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Enhanced degradation of *p*-nitrophenol in soil in a pulsed discharge plasma-catalytic system

Tiecheng Wang[a], Na Lu[a,b], Jie Li[a,b,*], Yan Wu[a,b], Yan Su[c]

[a] Institute of Electrostatics and Special Power, Dalian University of Technology, Dalian 116024, PR China
[b] Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education of the People's Republic of China, Dalian 116024, PR China
[c] Faculty of Chemical, Environmental and Biological Science and Technology, Dalian University of Technology, Dalian 116024, PR China

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ABSTRACT

A pulsed discharge plasma-TiO_2 catalytic (PDPTC) system was developed to investigate the degradation of *p*-nitrophenol (PNP) in soil. The effects of TiO_2 amount, soil pH and air moisture on PNP degradation were evaluated, and PNP degradation processes were predicted with Gaussian 03W combined with density functional theory (DFT). Experimental results showed that 88.8% of PNP could be smoothly removed in 10 min in the PDPTC system with the specific energy density of 694 J g_{soil}^{-1}, compared with 78.1% in plasma alone system. The optimum TiO_2 amount was 2% in the present study, and higher TiO_2 amount exhibited an inhibitive effect. Alkaline soil was favorable for PNP removal. The increase of air moisture to a certain extent could enhance PNP removal. A DFT calculation presented that there was a high preference for the –*ortho* and –*para* positions with respect to the functional –OH group of PNP molecule for •OH radicals attack. The main intermediates were hydroquinone, benzoquinone, catechol, phenol, benzo[d][1,2,3]trioxole, acetic acid, formic acid, NO_2^-, NO_3^- and oxalic acid. The generation of hydroxylated intermediates, NO_2^- and NO_3^- suggested that the experimental results were consistent with those of the theoretical prediction.

1. Introduction

Phenols, widely used as chemical intermediates in the manufacture of dyes, pesticides and medicines, are of great environmental interest because of their toxicity and stability [1]. Most phenols in soil come from fugitive emissions during their production and use, causing serious health hazards. Therefore, remediation of these phenols contaminated soil has been called to task. Several technologies such as chemical methods [2,3], bioremediation [4,5], electrokinetics remediation [6], and photocatalysis [7] have been employed to remedy phenols contaminated soils. With the strengthening of industrial standard and the increasing of economic values of lands, high efficient and rapid soil remediation method is becoming a necessity. In this case, the conventional remediation technologies will not meet the requirement of high efficient and rapid remediation due to the drawbacks such as second pollution and time-consuming.

Recently, non-thermal discharge plasma, one of the advanced oxidation processes, has been widely exploited for organic pollutants removal [8,9]. Chemical effects (such as •OH, •O, H_2O_2 and O_3) and physical effects (such as strong electric field and ultraviolet (UV) light) in the discharge processes have been both received great attention [9,10]. In our previous studies, the chemical effects in discharge plasma were confirmed to play a decisive role in pentachlorophenol removal in soil [11,12]. The physical effects in discharge plasma possess parts of discharge energy, and they played important roles in organic pollutants removal in water [9]. If these physical effects can be sufficiently utilized for pollutants removal in soil, it is of great benefit to enhance the soil remediation.

Anatase TiO_2, an economic and photosensitive semiconductor material with a band gap of about 3.2 eV, can be excited by strong electric field and UV light radiation to generate electron–hole pair [13]. The electrons and holes are capable of initiating oxidation and reduction reactions on the surface of TiO_2 particles. Heterogeneous photocatalysis of organic pollutants using TiO_2 under UV-irradiation for soil remediation has been received great attention, and the results suggested that the photogenerated electrons could reduce the organic compounds or react with electron acceptors such as O_2, reducing it to superoxide radical anion $O_2^{\bullet -}$, and the photogenerated holes could oxidize organic pollutants, OH^- ions and H_2O molecule to •OH radicals [7]. Moreover, it has been proved that the physical effects in discharge plasma process could be employed to excite TiO_2, resulting in accelerated formation of active species, and thus the degradation efficiency and energy efficiency of organic pollutants were enhanced in water [9,14]. Therefore, the physical effects in discharge plasma are expected

* Corresponding author at: Institute of Electrostatics and Special Power, Dalian University of Technology, No.2 Linggong Road, Ganjingzi District, Dalian 116024, PR China. Tel.: +86 411 84708576; fax: +86 411 84709869.
E-mail address: lijie@dlut.edu.cn (J. Li).

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to be utilized to improve organic pollutants removal in soil in the presence of TiO_2 catalyst.

The aim of this study is to investigate organic pollutant degradation by pulsed discharge plasma-TiO_2 catalytic (PDPTC) system. *p*-Nitrophenol (PNP) was used as the model pollutant, which has been widely used as an important raw material for production of insecticides, herbicides and various synthetic compounds [1], and has been listed as the 129 priority toxic pollutants by U.S. Environmental Protection Agency [15]. The effects of some factors, such as TiO_2 amount, soil pH and air moisture on PNP removal were evaluated. Furthermore, PNP degradation process was predicted by the Gaussian 03W program [16], and its main degradation intermediates were analyzed.

2. Experimental

2.1. Materials

PNP was used in the study, and its detailed introduction was presented in S1 of Supplementary Data (SD).

Soil samples were collected from a suburb of Dalian, China. The details were presented in S2 of Supplementary Data. The original PNP concentration in the soil was 800 mg kg^{-1}. Soil pH was adjusted with NaOH and H_2SO_4 solutions as described by Hultgren et al. [17].

TiO_2 (Degussa, P25) (BET area = 50 m^2 g^{-1}) was used as the catalyst.

2.2. Treatment of contaminated soil sample

The schematic diagram of the experimental apparatus was illustrated in Fig. S1 of Supplementary Data, which was similar with our previous work [11]. The details of the reactor were showed in S3 of Supplementary Data. The pulse frequency, pulsed discharge voltage and pulse-forming capacitance C_p were 100 Hz, 20 kV and 200 pF, respectively, and the input energy per pulse was 0.023 J.

In each experiment, a certain amount of TiO_2 was added into PNP contaminated soil and then homogenized. The soil sample (approximately 2.0 g) was spread on the ground electrode with a thickness of about 1.3 mm. Prior to discharge treatment, the moisture content of the soil sample was adjusted to 20% with deionized water. Air was injected from one side of the reactor and out from the other side with flow rate of 0.5 l min^{-1}. Air moisture was adjusted by making the air pass through a scrubbing bottle containing deionized water, and a heating unit was used to adjust water vapor from the scrubbing bottle. Herein the moisture content (g m^{-3}) means the mass of water vapor in a stere of air.

2.3. Extraction and analysis

After discharge treatment, PNP in soil was extracted immediately, and the extraction procedure was described in S4 of Supplementary Data. The extractions produced average recoveries of 90.1–95.3%. PNP concentration, intermediates and total organic carbon (TOC) were analyzed and the details were shown in S5 of Supplementary Data.

The input energy per discharge, specific energy density and energy efficiency were defined as shown in S6 of Supplementary Data.

All experiments were conducted in duplicates.

3. Results and discussion

3.1. Effect of TiO_2 amount on PNP degradation

The effect of TiO_2 amount (w/w) on PNP degradation was presented in Fig. 1. Herein, soil pH and air moisture were 7.51 and 15.1 g m^{-3}, respectively. The introduction of TiO_2 enhanced PNP removal in soil. When the TiO_2 amount increased from 0 to 2%, PNP degradation efficiency increased by 10.7% at the SED of 694 J g_{soil}^{-1}. However, further increase presented an inhibitive effect. Maximum PNP degradation efficiency was obtained at the TiO_2 amount of 2% in the present study.

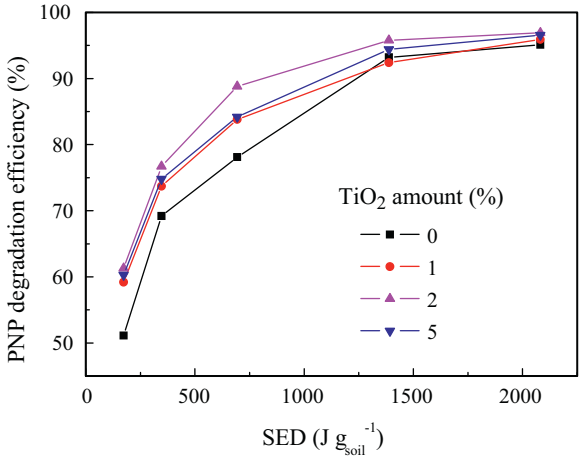

Fig. 1. Effect of TiO_2 amount on PNP degradation.

Less TiO_2 addition (<2%) does not sufficiently utilize the energy of physical effects, therefore as the TiO_2 amount increases, more photons may be adsorbed on the catalyst surface, and then more active species are formed, accelerating PNP degradation processes. However, at higher TiO_2 amount, particles aggregation may reduce the interfacial area between pollutants and catalyst surface sites, and thus the number of active sites on the catalyst surface is decreased, resulting in the decrease of PNP degradation. Sohrabi et al. [18] found that aggregation of TiO_2 particles at high concentrations caused a decrease in the number of surface active sites. Wang et al. [7] reported that 0.5% of TiO_2 was effective for PNP photodegradation in soil, and further increase of the TiO_2 amount from 0.5 to 2% had no significant enhancement effect.

In addition, TOC removal efficiency was enhanced in the PDPTC system. At SED of 1387 J g_{soil}^{-1}, TOC removal efficiency was 45.8% at TiO_2 amount of 2%, compared with 28.3% in plasma alone system.

3.2. Effect of soil pH

The effect of soil pH on PNP degradation was presented in Fig. 2. TiO_2 amount and air moisture were 2% and 15.1 g m^{-3}, respectively.

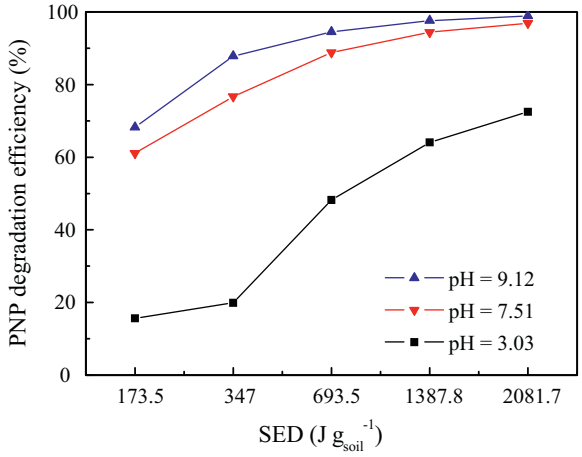

Fig. 2. Effect of soil pH on PNP degradation.