

Enhanced photodegradation of phenolic compounds by adding TiO_2 to soil in a rotary reactor

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Abstract: Photodegradation of pentachlorophenol (PCP) and *p*-nitrophenol (PNP) in soil was carried out in a designed rotary reactor, which can provide the soil particles with continually uniform irradiation, and on a series of thin soil layers. TiO_2 , as a kind of environmental friendly photocatalyst, was introduced to the soil to enhance the processes. Compared with that on the soil layers, photodegradation of PCP at initial concentration of 60 mg/kg was improved dramatically in the rotary reactor no matter whether TiO_2 was added, with an increase of 3.0 times in the apparent first-order rate constants. The addition of 1 wt% TiO_2 furthered the improvement by 1.4 times. Without addition of TiO_2 , PNP (initial concentration of 60 mg/kg) photodegradation rate in the rotary reactor was similar to that on the soil layers. When 1 wt% additional TiO_2 was added, PNP photodegradation was enhanced obviously, and the enhancement in the rotary reactor was 2 times of that on the soil layers, which may be attributed to the higher frequency of the contact between PNP on soil particles and the photocatalyst. The effect of soil pH and initial concentrations of the target compounds on the photodegradation in the rotary reactor was investigated. The order of the degradation rate at different soil pH was relative to the aggregation of soil particles during mixing in the rotary reactor. Photodegradation of PCP and PNP at different initial concentrations showed that addition of TiO_2 to enhance the photodegradation was more suitable for contaminated soil with higher concentration of PCP, while was effective for contaminated soil at each PNP concentration tested in our study.

Keywords: TiO_2 ; photodegradation; phenolic compounds; soil remediation

Introduction

Phenolic compounds are widely used as intermediates in the production of dyes, plastics and pharmaceuticals. Consequently, most phenols in soil come from industrial waste sources; some however originate from their use as fungicides, bactericides, and insecticides or the degradation of some organophosphate pesticides or herbicides (Barles *et al.*, 1979; Nakagawa and Crosby, 1974). Some contaminated lands, rich in phenolic compounds, have been left at the center of the city during the migration of some chemical factories in China. These lands are of high economic values because of their locations, and, hence, need to be remedied rapidly.

Photolysis on soil surface is an important degradation pathway for a variety of organic pollutants (Choudhury and Dureja, 1997; Balmer *et al.*, 2000; Si *et al.*, 2004a; Fan *et al.*, 2005). Soil moisture, soil pH, and soil components were found to be important factors in photodegradation (Romero *et al.*, 1998; Frank *et al.*, 2002; Si *et al.*, 2004b; Graebing *et al.*, 2002, 2003). Some other studies have demonstrated that small additions of semiconductor oxides, such as TiO_2 , to soil greatly increased the rate and extent of organic pollutants photodegradation under UV or sunlight irradiation (Higarashi and Jardim, 2002; Zhao *et al.*, 2004; Quan *et al.*, 2005). However, compared with that in homogeneous or heterogeneous aqueous systems, the photodegradation of organic pollutants in soil were substantially slower

due to light attenuation by the soil (Nilles and Zabik, 1975; Hebert and Miller, 1990). Presently the most common experimental approach to study photodegradation of organic compounds on soils was to expose a series of thin, spiked soil layers to a light source. In these systems, only the fraction of the total compound actually exposed to light could be degraded. Therefore, the reported photodegradation rate coefficient of the compounds, determined by measuring the total loss of compound from the soil layers as a function of time, always depended on the layer thickness of the soil and transport of the compound in soil.

In order to gain higher and more actual photodegradation rate, a rotary photoreactor was designed and used to study the photodegradation of phenolic compounds in soil. In the rotary reactor, the soil particles were mixed continually around the lamp and accepted uniform UV irradiation, excluding the influence of compounds transport in soil. TiO_2 , as an environmental friendly photocatalyst, was introduced into the soil for further improvement in photodegradation. Pentachlorophenol (PCP) and *p*-nitrophenol (PNP), with different photochemical and soil adsorption characteristics, were selected as the target compounds. PCP has been used for many years for its fungicide, bactericide and insecticide action, especially for wood preservation, and it is commonly found in contaminated soils at wood treatment sites (Tse and Lo, 2002). PNP was a widely used intermediate in chemical industries and was released

to soil from fugitive emissions during its production and use. Because of their toxicities, both of them are listed in the priority pollutants of the US Environmental Protection Agency.

1 Experimental

1.1 Materials

All chemicals were analytical reagent grade and were used as received. PCP and PNP were purchased from Tianjin Nankai Chemical Company and Shenyang City Reagent No.3 Factory respectively. Soil was collected from the suburb of Dalian, China. The soil properties were as follows: the contents of sand, silt, clay, and organic matters were 74%, 17%, 9%, and 0.27%, respectively; bulk density was 1.01 g/cm³. Before use, the soil was air-dried and sieved through a 140-meshed sieve. TiO₂ sol, prepared according to the method described by Yu *et al.* (2001), was annealed at 500°C in the muffle for 2 h, resulting in TiO₂ nanoparticles. The XRD pattern, identified by X-ray diffractometer (LabX-6000, Shimadzu, Japan) employing Cu K α radiation at 40 kV, 30 mA over the 2 θ range of 20–100°, showed 93% of TiO₂ in anatase phase and 7% in rutile phase. The crystallite size was in the range of 16 nm, determined by the Sherrer equation.

1.2 Preparation of the soil samples

A given mass of air-dried soil was mixed with an acetone solution of PCP or PNP, and was homogenized on a shaking machine for 24 h. Then, the solvent was allowed to evaporate at room temperature. This method gave a uniform PCP or PNP distribution in the soil at about 20, 60, or 100 mg/kg. For the experiments with respect to the effect of soil pH on the photodegradation, pH of the soil was adjusted with solutions of Ca(OH)₂ and H₂SO₄ and then allowed air-dried before adding target compounds. Soil pH was measured according to the method described by Wei (1992).

1.3 Irradiation of soil samples

The photoreactor (Fig.1) consisted of a rotary evaporator motor turning a soil container at 50 r/min. The soil container was made up of two cylinders with different diameters. The inner cylinder, made of quartz glass, was 28 cm in length and 7 cm in diameter. The outer cylinder had the same length as the inner one and was thick in the mid and thin at the ends. Its thick part was 10 cm in diameter and 10.5 cm in length, which was approximate to the length of the lamp's illuminating part. In the side of this part, there is indentations, which continually mixed the soil particles and provided them with uniform light exposure. The diameter of the thin ends of the outer cylinder was approximate to the inner cylinder, and they were pressed together through the flexible materials between them. Then, a chamber was formed

between the inner cylinder and the outer cylinder, where 5 g contaminated soil was placed in. A 300 W high pressure mercury lamp (Shanghai Yaming Lighting Corporation) whose primary radiation is emitted at 365 nm, surrounded by a water-cooled quartz condenser, was placed in the center of the soil container as the light source. The irradiation intensity reaching the soil was 280 μ W/cm².

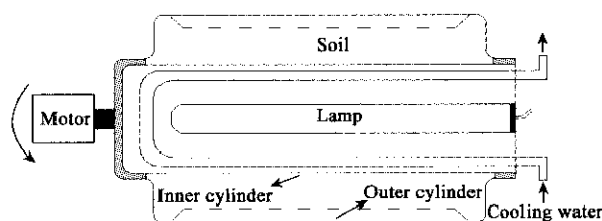


Fig.1 Diagram of the rotary photoreactor used in the experiment

To compare the photodegradation of the target compounds in the rotary photoreactor with that on the soil layers, thin contaminated soil layers, with an initial target compound concentration of 60 mg/kg and a depth of about 0.19 mm, spread on the bottom of glass Petri dishes, were placed below the same lamp where the average incident irradiation intensity was equal to that reaching the soil in the rotary reactor. Concentration of the target compounds in the soil layers were measured after desirable irradiation time.

The dark controls of the contaminated soils were performed respectively in the rotary reactor and on the soil layer in the same procedures for the photodegradation experiments but without light irradiation.

1.4 Analytical procedure

After irradiation was terminated in the set time, two replicates of about 1.2 g soil samples, with the exception of PCP contaminated acidic soil, were mixed with 10 ml deionized water and shaken on a shaking machine for 2 h to extract the target compounds from the soil. After extraction, the solution was separated from the soil by centrifugation at 5000 r/min. The PCP contaminated acidic soil samples were extracted using NaOH solution (pH=10) according to the same procedure. The extractions produced average recoveries of 89.6%–91.9% for PCP and 87.9%–91.6% for PNP at different soil pH and target compound concentrations, and the relative standard deviations are 1.4%–1.9% for PCP and 1.3%–1.8% for PNP, respectively. The data of PCP and PNP concentrations were calibrated by the recoveries.

The extracts were filtered with 0.45- μ m membranes and analyzed by HPLC (PU-1580, UV-1575, Jasco, Japan) equipped with a Kromasil ODS column (250 mm \times 4.6 mm, 5.0 μ m). A mobile phase of methanol/water containing 1% acetic acid

(V/V, 4/1) was employed at a flow rate of 1.0 ml/min and the wavelength was set at 254 nm for PCP analysis. For PNP analysis, a mobile phase of methanol/water (V/V, 5/3) at 0.8 ml/min was used and the wavelength was set at 320 nm.

2 Results and discussion

2.1 Photodegradation in the rotary reactor

Fig.2 shows the degradation of PCP and PNP (initial concentrations were both 60 mg/kg) in the rotary reactor and on the soil layers under UV irradiation with and without addition of 1 wt% TiO₂. No obvious changes were observed in PCP and PNP concentration after 6 h in dark control in the two reaction systems. However, PCP and PNP degradation occurred when the contaminated soils were irradiated by UV light, and the degradation followed pseudo-first order kinetics. Addition of 1 wt% TiO₂ enhanced the photodegradation of them. For PCP photodegradation on the soil layers without addition of TiO₂, the apparent first-order rate constant was 0.1307 h⁻¹, and

51.9% of the original PCP was removed in 6 h. The PCP photodegradation was improved dramatically in the rotary reactor, with an increase of 3.0 times in the degradation rate constant. With addition of 1 wt% TiO₂, the degradation rate was improved by 1.4 times both on the soil layers and in the rotary reactor. PNP on the soil layers without additional TiO₂ had also been degraded under UV irradiation, while at a relative lower rate, with an apparent first-order rate constant of 0.07154 h⁻¹. A removal of 31.6% was obtained in 6 h. Different with that of PCP, without the addition of TiO₂, no significant improvement was observed in the photodegradation of PNP in the rotary reactor, where the apparent first-order rate constant was 0.07911 h⁻¹. However, the enhancement of additional TiO₂ was very remarkable in the photodegradation of PNP. The apparent kinetic first-order rate constant in the presence of 1 wt% TiO₂ on the soil layers and that in the rotary reactor were 0.1593 h⁻¹ and 0.3498 h⁻¹ respectively, which were 2.2 times and 4.4 times of that without addition of TiO₂.

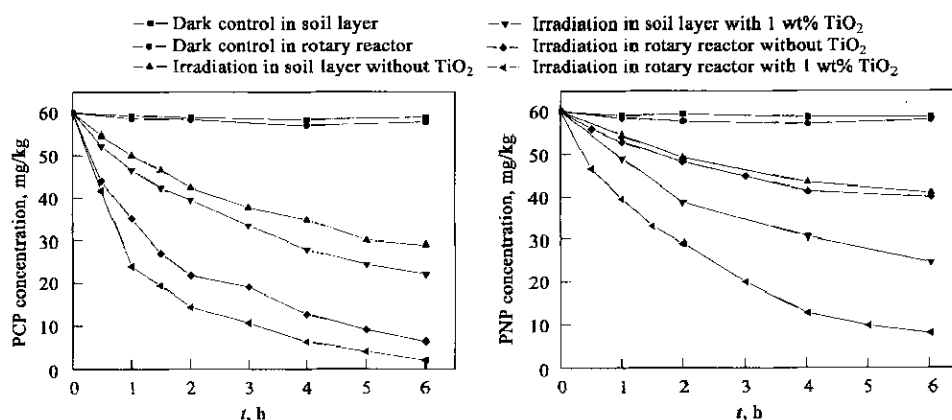


Fig.2 Photodegradation of PCP and PNP in the rotary reactor and on the soil layers with and without addition of TiO₂ (initial concentrations were both at 60 mg/kg)

These results indicated that, in the absence of additional TiO₂, photodegradation of PCP under UV irradiation was relatively easy, and its lower degradation rate in the UV irradiated soil layers may be attributed to the light attenuation by the soil and its slow transport in the soil. When the PCP contaminated soil was irradiated in the rotary reactor, which can provide the soil particles with continually uniform light exposure, they can be degraded rapidly. The improvement of additional TiO₂ was then relatively slight in the PCP photodegradation. Photodegradation of PNP was slower than PCP, and its relatively weaker adsorbability to soil resulted in higher mobility in soil. Therefore, on the soil layers, there is enough PNP in the irradiated zone to be degraded. This may be the reason for the negligible change in the photodegradation rate in the rotary reactor compared with that on the soil layers. Addition of 1 wt% TiO₂ was more

effective for PNP photodegradation, especially in the rotary reactor. It had been reported that, in the presence of TiO₂, the photodegradation underwent the adsorbing of the target compounds to the catalyst surface before the surface react on the catalyst. Therefore, compared with that on the soil layers, the rather higher degradation rate in the rotary reactor in the presence of 1 wt% additional TiO₂ may be attributed to the higher frequency of contact between PNP on soil particles and the photocatalyst.

2.2 Effect of soil pH

Soil pH is a key parameter in both the adsorption of organic pollutants on soil particles (Hultgren *et al.*, 2002) and the physicochemical properties of TiO₂. Therefore, soil pH is important in the photodegradation of organic pollutants in soil. Fan *et al.* (2005) studied the effect of pH on the solar light photodegradation of atrazine, and found that both

atrazine photolytic rate and photolytic depth were greater in acid soil (pH 3.34, 5.58) or base soil (pH 10.01) than that in neutral soil (pH 8.63). In the photodegradation of Diuron on soil surface with additional TiO_2 as the photocatalyst, rise in the soil pH by adding $\text{Ca}(\text{OH})_2$ did not significantly alter the degradation compared with soil that received no lime (Higarashi and Jardim, 2002). However, Quan *et al.* (2005) found that, with the addition of 1 wt% TiO_2 , the photodegradation rate of *p,p'*-DDT on soil surfaces increased with increasing soil pH. All these researches were performed on thin soil layers. Effect of soil pH on the photodegradation of PCP and PNP in the rotary reactor was investigated in our experiments with and without the addition of 1 wt% TiO_2 . Fig.3 shows that photodegradation of PCP and PNP was fastest at pH 6.3 and the lowest at pH 4.7 in the absence or presence of 1 wt% TiO_2 . For PCP (Table 1, a), the apparent pseudo-first-order rate constants were 0.1068 h^{-1} , 0.3898 h^{-1} , and 0.1989 h^{-1} corresponding to the pH of 4.7, 6.3, and 9.4 without the addition of

TiO_2 , and were 0.1933 h^{-1} , 0.5414 h^{-1} , and 0.2679 h^{-1} respectively when 1 wt% TiO_2 was added. For PNP (Table 1, b), the apparent pseudo-first order rate constants were 0.02311 h^{-1} , 0.07911 h^{-1} , and 0.04499 h^{-1} or 0.05305 h^{-1} , 0.3498 h^{-1} , and 0.1235 h^{-1} respectively in the absence or presence of 1 wt% additional TiO_2 corresponding to the pH of 4.7, 6.3, and 9.4. This result was different with that on the soil layers found in our previous work (Quan *et al.*, 2005). It has been observed that, in our experiments, alkaline soil and acidic soil were more easily to aggregate in the mixing by the rotary photoreactor, and higher aggregation was found in the acidic soil than in alkaline soil. Aggregation in soil particles impeded the organic pollutants to be irradiated by UV light. This may be the reason for the order of photodegradation rates: acidic soil (pH 4.7) < alkaline soil (pH 9.4) < neutral soil (pH 6.3). The results indicated that exposure to UV light is the dominating factor in the photodegradation of organic compounds in soil.

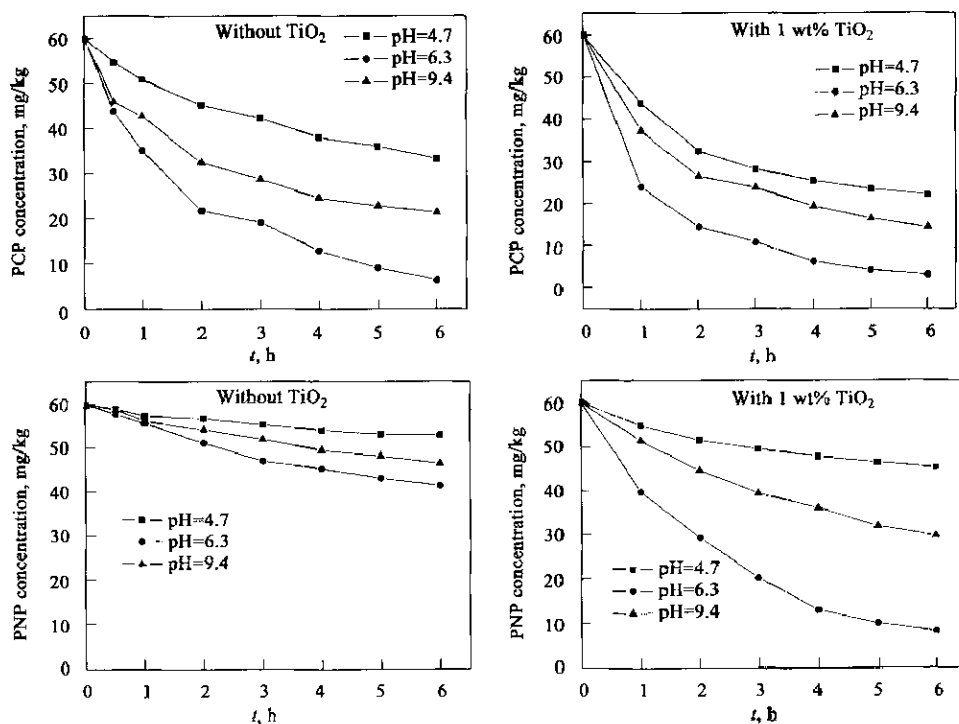


Fig.3 Effect of soil pH on the photodegradation of PCP and PNP in the rotary reactor with and without addition of TiO_2

2.3 Effect of initial concentration

Fig.4 illustrates the effect of initial target compound concentration from 20 to 100 mg/kg on the photodegradation of PCP (a) and PNP (b) in the rotary reactor. The apparent first-order rate constants k_T and the corresponding $t_{1/2}$ values are given in Table 2. Because, in the addition of 1 wt% TiO_2 , PCP and PNP at initial concentration of 20 mg/kg were degraded so fast that the target compound concentration decreased in a short time to a very low value, the apparent rate constants for 20 mg/kg in the addition of 1 wt% TiO_2

were calculated from the data in the first 2 h. For PCP, the degradation rate decreased with increasing initial concentration no matter whether additional TiO_2 was added. At initial concentration of 100 mg/kg, the apparent first-order rate constants of PCP photodegradation were 0.1917 h^{-1} and 0.4284 h^{-1} respectively in the absence and presence of 1 wt% TiO_2 , indicating 2.2 times improvement in the photodegradation rate by the addition of 1 wt% TiO_2 , which was higher than that at initial concentration of 60 mg/kg. This result indicated that addition of TiO_2 to

Table 1 Apparent first-order rate constants k_T and $t_{1/2}$ of the photodegradation of PCP and PNP at different soil pH in the rotary reactor

Soil pH	Without addition of TiO ₂			With 1 wt% additional TiO ₂		
	k_T , h ⁻¹	R	$t_{1/2}$, h	k_T , h ⁻¹	R	$t_{1/2}$, h
PCP						
4.7	0.1068	0.9854	6.490	0.1933	0.9553	3.586
6.3	0.3898	0.9920	1.778	0.5414	0.9845	1.280
9.4	0.1989	0.9568	3.485	0.2679	0.9659	2.587
PNP						
4.7	0.02311	0.9752	29.99	0.05305	0.9680	13.07
6.3	0.07911	0.9618	8.762	0.3498	0.9943	1.982
9.4	0.04499	0.9938	15.41	0.1235	0.9949	5.613

enhance the photodegradation was more suitable for contaminated soils with higher PCP concentration. For PNP, when no additional TiO₂ was added, alteration in the degradation rate caused by changing the initial concentration was not obvious. However, with the

addition of 1 wt% TiO₂, the degradation rate decreased evidently with the increase in the initial concentration, and TiO₂ was found to be effective for PNP at each initial concentration tested in our study.

Table 2 Apparent first-order rate constants k_T and $t_{1/2}$ of the photodegradation of PCP and PNP at different initial concentration in the rotary reactor with and without addition of TiO₂

C_0 , mg/kg	Without addition of TiO ₂			With 1 wt% additional TiO ₂		
	k_T , h ⁻¹	R	$t_{1/2}$, h	k_T , h ⁻¹	R	$t_{1/2}$, h
PCP						
20	0.5743	0.9965	1.207	1.4645	0.9885	0.4733
60	0.3898	0.9920	1.778	0.5414	0.9845	1.280
100	0.1917	0.9959	3.616	0.4284	0.9549	1.618
PNP						
20	0.09050	0.9882	7.659	0.8550	0.9695	0.8107
60	0.07911	0.9618	8.762	0.3498	0.9943	1.982
100	0.05910	0.9833	11.73	0.2261	0.9876	3.066

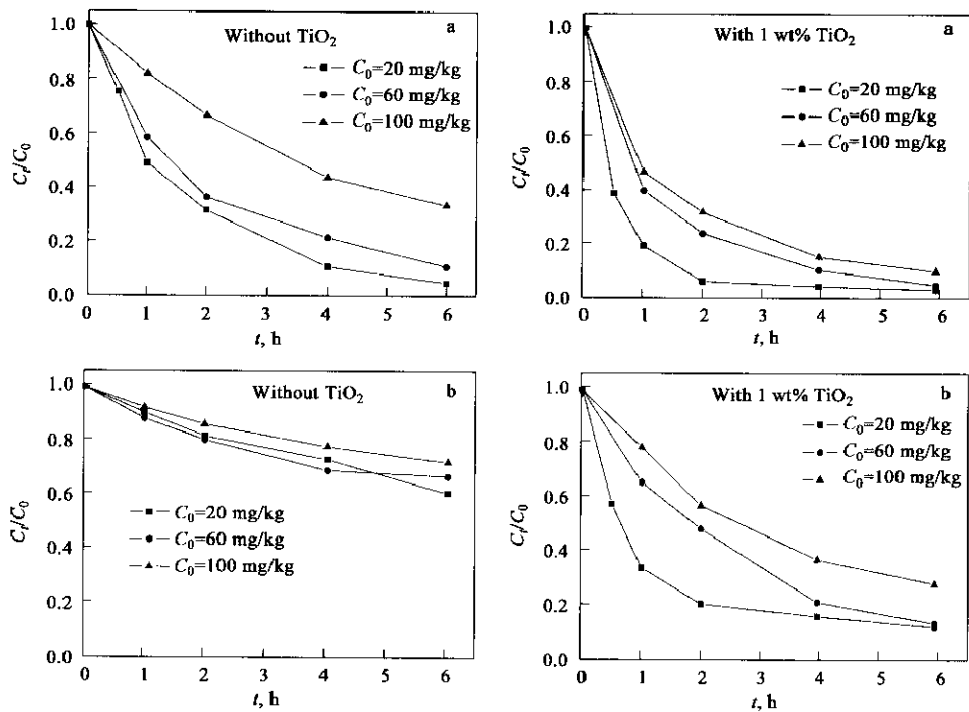


Fig.4 Kinetics of PCP (a) and PNP (b) photodegradation at different initial concentrations with and without addition of TiO₂

3 Conclusions

In the designed rotary reactor, PCP photodegradation in soil without addition of TiO₂ was much faster than that on the soil layers due to the more chance to accept UV irradiation in the rotary reactor. The addition of TiO₂ improved the degradation, and the enhancement in the first-order rate constant by adding 1 wt% TiO₂ was approximately equal in the rotary reactor and on the soil layers. For PNP photodegradation in soil without addition of TiO₂, no obvious changes were found in the degradation rate

between in the rotary reactor and on the soil layers. However, the presence of additional TiO₂ in the soil improved the degradation dramatically, and the degradation rate in the rotary reactor was two times of that on the soil layers, which was attributed to the higher frequency of contact between PNP on soil particle and the photocatalyst.

Soil pH affected the photodegradation in the rotary reactor through affecting the aggregation of the soil particles during mixing, which affected the efficiency of the UV irradiation on the target compounds.

The results obtained at different initial concentrations indicated that addition of TiO_2 to improve the photodegradation was more suitable for contaminated soil with higher concentration of PCP, while was effective for contaminated soil at each PNP concentration tested in our study.

This laboratory experiment showed that the rotary reactor could produce higher degradation rate in the photodegradation of phenolic compounds in soils and may be useful in rapid remediation of phenolic compounds contaminated soils from industrial areas.

References:

- Balmer M M, Goss K U, Schwarzenbach R P, 2000. Photolytic transformation of organic pollutants on soil surfaces—an experimental approach[J]. *Environ Sci Technol*, 34: 1240—1245.
- Barles R W, Daughton C G, Hsieh D P, 1979. Accelerated parathion degradation in soil inoculated with acclimated bacteria under field conditions[J]. *Arch Environ Contam Toxicol*, 8: 647—660.
- Choudhury P P, Dureja P, 1997. Studies on photodegradation of chlorimuron-ethyl in soil[J]. *Pestic Sci*, 51: 201—205.
- Fan X Z, Lu B, Gong A J, 2005. Dynamics of solar light photodegradation behavior of atrazine on soil surface[J]. *J Hazard Mater*, B117: 75—79.
- Frank M P, Graebing P, Chib J S, 2002. Effect of soil moisture and sample depth on pesticide photolysis[J]. *J Agric Food Chem*, 50: 2607—2614.
- Graebing P, Frank M, Chib J S, 2002. Effect of fertilizer and soil components on pesticide photolysis[J]. *J Agric Food Chem*, 50: 7332—7339.
- Graebing P, Frank M P, Chib J S, 2003. Soil photolysis of herbicides in a moisture- and temperature-controlled environment[J]. *J Agric Food Chem*, 51: 4331—4337.
- Hebert V R, Miller G C, 1990. Depth dependence of direct and indirect photolysis on soil surfaces[J]. *J Agric Food Chem*, 38: 913—918.
- Higarashi M M, Jardim W F, 2002. Remediation of pesticide contaminated soil using TiO_2 mediated by solar light[J]. *Catal Today*, 76: 201—207.
- Hultgren R P, Hudson R J M, Sims G K, 2002. Effects of soil pH and soil water content on prosulfuron dissipation[J]. *J Agric Food Chem*, 50: 3236—3243.
- Nakagawa M, Crosby D G, 1974. Photodecomposition of nitrofen[J]. *J Agric Food Chem*, 22: 849—853.
- Nilles G P, Zabik M J, 1975. Photochemistry of bioactive compounds. Multiphase photodegradation and mass spectral analysis of basagran[J]. *J Agric Food Chem*, 23: 410—415.
- Quan X, Zhao X, Chen S *et al.*, 2005. Enhancement of *p, p'*-DDT photodegradation on soil surfaces using TiO_2 induced by UV-light[J]. *Chemosphere*, 60: 266—273.
- Romero E, Dios G, Mingorance M D *et al.*, 1998. Photodegradation of mecoprop and dichlorprop on dry, moist and amended soil surfaces exposed to sunlight[J]. *Chemosphere*, 37: 577—589.
- Si Y B, Yue Y D, Chen H M *et al.*, 2004a. Photodegradation of bensulfuron-methyl on soil surface[J]. *Pest Manag Sci*, 60: 286—290.
- Si Y, Zhou J, Chen H *et al.*, 2004b. Effects of humic substances on photodegradation of bensulfuron-methyl on dry soil surfaces[J]. *Chemosphere*, 56: 967—972.
- Tse K K C, Lo S L, 2002. Desorption kinetics of PCP-contaminated soil: effect of temperature [J]. *Wat Res*, 36: 284—290.
- Wei F S, 1992. Modern methods of soil components analysis [M]. Beijing: China Environmental Science Press.
- Yu J G, Zhao X J, Zhao Q N, 2001. Photocatalytic activity of nanometer TiO_2 thin films prepared by the sol-gel method[J]. *Mater Chem Phys*, 69: 25—29.
- Zhao X, Quan X, Zhao H *et al.*, 2004. 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]. *J Photochem Photobiol A*, 167: 177—183.

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