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**Evaluation of the Potential of Pentachlorophenol Degradation in Soil by Pulsed  
Corona Discharge Plasma from Soil Characteristics**

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**S1 Soil Pretreatment Procedure.** The soil samples were pretreated as follows. Firstly, the soil samples were air-dried for 3 days, passed through a 20 mesh standard sieve, and washed with n-hexane and acetone (v/v = 1: 1) for 12 h to remove residual impurities to eliminate their impacts on analysis processes, and then air-dried before use.

**S2 Contaminated Soil Preparation.** PCP contaminated soil samples were artificially prepared by adding 400 mg L<sup>-1</sup> of PCP acetone solution to a given amount of the pretreated soils, vigorously homogenized and then placed in a fume hood until acetone evaporated entirely. This method gave a uniform PCP distribution in the soil samples at about 200 mg kg<sup>-1</sup>.

**S3 Detailed Reactor Introduction.** The high voltage electrode comprised of seven 9<sup>#</sup> stainless-steel hypodermic pinheads which were distributed uniformly in a circle of 40 mm diameter with inter-distance of 15 mm, and secured within a resin disc. Silicone insulation encased the hypodermic pinheads that protruded from the resin disc, with only 5 mm of length exposed beyond the silicone insulator. The hypodermic pinheads were sealed in a Plexiglas<sup>TM</sup> cylinder (50 mm inner diameter and 50 mm length), as shown in part (a) of Figure S1 (□). The ground electrode was a wire netting (200 mesh), which was embedded into a Plexiglas<sup>TM</sup> cylinder (40 mm inner diameter and 50 mm length), as shown in part (b) of Figure S1 (□). The part (a) and part (b) were connected through thread seal, forming the reactor system, as shown in Figure S1 (□).

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The distance between the high voltage electrode and the ground electrode was 12 mm.

**S4 Roles of Active Species.** In order to investigate the roles of active species, PCP degradation experiments by PCDP under pure oxygen atmosphere and by pure ozonation were performed, respectively, and PCP removal efficiencies and O<sub>3</sub> utilization efficiencies were obtained. O<sub>3</sub> concentrations were measured as described by Suarasan et al. (1), under PCP uncontaminated and contaminated soils, respectively, and the difference were considered as consumed O<sub>3</sub> by PCP. Specially, ozonation experiments were conducted in series reactors as shown in Figure S3, where the reactor I was used for ozone generation by PCDP under pure oxygen atmosphere, and the reactor II was for pure ozonation.

**S5 Sampling Procedures.** (i) For neutral and alkaline soils, after each experiment, all the soil samples were mixed with 50 mL NaOH solution (pH = 11.0) in an airtight sealed conical flask and then shaken on a shaker at 300 rpm for 12 h to extract PCP from the soil samples, then the mixture was centrifuged at 3000 rpm for 15 min. After centrifugation the extract was passed through a 0.45 µm filter, 1 mL filtrate was used for PCP analysis, 5 mL for Cl<sup>-</sup> analysis and 15 mL for mineralization analysis. (ii) For acidic soils and HA added soils, after each experiment, all the soil samples were mixed with 50 mL methanol in an airtight sealed conical flask and then shaken on a shaker at 300 rpm for 12 h to extract PCP from the soil samples, then the mixture was centrifuged at 3000 rpm for 15 min. After centrifugation the extract was passed

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through a 0.45  $\mu\text{m}$  filter, 1 mL filtrate was used for PCP analysis.

**S6 Analysis Methods.** (i) PCP concentration was determined by HPLC system equipped with a Hypersil ODS (25  $\mu\text{m}$ , 4.6  $\times$  250 mm) reverse phase column. The mobile phase consisted of a mixture of 1% aqueous acetic acid and methanol (v/v = 20: 80) with a total flow rate of 1.0 mL min<sup>-1</sup>, the detection wavelength of PCP was set at 220 nm. (ii) Organic acids and chloride ions were detected by IC (ICS-90, U.S.) equipped with AMMSIII4mm suppressor, Dionex IonPac AS9-HC column and DS5 conductance detection. The mobile phase was 9 mmol L<sup>-1</sup> sodium carbonate solution with a flow rate of 1.0 mL min<sup>-1</sup>, and the regenerant was 50 mmol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution with a flow rate of 1.0 mL min<sup>-1</sup>. (iii) HPLC/MS (HP1100/MSD, Agilent Co., U.S.) was used for qualitative analysis of intermediates and final products, and the analyses were performed with electrospray ionization in the negative mode. Nitrogen was used as dry gas at the flow rate of 8 L min<sup>-1</sup> and temperature was 350 °C. The nebulizer pressure was 35 psi. In the full-scan mode, the m/z range was 80 to 800 in the negative-ion (NI) mode. The treatment procedures of samples before HPLC/MS analysis were as follows. First, the intermediates in treated soils were extracted with methylene chloride and hexane (v/v = 1: 1) for 4 times, and then the mixture was centrifuged at 3000 rpm for 15 min, the extract was collected. Second, the extract was passed through a chromatographic column, and then methanol used as eluting reagent. Finally, the eluting reagent was condensed before analysis for HPLC/MS. (iv) The Fourier transform infrared spectroscopy (FTIR) was applied in the characterization of

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the chemical bonds of the soil samples. Sample discs were prepared by mixing 1 mg of the soil samples with 500 mg of KBr in an agate mortar and scanned in a range from 4000 to 400  $\text{cm}^{-1}$  using an EQUINOX55 spectrophotometer, 100 scans were taken at a resolution of 4  $\text{cm}^{-1}$ . (v) The mineralization of PCP was determined by a Total Organic Carbon analyzer (TOC-5000A Shimadzu). 5 mL of the extract was used for Total Carbon (TC) analysis and another 5 mL for Inorganic Carbon analysis (IC).

**S7 Ozone Utilization Efficiency and Chlorine Found in Organic Products.** The ozone utilization efficiency was calculated from the follow:

$$\text{Ozone utilization efficiency} = \frac{\text{removed PCP (mg)}}{\text{ozone consumed (mg)}} \quad (1)$$

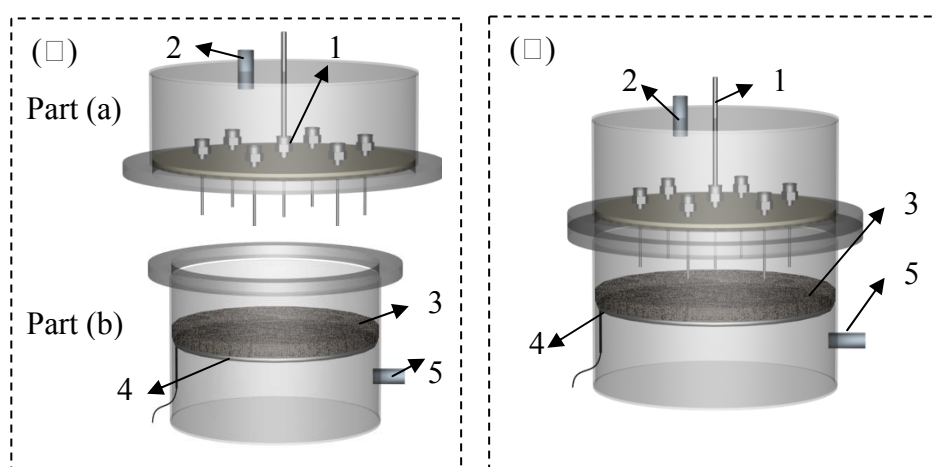
Amount of chlorine hypothetically found in organic products (Org. Cl) was defined as (2):

$$[\text{Org. Cl}]_t = [\text{T-Cl}]_0 - [\text{T-Cl}]_t - [\text{Cl}^-]_t \quad (2)$$

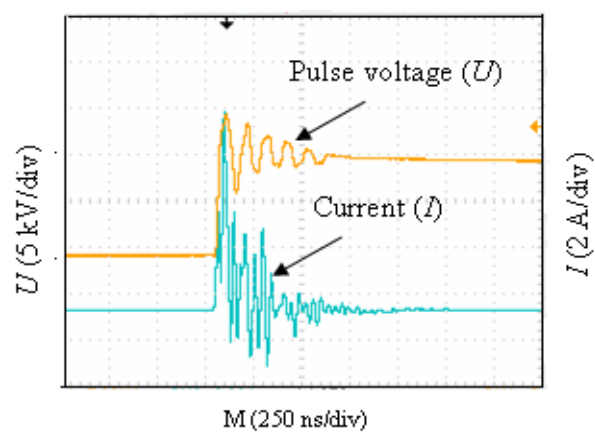
$$\eta_{\text{Cl}^-} (\%) = \frac{[\text{Cl}^-]}{[\text{T-Cl}]_0} \times 100\% \quad (3)$$

Where  $[\text{T-Cl}]_0$  was the initial stoichiometric amount of organic chlorine,  $[\text{T-Cl}]_t$  was the stoichiometric amount of organic chlorine in the remaining PCP during discharge treatment,  $[\text{Cl}^-]$  was the amount of  $\text{Cl}^-$  determined by IC, and  $\eta_{\text{Cl}^-}$  was the

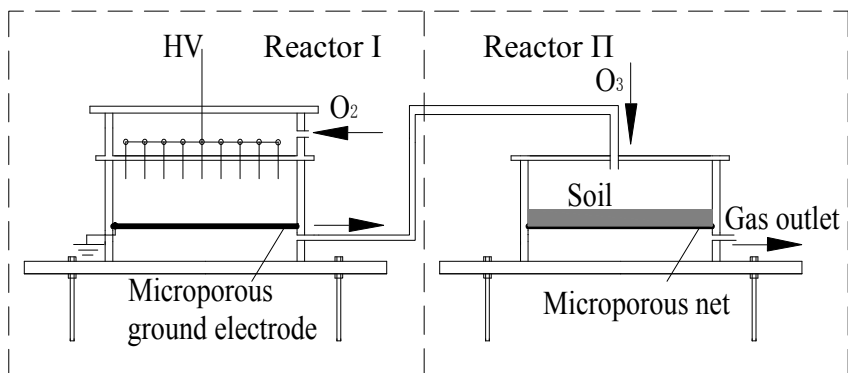
dechlorination efficiency.



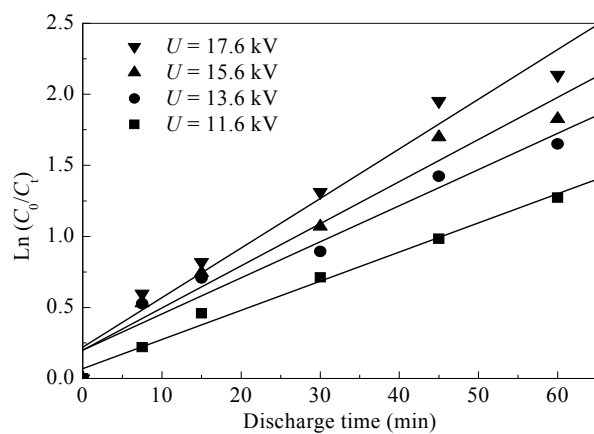
**Figure S1.** Section view of the reactor (1. high voltage electrode; 2. gas inlet; 3. soil layer; 4. ground electrode; 5. gas outlet). (□) partial view of the reactor; (□) total view of the reactor.



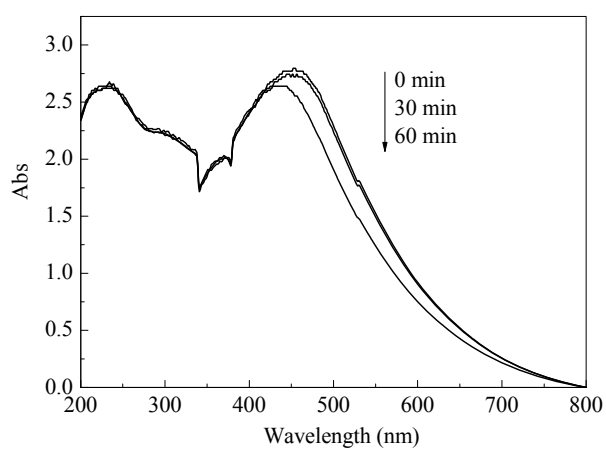
**Figure S2.** Typical pulsed voltage and current waveforms obtained in the experiment.



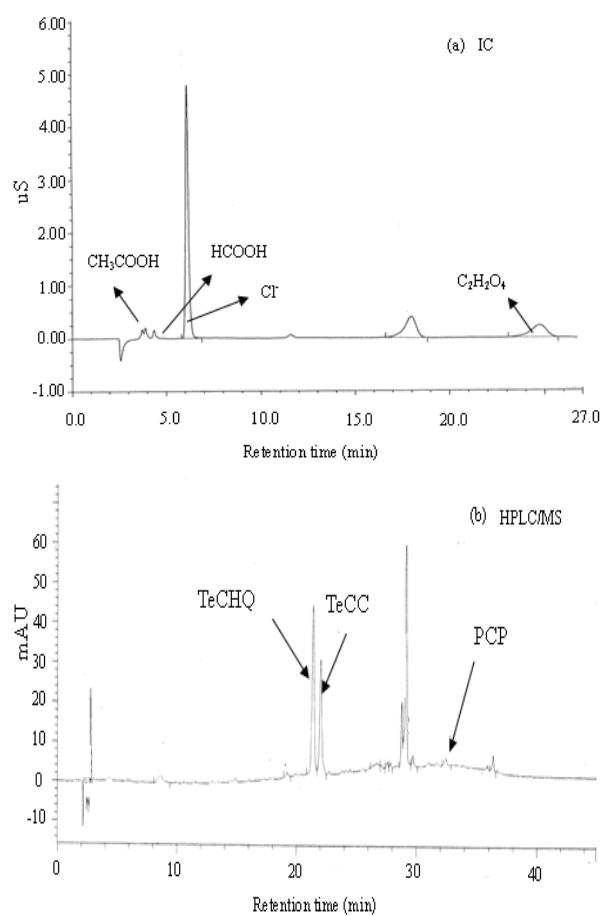
**Figure S3.** Schematic diagram of the experimental setup for pure ozonation.



**Figure S4.** Degradation kinetic curves of PCP in soil under different pulse voltages.



**Figure S5.** Variations of UV/VIS absorbance spectrum of HA desorbed from soil samples.



**Figure S6.** Total ion chromatograph (TIC) of intermediates of PCP degradation after 45 min discharge treatment ((a) IC; (b) HPLC/MS).



**Table S1.** The brief comparison of the present method with other technologies.

System	Initial PCP concentration (mg kg <sup>-1</sup> )	Treatment time	PCP removal (%)	Reference
Fungi	672	56 d	89%	3
Nanoscale iron/H <sub>2</sub> O <sub>2</sub>	1000	40 h	78%	4
Catalytic oxidation	67	3 d	60-70%	5
Biotreatment	10-30	28-35 d	100%	6
This study	200	60 min	87%	-

**Table S2.** The energy efficiencies under different pulse voltages after 60 min of treatment.

Pulse voltage (kV)	Energy efficiency (mg kJ <sup>-1</sup> )
11.6	2.05
13.6	1.85
15.6	1.52
17.6	1.25

**Table S3.** Remediation of PCP contaminated soils by PCDP and pure ozonation

Time (min)	O <sub>3</sub> consumed (mg)		PCP degradation efficiency (%)		O <sub>3</sub> utilization efficiency (mg/mg)	
	PCDP	Ozonation	PCDP	Ozonation	PCDP	Ozonation
15	0.12	0.13	85	63	7.1	4.9
30	0.16	0.18	98	78	6.3	4.4

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