Depth dependence of *p*-nitrophenol removal in soil by pulsed discharge plasma

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HIGHLIGHTS

- PNP degradation and active species diffusion in soils was studied during pulsed discharge process.
- Organic matter blocks active species transport and inhibits PNP degradation.
- Metal oxides affect PNP degradation through catalyzing ozone decomposition.
- Soil moisture benefits active species transfer, and thus promotes PNP degradation.
- Intermediates distribution in soils confirms diffusion behaviors of active species.

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ABSTRACT

A series of soil column experiments were performed to investigate *p*-nitrophenol (PNP) degradation and active species diffusion behaviors in soil layers during pulsed discharge processes. The effects of organic matter, metal oxides, soil moisture, discharge voltage, treatment time, and pollutant concentration on PNP degradation and active species transport were evaluated. PNP degradation efficiency was inversely proportional to organic matter content, due to its adsorption for PNP and blocking for active species transport. For layer 0–2 mm, 99.2% of PNP was removed after 45 min of discharge treatment in column packed with quartz sand, followed in descending order, by sand (85.0%), by sandy soil (77.9%), and by clay soil (61.9%). Metal oxides affected PNP degradation through catalyzing ozone decomposition. Moist soil, higher discharge voltage, and lower PNP initial concentration benefitted active species diffusion and thus promoted PNP degradation. PNP degradation processes in soil layers followed first-order kinetic model, and the reaction rate constant decreased from 0.0458 min^{-1} in soil layer 0–2 mm to 0.0078 min^{-1} in soil layer 10–12 mm. PNP mineralization and degradation intermediates were also identified in soil layers. The distribution of intermediates in soil layers confirmed the different diffusion behaviors of active species.

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1. Introduction

The contamination of the subsurface by organic compounds resulting from leaky fuel storage tanks, refineries, factories, oil spills, and improper waste disposal has been of concern for many decades [1–5]. Considerable efforts have been made to understand the consequences of the contamination and to develop proper technologies for remediating subsurface areas contaminated with various organic compounds [6–9]. Recently, advanced oxidation processes (AOPs) have been viewed as promising alternatives for removing certain recalcitrant organic compounds such as polycyclic aromatic hydrocarbons and chlorinated organic compounds, because of their ability to rapidly oxidize refractory organic contaminants [10,11]. Among the AOPs, pulsed discharge plasma has received great attention in pollution control [12,13].

In our previous studies, pulsed discharge plasma has also been employed to remediate organic pollutants contaminated soils [14–17]. The main principle is as follows: when organic pollutants contaminated soil is placed in the discharge plasma region, the organic pollutants will be excited, ionized or dissociated by high energy electrons and various chemical active species (·OH, ·O, H_2O_2 and O_3 etc.); and simultaneously, physical effects generated concomitantly during the discharge process such as strong electric field and UV light irradiation, can also act on organic pollutants in soil. Because of high oxidative potential of active species and the

actions of physical effects, organic pollutants in soil can be removed effectively and rapidly. However, previous studies have only been conducted in thin soil layer (about 1.3–3.6 mm), and in that case, the pollutant removal rate was calculated by measuring the changes of pollutant concentration in the whole soil. Although these studies addressed the contributions of various operational parameters during discharge plasma process, little progress has been made in exploring the degradation characteristics of pollutants and transfer characteristics of the chemical active species in soil layers.

When organic pollutants in deep soil layer are oxidized and removed, there exist at least two processes, e.g., the transfer processes of organic pollutants and oxidants in different media, and chemical reaction processes between them. More importantly, these two processes affects mutually. On the one hand, the gas phase oxidants may diffuse from air in soil pores to water in soil pores by gas–liquid surface, and the pollutants absorbed in soil particle may transfer to the water in soil pores by solid–liquid surface, and thus the chemical reactions will occur in the water in soil pores; on the other hand, the transfer processes of the organic pollutants and oxidants can influence the chemical reactions, and inversely, the occurrence of the chemical reactions can also improve the transfer processes [18,19]. Therefore, it is necessary to explore the degradation characteristics of pollutants and transfer behaviors of the active species in soil layers.

In the present study, a multi-layer soil sampling device was developed to investigate the degradation characteristics of pollutants and diffusion behaviors of the active species during pulsed discharge treatment process. *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 [20], and has been listed as one of the 129 priority toxic pollutants by US Environmental Protection Agency [21]. The objectives of this research were to explore the effectiveness of PNP degradation in soil layers, and to evaluate the effects of soil characteristics, discharge parameters, and pollutant concentration on PNP degradation and active species diffusion in soil layers. PNP mineralization behavior and intermediates distribution in soil layers were also identified. A brief mechanism of PNP degradation with possible intermediates was also discussed. This study may contribute to a reliable method for deep soil remediation using pulsed discharge plasma.

2. Experimental

2.1. Materials

PNP (purity > 95%) was purchased from the Chemical Plant of Tianjin, China. All other organic and inorganic reagents used were analytical grade (Tianjin Fuyu Refinery Chemical Co., Ltd. and Shenyang Chemical Reagent Factory, China) and were used as purchased without further purification.

In this study, four different types of porous media (quartz sand, sand, sandy soil, and clay soil) were employed. Quartz sand and sand were purchased from a chemical plant of Dalian, China. Soils were collected from a suburb of Dalian, China. Before use, the porous media were all pretreated as follows: firstly, they were passed through a 20 mesh standard sieve, and washed with *n*-hexane and acetone (v/v = 1:1) for several times to remove residual impurities to eliminate their impacts on analysis processes, and then air-dried. The main properties of these porous media were presented in Table 1. The contents of metal oxides of the porous media were analyzed by XRF (S4 EXPLORER, Germany), and the results were shown in Table 2. The preparation of PNP contaminated soils or sands was the same as previous study [16].

Table 1
Main properties of the porous media used in this study.

Soil matrix	Quartz sand	Sand	Sandy soil	Clay soil
pH	8.18	7.73	7.30	7.51
Organic matter (%)	0.03	0.28	2.38	5.54
Particle size (mesh)	20–30	20–30	20–30	20–30

Table 2
Results of XRF analysis of different media.

Oxides	Contents (wt.%)			
	Quartz sand	Sand	Sandy soil	Clay soil
SiO_2	98.95	90.01	79.37	56.02
Al_2O_3	0.54	4.03	10.23	17.61
Fe_2O_3[a]	0.40	1.15	3.04	8.86
K_2O	0.03	2.13	2.19	4.09
CaO	0.01	0.06	1.00	2.36
MnO	0.01	0.10	0.42	2.12
MgO	0.01	0.04	0.03	1.81
Na_2O	–	2.01	1.05	0.85
P_2O_5	–	0.01	0.08	0.16
BaO	–	–	0.03	0.11
CuO	–	0.01	0.01	0.10
TiO_2	–	0.03	0.04	0.09
ZrO_2	–	0.08	0.05	0.07
ZnO	–	0.02	0.01	0.05
L.O.I.[b]	0.05	0.32	2.45	5.70
Total	100.00	100.00	100.00	100.00

[a] Fe_2O_3: Total iron.
[b] L.O.I.: Loss on ignition.

2.2. Treatment of contaminated soil samples

The schematic diagram of the experimental apparatus could be seen in Fig. 1, which consisted of a pulsed high-voltage power supply and a reactor vessel. High-voltage pulses were generated using the combination of a 0–50 kV adjustable DC power supply, a storage capacitor (C_e), an adjustable trim capacitance (C_p) and rotation spark gap switches (RSG1, RSG2). In the power supply system, C_e and C_p were charged respectively by the changes of the rotation spark gap switches position, and then C_p was discharged towards to the reactor, forming pulse discharge. The pulse rise time was less than 100 ns, and the pulse width was less than 500 ns. The pulse frequency and adjustable trim capacitance C_p were 50 Hz and 200 pF, respectively. The sectional view of the discharge reactor was illustrated in Fig. 2, and herein, Fig. 2(a) was the reactor vessel, and Fig. 2(b) was the schematic diagram of multi-layer soil sampling device. The high voltage electrode comprised of seven 9[#] stainless-steel hypodermic pinheads which were distributed
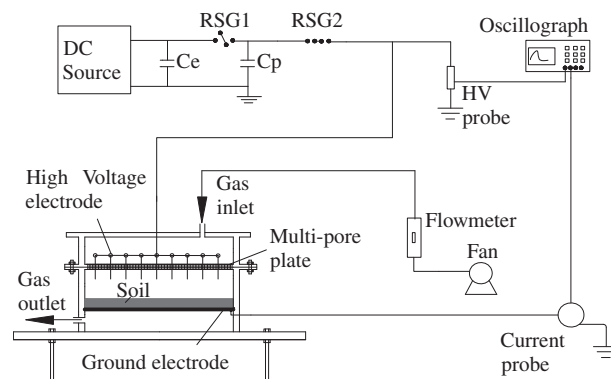

Fig. 1. Schematic diagram of the experimental apparatus.