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Photocatalytic degradation of polycyclic aromatic hydrocarbons on soil surfaces using TiO_2 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 TiO_2 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 TiO_2, 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 TiO_2 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 TiO_2 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% TiO_2 were different at UV irradiation wavelengths of 254, 310 and 365 nm, respectively. The synergistic effect of UV irradiation and TiO_2 catalysis was efficient for degradation of PAHs in contaminated soil.

Keywords: Photocatalysis; Polycyclic aromatic hydrocarbons (PAHs); Soil; TiO_2; 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 semiconductor 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 TiO_2 under UV-irradiation and/or solar light has demonstrated successful performance in various remediation systems of polluted soil. The addition of small amounts of TiO_2 (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 TiO_2 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, 2,7-dichlorodibenzodioxin were mixed with TiO_2 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 TiO_2 has been extensively studied in the past few years. Catalyst TiO_2 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 TiO_2 in an aqueous dispersion under UV irradiation. The pH of the dispersion and Ph/TiO_2 value had little effect on the photooxidation rate of phenanthrene catalyzed by TiO_2 [18]. In fact, PAH compounds exist as a mixture of multi-ring structures (i.e. 2-through 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 TiO_2 illuminated with ultraviolet light. In order to enhance TiO_2 utilization rate, García-Martínez et al. [19] reported the photocatalytic degradation of naphthalene in water using TiO_2, 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 TiO_2 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 TiO_2 were purchased from Degussa (P25, anatase, surface area $\sim 50\,m^2\,g^{-1}$, 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 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.

Table 1
Characteristics 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

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.% TiO_2.

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 $1071\,\mu W\,cm^{-2}$. 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-