Degradation Characteristics of Pentachlorophenol in Soil under Different Plasmas Using Pulsed Electrical Discharge

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Abstract—Pentachlorophenol (PCP) is a wood preserving agent that is commonly found in contaminated soils at wood treatment sites. The degradation characteristics of PCP under different plasmas (such as O₂ plasma, air plasma and N₂ plasma) were studied using pulsed discharge plasma. PCP degradation efficiencies in soil were greatly influenced by different plasmas. The removal efficiency ranked in the following order: O₂ plasma > air plasma > N₂ plasma. Almost 90%, 65% and 20% of PCP removal could be achieved within 15 min of discharge treatment under O₂, air and N₂ plasmas with the energy yields of 2.69, 1.95 and 0.60 g/kWh, respectively. The FT-IR results under diverse plasmas revealed that partial C-Cl bonds in PCP were cleaved during pulsed discharge plasma treatment. The mineralization of PCP was confirmed by the regular decrease in quantity of total organic carbon (TOC) and the quantitative release of chloride ions. Dechlorination corresponded to about 78%, 57% and 12% of total conversion of PCP under O₂, air and N₂ plasmas, respectively. The trend of the amount of organic chlorine in organic products indicated that the chlorinated intermediates were produced during pulsed discharge plasma treatment, and then they were undergone the dechlorination reactions as the process continued. Ozone played a decisive role for the removal process. However, in the case of N₂ plasma, hydroxylation of PCP and atomic N, N₂⁺ and N⁺ attack might be the degradation pathways for PCP degradation.

Keywords—Contaminated soil, pulsed corona discharge, different plasmas, pentachlorophenol

I. INTRODUCTION

Pentachlorophenol (PCP) is a general biocide and has been used extensively for a variety of purposes such as agriculture and timber preservation. Worldwide use of PCP has led to severe contamination problems particularly around former timber treatment plants [1]. PCP is toxic to humans and may target and/or damage the liver, kidney, hematopoietic system, pulmonary system and central nervous system [2]. Due to its acute and chronic toxicity and carcinogenic nature, PCP was listed as one of priority pollutants by the United States Environmental Protection Agency in 1979 [3]. Therefore, there is considerable interest in the remediation of sites contaminated by PCP.

Various methods have been employed to removal PCP from PCP contaminated soils, such as bioremediation [4], air stripping and incineration [5] and electrokinetic remediation [6]. Bioremediation process is a slow process and requires keeping rigorous conditions for microorganisms’ growth. The use of air stripping based on the phase transfer and non-degradation of the compound. Electrokinetic technology is limited by the solubility and desorption of organic pollutants in soil. Recently, electrical discharge technologies, especially pulsed discharge plasma, have attracted a great deal of attention for the degradation of organic compounds [7-9]. Because of the relatively short pulses and the fast pulse rise time (nanosecond level), pulsed discharge plasma has a higher energy efficiency compared to other advanced oxidation processes [8]. Many studies have been carried out using pulsed discharge plasma for oxidizing organic pollutants in water [8-11] or inactivating microorganisms [12]. In our previous research, we have studied the potential of PCP degradation in soil by pulsed discharge plasma from soil characteristics [13]. Depending on the composition of the gas phase (such as Ar, O₂, N₂ and air), a variety of chemically active species are formed, such as •O, •OH, •H radicals and N atom [14, 15]. •O, •OH and O₃ have powerful oxidation potentials and all play important roles in chemical reactions. N atom is also a relatively high density of reactive species produced by electron collisions of N₂. The degradation pathways of organic compounds were different due to the difference of oxidative potentials of the active species in Ar, O₂, air or without gas [16, 17].

The aim of this study is to investigate the degradation characteristics of PCP in soil by different plasmas. The pulsed discharge plasmas were produced under air, O₂ and N₂, respectively. The degradation efficiency, energy yield and specific energy density were evaluated under different plasmas. The detection of active species such as O₂ and H₂O₂ were also conducted. The roles of active species on PCP removal were discussed, and mineralization and dechlorination of PCP in soil were also investigated under different plasmas.

II. EXPERIMENTAL

A. Materials

PCP (purity > 95%) was purchased from the Chemical Plant of Nankai University, China. All other...
grade (Tianjin Fuyu Refinery Chemical Co., Ltd. and Shenyang Chemical Reagent Factory, China) and used as received without any purification.

Soil samples used in the study were collected from a suburb of Dalian, China. The pretreatment process, the soil properties and the preparation of contaminated soil samples were the same as our previous research [13]. The original PCP concentration in the soil is 200 mg/kg.

B. Soil treatment

The schematic diagram of the experimental apparatus was illustrated in Fig. 1. The reaction system consisted of a pulsed high-voltage power supply and a reactor vessel. The pulse frequency and pulse-forming capacitance \( C_p \) were 50 Hz and 25 pF, respectively. The high voltage electrode comprised of seven stainless-steel hypodermic hollow needles with inner diameter of 0.7 mm and outer diameter of 1.0 mm, and the ground electrode was a wire netting (200 mesh). The distance between the high voltage electrode and the ground electrode was 12 mm. The peak pulse voltage and current were measured with oscilloscope (Tektronix TDS2014) equipped with voltage probe (Tektronix P6015A) and current probe (Tektronix P6021).

In each experiment, PCP contaminated soil samples (approximately 5.0 g) were spread on the ground net electrode with a thickness of about 3.6 mm. Prior to discharge treatment, the moisture content of soil was adjusted to about 10% with deionized water. The carrier gas (0.5 L/min) was injected into the discharge area through the seven 9# stainless-steel hypodermic pinheads and vented through the soil layers. The pulse voltage used in the study was 18 kV unchanged unless special illustration.

C. Extraction and analysis

After each experiment, the soil sample was mixed with 50 mL NaOH solution (pH = 11) in an airtight sealed conical flask and then shaken on a shaker at 300 rpm for 12 h to extract PCP, then the mixture was centrifuged at 3000 rpm for 15 min and finally the extract was collected.

The extract was filtered through 0.45 μm membranes and then a 25 μL aliquot of the filtrate was injected into a HPLC system (SCL-10ACP, Shimadzu, Japan) equipped with a Hypersil ODS (25 μm, 4.6 × 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, and the wavelength of UV detection was set as 220 nm. The recoveries were 81.5-86.9% (n = 5).

Chloride ion was detected by ion chromatography (IC, ICS-90, USA) equipped with AMMSIII 4 mm suppressor, Dionex IonPac AS9-HC column and D5S conductance detection. The mobile phase was 9 mmol/L sodium carbonate solutions with a flow rate of 1.0 mL/min, and the regenerant was 50 mmol/L H₂SO₄ solutions with a flow rate of 1.0 mL/min. Total organic carbon was determined using a Total Organic Carbon analyzer (TOC-5000A Shimadzu) after the sample mineralization. The Fourier transform-infrared spectroscopy (FT-IR, EQUINOX55 spectrophotometer) was applied in the characterization of the chemical bonds of the soil samples.

The oxidation power measured with ozone equivalent concentration \( (C_{O3}) \) was detected using 50 mL KI solutions absorption as described by Suarasan et al. [18]. After a period of discharge time, soil sample was mixed with 30 mL water in an airtight sealed conical flask and then shaken on a shaker at 300 rpm for 1 h to extract H₂O₂. The H₂O₂ concentration in the extract was determined by a UV-vis spectrophotometry (U-2800) at wavelength of 400 nm as described by Robin [19].

The total organic chlorine concentration \([\text{tot. org. Cl}}\) at time \( t \) was defined as [20, 29]:

\[
[tot. \text{org. Cl}]_t = 5[PCP]_0 - [Cl^-]_t \quad (1)
\]

where \([PCP]_0\) was the initial PCP concentration and \([Cl^-]\) was the chloride concentration at time \( t \).

The corresponding organic chlorine concentrations in PCP \([\text{org. Cl in PCP}}\) in intermediates \([\text{org. Cl in intermediates}}\) are then:

\[
[\text{org. Cl in PCP}]_t = 5[PCP]_0 - [PCP]_t \quad (2)
\]

\[
[\text{org. Cl in intermediates}]_t = [\text{tot. org. Cl}]_t - [\text{org. Cl in PCP}]_t = 5[PCP]_0 - [PCP]_t - [Cl^-]_t \quad (3)
\]

The dechlorination efficiency \( \eta_{Cl^-} \) was defined as [20]:

\[
\eta_{Cl^-} (\%) = \frac{[Cl^-]_t}{5[PCP]_0} \times 100\% \quad (4)
\]

The input energy per discharge can be obtained by the following equation,

\[
E_{in} = \int_0^T UI \, dt \quad (5)
\]
where \( U \) and \( I \) are the discharge voltage (V) and current (A) at time \( t \) (ns), respectively. \( E_{in} \) is the input energy per discharge (J/discharge). \( T \) is the total time (ns) of one discharge.

The specific energy density (SED) can be calculated by the following equation,

\[
\text{SED} = \frac{E_{in} N}{M_{\text{soil}}} \tag{6}
\]

\[N = 60 f t \tag{7}\]

where \( M_{\text{soil}} \) is the total amount of treatment soil (g), \( N \) is the discharge number, \( f \) is the pulsed frequency (Hz) and \( t \) is the time for PCP degradation (s).

The energy yield \( G \) is defined as the removed PCP divided by input energy.

\[
G = \frac{m_{\text{PCP}}}{E_{in} N} \tag{8}
\]

where \( m_{\text{PCP}} \) is the amount of PCP removed (mg).

The average PCP degradation rate (\( \nu \)) is defined as follows,

\[
\nu = \frac{m_{\text{PCP}}}{t} \tag{9}
\]

III. RESULTS AND DISCUSSION

A. PCP removal under different plasmas

PCP degradation by different plasmas under different specific energy densities (SED) was illustrated in Fig. 2, and herein the different plasmas were triggered under \( \text{N}_2 \), \( \text{O}_2 \) and air atmospheres, respectively. It could be observed that the increase of SED enhanced PCP degradation efficiency within the same treatment time (15 min) for all kinds of plasmas used in the study. At higher SED, more energetic electrons are produced, leading to the accelerated formation of active species [18], which was beneficial for PCP degradation. The greatest PCP degradation efficiency was achieved under \( \text{O}_2 \) plasma, and followed by air plasma and the lowest under \( \text{N}_2 \) plasma when the SED was kept unchanged. For example, almost 90% of PCP removal was achieved within 15 min of discharge treatment under \( \text{O}_2 \) plasma with the SED of 243 J/g soil, and about 65% under air plasma, while it was only 20% within the same treatment time under \( \text{N}_2 \) plasma.

Under \( \text{O}_2 \) plasma, the input energy was mainly consumed to produce the O-reactants, whose concentrations were larger than those under air plasma, resulting in greater degradation efficiency under \( \text{O}_2 \) plasma than that under air plasma. In the case of \( \text{N}_2 \) plasma, the atomic \( \text{N} \), \( \text{N}_2^+ \) and \( \text{N}^- \) can be created by high voltage discharge [21], but no ozone and oxygen participated in PCP degradation. Hence the atomic \( \text{N} \), \( \text{N}_2^+ \) and \( \text{N}^- \) attack may be the degradation pathways for PCP degradation under \( \text{N}_2 \) plasma. The roles of atomic \( \text{N} \), \( \text{N}_2^+ \) and \( \text{N}^- \) on 4-chlorophenol degradation by pulsed high voltage discharge were also confirmed by Zhang [11].

Table 1 shows the changes of PCP degradation efficiency (\( \eta \)), \( G \), \( \nu \), ozone equivalent concentration (\( C_{\text{O}_3} \)) and \( \text{H}_2\text{O}_2 \) concentration (\( C_{\text{H}_2\text{O}_2} \)) under different plasmas after 15 min of discharge treatment. Herein the \( C_{\text{O}_3} \) and \( C_{\text{H}_2\text{O}_2} \) were measured in PCP contaminated soil and in clean soil, respectively. Greatest \( C_{\text{O}_3} \) and \( C_{\text{H}_2\text{O}_2} \) were detected in \( \text{O}_2 \) plasma, and no \( \text{O}_3 \) in \( \text{N}_2 \) plasma.
Furthermore, greater PCP degradation efficiency, higher energy yield, larger specific energy density and faster PCP degradation rate were obtained in O₂ plasma. As compared with PCP contaminated soil, higher CO₃ and CΗ₂O₂ occurred in clean soil. These results indicated that O₃ and H₂O₂ both played certain roles in PCP degradation. In our previous study, the main role of O₃ in PCP degradation by pulse discharge plasma was evaluated through the comparison with pure ozonation [13].

The light-emission pictures recorded under different plasmas were presented in Fig. 3. Under the same peak pulse voltage, the brightest light appeared in the case of N₂ plasma, and followed by air plasma, and the faintest light showed in O₂ plasma. These results indicated that different discharge states presented under different plasmas, and the strongest discharge occurred in N₂ plasma. However, the lowest PCP degradation efficiency was achieved in N₂ plasma. From this result, we could also induce that O₃ played a dominant role in PCP degradation in air plasma.

B. Effect of treatment time on PCP degradation

The effect of discharge treatment time on PCP degradation under different plasmas was shown in Fig. 4. PCP degradation efficiency increased with treatment time. However, as the reaction proceeded, the oxidation rate of PCP declined gradually. For example, about 90%, 65% and 20% of PCP removal were achieved within 15 min of discharge treatment under O₂, air and N₂ plasmas, respectively. However, there was only an enhancement of 10%, 24% and 8% under O₂, air and N₂ plasmas, respectively, as the treatment time increased from 15 to 60 min. This could be due to the intensified interaction of the second or later generation of intermediates with active species, which resulted in the decrease of the amount of active species reacted with PCP, especially in air and N₂ plasmas.

C. FT-IR analysis

In order to further understand the characteristics of PCP degradation under different plasmas, the transmission FT-IR spectrometry was applied for the analysis of the chemical bonds of the soil samples before and after treatment, and the solid-state FT-IR spectra of soil samples treated under different plasmas were presented in Fig. 5. It could be observed that no additional peaks appeared for all the treated soil samples as compared with original soil sample. The band at ~ 3623 cm⁻¹ could be caused by free OH groups and the band at ~ 3430 cm⁻¹ by hydrogen-bonded OH groups [22, 23]. The band around 1630 cm⁻¹ was mainly associated with the aromatic ring stretching of C=C groups [24, 25]. The peak at ~ 1040 cm⁻¹ was usually assigned to C-O stretches in lactonic, ether and phenol groups [26]. It could be found that the intensity of these peaks decelerated after 60 min of pulsed discharge plasma treatment under O₂ and air plasmas, especially around 1040 cm⁻¹, suggesting that PCP was decomposed greatly.
after discharge treatment under O$_2$ and air plasmas. However, no obvious peak around 1850-1650 cm$^{-1}$ appeared for both of the treated soil samples, which was usually caused by the stretching vibration of C=O in ketones, aldehydes and carboxyl groups [24, 25]. The reason might be that the amounts of products possessing C=O were so much less that they were beyond the limits of detection of the FT-IR spectrometry. In addition, no obvious change in the intensity of peak could be seen for the soil sample treated under N$_2$ plasma as compared with original soil sample.

As compared with original soil sample, the lack of an observable new peak in the region of 900-500 cm$^{-1}$ was noted for all the treated soil samples. However, the intensity of ~800 and ~690 cm$^{-1}$ band decreased obviously after pulsed discharge plasma treatment under O$_2$ and air plasmas. The C-Cl stretching vibrations in chlorophenols lie in the region 900-700 cm$^{-1}$ [25]. In our case the ~800 and ~690 cm$^{-1}$ bands could be attributed to stretching vibration of C-Cl. These results revealed that C-Cl bonds in PCP were cleaved partially during pulsed discharge plasma treatment.

The trends in the peak intensity, among O$_2$, air and N$_2$, were consistent with those in the degradation efficiencies. That was, the greater the degradation efficiency was, and the weaker the peak intensity appeared.

D. Dechlorination and mineralization

Due to the possibility of the formation of intermediates, the degradation rate of the target compound does not always correspond to the mineralization of the organics. Therefore, it is necessary to investigate the dechlorination and mineralization of PCP in soil during pulsed discharge plasma treatment.

In the present study, the results of the dechlorination and mineralization of PCP under diverse plasmas were shown in Fig. 6. The dechlorination efficiency in Fig. 6(a) was lower than PCP degradation efficiency as shown in Fig. 4, under each kind of plasma. For example, the percentage of PCP dechlorination increased up to 78%, 57% and 12% within 60 min of pulsed discharge plasma treatment under O$_2$, air and N$_2$ plasmas, respectively. Correspondingly, the percentages of PCP degradation were 100%, 90% and 28% within the same time period under O$_2$, air and N$_2$ plasmas, respectively. These results indicated that the intermediates containing chlorine were continuously degraded at the later stage of experiments [20]. Furthermore, in order to corroborate the number of the released Cl$, the chloride formation yields, defined as the mole of chloride formed per mole of PCP degrade [27], have been calculated and included in Fig. 6(b). The chloride formation yield increased with treatment time, which was achieved to 4.2, 3.4 and 1.6 within 60 min of pulsed discharge plasma treatment under O$_2$, air and N$_2$, respectively. The obtained results presented that almost four, three and one chlorine atoms were released from a molecule of PCP after 60 min of discharge treatment in O$_2$, air and N$_2$, respectively. It also revealed the differences in PCP degradation from the changes of dechlorination and chloride formation yield under diverse plasmas.

The mineralization of PCP in soil was shown in Fig. 6(c). It could be observed that the mineralization rate under each kind of plasma was higher at the beginning of
pulsed discharge plasma treatment, but diminished with treatment time. The result indicated that aliphatics, such as carboxylic acids produced by ring opening reactions, were formed during pulsed discharge plasma treatment. The aliphatics were more resistant to mineralization [28]. The organic chlorine concentration in intermediates was calculated based on the report by Ho and Bolton [29], and the result was showed in Fig. 7. It could be seen that the amount of organic chlorine in intermediates firstly increased as pulsed discharge plasma treatment, and then decreased as the process continued under O2 and air plasmas. These results indicated that the chlorinated intermediates were produced during pulsed discharge plasma treatment, and then they were undergone the dechlorination reactions as the process continued. However, the amount of organic chlorine in intermediates increased during pulsed discharge plasma treatment under N2 plasma. It might be due to the much lower dechlorination efficiency. The detailed intermediate products would be confirmed in a future study.

IV. CONCLUSION

PCP degradation characteristics in soil by pulsed discharge plasma were investigated under different plasmas in the present study. The results showed that PCP degradation efficiency was greatly influenced by the types of plasma. The greatest PCP degradation efficiency and highest energy yield were achieved in O2 plasma.

C-Cl bonds in PCP were partially cleaved during pulsed discharge plasma treatment. The dechlorination efficiency was lower than PCP degradation efficiency in all kinds of plasmas. The chlorinated intermediates were produced during pulsed discharge plasma treatment, and then they were undergone the dechlorination reactions as the process continued, especially under O2 and air plasmas.

Ozone played a decisive role for the removal process. However, atomic N, N2, and N+ attack might play a certain role in PCP degradation, especially in N2 plasma.

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