



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

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ABSTRACT

A pulsed discharge plasma-TiO₂ catalytic (PDPTC) system was developed to investigate the degradation of *p*-nitrophenol (PNP) in soil. The effects of TiO₂ 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 TiO₂ amount was 2% in the present study, and higher TiO₂ 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, NO₂⁻, NO₃⁻ and oxalic acid. The generation of hydroxylated intermediates, NO₂⁻ and NO₃⁻ suggested that the experimental results were consistent with those of the theoretical prediction.

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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, H₂O₂ and

O₃) 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 TiO₂, 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 TiO₂ particles. Heterogeneous photocatalysis of organic pollutants using TiO₂ 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 O₂, reducing it to superoxide radical anion O₂^{•-}, and the photogenerated holes could oxidize organic pollutants, OH⁻ ions and H₂O molecule to •OH radicals [7]. Moreover, it has been proved that the physical effects in discharge plasma process could be employed to excite TiO₂, 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

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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 = $50 \text{ m}^2 \text{ g}^{-1}$) 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

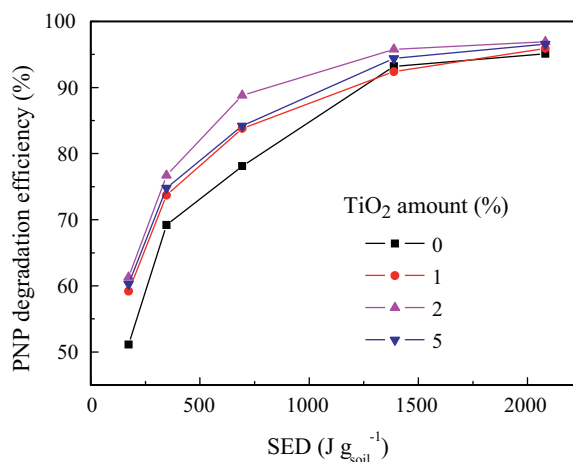


Fig. 1. Effect of TiO_2 amount on PNP degradation.

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 $694 \text{ J g}_{\text{soil}}^{-1}$. However, further increase presented an inhibitive effect. Maximum PNP degradation efficiency was obtained at the TiO_2 amount of 2% in the present study.

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 $1387 \text{ J g}_{\text{soil}}^{-1}$, 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.

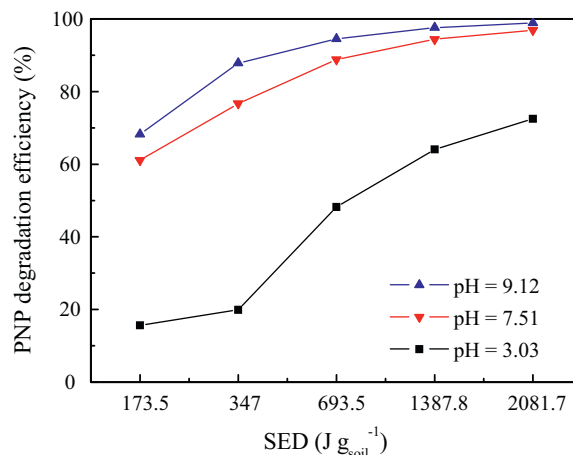


Fig. 2. Effect of soil pH on PNP degradation.

Greatest PNP degradation efficiency occurred in alkaline soil, and followed by neutral soil, and the lowest in acidic soil. At SED of $694 \text{ J g}_{\text{soil}}^{-1}$, PNP degradation efficiencies were 48.2%, 88.8% and 94.5% in acidic, neutral, and alkaline soils, respectively.

The characteristics of electron–hole pairs are influenced by pH changes. High OH^- ion content could enhance the separation of electron–hole pairs, and then more $\cdot\text{OH}$ radicals were generated [7]. On the other hand, the changes of pH could affect the ionization state of PNP [19]. PNP is primarily in the molecular state when the pH is lower than $\text{p}K_a$ of PNP ($\text{p}K_a = 7.15$), and it exists in ionic form when the pH is higher than the $\text{p}K_a$. The weaker adsorption occurs between the ionic PNP and soil particles, and thus PNP has more chances to react with active species at pH 9.12 and 7.51. Thorstensen et al. [20] reported that in acidic soil, some weak acidic compounds had higher adsorbility on soil particles. The lower degradation efficiency of PNP in acidic soil might be attributed to the stronger adsorption of PNP on soil particles. On the other hand, NO_x could also be generated through pulsed discharge plasma established in humid air [10], which suppressed O_3 generation, and therefore, resulting in the decrease of PNP degradation. Furthermore, the ionic form of organic pollutant was generally more reactive towards oxidants than the molecular form [21]. Therefore, higher PNP degradation efficiencies occurred at soil pH 9.12 and 7.51.

3.3. Effect of air moisture

The effect of air moisture on PNP degradation was presented in Fig. 3. Herein, the soil pH value was 7.51. PNP degradation efficiency firstly increased up to a certain point, and then decreased slowly with the increase of the air moisture. PNP degradation efficiency enhanced from 72.0% to 88.8% when the air moisture increased from 0 to 15.1 g m^{-3} , while it decreased to 65.8% at the air moisture of 48.6 g m^{-3} . Greatest PNP degradation efficiency was obtained at the air moisture of 15.1 g m^{-3} in the present study.

The presence of water molecules is considered to play an important role in the formation of active species on the surface of TiO_2 . On the one hand, water molecules can promote the active species generation through the following reactions [10,22,23]:

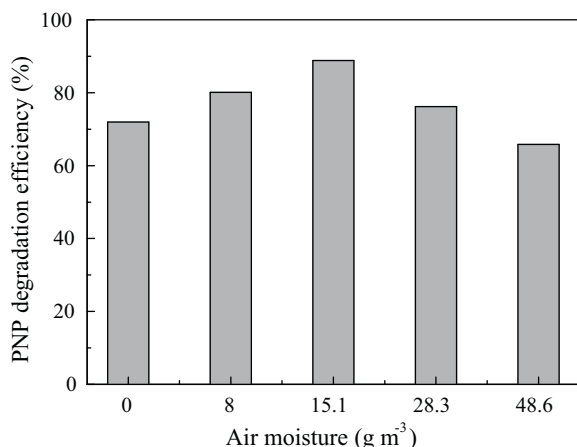
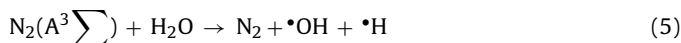
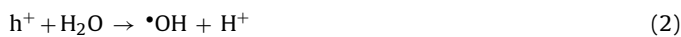


Fig. 3. Effect of air moisture on PNP degradation.

The active species can react with organic pollutant, and then enhance its degradation efficiency; on the other hand, the presence of excessive amount of water molecules could compete for the activated surface of TiO_2 and occupied it, resulting in the decrease of pollutant removal efficiency [24]. Therefore, a positive effect of air moisture occurred firstly in the present experiment, and followed by a negative effect. Similar results were also observed by Date et al. [25], where the increase of air moisture to a certain extent could enhance the activity of TiO_2 , and further increase would exhibit an inhibitive effect.

In addition, a certain amount of water molecules could enhance the generation of $\cdot\text{OH}$ radicals [26], and thus improved PNP removal. The important role of $\cdot\text{OH}$ radicals played in PNP removal could be confirmed by the increase of PNP degradation efficiency with air moisture increased from 0 to 15.1 g m^{-3} in Fig. 3, because the presence of water and N_2 molecules in humid air could inhibit O_3 production during non-thermal discharge plasma process [10]. However, with the further increase in air moisture, more high-energy electrons were captured by water molecules, and the generation of O_3 was further suppressed and the formation of $\cdot\text{OH}$ radicals also decreased, resulting in the decrease of PNP degradation efficiency [27].

3.4. Theoretical prediction of PNP degradation

In order to predict the primary intermediates, the attack of active species such as $\cdot\text{OH}$ radicals was discussed by theoretical calculation. There are several shortcut methods for determining the attack positions of the $\cdot\text{OH}$ radicals. One of the most successful theories is the “frontier orbital theory”, which states that in electrophilic reactions, the attack point is at the position of the greatest electron density in the highest occupied molecular orbital (HOMO) of the aromatic molecule [28]. The HOMO coefficients for PNP were shown in Fig. 4. The italic data in parentheses in Fig. 4 represented the HOMO coefficients. These results indicated that there was a high preference for the two *-ortho* positions with respect to the functional $-\text{OH}$ group for $\cdot\text{OH}$ radical attack.

The main bond lengths, bond angles and atomic charges of PNP were calculated with the help of Gaussian 03W, and the results were shown in Table 1. The corresponding PNP structure could be seen in Fig. 4. As could be found in Table 1, the length of C(4)–N(13) bond was 1.462 \AA , which was the longest in PNP molecule, and therefore it would be potential firstly to be attacked by active species such as $\cdot\text{OH}$ radicals [29]. After the $\cdot\text{OH}$ radicals attacked the bond of C(4)–N(13) with the $-\text{NO}_2$ group removed from the aromatic ring, intermediates such as phenol, hydroquinone, benzoquinone and catechol would be generated. On the other hand, the atomic charge can indicate its electronegativity to some extent in quantum chemistry. Endou et al. [30] have tested the validity of

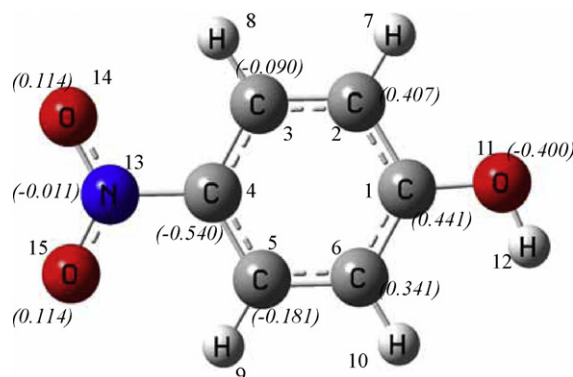


Fig. 4. HOMO coefficients for PNP.

Table 1
Main bond lengths, bond angles and atomic charges of PNP.

Bond name	Bond length (Å)	Name of bond angle	Bond angles (°)	Atom	Atomic charges
C(1)–C(2)	1.386	O(11)–C(1)–C(2)	117.102	C(1)	0.349
C(1)–C(6)	1.403	O(11)–C(1)–C(6)	122.625	C(2)	–0.112
C(1)–O(11)	1.357	C(2)–C(1)–C(6)	120.273	C(3)	–0.091
C(2)–C(3)	1.386	C(3)–C(2)–C(1)	119.835	C(4)	0.241
C(2)–H(7)	1.084	C(4)–C(3)–C(2)	119.299	C(5)	–0.092
C(3)–C(4)	1.397	C(5)–C(4)–C(3)	121.505	C(6)	–0.142
C(3)–H(8)	1.083	C(3)–C(4)–N(13)	119.321	H(7)	0.116
C(4)–C(5)	1.394	C(5)–C(4)–N(13)	119.174	H(8)	0.141
C(4)–N(13)	1.462	C(6)–C(5)–C(4)	119.131	H(9)	0.141
C(5)–C(6)	1.389	C(1)–C(6)–C(5)	119.957	H(10)	0.095
C(5)–H(9)	1.083	C(4)–N(13)–O(14)	117.777	O(11)	–0.542
C(6)–H(10)	1.087	C(4)–N(13)–O(15)	117.797	H(12)	0.326
N(13)–O(14)	1.232	O(14)–N(13)–O(15)	124.426	N(13)	0.381
N(13)–O(15)	1.233	–	–	O(14)	–0.403
O(11)–H(12)	0.967	–	–	O(15)	–0.406

the qualitative electronegativity using quantum chemical calculations based on the density functional theory. In the present study, the atomic charges of C(2) and C(6) had larger negative values than those of C(3) and C(5), which indicated that the electronegativities

of C(2) and C(6) were stronger than those of C(3) and C(5), and thus C(2) and C(6) would be attacked more easily by electrophilic radicals. Therefore, the substituted intermediates of the two *-ortho* positions with respect to the functional *-OH* group were much easier to generate than those of the two *-meta* positions.

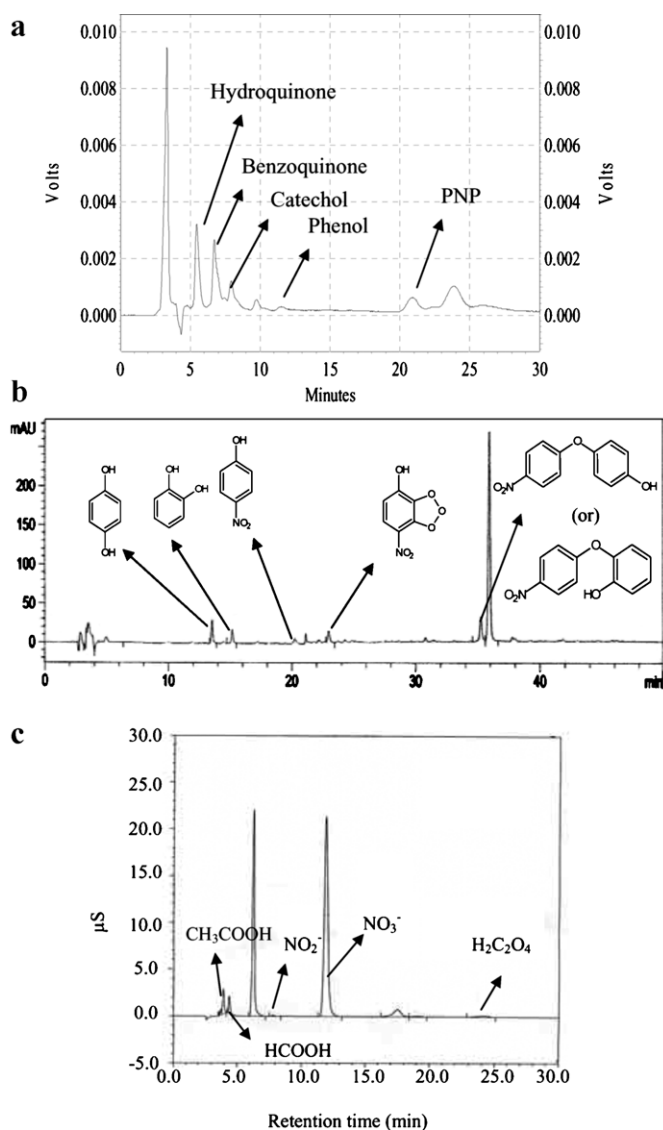


Fig. 5. Total ion chromatograph (TIC) of intermediates of PNP degradation after 30 min of discharge treatment in PDPTC system: (a) HPLC, (b) HPLC/MS, and (c) IC.

3.5. Intermediates of PNP degradation in PDPTC system

PNP degradation intermediates in soil were analyzed using ion chromatography (IC), HPLC and HPLC/MS. The total ion chromatogram of the intermediates after 30 min of discharge treatment was shown in Fig. 5. As presented in Fig. 5(a), hydroquinone, benzoquinone, catechol and phenol were detected as the intermediates using HPLC system. Hydroquinone, catechol, benzo[d][1,2,3]trioxole, and the dimer of PNP with diphenol were monitored using HPLC/MS system in Fig. 5(b). In addition, acetic acid, formic acid, NO₂⁻, NO₃⁻ and oxalic acid were identified by IC in Fig. 5(c). Herein the formation of NO₂⁻ and NO₃⁻ in the case of pulsed discharge in air atmosphere was eliminated through control experiments.

Considering these intermediates, the hydroxylated products were the major intermediates, and which were based on the substitution of *-ortho* and *-para* positions with respect to the functional *-OH* group. In addition, the formation of NO₂⁻ and NO₃⁻ indicated that the broken of the bond of C(4)–N(13) occurred with the *-NO₂* group removed from the aromatic ring during PNP degradation process. These experimental results were consistent with those of the theoretical prediction.

Based on these intermediates, it could be deduced that PNP was first oxidized into kinds of hydroxylated intermediates, and then further oxidized into acetic acid, formic acid and oxalic acid after aromatic rings were broken. The organic acids could also be further decomposed into carbon dioxide. The detailed degradation mechanisms of PNP in soil in the PDPTC system would be still further studied.

4. Conclusions

We have investigated the feasibility of utilizing TiO₂ catalyst to promote PNP degradation in soil in a PDPTC system. Greater PNP degradation performance was presented in this system, compared with in plasma alone system. The increase of TiO₂ amount to a certain extent could enhance PNP degradation, while further increase would present a negative effect. By influencing the ionization state of PNP and the physicochemical properties of TiO₂, soil pH exhibited significant effects on PNP degradation, and greatest PNP degradation efficiency occurred at alkaline soil. The change of air moisture could affect the formation of active species and the

activity of TiO₂ catalyst, and therefore there exists appropriate air moisture for PNP degradation.

The degradation intermediates, analyzed from PNP degradation experiment, were consistent with those predicted using the Gaussian 03W combined with density functional theory.

This study is a fundamental research effort, trying to offer an alternative solution to utilize catalyst to improve pollutant removal in soil. Further work needs to be carried out from exploring the enhancement mechanisms for PNP degradation in soil in this PDPTC system.

Supplementary data

Text S1–S6 include introduction of PNP and other reagents, details of the soil sample, reactor introduction, extraction procedure, analysis methods, calculation of input energy per discharge, specific energy density and energy efficiency. Fig. S1 presents the schematic diagram of the experimental setup.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.08.041.

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