In-Situ Removal of Antibiotics in Soil by Cold Plasma

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Abstract

Cold atmospheric plasma (CAP) was examined for the remediation of antibiotic ciprofloxacin-polluted soil. Experiments were conducted in two different electrode configurations of dielectric barrier discharge (DBD) reactors (i.e. cylinder-to-cylindrical grid and plane-to-grid) driven by a high voltage nanosecond pulse generator. The aforementioned DBD reactor configurations correspond to ex-situ and in-situ soil remediation, respectively. Initial concentration of ciprofloxacin in soil was 200 mg/kg, and the effect of CAP operating conditions such as treatment time, applied voltage and pulse frequency were investigated and optimized. Increase of pulse frequency, applied voltage and plasma treatment time resulted in the increase of degradation efficiency of ciprofloxacin. In the plane-to-grid reactor, ciprofloxacin was completely removed after 5 minutes of CAP treatment in the optimized conditions. In addition, preliminary results showed that complete removal of ciprofloxacin can be also achieved in the cylinder-to-cylindrical grid reactor, indicating that DBD can be also applied for the in-situ remediation of ciprofloxacin-polluted soils.

Keywords: Soil remediation; DBD plasma; Ciprofloxacin; Antibiotics

1. Introduction

Antibiotics are extensively used in clinical settings to treat or prevent human diseases, in veterinary science for farm and domestic animal health and in agriculture for crop protection. Once antibiotics are found in the environment, they pose a serious threat for soil and water quality since they inhibit active microorganisms of the ecosystem that could be vital in many subsurface processes. More importantly, the continuous presence of antibiotics in the soil and water will gradually allow harmful microbes and bacteria to develop resistance to these medicines that our defense depends on (Thiele-Bruhn, 2003). It is therefore necessary to develop efficient, cost-effective and environmentally friendly methods for the decontamination of antibiotics-polluted soils. Ciprofloxacin is one of the most widely used antibiotics and one of the most persistent in the environment, which also possesses genotoxic properties. The concentration of ciprofloxacin in digested sludge and contaminated soil has been found in the range 0.3-3 mg/kg, whereas much higher concentrations have been reported in wastewater treatment plants effluents (i.e. 50 mg/L) (Martinez-Carballo et al., 2007). Given that ciprofloxacin is strongly adsorbed onto soil surface and is recalcitrant to biodegradation, it is of vital importance to be removed from soil layers. Over the years various technologies have been proposed to remediate wastewater or sludge polluted by ciprofloxacin and/or other antibiotics (e.g. bioremediation, photocatalytic oxidation, adsorption, etc.), but studies regarding the removal of antibiotics from agricultural soils are scarce (Zhang et al., 2012). In this study, cold atmospheric plasma (CAP) was examined as an advanced oxidation process (AOP) for the remediation of ciprofloxacin-polluted soil. The experiments were conducted in two different electrode configurations of dielectric barrier discharge (DBD) reactors (i.e. cylinder-to-cylindrical grid and plane-to grid) (Aggelopoulos et al., 2016; Aggelopoulos et al., 2018) where a high voltage nanosecond pulse generator provided the applied voltage to produce the plasma species. The residual ciprofloxacin concentration was determined by HPLC analysis and the effect of CAP operating conditions such as treatment time, applied voltage and discharge frequency was investigated and optimized.

2. Experimental Section

2.1. Materials and preparation of contaminated soil

Silicate sand was used as a model soil with a narrow grain size distribution (100-400μm). Before the experiments, the soil was washed with Tetramethylammonium Hydroxide (TMAH) 2% w/v in MeOH, to remove any impurities that could complicate or interfere with the HPLC analysis. Contamination of the soil with ciprofloxacin was realized by immersing a pre-weighed sample of the washed soil in a specific volume of a 2% TMAH in MeOH ciprofloxacin solution of predetermined concentration. After thorough agitation/mixing by magnetic stirring, the soil sample was placed into a fume hood (P<50mbar, T<40^{o}C) where methanol was allowed to evaporate furnishing thus a dry soil sample containing ciprofloxacin. In this manner, contaminated soil samples were generated with initial ciprofloxacin concentration in soil equal to 200 mg/kg.

2.2. *Experimental setup*

The schematic diagram of the experimental setup is shown in Fig. 1. A high voltage nanosecond pulse generator provided the applied voltage, whereas during CAP soil treatment its waveform was monitored by a digital oscilloscope (Rigol MSO2302A, 300MHz, 2 GSamples/s) and a high voltage divider (TT-HPV-Testec, 220 MHz).

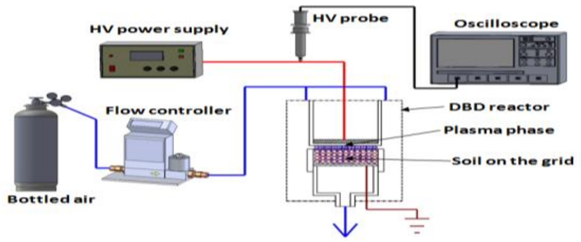

Figure 1. Schematic diagram of the experimental setup for the treatment of ciprofloxacin contaminated soil.

CAP experiments were conducted using two different configurations of DBD reactors. The first one was a plane-to-grid reactor (Aggelopoulos et al., 2018) suitable for ex-situ soil remediation. The second one was a cylinder-to-cylindrical grid reactor, which is presented for the first time, and it can be potentially used for in situ soil remediation (Fig. 2). It consists of a cylindrical HV electrode made of stainless still (d=20mm), surrounded by a cylindrical quartz tube with d=30mm and thickness 1.6mm, playing the role of the dielectric barrier. The grounded electrode was a stainless steel grid attached at the outer surface of the quartz tube. The polluted soil was placed in the space between the HV electrode and quartz tube to ensure that plasma species are created inside the soil and not in the gas phase above it.

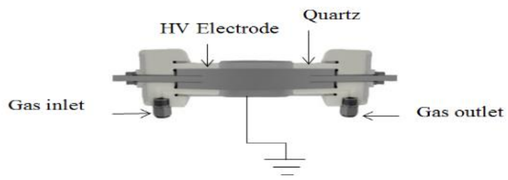

Figure 2. Cross section of of the cylinder-to-cylindrical grid DBD reactor.

During the experiments, dry compressed air (Respal TM) was streamed into the reactor and an Aalborg GFC17 gas mass flow controller (Fig. 1) controlled its flow rate (i.e. 1 L/min). In each experiment, 5g of contaminated soil were loaded in each reactor.

2.3. *Chemical analysis*

After CAP treatment, the residual ciprofloxacin was recovered from each soil sample. The recovery of the organic matter was carried out by four successive washes with 2% TMAH w/v in MeOH and one wash with MeOH followed by neutralization (pH=5) with acetic acid. The extracts were placed into a fume hood (P<50MBAR, T<40C), where methanol was allowed to evaporate. After that they were dilluted in certain volume and analyzed by high-performance liquid chromatography (HPLC). Prior to analysis, the extracts were filtered to remove soil debris.

3. Results and Discussion

Dry contaminated soil samples were treated in both DBD reactors, where CAP treatment time varied from 30 seconds to 5 minutes at various values of applied voltage and pulse frequency. In Figure 3, the effect of applied voltage and pulse frequency is presented as a function of treatment time in the plane-to-grid DBD reactor. Ciprofloxacin degradation efficiency was an increasing function of pulse frequency and applied voltage regardless of treatment time. Fig. 3.a shows the effect of pulse frequency when applied voltage was constant at 18 kV. For pulse frequency equal to 200Hz, ciprofloxacin was completely removed within 3 minutes of CAP treatment, whereas for pulse frequency 500Hz degradation efficiency was 100% within 1 minute of plasma treatment. At lower pulse frequency (i.e. 100Hz) degradation efficiency exceeds 80% within 5 minutes. The effect of applied voltage on ciprofloxacin degradation is shown in Fig. 3b for a constant pulse frequency of 100 Hz. The examined values of applied voltage was 15kV, 18kV and 21kV. Degradation efficiency was an increasing function of the applied voltage regardless of plasma treatment time. Over the whole range of applied voltages, ciprofloxacin degradation efficiency was approximately 90% after 5 minutes of soil treatment.

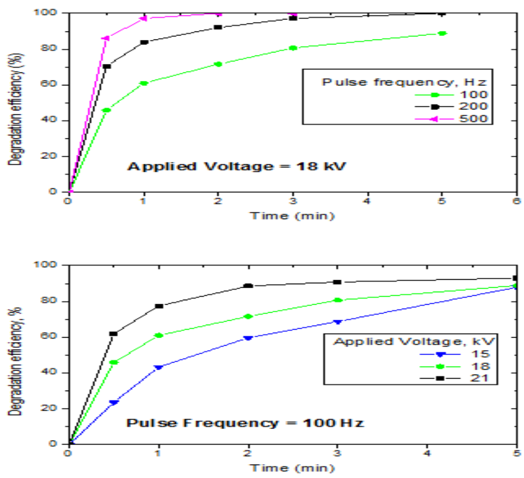

Figure 3. Ciprofloxacin degradation efficiency as a function of plasma treatment time for different values of (a) pulse frequency and (b) applied voltage.

Soil remediation experiments, were also conducted in a cylinder-to-cylindrical grid DBD reactor. Results of this study are not presented in this paper, as a complete series of experiments has not been conducted yet. However, preliminary experiments show that removal of ciprofloxacin can be achieved within short treatment times (i.e. 5min) in mild conditions (low applied voltage and pulse frequency), indicating that DBD can be also applied for the in-situ degradation of antibiotics in soil.

4. Conclusions

CAP was examined as an advanced oxidation method to remove antibiotic ciprofloxacin from soil. Two configurations of DBD reactors were tested, corresponding to ex-situ and in-situ soil remediation. Results so far, have shown that ciprofloxacin can be completely removed from soil within few minutes at both DBD reactors. Current study indicate that CAP can be very efficient for the ex-situ and in-situ remediation of wide-used antibiotics in soil. In future work, the intermediates of ciprofloxacin degradation during CAP treatment will be identified by liquid chromatography-mass spectrometry (LC-MS) in order to propose a possible ciprofloxacin degradation pathway in soil.

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