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Evaluation of the potential of soil remediation by direct multi-channel pulsed corona discharge in soil

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HIGHLIGHTS

- In situ multi-channel pulsed discharge in soil was developed for soil remediation.
- Effects of operational parameters on PNP degradation were evaluated.
- Roles of ozone, H_2O_2, and $^{\bullet}OH$ radicals in PNP degradation were discussed.
- Possible pathway of PNP degradation in soil in such a system was proposed.

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ABSTRACT

A novel approach, named multi-channel pulsed corona discharge in soil, was developed for remediating organic pollutants contaminated soil, with *p*-nitrophenol (PNP) as the model pollutant. The feasibility of PNP degradation in soil was explored by evaluating effects of pulse discharge voltage, air flow rate and soil moisture on PNP degradation. Based on roles of chemically active species and evolution of degradation intermediates, PNP degradation processes were discussed. Experimental results showed that about 89.4% of PNP was smoothly degraded within 60 min of discharge treatment at pulse discharge voltage 27 kV, soil moisture 5% and air flow rate 0.8 L min^{-1}, and the degradation process fitted the first-order kinetic model. Increasing pulse discharge voltage was found to be favorable for PNP degradation, but not for energy yield. There existed appropriate air flow rate and soil moisture for obtaining gratifying PNP degradation efficacy. Roles of radical scavenger and measurement of active species suggested that ozone, H_2O_2, and $^{\bullet}OH$ radicals played very important roles in PNP degradation. C—N bond in PNP molecule was cleaved, and the main intermediate products such as hydroquinone, benzoquinone, catechol, phenol, acetic acid, formic acid, oxalic acid, NO_2^- and NO_3^- were identified. Possible pathway of PNP degradation in soil in such a system was proposed.

1. Introduction

With the quick development of industrial production and urbanization, lots of relocated or closed industrial enterprises caused serious soil pollution [1,2]. In these polluted sites, a large number of toxic contaminants have been continually entered into plant sites including petroleum hydrocarbon, heavy metals, pharmaceuticals and persistent organic pollutants [3–5]. With the increasing of economic values of lands, these polluted sites are faced with quick commercial utilization, but lots of toxic contaminants in soil bring great threat to human health, especially organic pollutants [6–8]. Therefore, rapid and high-efficient remediation for these sites is of great importance. Lots of methods had been proposed for soil remediation, such as physical remediation [8], traditional chemical remediation [9], and bioremediation [10]; however, there exist some drawbacks such as second pollution and time-consuming, and they cannot meet the requirement of high efficient and rapid remediation, and thus it is urgent to develop new methods for soil remediation.

Recently, advanced oxidation processes (AOPs) are receiving great emphasis on pollution control [11–13]. Among the AOPs, non-thermal discharge plasma is a promising approach [12,13]. During discharge plasma processes, the ensuring electron-molecule interactions generate highly reactive non-thermal plasma, which are strongly oxidizing environments due to the presence of large number of chemically active species, such as ozone, H_2O_2, $^{\bullet}OH$ radicals,

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O atoms, and ions (O_2^-, O_2^+, H_3O^+, O_3^-) [13]. Research on pollutants degradation in environment by non-thermal discharge plasma has mainly concerned about wastewater treatment and gas purification [14–16], while only few investigations have been published related to soil remediation so far. Peurrung and Peurrung [17] has reported that it might be feasible for in situ electrical corona to detoxify soil and studied the propagation of corona through a soil. Gas phase dielectric barrier discharge (DBD) plasma was employed to remediate kerosene contaminated soil by Redolfi et al. [18], and it was found that kerosene in soil could be oxidized efficiently. In our previous research, pulsed corona discharge plasma and DBD were both employed to remove organic pollutants from soil, such as pentachlorophenol, nitrophenol, and chloramphenicol [19–21]. However, the published literatures related to soil remediation by non-thermal discharge plasma were mainly used gas phase discharge plasma, where the discharge plasma occurred in gas phase firstly, and then the generated chemically active species permeated into contaminated soil layer to oxidize pollutants; in that case, some short-lived active species would disappear before entering soil layer and only long-lived active species participated in pollutants degradation.

Therefore, in order to sufficiently utilize the efficacy of discharge plasma for soil remediation, a novel approach for discharge plasma initiation, namely direct multi-channel pulsed discharge plasma in soil, was developed in this study to remedy contaminated soil. In this approach, the discharge plasma was triggered directly in contaminated soil. *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 [22], and has been listed as the 129 priority toxic pollutants by U.S. Environmental Protection Agency [23]. The present study was mainly focused on exploring the feasibility of PNP contaminated soil remediation by this multi-channel discharge plasma, and experiments under various conditions were carried out to investigate the effects of electric factors, carrier gas, and soil moisture on PNP degradation. The roles of chemically active species (O_3, H_2O_2, •OH radicals) in PNP degradation were also identified. Furthermore, PNP degradation mechanisms were discussed based on the evolution of degradation intermediates. This is, to the best of our knowledge, the first study in which organic pollutant contaminated soil was remedied by multi-channel discharge plasma system. It is expected to contribute to an alternative for soil remediation by non-thermal discharge plasma.

2. Experiments and methods

2.1. Materials

PNP (analytical reagent) was purchased from the Chemical Plant of Tianjin, China. All other organic and inorganic reagents used were analytical grade and were used as purchased without further purification. Soil samples were collected from a suburb of Dalian, China. Soil pretreatment process, soil properties and the preparation of contaminated soil samples were the same as our previous research [20]. PNP initial concentration in the contaminated soil was 300 mg kg^{-1}.

2.2. Multi-channel pulse discharge plasma system

The schematic diagram of the experimental apparatus was illustrated in Fig. 1. The reaction system consisted of a pulsed high-voltage power supply, a reactor vessel, and detector. Pulses high-voltage was generated using the combination of a 0–50 kV adjustable DC power source, a storage capacitor (C_e), an adjustable trim capacitance (C_p) and rotation spark gap switches (*RSG1* and *RSG2*). The pulse rise time was less than 100 ns, and the pulse width was less than 500 ns. The trim capacitance was 500 pF and the pulse repetition capacitance was 50 Hz in the present research. The reactor vessel was made of Plexiglas™ cylinder (40 mm inner diameter and 100 mm length). 13 stainless-steel hypodermic needles (inner diameter of 0.7 mm and outer diameter of 1.0 mm) were used as high voltage electrode to form multi-channel discharge plasma, which were distributed uniformly in a diffused-air plate with only 2 mm of length protruded from the plate, and the distance of adjacent needle was 10 mm, as shown in Fig. 1(b). Stainless-steel plate was used as ground electrode. The distance between the high voltage electrode and the ground electrode was 16 mm. The peak pulse voltage and current were measured with a Tektronix TDS2014 digital oscilloscope equipped with a Tektronix P6015A high voltage probe and a Tektronix A6021 current probe. The typical pulsed voltage and current waveforms obtained in the experiment were shown in Fig. 2.

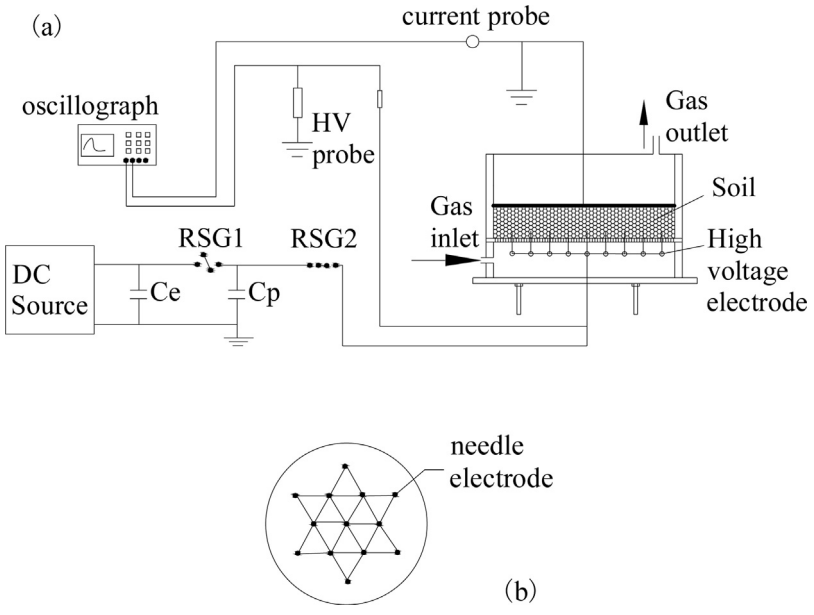

Fig. 1. Schematic diagram of the experimental apparatus (a) experimental system and (b) needle electrode distribution.