

Photodegradation of Polycyclic Aromatic Hydrocarbon Phenanthrene on Soil Surface

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Abstract—Photodegradation of Polycyclic Aromatic Hydrocarbons (PAHs) is a main environmental behavior and plays an important role in the fate of PAHs in environment. In order to understand the photodegradation law of Polycyclic Aromatic Hydrocarbons (PAHs) in soil, aeolian sand in blow-sand region of Northern Shaanxi was chosen as typical soil and phenanthrene (Phe) as typical pollutant of PAHs. Photodegradation law of Phe on soil surface was simulated. In addition, effects of initial Phe concentration, light intensity, time and pH on photodegradation of Phe in aeolian sand was assessed. Results show that the photodegradation of Phe followed pseudo first-order kinetics. Photodegradation rate constant of Phe increased with the increasing of irradiation intensity which the order was as followed: 125W>100W>75W>50W. Irradiation intensity enhances photodegradation of PAHs on soil surfaces. Photodegradation half-life of Phe ranged from 2.474 hours to 3.095 hours under different irradiation intensity. Degradation rate increases as pH increase and photodegradation is more rapid in alkaline medium. Photodegradation rate is the lowest as initial concentration is the largest.

Keywords—photodegradation; Phenanthrene(Phe); aeolian sand; photodegradation kinetics; influence factors

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) is a kind of typical persistent organic pollutants, mainly derived from natural and anthropogenic sources, generated during the incomplete combustion of solid and liquid fuels or derived from industrial activities. PAHs are known to be widespread pollutants which are teratogenic, carcinogenic and mutagenic toxic^[1-4]. In US EPA priority pollutants list, there are 16 PAHs included^[5]. Thus PAHs are ubiquitous pollutants that occur in natural phase such as soil, sediment, water and air, and are harmful to environment and human health. Because of low solubility, PAHs are easy to go into the water phase. Most of PAHs can be adsorbed on soil in environment and only few can enter into the water body. So soil is a very important focus place and medium bearing PAHs. Migration of PAHs in soil is slow and it mainly focused on the soil surface layer^[6]. The main processes which can successfully remove and eliminate the organic pollutants in environment mainly include: microbiological transformation and degradation, volatilization, photodegradation and so on^[7]. Among these

processes, photodegradation is one of the major abiotic transformation processes for PAHs in the environment^[8]. Thus it is importance to investigate photodegradation of PAHs in environment. It can help us to develop efficient and economical degradation technologies for PAHs.

Over the past few years, much work has been done in characterizing photolytic reactions of PAHs in aqueous^[9-11]. On the other hand, Photodegradation of organic matter in soil is influenced by various environmental factors which include irradiation intensity, soil composition and the nature of physical and chemical properties, organic matter and so on. The photodegradation of organic pollutants in the soil depends not only on the degradation rate, but also on the soil thickness, moisture, diffusion and migration of pollutants and other processes. Soil can effectively block light and reduce light penetration^[12]. When other conditions are same, the photodegradation of organic matter in soil was accelerated with different pH and depth in soil^[13]. The photochemical degradation of PAHs in soil usually occurred in the soil/air interface which its thickness less than 1mm. Direct photodegradation process generally occurred mainly in soil surface layer of 0.2-0.4 mm. Thickness about 0.5 mm can block the 95% incident light. Only little can penetrate through the 1.5 mm or deeper in soil layer^[14]. The photodegradation in a certain thickness of soil followed pseudo-first-order kinetics^[15-16]. But sometimes the secondary rate constant or Hoerl function can better reflect the relationship between various factors^[17-18]. Humus effect on the photodegradation of DDT was accord with Langmuir-Hinshel Wood model^[19].

Recent studies have focused on the photodegradation of PAHs in the soils. However, comparatively little research effort has been directed at examining the photodegradation of Phenanthrene(Phe) on aeolian sand, and the fate of Phe adsorbed on aeolian sand surfaces has not been fully explored.

The purpose of this study therefore was to investigate photodegradation of PAHs on aeolian sand surfaces under irradiation. Phenanthrene was chosen as a representative compounds for PAHs. Halogen tungsten lamp was use to simulate the natural light. Using photochemical test on soil surface, photodegradation kinetic model and influence factors were discussed. Result is of great importance to investigate the transport and transformation of PAHs.

II. MATERIALS AND METHODS

A. Chemicals and apparatus

Phenanthrene was purchased from Aladdin Industrial Corporation and the purity was 95% used without further purification. Methanol (Analytical Reagent, AR) was purchased from Beijing Chemical Works, China. Anhydrous calcium chloride (AR) was purchased from Tianjin Fengchuan Chemical Reagent Science And Technology Co., Ltd. The type of constant temperature drying oven was DHG-9070A and was purchased from Shanghai Yiheng Technical Co., Ltd. Millie-Q water purification machine was Gradient A10 from Millipore Corporation, USA. Ultraviolet spectrophotometer was purchased from Purkinje General and the type of pH meter was JSM-6460LV. Oscillator, ultrasonic bath and centrifuge was also needed in the experiment. Tungsten halogen lamps were used as the irradiation sources which the wattages were 50, 75, 100 and 125 respectively.

B. Soil samples

Surface soil samples were collected from the blow-sand region of the Northern Shaanxi. The soil was the typical eolian sand in this area. Impurities were removed from the soil samples and air dried. Then the soil samples were passed through a 1-mm sieve and stored in a dark chamber before use. After autoclaving, the soil samples were mixed with methanol solution. Then let the methanol volatile completely.

C. Photodegradation experiments

In all photodegradation experiments, different replicates of 25g polluted soil samples were evenly spread on Petri dishes which diameter was 9cm and located in a chamber. The soil thickness was 2cm. Put the Petri dish with polluted soil samples under the irradiation of tungsten halogen lamp which the distance was 30cm. Light-proof Petri dish also containing 25 g of uniformly spread soil samples was used as controls for the measurement of non-photodegradation PAHs loss for all experimental treatments. Temperature within the chamber was held constant at 25°C throughout all experiments. Soil samples were taken at 1 hour intervals from the Petri dishes exposed to light.

The effect of irradiation intensity on the photodegradation was investigated by conducting experiments. Five different levels of irradiation intensity were employed in the range of no light, 50W, 75W, 100W and 125W. The effect of time about 0h, 1h, 2h, 3h, 4h and 5h on the degradation of PAHs was also examined. The pH of soil samples on the Petri dishes were adjusted from 3 to 11. Initial Phe concentration in the soil samples were 60mg/g, 90mg/g, 120mg/g, 150mg/g, 180mg/g, respectively.

D. Analytical methods

Concentrations of PAHs in the irradiated and non-irradiated soil samples were obtained by the following method: the soil samples were transferred into 50mL centrifugal tubes and added with 10mL methanol. The centrifugal tubes were covered by tinfoil to prevent the

light irradiation. The mixtures were extracted for 30min in an ultrasonic bath extractor at the controlled temperature below 10°C. After extraction, the mixtures were then centrifuged at 4000 r/min for 5 min to separate the supernatant from the soil samples. The same extraction process was repeated three times. The effluent samples were collected and diluted to appropriate concentration for later analysis. Quantification of PAHs in methanol solutions was conducted using an ultraviolet spectrophotometer with a wavelength set at 250 nm.

III. RESULTS AND DISCUSSION

A. Physical and chemical properties of soil

Mechanical composition of aeolian sand was fine. Particle size between 0.074 to 0.250mm was more than 90%, more than 0.25mm was only 0.1% and less than 0.074mm was less than 9%. The coefficient of nonuniformity was about 1.35. Mineral element of the experimental soil samples was analyzed by energy spectrum analysis and the main chemical component was SiO₂.

B. Law of photodegradation

Degradation law of Phe measured at 1 hour intervals were shown in fig.1. It was observed that degradation of Phe under dark condition mainly occurred in the first hour which was achieved 7.18%. Then the concentration of PAHs was not altered obviously and degradation rate in five hours was only 9.97%. On the contrary, concentration of Phe decreased when irradiation time prolonged. Photodegradation rate was fast in the first four hours and then became slow. Residual rate of Phe was 36.84% after four hour irradiation. It showed that photochemical reaction rate was faster in the early irradiation with more molecules of PAHs on soil surface. Phe concentration on soil surface decreased and photoreaction rate also decreased. Hence, the results indicated that the degradation degree of PAHs on soil surfaces was related to irradiation on soil surface.

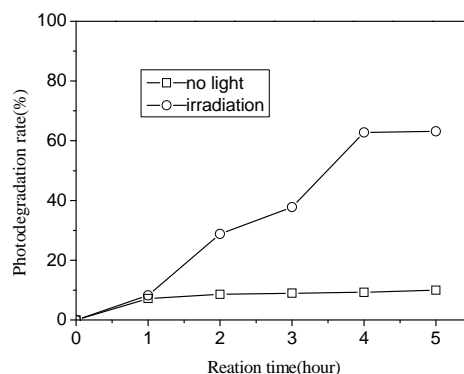


Figure 1. Photodegradation curves of Phe

C. Irradiation intensity effect

It is well established that light intensity is an important factor which affects photodegradation of organics. Photodegradation rate increases with the irradiation intensity enhanced^[19]. Effect of irradiation

intensity on Phe degradation was investigated in 5 hours and photodegradation rate of Phe in eolian sand was shown in Fig.2.

It was observed that intensity increased from 50W to 125W, the degradation rate of Phe increased from 63.16% to 73.55% after 5h reaction. The degradation rate of Phe under same conditions was in the sequence 125W>100W>75W>50W >no irradiation.

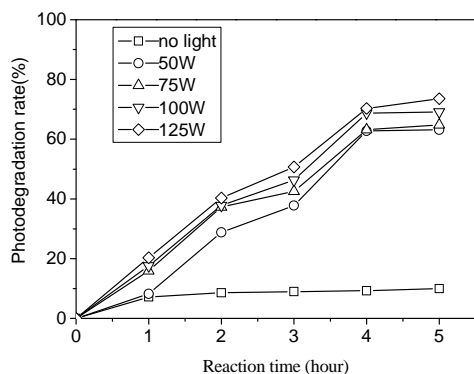


Figure 2. Effect of irradiation intensity

The results indicated that the irradiation intensity enhanced the degradation of the Phe on soil surfaces. Theoretically, at a given depth, the rate of photoreaction was assumed to obey a first-order rate law^[5, 16]. On the other hand, greater irradiation intensity provided more energy for Phe particles, and the reaction rate therefore increased with increased irradiation intensity^[20].

D. pH effect

Soil pH is an important influencing factor and appropriate pH could speed up the photodegradation of organics^[21]. Effect of pH was showed in Fig.3. Results indicated that pH had less effect on photodegradation of Phe. With pH increases, the degradation rate slightly ascended. This is because acid and alkali could not play a role in the dry sand like in solution where can provides hydrogen ions and hydroxyl.

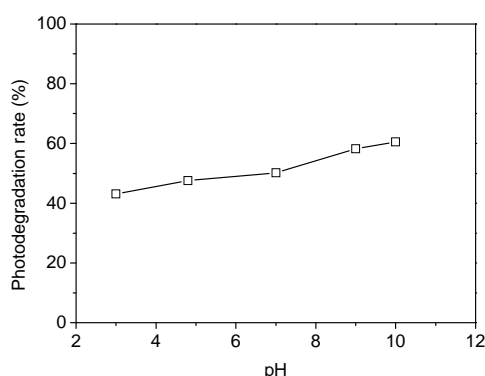


Figure 3. Effect of pH

E. Initial concentration effect

Figure 4 showed the effect of initial concentration on the photodegradation of Phe under 125W with different

initial concentration. Content of Phe decreased after 5 hours and degradation percentages were 64.35%, 59.87%, 55.79%, 52.67% and 49.03% respectively. Result showed that photodegradation rate was obviously influenced by initial concentration. Higher concentration of Phe makes the solution less permeable to light irradiation under the same irradiation intensity. It can also be confirmed that PAHs should be effectively photodegraded on soil surface.

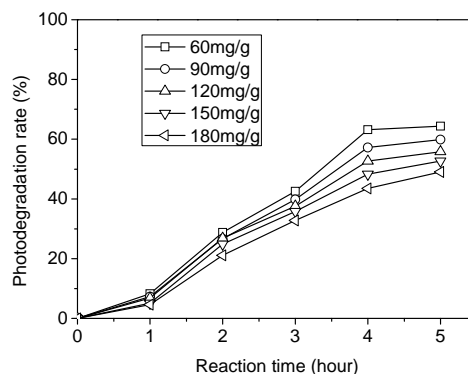


Figure 4. Effect of initial concentration

F. Photodegradation kinetics

Concentration gradient of organic in soil vertical depends on the photodegradation, which follows the pseudo first-order rate equation^[15]. Most direct photodegradation of organic pollutants in homogeneous system obeyed the pseudo first-order rate equation^[5]. Equation and parameters were fitted with the photodegradation data of Phe in the soil under different irradiation intensity. Results were listed in Table 1.

The fitting result showed that photodegradation of Phe followed the pseudo-first order kinetics. The pseudo-first order rate constant was increased as the irradiation intensity increased. The maximum was 0.2806h which the irradiation intensity was 125W. Half-life was shortened when irradiation intensity was enhanced. The minimum was 2.474h which irradiation intensity was 125W.

IV. CONCLUSION

Results of the present work suggested that photodegradation was a successful way to remediate PAHs-contaminated soils. Degradation rate of Phe on aeolian sand increased with time prolonged. The process follows pseudo-first order kinetics. It was significantly influenced by irradiation intensity and initial concentration.

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TABLE 1. PHOTODETRADATIN KINETIC PARAMETERS OF PHE UNDER DIFFERENT IRRADIATION INTENSITY

<i>Irradiation Intensity /W</i>	<i>Pseudo first-order kinetics</i>	<i>Rate constant /h</i>	<i>Half-life /h</i>	<i>Correlation coefficient R</i>
55	$C_t = 2.617e^{-0.2239t}$	0.2239	3.095	0.9696
75	$C_t = 2.512e^{-0.2242t}$	0.2242	3.056	0.9829
100	$C_t = 2.589e^{-0.2553t}$	0.2553	2.717	0.9792
125	$C_t = 2.603e^{-0.2806t}$	0.2806	2.474	0.9895

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