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Photochemical behavior of benzo[a]pyrene on soil surfaces under UV light irradiation

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Abstract: The rates of photodegradation and photocatalysis of benzo[a]pyrene (BaP) on soil surfaces under UV light have been studied. Different parameters such as temperature, soil particle sizes, and soil depth responsible for photodegradation, catalyst loads and wavelength of UV irradiation blamed for photocatalysis have been monitored. The results obtained indicated that BaP photodegradation follows pseudo-first-order kinetics. BaP photodegradation was the fastest at 30°C. The rates of BaP photodegradation at different soil particle size followed the order: less than 1 mm > less than 0.45 mm > less than 0.25 mm. When the soil depth increased from 1 mm to 4 mm, the half-life increased from 13.23 d to 17.73 d. The additions of TiO₂ or Fe₂O₃ accelerated the photodegradation of BaP, and the photocatalysis of BaP follows pseudo-first-order kinetics. Changes in catalyst loads of TiO₂ (0.5%, 1%, 2%, and 3% (wt)) or Fe₂O₃ (2%, 5%, 7%, and 10% (wt)) did not significantly affect the degradation rates. Both BaP photocatalysis in the presence of TiO₂ and Fe₂O₃ were the fastest at 254 nm UV irradiation.

Keywords: photodegradation; photocatalysis; benzo[a]pyrene; UV-irradiation

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of major contaminants that are ubiquitous in the environment. In industrial countries, anthropogenic activities are a principal source of PAHs in soil (Jones *et al.*, 1989a, b). PAHs, especially those with four or more rings and their metabolites, are considered as hazardous pollutants due to their toxicity, mutagenicity and carcinogenicity, and are classified as compounds with significant human health risk (Kalf *et al.*, 1997). Benzo[a]pyrene (BaP) is a typical high molecular weight PAH with five rings, and it has been classified by the US Environmental Protection Agency (USEPA) as a priority pollutant (Juhász and Naidu, 2000). BaP is one of the most potential carcinogenic PAHs, and as such, is the most studied compound of the PAH class (Kot-Wasik *et al.*, 2004).

The main processes which successfully remove and eliminate PAHs from the environment include: microbiological transformation and degradation, volatilization, photo-oxidation, chemical oxidation, bioaccumulation and biological uptake (Saftic *et al.*, 1992; Wilson and Jones, 1993). However, some of the HMW PAHs are recalcitrant, as biological processes are always ineffective in removing them. Photodegradation is an important transformation pathway for most PAHs in the environment, because this process preferentially attacks the same tertiary carbon atoms that tend to block biodegradation (Atlas and Bartha, 1998).

BaP photochemical behaviour has essentially been studied in different liquid media (Fasnacht, 2002,

2003), in diesel particulate matter and on the various adsorbent surfaces (alumina, silica gel, controlled pore size glass, flaked graphite and coal stack ashes) from the vapor phase (Yokley *et al.*, 1986; Matsuzawa *et al.*, 1998, 2001), but little is known about the photochemical behaviour of BaP on soil surfaces.

The photodegradation of organic compounds on soil are affected by many factors. Miller and Zepp (1983) found that soil particle size, mineral composition, light absorption characteristics, and moisture content affected the nature of soil photoreactions of pesticides. Because light penetrating into soils is very limited (Miller *et al.*, 1989a; Herbert and Miller, 1990) and is wavelength dependent, the fraction of total compound actually exposed to light depends on the type of soil, the thickness of the soil layer, and the light absorption spectrum of the compound. Since temperature and humidity strongly influence the compound's sorption behavior and rate of disappearance from soil (Goss and Eisenreich, 1996), these parameters also need to be considered.

The feasibility of using heterogeneous photocatalysis in the treatment of highly contaminated soil was recently demonstrated. Zhao *et al.* (2004b) found that the addition of α -Fe₂O₃ or TiO₂ enhanced the photocatalytic degradation of γ -HCH on soil surfaces. However, the results of Higarashi and Jardim (2002) contradicted this as they found that both the catalyst and the Diuron concentration had no influence on the kinetics of the pesticide degradation.

In this paper, main factors that influence the photodegradation of BaP on soil surfaces such as temperature, soil particle size and soil thickness were

investigated under irradiation of UV light. In addition, the effects of Fe₂O₃ or TiO₂ concentration and UV-irradiation wavelength on BaP photocatalytic degradation were also examined.

1 Materials and methods

1.1 Chemicals

Benzo[a]pyrene (BaP, 97%) was purchased from Fluka, Germany, and used without further purification. Table 1 outlines the physical-chemical properties of BaP (Sims and Overcash, 1983). Methanol (HPLC grade) was purchased from Shandong Yuwang Company, China. Hexane and dichloromethane were purchased from Tianjin Concord Technical Company, China. TiO₂ particles were purchased from Degussa (P25, anatase, surface area about 50 m²/g, mean diameter 20 nm). Fe₂O₃ was purchased from Beijing Chemical Company, China.

Table 1 Structure and physico-chemical properties of BaP

No. of rings	Mp, °C	Bp, °C	Sol, mg/L	lg K _p	Vapour pressure, torr at 20°C
5	179	496	0.0038	6.04	5.0 × 10 ⁻⁷

Notes: Mp, Melting point; Bp, boiling point; Sol, aqueous solubility; lgK_p, logarithm of the octanol: water partitioning coefficient

1.2 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 air-drying, soil samples were divided into different particle sizes by passing them through 1 mm, 0.45 mm and 0.25 mm sieves, respectively. To prepare a sterile soil, the sieved soil was autoclaved at 121°C for 30 min twice, and stored in the dark before use. The characteristics of the soil are shown in Table 2. Mineral components of the soil were analyzed by X-ray fluorescence (XRF) and the results are listed in Table 3.

Table 2 Characteristics of the soil

pH	TOC, %	Texture, %			Bulk density, g/cm ³
		Sand	Silt	Clay	
6.8	1.78	21.4	46.5	32.1	2.53

The soil sample was spiked with a methanol solution of BaP, mixed thoroughly and then air-dried for the evaporation of methanol. This method gave a uniform BaP distribution in the soil at 40 mg/kg.

1.3 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

Table 3 Main components of the soil

Component	Content	Component	Content	Component	Content
As, mg/kg	8.95	Mn, mg/kg	577.70	Zn, mg/kg	70.45
Ba, mg/kg	676.65	Ni, mg/kg	26.70	Zr, mg/kg	276.95
Ce, mg/kg	123.00	P, mg/kg	630.30	SiO ₂ , %	68.22
Cl, mg/kg	49.55	Pb, mg/kg	37.00	Al ₂ O ₃ , %	13.41
Co, mg/kg	11.70	Rb, mg/kg	109.75	Fe ₂ O ₃ , %	4.19
Cr, mg/kg	67.65	Sr, mg/kg	189.75	MgO, %	1.13
Cu, mg/kg	36.70	Th, mg/kg	13.00	CaO, %	1.16
Ga, mg/kg	17.90	Ti, mg/kg	4459.40	Na ₂ O, %	1.78
La, mg/kg	65.90	V, mg/kg	76.35	K ₂ O, %	2.43

between the lamps and samples was 150 mm. UV lamps (20 W, model UV-A, UV-B and UV-C) were changed for wavelength variation, and available wavelengths in the experiment were 254, 310, and 365 nm, respectively. Petri dishes containing experimental soil samples were placed on the shelves for photo irradiation. The temperature within the chamber was adjusted through refrigerator, heater, and fans in the chamber. During different intervals of the exposure, three replicate samples and dark control samples were taken from the chamber and transferred into 100 ml Teflon tubes.

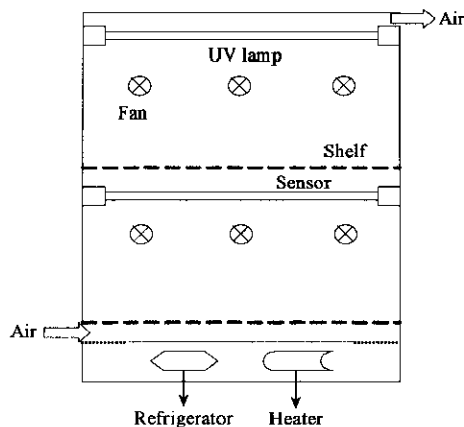


Fig.1 Device for photodegradation of benzo[a]pyrene on soil surfaces

1.4 Photo irradiation

1.4.1 Effect of chamber temperature

To study the influence of chamber temperature, 5 g of soil samples of 1 mm particle size were evenly spread on the Petri dishes (9 cm in diameter) and replicated thrice. Chamber temperature varied from 20°C to 30°C. Light proof Petri dishes containing the same soil samples were set as control for the measurement of non photodegraded BaP loss throughout all the experiments. Wavelength of UV lamps used throughout all the experiments was 254

nm unless otherwise indicated. All the Petri dishes were randomly placed on the shelf, and sampling was performed during the irradiation with the sampled soil sacrificed.

1.4.2 Effect of soil particle size

To study the influence of soil particle sizes on the photodegradation of BaP, 5 g of soil samples of particle sizes 0.25, 0.45, and 1 mm, respectively, were evenly spread on the Petri dishes (9 cm in diameter) and replicated thrice. Chamber temperature was 30°C throughout all the experiments. Irradiation, sampling, and analyses were then performed as described above.

1.4.3 Effect of soil depth

To test the effect of soil depth on photodegradation of BaP, soil samples (size = 1 mm) at a weight of 2.5, 4, 5, 6, and 10 g were evenly spread on the Petri dishes (9 cm diameter), respectively. Three replicates were prepared. Soil depth was calculated using soil weight, soil bulk density, and bottom area of the Petri dishes. Irradiation, sampling, and analyses were then performed as described above.

1.4.4 Photocatalytic degradation of BaP

To study the photocatalytic degradation of BaP in the soil, soil samples were added with TiO₂ or Fe₂O₃ to test their catalytic effects. Soil samples in the Petri dishes at a weight of 5 g and a particle size of 1 mm were added with 0.5%, 1.0%, 2.0%, and 3.0% of TiO₂ (wt) or 2.0%, 5.0%, 7.0%, and 10.0% of Fe₂O₃ (wt). Each sample was replicated thrice. Irradiation, sampling, and analyses were then performed as described above.

To test the synergistic effect of irradiation wavelength and catalytic compounds, the wavelengths were varied with 254, 310, and 365 nm, and amounts of TiO₂ or Fe₂O₃ added was 2%, or 7%, respectively.

1.5 Soil extraction and HPLC analysis

Concentrations of the BaP in irradiated and nonirradiated 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°C. The mixture was then centrifuged at 4000 r/min for 5 min to separate the supernatant from the soil. 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 2 ml mixture 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 BaP in methanol solutions was done by an HPLC (Hewlett-Packard 1090-II Series) 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, and detector wavelength was 295 nm. The

injection volume was 10 µl. The extraction recovery of BaP under given conditions was higher than 85% (recovery experiments).

2 Results and discussion

2.1 Effect of chamber temperature

The photodegradation loss can be obtained from the following calculation:

$$L = (C_N - C_t)/C_0 \times 100\% \quad (1)$$

Where L is the photodegradation loss at time t , C_0 is the original concentration of BaP, C_N is the concentration of BaP non-irradiated soil sample at time t , C_t is the concentration of BaP irradiated sample at time t .

The photodegradation losses of BaP versus time on soil surfaces at the temperature 30°C, 25°C and 20°C are shown in Fig.2. BaP degradation was the fastest at 30°C, while the difference was not significant between 25°C and 20°C. The photodegradation loss of BaP at the three temperatures increased rapidly during the first 8 d of the experiment, with the degradation loss being about 40% at 30°C and about 20% at 25°C and 20°C respectively. Our study showed that temperature greatly influenced the BaP breakdown on the soil surface during UV irradiance. The reasons for this may be that increased temperatures decreased PAHs sorption by soils (Podoll *et al.*, 1989) and increased their solubility and vapour pressure (Miller *et al.*, 1989b). Moreover, temperature may influence the velocity of photochemical reaction. Maliszewska-Kordybach (1993) investigated the effect of temperature on the range and rate of disappearance of four PAHs (fluorine, anthracene, pyrene and chrysene) added as a mixture of pure compounds to two different soils (light loam and loamy sand) and found that an increase in temperature from 10°C to 25°C enhanced the losses of all the four PAHs from both soils. Our study showed similar results as the above, this indicates that increased temperature may enhance the degradation loss of PAHs in soil. Coover and Sims (1987) studied the influence of temperature on the apparent loss kinetics of 16 PAHs in an unacclimated agricultural soil and found that increasing the soil

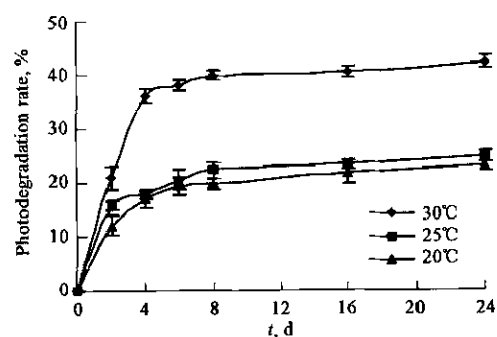


Fig.2 Effect of temperature on BaP photodegradation on soil surfaces under UV irradiation

temperature in the range of 10—30°C improved the rate and extent of apparent loss of lower molecular weight PAHs, but had little effect on the loss of five- and six-ring compounds. Our study however showed a different result. The reason for this may be that the soil used in their study was contaminated with a mixture of 16 PAHs, while that of our study was contaminated by only one single PAH, hence antagonistic effects of PAHs did not exist.

2.2 Effect of soil particle size

Soil particle sizes influence the sorption and desorption of PAHs in soil. Therefore, we also used photodegradation losses to show the results. The photodegradation loss can be obtained from the Equation (1). In this study, we chose three different soil particle sizes (diameter less than 1 mm, less than 0.45 mm, and less than 0.25 mm). Fig.3 is a graphical comparison of the BaP photodegradation losses at different soil particle sizes. Clearly, soil particle size influenced the photodegradation. BaP degradation was the fastest when soil particle size was less than 1 mm. These results were similar to those obtained for the photolytic losses of cypermethrin, deltamethrin, and fenvalerate at different soil particle sizes, where the photodegradation loss for diameter less than 1 mm soil sample was the fastest and that for less than 0.25 mm soil sample was the slowest (Yue *et al.*, 1993). Soil particles less than 1 mm are more loosely packed, leaving more room for light to scatter and permeate the soil than the other two soil particle sizes. Our study was performed on air-dried soil, so the photodegradation by hydroxyl radical was almost eliminated. Singlet oxygen plays a main role in photodegradation. The singlet oxygen penetration is dependent upon soil porosity and soil depth. However, a different behavior was observed for PAHs photodegradation in clay soil, where PAHs photodegradation was not affected by particle size (Huang *et al.*, 1997). The particle ranges they studied were 0.05 to 0.08 mm and 0.08 to 0.12 mm, which were too small to express the difference between the particles. In the current experiment, the photodegradation losses of all the treatments did not show any significant

change after 8—10 d irradiation, indicating that direct photodegradation was no longer happening, while indirect photodegradation proceeded slowly.

2.3 Effect of soil depth

Soil depth is an important consideration in a photolysis study. The photodegradation rate is determined not only by photolysis itself but also is a function of the layer thickness (Balmer *et al.*, 2000). Photodegradation of organic contaminants in soil will be restricted to a certain thickness, which depends on many factors such as light wavelength distribution, soil characteristics, and photodegradation mechanism (Miller *et al.*, 1989a; Balmer *et al.*, 2000). In this experiment, five thickness levels (1.0, 1.6, 2.0, 2.4, 4.0 mm) were tested.

BaP photodegradation were fitted to the first-order equation:

$$\ln C_0 / C = kt \tag{2}$$

where C_0 and C are the BaP concentration at time zero and t , respectively, and k is the rate constant. First-order degradation rate constants were determined by analysis. Half-lives $t_{1/2}$ were calculated using Eq.(3) which was derived from Eq.(2) by replacing C with $C_0/2$:

$$t_{1/2} = \ln 2/k = 0.6931/k \tag{3}$$

The results are listed in Table 4. It shows that increasing depth of soil sample leads to an increase in half-life ($t_{1/2}$) and a decrease in rate constant (k). Researchers obtained the similar results (Herbert and Miller, 1990; Balmer *et al.*, 2000; Gong *et al.*, 2001; Frank *et al.*, 2002; Zhao *et al.*, 2004a). Our results showed that the relationship of BaP half-life with soil depth was linear (significant correlation, $p < 0.01$ (Fig. 4). Soil depth had a much great effect on photodegradation in soil because it influenced the light penetration and soil ventilation. Frank *et al.* (2002) studied the effects of soil depth and moisture on niclosamide photolysis. They concluded that when moisture was maintained, only a gradual increase in half-life with soil depth was observed, and the relationship of that increase with depth was strongly linear.

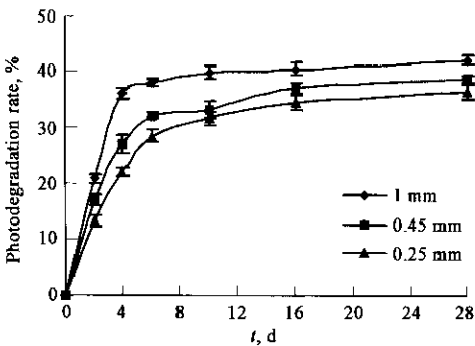


Fig.3 BaP photodegradation of different soil particle sizes under UV irradiation

Table 4 Kinetic parameters for BaP photodegradation at different soil depth

Soil depth, mm	<i>k</i> , 10 ³ d ⁻¹	<i>t</i> _{1/2} , d	<i>r</i>
1.0	5.24	13.23	0.9582
1.6	4.65	14.93	0.9594
2.0	4.58	15.13	0.9551
2.4	4.38	15.82	0.9629
4.0	3.91	17.73	0.9691

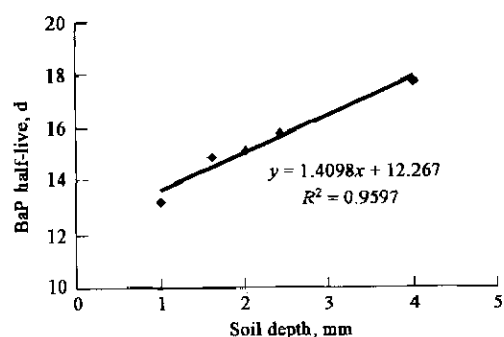


Fig.4 Variation in half-life in relation to soil depth

2.4 Photocatalytic degradation of benzo[a]pyrene

Many studies have been carried out to investigate the TiO_2 photocatalytic degradation of PAHs in aqueous solutions (Das *et al.*, 1994; Ireland *et al.*, 1995; Pal and Sharon, 2000; Wen *et al.*, 2002). All these studies concluded that TiO_2 can efficiently photocatalyse the degradation of PAHs on irradiation with artificial light as well as sunlight. However, the application of the photocatalytic method using TiO_2 to degrade PAHs adsorbed on soil surfaces remains unknown. In our study, different dosages of TiO_2 (0, 0.5%, 1%, 2% and 3% (wt)) were used to evaluate the effect of TiO_2 on photodegradation of BaP on soil surfaces under UV light. The results presented in Table 5 show that TiO_2 accelerated the photodegradation of BaP, but changes in the concentration of TiO_2 from 0.5% to 2% (wt) had no significantly different effect on BaP degradation, demonstrating that 0.5% TiO_2 (wt) or less was enough. The pseudo-first-order rate constants in the presence of 0, 0.5%, 1%, 2% and 3% TiO_2 (wt) in soil were 1.91×10^{-3} , 6.71×10^{-3} , 7.23×10^{-3} , 7.76×10^{-3} , and $7.30 \times 10^{-3} \text{ h}^{-1}$, respectively. These results are similar to the observation by Higarashi and Jardim (2002), who studied the effect of the TiO_2 concentration on the rate of Diuron degradation.

Effects of Fe_2O_3 ranging from 0, 2%, 5%, 7%, to 10% (wt) on BaP photodegradation were investigated. The pseudo-first order constants of BaP photodegradation corresponding to different dosage of Fe_2O_3 are presented in Table 5. The results were similar to the effect of TiO_2 concentration on BaP photodegradation. Changes in the concentration of Fe_2O_3 from 2% to 10% (wt) did not result in any significantly different BaP degradation. However, the concentration of 2% Fe_2O_3 (wt) clearly accelerated the photodegradation of BaP, the pseudo-first-order rate constant was increased from $1.91 \times 10^{-3} \text{ h}^{-1}$ in natural soil to $6.25 \times 10^{-3} \text{ h}^{-1}$. In comparing the rate constants for different dosages of TiO_2 with those of Fe_2O_3 in BaP photodegradation, it can be seen that the photocatalytic degradation rates of BaP in the presence of TiO_2 are slightly higher than those in the presence of Fe_2O_3 . Semiconductors (such as TiO_2 ,

Table 5 Kinetic parameters for the photocatalytic degradation of BaP on soil surfaces under UV light

Photoreactive condition	k , 10^{-3} h^{-1}	$t_{1/2}$, h	r^2
Natural soil sample	1.908	363.22	0.9122
TiO_2 (0.5% wt)	6.713	103.26	0.9620
TiO_2 (1% wt)	7.225	95.94	0.9662
TiO_2 (2% wt)	7.758	89.34	0.9558
TiO_2 (3% wt)	7.300	94.95	0.9655
Fe_2O_3 (2% wt)	6.246	110.97	0.9802
Fe_2O_3 (5% wt)	6.771	102.37	0.9827
Fe_2O_3 (7% wt)	6.942	99.85	0.9630
Fe_2O_3 (10% wt)	6.675	103.84	0.9700

Fe_2O_3 , and ZnO) are important due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and an empty conduction band (Chakrabarti and Dutta, 2004). The content of Fe_2O_3 is higher than other semiconductor oxides (such as TiO_2 , ZnO , MnO_2 , and MgO) in soil, so the effect of Fe_2O_3 on the photodegradation of BaP can not be neglected.

A successful direct photolysis demands two requirements to be met: the emission spectra of the light sources should overlap the spectra of the target compound (Miller and Olejnik, 2001). The effects of different wavelengths on photocatalysis of BaP have been studied under six different conditions: UV irradiation in the presence of TiO_2 and Fe_2O_3 at 254, 310, and 365 nm, respectively. The concentration of TiO_2 and Fe_2O_3 added to soil samples were 2% and 7% (wt), respectively. Fig.5 shows that the influence of wavelengths on photocatalysis is significant. The photodegradation rate of BaP in the presence of TiO_2 followed the order of 254 nm irradiation > 310 nm irradiation > 365 nm irradiation (Fig.5a). The pseudo-first-order rate constants were 0.0078 h^{-1} , 0.0061 h^{-1} , and 0.005 h^{-1} corresponding to the wavelengths of 254 nm, 310 nm, and 365 nm, respectively. The probable reason is that the shorter wavelength was, the more the photons and higher energy illuminate. In the case of Fe_2O_3 , the results were different. The photodegradation rate of BaP in the presence of Fe_2O_3 followed the order of 254 nm irradiation > 365 nm irradiation > 310 nm irradiation (Fig.5b). The pseudo-first-order rate constants were 0.0069 h^{-1} , 0.0045 h^{-1} , and 0.0033 h^{-1} corresponding to the wavelengths of 254 nm, 365 nm, and 310 nm, respectively. At 310 nm irradiation, less BaP molecules can be directly degraded. At the same wavelength, BaP photodegradation rate in the presence of TiO_2 was faster than that in the presence of Fe_2O_3 , despite the fact that the concentration of TiO_2 was less than Fe_2O_3 . The reason could be that more e

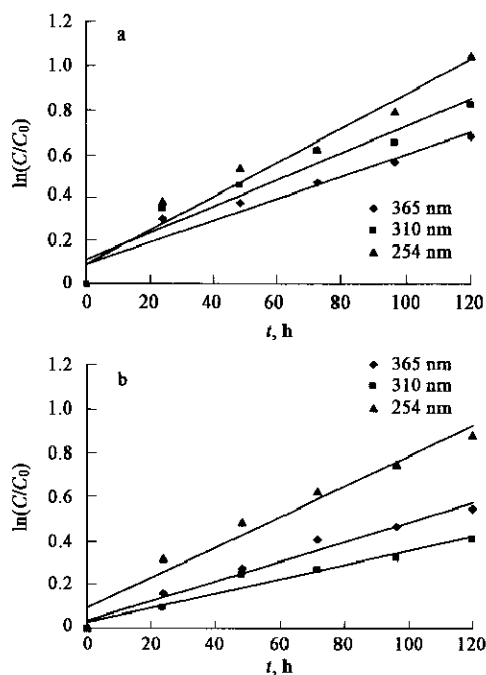


Fig.5 Photocatalytic degradation of BaP on soil surface under different wavelength UV irradiation
a. added TiO_2 ; b. added Fe_2O_3

and h^+ were produced from the excited TiO_2 than from the Fe_2O_3 .

3 Conclusions

Photodegradation is a major degradation process which can naturally clean up the soil. Photodegradation rate of BaP is affected by soil characteristics and environmental factors. According to our study, BaP photodegradation follows pseudo-first-order kinetics, and soil depth has a much greater effect on photodegradation of BaP in soil. The rate constant of photodegradation ranged from 5.24 to $3.91 \times 10^{-2} \text{ d}^{-1}$ within a soil depth of 1.0 – 4.0 mm . In addition, the increase of soil particle sizes left more room for light to scatter and permeate the soil thereby speeding up the photodegradation. The loss of photodegradation at 30°C was greater than those at 25 and 20°C .

BaP photocatalysis also follows pseudo-first-order kinetics. The addition of TiO_2 (2% wt) or Fe_2O_3 (7% wt) decreased the half-life of photodegradation from 363.22 h to 89.34 h or 99.85 h, respectively. This result suggests that semiconductors can be used to degrade soil bound BaP efficiently. However, the addition of TiO_2 (0.5%, 1%, 2%, and 3% (wt)) or Fe_2O_3 (2%, 5%, 7%, and 10% (wt)) had no significant difference on the rate of BaP photodegradation. At different wavelength irradiation, the rates of BaP photodegradation were different in the presence of TiO_2 (2% wt) or Fe_2O_3 (7% wt).

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