Degradation of pentachlorophenol in soil by pulsed corona discharge plasma

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ABSTRACT

The remediation of pentachlorophenol (PCP) contaminated soil using pulsed corona discharge plasma was reported in this study. The effect of practical run parameters such as peak pulse voltage, pulse frequency, gas atmospheres (air, O_2, Ar and N_2), air flow rate and pollution time on PCP degradation was investigated, and the intermediate products were also studied. The results indicated that PCP degradation efficiency increased with an increase in peak pulse voltage or pulse frequency, due to the enhancement of energy input. There existed a maximal PCP degradation efficiency with the change of air flow rate. PCP degradation efficiencies under oxygen and air atmospheres were achieved 92% and 77% after 45 min of discharge treatment at 14.0 kV, respectively, which were only 19% and 8% under argon and nitrogen atmospheres, respectively. O_3 played an important role in PCP degradation. However, other processes also contributed to PCP degradation, such as N, N_2^+, N^+ and $^\bullet OH$. The pollution time evidenced slight influence on PCP degradation. The main intermediate products produced during the treatment process were identified as tetrachlorocatechol, tetrachlorohydroquinone, acetic acid, formic acid and oxalic acid by HPLC/MS and ion chromatography. This study is expected to provide reference for the application of pulsed corona discharge in soil remediation.

1. Introduction

Soil contamination by organic compounds has become an issue of concern around the world [1]. Efforts to explore effective methods to treat soil contaminated with pesticides and other compounds have led to the study of alternative remediation strategies, such as bioremediation [2,3], chemical remediation [4] and electrokinetic remediation [5]. Bioremediation process is relatively slow and requires keeping the experimental conditions conducive to the viability and growth of the microorganisms. Conventional chemical remediation may bring secondary pollution, and then increase the cost of treatment [4]. Electrokinetic technology is limited by the solubility and desorption of organic pollutants in soils [6]. Thus, it is highly recommended to find feasible methods to remediate organic pollutants contaminated soils, especially for those polluted sites required for quick remediation.

Advanced oxidation processes (AOPs) are receiving great emphasis on pollution control because of their ability to rapidly oxidize refractory organic contaminants [7]. Among the AOPs, low-temperature plasma has been demonstrated as an end-of-pipe technology for pollution control [8]. Currently, low-temperature plasma, especially pulsed corona discharge, has received a great attention in environmental protection field [9,10]. Two kinds of processes (chemical and physical processes) exist during pulsed corona discharge, which are thought to occur simultaneously in synergism for direct or indirect degradation of organic compounds [11]. The chemical processes are mainly due to the formation of various active radicals, such as $^\bullet OH$, $^\bullet H$, $^\bullet O$, $^\bullet O_2$ and $^\bullet HO_2$, and active molecules, such as H_2O_2 and O_3. All these active species have high oxidation potentials to break the molecular bonds of organic contaminants. The physical processes include strong electric field, ultraviolet light, shock waves and pyrolysis. In wastewater treatment, Clements et al. [12] firstly investigated pre-breakdown phenomena in water using high-voltage pulse. Since then, this technology has been widely studied in wastewater treatment, involving sterilization [13], decolorization [9] and removal of refractory organic pollutants [14]. In addition, low-temperature plasma has also been largely studied in air pollution control [15,16]. However, the most noteworthy is the tentative application of low-temperature plasma in the removal of organic pollutant from solid phase [17,18].

In view of wide application of low-temperature plasma technology as mentioned above, it is suggested that it may be powerful enough to treat organic pollutants in solid phase, e.g. soil. When organic pollutants contaminated soil was placed in the discharge plasma region, the organic pollutants may be excited, ionized and

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dissociated by high energy electrons, and various active radicals, such as $\cdot OH$, $\cdot H$, $\cdot O$, $\cdot O_2$ and $\cdot HO_2$, and active molecules, such as H_2O_2 and O_3 can react with pollutants. Simultaneously, physical effects, generated concomitantly during the discharge process such as strong electric field, UV light and shock waves, 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 may be removed effectively and rapidly. Therefore, remediation of pentachlorophenol (PCP) contaminated soil was conducted using pulsed corona discharge plasma in this study. PCP was mainly used as wood preservative and pre-harvest herbicide [19] and listed as one of priority pollutants by the United States Environmental Protection Agency in 1979 due to its acute and chronic toxicity and carcinogenic nature [20]. Experiments under various conditions were carried out to investigate the effects of electric factors and carrier gases on PCP degradation. The roles of different radicals formed under different gas atmospheres in PCP degradation were discussed. The intermediate products were also identified. This study may contribute to the application of pulsed corona discharge plasma in the remediation of practical PCP contaminated soils.

2. Experimental

2.1. Materials

PCP (purity > 95%) was purchased from the Chemical Plant of Nankai University, 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.

Soil samples used in this study were collected from a suburb of Dalian, China. The soil samples were pretreated as follows. Firstly, they were air-dried for 3 d, 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 were further air-dried before use. The soil properties were as follows: the contents of sand, silt, clay and organic matters were 3.00%, 70.7%, 26.3% and 5.44%, respectively; bulk density 1.12 g cm^{-3}; porosity 12.8%; pH 7.9; loss on ignition 5.80%.

The PCP contaminated soil samples were artificially prepared by adding appropriate amount of PCP acetone solution into a given amount of pretreated soil. The soil was vigorously homogenized for several hours (such as 4, 24, 48, 72 and 96 h) to gain soil samples with different pollution times, and then placed in the fume hood until acetone evaporated entirely, which was confirmed by weight loss. This method gave a uniform PCP distribution in the soil at about 200 mg kg^{-1}. The pH values of the soils were determined for a mixture of soil and water at a ratio of 1:2.5 (soil:water = w/w) as described by Wei [21].

2.2. Treatment of contaminated soil samples

The schematic diagram of the experimental apparatus and a sectional view of the reactor were illustrated in Figs. 1 and 2, respectively. The reaction system 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). 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 0–150 Hz adjustable and 25 pF, respectively. The high-voltage electrode comprised of seven 9$^\#$ stainless-steel hypodermic pinheads which were distributed uniformly in a circle of 50 mm diameter and secured
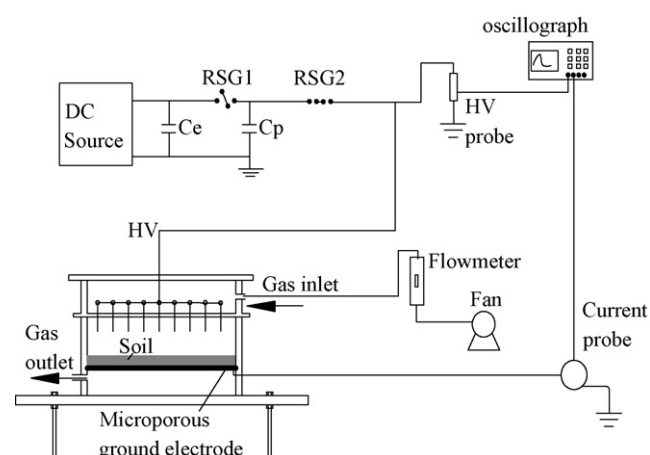

Fig. 1. Schematic diagram of the experimental apparatus.

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^{TM} cylinder (50 mm inner diameter and 50 mm length), herein named as part (a) of the reactor. The ground electrode was a wire netting (200 mesh), which was embedded into a Plexiglas^{TM} cylinder (50 mm inner diameter and 50 mm length), herein named as part (b). The part (a) and part (b) were connected to form the reactor system. The distance of adjacent needle was 15 mm. The distance between the high-voltage electrode and the ground electrode was 12 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, and then the electric power was calculated through the integral of pulse voltage and current under time.

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 20% with deionized water. Carrier gas was injected into the reactor from the top of the Plexiglas^{TM} cylinder. Concentration of PCP in the soil layers was measured after desirable treatment time.

The control experiments were performed on the soil layers in the same procedures as the discharge experiments but without discharge.
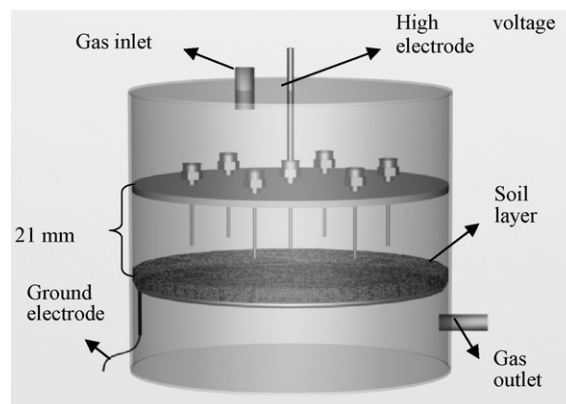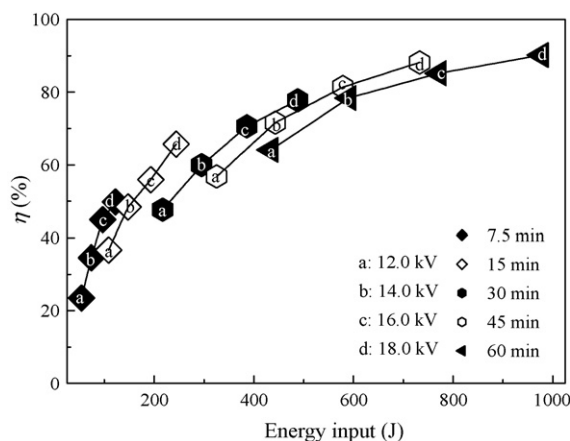

Fig. 2. Section view of the reactor.

Fig. 3. Effect of energy input on PCP degradation under different pulse voltages (conditions: pulse frequency 67 Hz; air flow rate 3.0 L min^{-1}; pollution time 4 h).
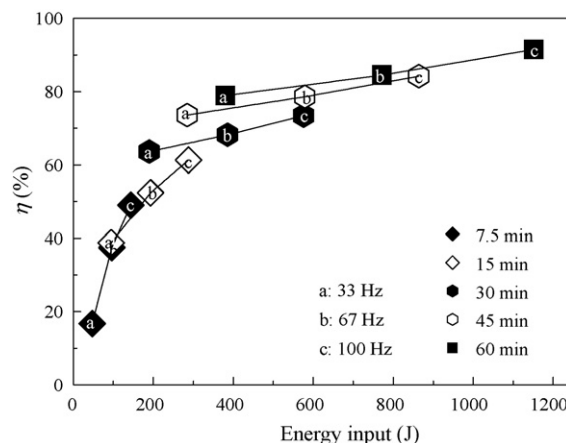

Fig. 4. Effect of energy input on PCP degradation under different pulse frequencies (conditions: pulse voltage 16.0 kV; air flow rate 3.0 L min^{-1}; pollution time 4 h).

2.3. Extraction and analysis

In order to analyze the residual PCP in soil, after each discharge experiment, all the soil samples were 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 from the soil samples, 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 mm × 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^{-1}. PCP was determined by UV/VIS detection at a wavelength of 220 nm. The recoveries were 81.5–86.9% for PCP in soils in this study ($n = 5$).

HPLC/MS (HP1100/MSD, Agilent Co., USA.) was used for qualitative analysis of intermediates and final products of the reaction. Analyses were performed with electrospray ionization in the negative mode. Nitrogen was used as dry gas at the flow rate of 8 L min^{-1} and temperature was 350 °C. The nebulizer pressure was 35 psi. In the full-scan mode, the m/z range was 80–800 in the negative-ion (NI) mode. Organic acids (formic acid, acetic acid, oxalic acid) and chloride ions were detected by ion chromatography (IC, ICS-90, USA) equipped with AMMS III 4 mm suppressor, Dionex IonPac AS9-HC column and DS5 conductance detection. The mobile phase was 9 mmol L^{-1} sodium carbonate solution with a flow rate of 1.0 mL min^{-1}, and the regenerant was 50 mmol L^{-1} H$_2$SO$_4$ solution with a flow rate of 1.0 mL min^{-1}.

All experiments were conducted in duplicates.

3. Results and discussion

3.1. Effect of energy input on PCP removal under different pulse voltages

Pulsed corona discharge can generate a large number of active species (such as high energy electrons, ions, radicals, and O$_3$), ultraviolet light, shock waves, and heat etc, which are directly related to the pulse voltage. Increasing pulse voltage can improve the energy of each pulse. Hence, pulse voltage is an important parameter to evaluate the practical application of this technology in pollution control. The effect of energy input on PCP degradation efficiency under different pulse voltages was illustrated in Fig. 3. The increase of pulse voltage benefited PCP degradation, due to the enhancement of energy input. With the increase of pulse voltage from 12.0

to 18.0 kV, PCP degradation efficiency enhanced from 64 to 90% within 60 min of discharge treatment; correspondingly, the energy input increased from 244 to 976 J. In addition, under the condition of the same PCP degradation efficiency, less energy input was needed for higher pulse voltage with a shorter discharge time. For example, PCP degradation efficiency of 56% was achieved within 45 min of discharge treatment at pulse voltage of 12.0 kV with the energy input of 325 J; while 192 J was needed at pulse voltage of 16.0 kV within 15 min of discharge treatment. This phenomenon indicated that PCP degradation experiment conducted at a higher pulse voltage with a shorter treatment time could reduce the energy consumption. Furthermore, there was a remarkable influence for energy input on PCP degradation at early stage of discharge treatment (7.5 min), which weakened gradually with the treatment time continued. This could be due to the intensified competition for energy between the second or later generation of intermediates with PCP, leading to the decrease of energy consumed by PCP.

The energy efficiency was defined as the consumed energy divided by PCP removed. After 60 min of discharge treatment at 16.0 kV, the energy efficiency was 908 J mg^{-1}.

3.2. Effect of energy input on PCP removal under different pulse frequencies

In non-thermal plasma process, the energy injected into the reactor increases with the pulse frequency at a certain extent, which may benefit the removal of organic pollutants. The effect of energy input on PCP removal was performed under different pulse frequencies as shown in Fig. 4. The energy input increased with the pulse frequency, and thus PCP degradation efficiency enhanced. For example, when the pulse frequency increased from 33 to 100 Hz, the corresponding energy input enhanced from 95 to 288 J; correspondingly, PCP degradation efficiency increased by 23% within 15 min of discharge treatment. Under the condition of the same PCP degradation efficiency, less energy input was needed for lower pulse frequency with a longer discharge time. PCP degradation efficiency of 74% was achieved within 30 min of discharge treatment at pulse frequency of 100 Hz with the energy input of 576 J; while 285 J was needed at pulse frequency of 33 Hz within 45 min of discharge treatment. This phenomenon suggested that PCP degradation experiment conducted at a lower pulse frequency with a longer treatment time could reduce the energy consumption. Furthermore, similar with the role of pulse voltage, the influence of energy input on PCP degradation under different pulse frequencies weakened gradually as treatment time went on.
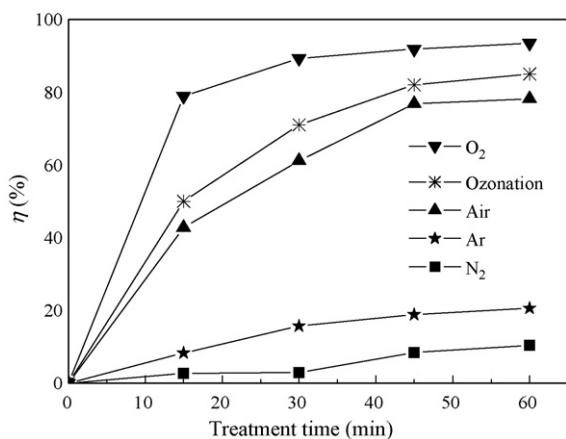
Fig. 5. Effect of gas atmospheres on PCP degradation in soil (conditions: pulse voltage 14.0 kV; pulse frequency 67 Hz; gas flow rate 3.0 L min^{-1}; pollution time 4 h) and pure ozonation treatment for PCP degradation.
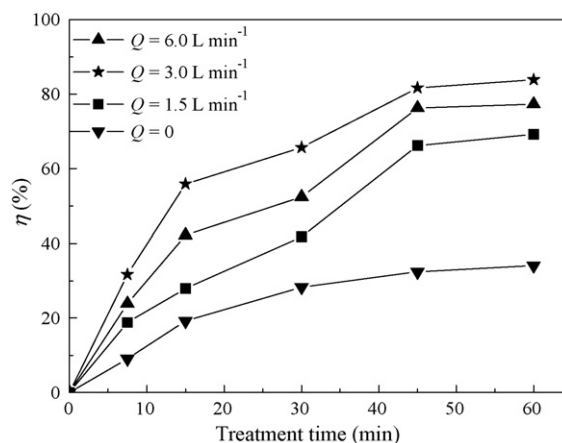

Fig. 6. Effect of air flow rate Q on PCP degradation in soil (conditions: pulse voltage 16.0 kV; pulse frequency 67 Hz; pollution time 4 h).

After 60 min of discharge treatment at 33, 67 and 100 Hz, the energy efficiencies were 481, 908, 1252 J mg^{-1}, respectively. Comprehensive consideration of PCP degradation efficiency and its energy efficiency, 67 Hz was chosen as the optimal pulse frequency.

3.3. Effect of gas atmosphere on PCP removal

Removal of organic pollutants using pulsed corona discharge is a complex process which may include multiple mechanisms acting simultaneously. The varieties and numbers of oxidative species are considerably different during discharge processes under different gas atmospheres [22]. In order to investigate the roles of different oxidative radicals in PCP degradation, experiments were conducted separately under oxygen, nitrogen, air and argon atmospheres. The experimental results for PCP degradation under different gas atmospheres were shown in Fig. 5. The degradation efficiencies obtained under oxygen and air atmospheres were much higher than those under argon and nitrogen atmospheres. PCP removal efficiencies of 92% and 77% were achieved in oxygen and air atmospheres after 45 min of discharge treatment, respectively; while only 19% and 8% removals of PCP were obtained in argon and nitrogen atmospheres at the same treatment time, respectively.

The dominant and strongly oxidative species in the discharge process are considered to be oxygen atom (O) and hydroxyl radicals (•OH), which are mainly produced by electron impact dissociation of H_2O and O_2, respectively. •OH radicals may react with each other to form H_2O_2, and O atoms may react with O_2 to form O_3. The O atoms and O_3 are produced only under atmospheres containing oxygen (not under argon or nitrogen atmosphere); while •OH radicals and their reaction products H_2O_2 are produced under humid atmosphere [23]. As reported in the literatures [22,23], the •OH radicals density was much higher under argon atmosphere than that under air atmosphere at the same condition. In addition, in order to investigate the contribution of O_3 to PCP degradation, the experiment of PCP degradation by pure O_3 treatment (without discharge) was conducted and the result was shown in Fig. 5. Herein, the concentration of O_3 was equal to that obtained by the discharge treatment under O_2 atmosphere. After 45 min of O_3 treatment, 82% of PCP was degraded, which was about 10% lower than that obtained by the discharge treatment under O_2 atmosphere. These results indicated that (1) in the case of O_2 atmosphere, there were other active species involved with the PCP reaction in addition to O_3; while in the case of argon atmosphere, PCP degradation was attributed mainly to the •OH radicals. (2) O_3 was the main active species for PCP degradation.

Under oxygen atmosphere, the input energy was mainly consumed to produce the O-reagents, whose concentrations were larger than those under air atmosphere, resulting in the larger degradation efficiencies under oxygen atmosphere than those under air atmosphere.

In general, N_2 is inactive and cannot participate in many chemical reactions. But when discharge occurred in gas atmosphere containing N_2, it can be dissociated to the atomic N, N_2^+ and N^+ [24]. The bond dissociation energy of N_2 (9.82 eV) is higher than that of O_2 (5.12 eV), and thus it is much easier for O_2 to dissociate than N_2 when pulse discharge occurs under air atmosphere. Therefore, more •O radicals and O_3 can be generated than N, N_2^+ and N^+ under air atmosphere. Furthermore, the oxidative potentials of •O radicals and O_3 are much stronger than those of atomic N, N_2^+ and N^+, so the PCP degradation efficiency was higher under air atmosphere that that under N_2 atmosphere. However, PCP degradation under N_2 atmosphere may be contributed to the attack of atomic N, N_2^+ and N^+. The roles of atomic N, N_2^+ and N^+ on 4-chlorophenol degradation by pulsed high-voltage discharge were confirmed by Zhang et al. [25].

3.4. Effect of air flow rate on PCP removal

As discussed above, PCP could be efficiently degraded under oxygen or air atmosphere. From the point of view of economy and universality, air was applied in the following experiments. The effect of air flow rate (Q) on PCP degradation was then studied in this part, and the experimental result was illustrated in Fig. 6. A certain range of maximal degradation rate existed along with the change of Q, which was obtained at Q = 3.0 L min^{-1} in the experiments. When Q increased from 1.5 to 3.0 L min^{-1}, PCP degradation efficiency increased to 85% after 60 min of discharge time. However, it decreased to 77% at Q = 6.0 L min^{-1}. In addition, about 39% removal of PCP could be obtained after 60 min of discharge treatment without gas bubbling, this may be due to that there existed originally some air in the discharge area, because the experiments were conducted at normal temperature and pressure. In addition, the existence of carrier gas could cause the change of discharge characteristics. Pulsed discharge occurred more easily with carrier gas supplement, as compared with that of no carrier gas supplement, which was due to the fact that low pressure was generated near the pinpoint when the carrier gas passed through it, and thus the density of the carrier gas would decrease, and therefore the corona onset voltage would decrease [26]. The results were similar with those of Zhang et al. [27], who pointed out that the increase of air flow rate was helpful to the transfer of ozone from gas phase to
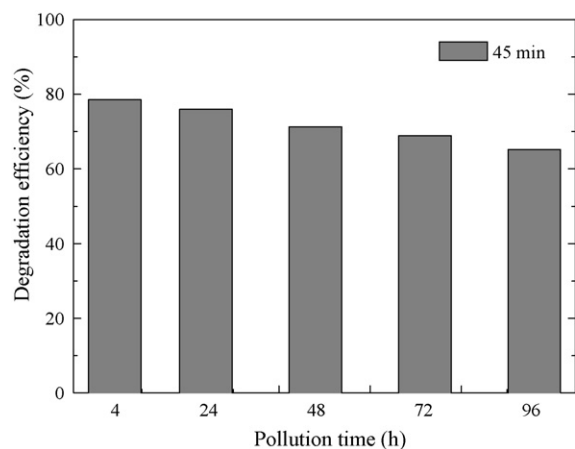
Fig. 7. Effect of pollution time on PCP degradation in soil (conditions: pulse voltage 16.0 kV; pulse frequency 67 Hz; air flow rate 3.0 L min^{-1}; treatment time 45 min).

liquid phase. However, with the further increase of air flow, the residence time of ozone in aqueous was shortened and the utilization efficiency of ozone was decreased. Choi et al. [28] and Shin et al. [29] reported that less time was required for ozone gas to break through soil layer as the gas flow rate increased. Similarly, it could be suggested that the increase of air flow rate was helpful to the transfer of active species from gas phase to soil layer, while the residence time of active species in soil layer was shortened with the further increase of air flow rate, resulting in the utilization efficiency of active species decreased.

3.5. Effect of pollution time on PCP removal

It is important to note that when organic pollutants are in contact with the soil for long periods of time, they may enter the inside of soil granules, then becoming more deeply adsorbed by soil and thus less available, which may diminish the capabilities of active species to oxidize sorbed organic pollutants. Hence the effect of the pollution time of PCP in soil on its degradation was investigated, and the experimental results were shown in Fig. 7. The pollution time evidenced slight influence on PCP degradation. There was only a decline of 13.4% in PCP degradation efficiency as pollution time persisted from 4 to 96 h, indicating that active species could penetrate into the inside of soil granules and reacted with PCP.

3.6. Analyses of intermediates

The intermediates and/or final products of PCP degradation in soils were analyzed using HPLC/MS and IC in order to understand the toxicity and biodegradability of soil sample after discharge treatment. The total ion chromatogram (TIC) of the intermediates of PCP degradation after 45 min of discharge treatment was shown in Fig. 8. Fig. 8(a) presented the TIC of untreated soil sample, and PCP was detected in the peak at retention time of 32.4 min. As shown in Fig. 8(b), PCP was degraded greatly after 45 min of discharge treatment, which could be confirmed by the remarkable decrease of the intensity of the peak of PCP as compared with that of untreated sample. More importantly, two new peaks appeared at the retention times of 21.4 and 22.0 min, which were confirmed as tetrachlorohydroquinone (TeCHQ) and tetrachlorocatechol (TeCC), respectively. In addition, acetic acid, formic acid, Cl$^-$ and oxalic acid were identified in Fig. 8(c) by IC in peaks at the retention times of 3.8, 4.3, 6.1 and 24.7 min, respectively.

The toxicity and biodegradability of contaminated medium depend on the composition of intermediates. The analyses of tox-
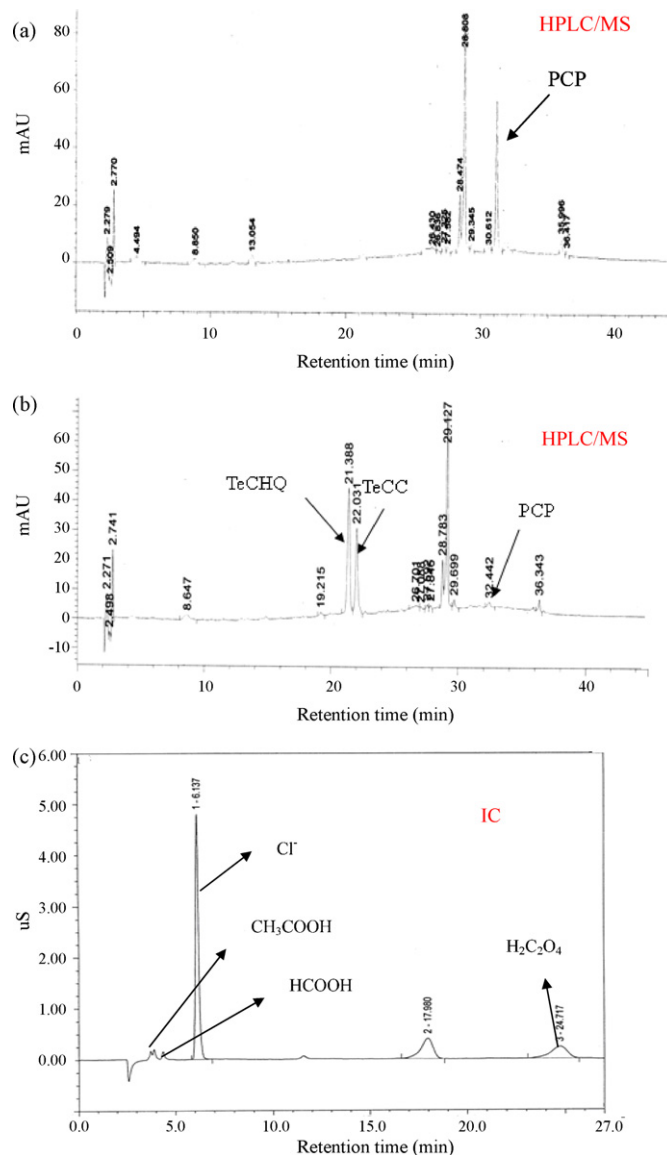

Fig. 8. Total ion chromatograph (TIC) of intermediates of PCP degradation (a: HPLC/MS, untreated sample; b: HPLC/MS, 45 min of discharge treatment; c: IC, 45 min of discharge treatment).

icity and biodegradability have been conducted from the aspect of intermediates by researchers. Hong and Zeng [19] detected TeCHQ, TeCC, acetic acid and formic acid during PCP degradation by ozonation and reported that the intermediates were increasingly less toxic and biodegradable with time. Anotai et al. [30] identified TeCC, TeCHQ and tetrachloro-p-benzoquinone as main intermediates during ozonation of PCP, and they reported that the toxicity of PCP solutions was reduced after ozonation treatment. As discussed in Section 3.3, ozonation of PCP in soil played a main role during the degradation process. Although PCP in soil was in solid phase, in view of the similar intermediates obtained in our study as those presented by Hong and Anotai, as well as the decisive role of ozonation of PCP played in the present research, it was deduced that the toxicity of the soil might be reduced and thus its biodegradability could be enhanced after pulsed corona discharge treatment. However, the detailed toxicity and biodegradability of the soil after discharge treatment were still needed to be further studied.

4. Conclusions

The application of pulsed corona discharge plasma in removing PCP in soil was studied. Under the studied conditions, increasing peak pulse voltage or pulse frequency resulted in higher PCP degradation efficiency, due to the enhancement of energy input, and thus more active species would be generated. There existed a maximal degradation efficiency of PCP with the change of air flow rate, due to the retention of active species and their utilizations. The investigation of roles of different radicals in PCP degradation process indicated that O_3 played a more important role during the degradation process. The pollution time showed small effect on PCP degradation. The intermediate products were monitored by HPLC/MS and IC. Identified products were tetrachlorocatechol, tetrachlorohydroquinone, acetic acid, formic acid and oxalic acid.

This study was a fundamental research effort, trying to offer an alternative solution for soil remediation. With further development, pulsed corona discharge plasma has the potential to be a viable treatment option for the remediation of PCP contaminated soils.

Acknowledgements

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