $H_2O_2$/UV processes, J. Hazard. Mater. 146 (2007) 496–501.

[38] J.M. Lee, M.S. Kim, B. Hwang, W. Bae, B.W. Kim, Photodegradation of Acid Red 114 dissolved using a photo-Fenton process with $TiO_2$, Dyes Pigments 56 (2003) 59–67.

[39] D. Bahnemann, P. Boule, Photocatalytic degradation of polluted waters, in: The Handbook of Environmental Chemistry, vol. 2. Part L: Environmental Photochemistry, Springer, Berlin, 1999.

[40] C.X. Wang, A. Yediler, A. Peng, A. Kettrup, Photodegradation of phenanthrene in the presence of humic substances and hydrogen peroxide, Chemosphere 30 (1995) 501–510.

[41] M. Kamiya, K. Kameyama, Photochemical effects of humic substances on the degradation of organophosphorus pesticides, Chemosphere 36 (1998) 2337–2344.

[42] K.T. Huster, P.N. Moza, A. Kettrup, Photochemical degradation of carboxin and oxycarboxin in the presence of humic substances and soil, Chemosphere 38 (1999) 3423–3429.

[43] Y.B. Si, J. Zhou, H.M. Chen, D.M. Zhou, Y.D. Yue, Effect of humic substances on photodegradation of bensulfuron-methyl on dry soil surfaces, Chemosphere 56 (2004) 967–972.

[44] K.H. Chan, W. Chu, Effect of humic acid on the photolysis of the pesticide atrazine in a surfactant-aided soil-washing system in acidic condition, Water Res. 39 (2005) 2154–2166.

[45] J. Bachman, H. Patterson, Photodecomposition of the carbamate pesticide carbofuran: kinetics and the influence of dissolved organic matter, Environ. Sci. Technol. 33 (1999) 874–881.

[46] A.J. Gong, C.M. Ye, X.J. Wang, Z.F. Lei, J.M. Liu, Dynamics and mechanism of ultraviolet photolysis of atrazine on soil surfaces, Pest Manage. Sci. 57 (2001) 380–385.

[47] R.G. Zepp, P.F. Schlotzhauer, Photoreactivity of selected aromatic hydrocarbons in water, in: P.R. Jones, P. Leber (Eds.), Polynuclear Aromatic Hydrocarbons, Ann Arbor Science Publishers, Ann Arbor, MI, 1979.

[48] G.B. Rong, L.B. Yuan, Q.R. Wang, Y. Yang, M.H. Li, Senior Organic Chemistry, 2007, Shanghai.

[49] J.R. Garbin, D.M.B.P. Milori, M.L. Simões, W.T.L. Silva, L.M. Neto, Influence of humic substances on the photolysis of aqueous pesticide residues, Chemosphere 66 (2007) 1692–1698.

[50] Y. Chen, C. Hu, J.H. Qu, M. Yang, Photodegradation of tetracycline and formation of reactive oxygen species in aqueous tetracycline solution under simulated sunlight irradiation, J. Photochem. Photobiol. A: Chem. 197 (2008) 81–87.