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Formation and roles of hydrogen peroxide during soil remediation by direct multi-channel pulsed corona discharge in soil

Tiecheng Wang [a,b], Guangzhou Qu [a,b], Qiuhong Sun [c], Dongli Liang [a,b], Shibin Hu [a,b,*]

[a] College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi Province 712100, PR China
[b] Key Laboratory of Plant Nutrition and the Agri-environment in Northwest China, Ministry of Agriculture, Yangling, Shaanxi 712100, PR China
[c] Institute of Soil and Water Conservation, Northwest A&F University, Yangling, Shaanxi Province 712100, PR China

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ABSTRACT

H_2O_2 is one of the most major active species generated in discharge plasma process. A multi-channel pulsed discharge plasma system was developed to investigate H_2O_2 formation characteristics during *p*-nitrophenol (PNP) contaminated soil remediation. Effects of gas varieties (air, O_2, Ar and N_2), air flow rate, and species scavengers on H_2O_2 formation were evaluated, and PNP degradation performance was also evaluated under various species scavengers. The experimental results revealed that the highest H_2O_2 concentration was obtained in O_2 plasma atmosphere, and followed in descends by air, Ar and N_2 atmospheres; and H_2O_2 formation rates in the case of O_2, air, Ar and N_2 were 2.9×10^{-7}, 1.8×10^{-7}, 1.2×10^{-7} and 8.9×10^{-8} mol L^{-1} s^{-1} under the condition of peak pulse discharge voltage of 27.0 kV and gas flow rate of 0.8 L min^{-1}, respectively. Increasing air flow rate to a certain extent was beneficial for H_2O_2 formation. The addition of *n*-butanol or $H_2PO_4^-$ into soil sample displayed negative effects on H_2O_2 formation, while the addition of HCO_3^- promoted H_2O_2 formation. Direct attack of high energy electrons to water molecules was the main pathway for H_2O_2 formation during direct pulse discharge plasma in soil; electrolysis reaction route of dissolved O_2 would take place to generate H_2O_2 and ozone decomposition in alkaline soil also played significant roles in H_2O_2 formation; however, the recombination of $\cdot$OH radicals exhibited relatively low contribution to H_2O_2 formation. PNP degradation efficiency decreased by 12.7%, 19.0% and 30.4% within 45 min's discharge plasma treatment at 27 kV with *n*-butanol, HCO_3^- and $H_2PO_4^-$ addition, respectively, which further confirmed the roles of high energy electrons and $\cdot$OH radicals in H_2O_2 formation.

1. Introduction

With the development of industrial production and urbanization, lots of relocated or closed industrial enterprises caused serious soil pollution [1,2]; in these sites, a large number of toxic pollutants have been continually released into plant sites including petroleum hydrocarbon, pharmaceuticals and heavy metals [1–3]. With the enhancement of economic values of lands, these polluted sites are faced with rapid commercial utilization especially in China, but lots of toxic pollutants in soil bring great threats to human health [4–6]. Therefore, rapid and high-efficient remediation for these sites is of great significance. Lots of methods have been proposed for soil remediation, such as physical remediation [6], traditional chemical remediation [7], and bioremediation [8]; however, there exist some drawbacks such as second pollution and time-consuming, and they cannot meet the requirements of high-efficient and rapid remediation, and thus it is urgent to develop new method for soil remediation.

Recently, advanced oxidation processes (AOPs) have been received great emphasis on pollution control [9–11]. Among the AOPs, non-thermal discharge plasma is an alternative approach [10,11]. During discharge plasma process, 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, $\cdot$OH radicals, O atoms, and ions (O_2^-, O_2^+, H_3O^+, O_3^-) [11]. Research on pollutants degradation in environment by non-thermal discharge plasma is mainly focused on wastewater treatment and gas purification [12–14], while only few investigations have been published related to soil remediation so far. Peurrung et al. [15] reported that it might be feasible for in-situ electrical corona to detoxify soil and he studied the propagation of corona

* Corresponding author at: College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi Province 712100, PR China.
E-mail address: shibinhu2014@126.com (S. Hu).

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through soil layer. Gas phase dielectric barrier discharge (DBD) plasma was employed to remediate kerosene contaminated soil by Redolfi et al. [16], 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 [17–19]. These published literatures related to soil remediation by non-thermal discharge plasma 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 process. Direct multi-channel pulsed discharge plasma in soil was developed in our recent research to remediate contaminated soil [20]; in this approach, the discharge plasma was triggered directly in contaminated soil, which enhanced the utilization efficiency of chemically active species; however, the detailed active species formation and roles were still unknown in this system.

H_2O_2 is considered to be one of the most major active species involved in the degradation of organic contaminants in discharge plasma process. H_2O_2 is a strong oxidant, and it can react with various compounds via direct oxidation or indirect oxidation. Generally, the indirect oxidation plays a more important role due to $\cdot OH$ radicals generation by H_2O_2 decomposition. In discharge plasma process, high energy electrons can attack H_2O_2 to generate $\cdot OH$ radicals; ozone can react with H_2O_2 to form $\cdot OH$ radicals, and the self-decomposition of H_2O_2 by UV irradiation can also produce $\cdot OH$ radicals, as shown in reactions (1)–(3) [10,21–23]. Furthermore, some metal ions (such as Fe^{2+} and Cu^{2+}) or metallic compounds are usually employed to catalytically decompose H_2O_2 to enhance oxidation capacity of discharge plasma system via $\cdot OH$ radicals generation [13,24]. For example, the typical Fenton reactions are initiated by reactions of H_2O_2 with Fe^{2+} (reactions (4)–(6)). Cu^{2+} can react with H_2O_2 to generate $\cdot OH$ radicals (reactions (7) and (8)). Therefore, analyzing the formation rate of H_2O_2 in the electrical discharge reactor and exploring the formation mechanism are very useful for evaluating organic pollutants degradation processes, enhancing the removal efficiency and improving the efficacy of discharge plasma system.

$$e^- + H_2O_2 \rightarrow OH^- + \cdot OH \quad (1)$$

$$O_3 + H_2O_2 \rightarrow \cdot OH + HO_2^- + O_2 \quad (2)$$

$$H_2O_2 + h\nu \rightarrow \cdot OH + \cdot OH \quad (3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (4)$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \quad (5)$$

$$\cdot OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (6)$$

$$Cu^{2+} + H_2O_2 \rightarrow (Cu^{2+}OOH^-)^+ + H^+ \quad (7)$$

$$(Cu^{2+}OOH^-)^+ \rightarrow Cu^+ + 1/2O_2 + \cdot OH \quad (8)$$

The objective of this study was to explore the formation of H_2O_2 in the direct multi-channel pulsed corona discharge in soil. The effects of gas types and gas flow rate on H_2O_2 formation were evaluated. The formation mechanisms of H_2O_2 were discussed via evaluating the influences of high energy electrons scavenger and active species capturers. The degradation of *p*-nitrophenol (PNP) in soil, used as the model pollutant, was also investigated under different species scavengers to evaluate the roles of active species.

2. Experiments and methods

2.1. Materials

PNP, titanium potassium oxalate, $NaHCO_3$, *n*-butanol, and NaH_2PO_4 were analytical grade and were used as purchased without further purification. Soil samples were the same as our previous research [20]. PNP initial concentration in the contaminated soil was 300 mg kg^{-1}.

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*, *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. 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. The electric power was calculated through the integral of pulse discharge voltage and current under time; and the energy yield for H_2O_2 generation was defined as the detected H_2O_2 concentration divided by total input energy.

In each experiment, 10 g soil samples were spread on the diffused-air plate. Carrier gas was injected into the reactor through the diffused-air plate. Discharge plasma was triggered after soil moisture was adjusted to a certain value. The soil moisture content was 15%, and peak pulsed discharge voltage was 27 kV in the present research.

2.2. Analysis

The processes of PNP extraction and PNP measurement were the same with previous research [20]. The H_2O_2 concentration was determined using titanium potassium oxalate method by a UV–vis spectrophotometry (U-2800) at wavelength of 400 nm as described by Sellers [25]. Detailedly, the titanium potassium oxalate solution (0.05 mol L^{-1}) was prepared with 136.0 mL

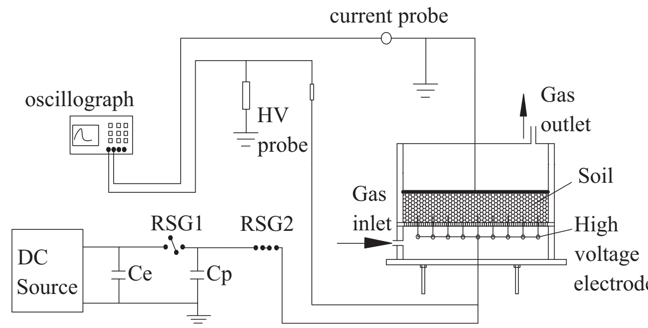

Fig. 1. Schematic diagram of the experimental apparatus.