Trifluralin-polluted soil treatment using nanosecond pulsed DBD plasma

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Abstract Cold atmospheric plasma (CAP) was examined as an advanced oxidation process (AOP) for the remediation of trifluralin in soil. Trifluralin is a commonly used herbicide, which is toxic and persistent in soil. CAP experiments were conducted using a cylinder-to-cylindrical-grid reactor layout, driven by a high voltage nanosecond pulse generator. This layout permits plasma discharges to be produced inside the pores of the soil. The initial concentration of the pollutant in a model sandy soil was set 200 mg/kg. The effect of CAP treatment was studied at different operational conditions (e.g. applied voltage and soil type). It was observed that increase of pulse voltage resulted in the increase of degradation efficiency of trifluralin. On the other hand, the use of a field loam soil seemed to decrease the degradation efficiency. In optimum operational conditions, CAP treatment seemed to have excellent performance; a complete removal of the pollutant was observed within a few minutes (3 min < t < 5min). At the same time, the system examined in the current study was proven to be highly-energy efficient.

Keywords: Soil remediation, DBD plasma, Trifluralin, Herbicides

1. Introduction

Pesticides include a variety of organic compounds such as insecticides, herbicides and fungicides. Herbicides are hazardous substances, which are widely used globally. As a result, there is an increasing accumulation of them in the terrestrial and aquatic environment (He et al., 2012; Kraemer et al., 2019). It exhibits a high soil persistence resulting from its low mobility. Trifluralin is designated as neurotoxic, embryotoxic, carcinogenetic and highly toxic to aquatic organisms. Considering these impacts, the removal of herbicide trifluralin from soil and aquatic systems is of great importance. Thermal treatment, chemical oxidation, biodegradation, etc. (Ding et al., 2019; Meng and Chi, 2017; Cheng et al., 2016) are some of the existing soil remediation approaches. However, there are several disadvantages in these methods, such as high energy demand, time-consuming procedures and use of additional chemicals.

In this study, a Cold Atmospheric Plasma (CAP) technique has been proposed as an Advanced Oxidation Process for the remediation of soil from trifluralin. The main novelty of study is that plasma discharges are directly generated within the pore-network of the contaminated soil. In order to investigate optimum operational conditions, a detailed parametric analysis (pulse voltage, soil type and energy efficiency) was performed towards the degradation of trifluralin.

2. Experimental section

2.1. Materials and preparation of trifluralin

Silicate sand (purchased from Sigma Aldrich >99%) was used as a model soil with narrow grain size distribution (100-400μm). Before the experiments, the soil was washed with MeOH, to remove any impurities that could complicate or interfere with the HPLC analysis. Contamination of the soil with trifluralin was realised by immersing a pre-weighed sample of the washed soil in a specific volume of MeOH trifluralin solution of predetermined concentration. After thorough agitation/mixing by magnetic stirring, the soil sample was placed into a fume hood (P<50mbar, T=50°C), where methanol was allowed to evaporate furnishing thus a dry soil sample containing trifluralin. In this manner, contaminated soil samples were generated with trifluralin concentration 200 mg/kg.

2.2. Experimental setup

The schematic diagram of the experimental setup is shown in Fig. 1 (Hatzisymeon et al. 2021). A high voltage nanosecond pulse generator provided the applied voltage, which ranged from 17 kV-28 kV. During CAP soil treatment the waveform was monitored by a digital oscilloscope (Rigol MSO2302A, 300 MHz, 2 GSamples/s) and a high voltage divider (TT-HPV-Testec, 220 MHz).

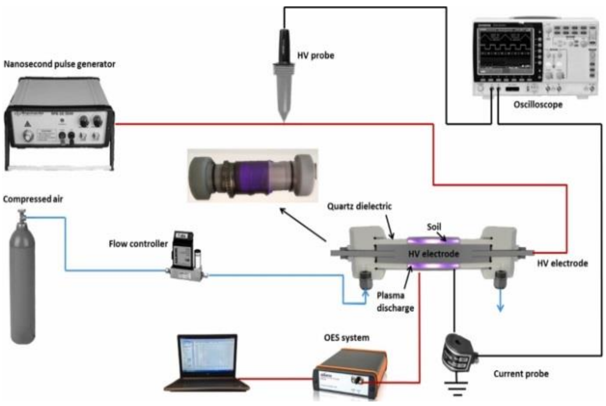


Figure 1. Schematic diagram of the experimental setup for the treatment of trifluralin contaminated soil.

Experiments have been conducted using a novel type of cylinder-to-cylindrical DBD reactor, which can be potentially used for in situ soil remediation (Fig. 2). It mainly consists of a cylindrical HV electrode made of stainless still (d=22 mm), which is surrounded by the polluted soil, where plasma species are created. The soil is held in a cylindrical quartz with d=30mm and thickness 1.6mm. The air passes vertically the reactor through a hole (d=1mm) at the top of the reactor and at the bottom there is a hole that acts as gas outlet forcing the gas phase to pass through the soil.

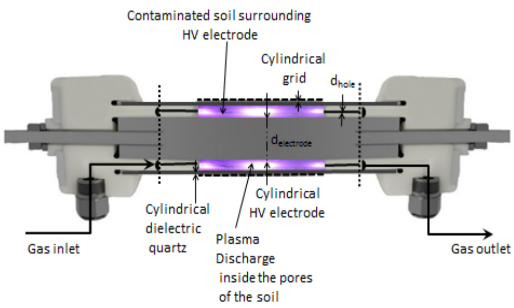


Figure 2. Cross section of of the cylinder-to-cylindrical grid DBD reactor.

2.3 Sample preparation and chemical analysis

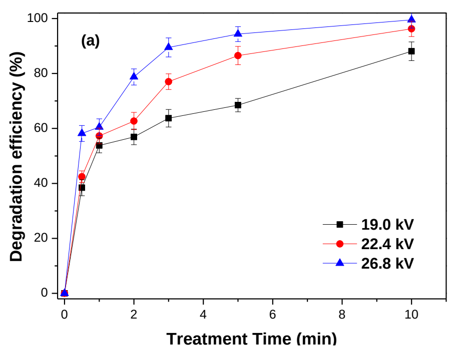
After CAP experiments, the residual of trifluralin was recovered from each sample of treated soil. The recovery of the organic matter was carried out by three successive washes with MeOH at 50°C. The extracts were placed into a fumehood (P<50 mbar, T<50°C), where methanol was allowed to evaporate. Finally, the extracts were dilluted in certain volume and analyzed by high-performance liquid chromatography (HPLC).

3. Results and Discussion

3.1. Effect of applied voltage and soil type on trifluralin degradation

CAP treatment in our in-situ nsp-DBD system varied from 30 sec to 10 min. Pulse voltage is a very crucial parameter, in order to determine optimum conditions. Values of pulse voltage examined were 19, 22.4 and 26.8 kV at dry model sandy soil. In Fig. 3.a, degradation efficiency of trifluralin is presented as a function of treatment time at the examined pulse voltage values. As it can be observed, degradation efficiency is an increasing function of pulse voltage. At pulse voltage 19.0, 22.4 and 26.8 kV, the removal of trifluralin was 56.9%, 62.7% and 78.8%, respectively, after 2 min of CAP treatment. It is remarkable that after 5 min of treatment, degradation of trifluralin surpassed 95% at 26.8 kV, whereas at the end of the experiment (10 min) the corresponding degradation efficiency was almost complete (99.5%).

CAP experiments were performed on two different soil types; a model sandy soil and a field loam soil. CAP performance on these soil types for the removal of trifluralin are shown in detail in Fig. 3.b. A decrease in the degradation efficiency was observed when a clay loam soil was used. After 2 min of treatment, the degradation of trifluralin in sandy soil was 78.8% and declined to 38.5% in loamy silty soil. However, at longer treatment times (i.e. 10 min), a respectable degradation efficiency of 74.6% was achieved for the loam soil.



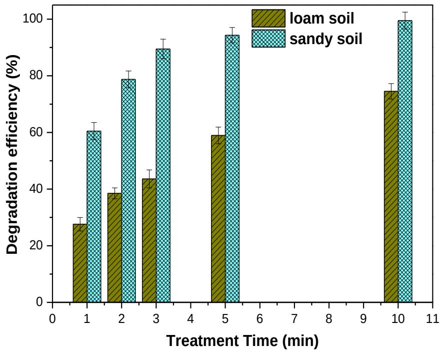


Figure 3. Trifluraliin degradation efficiency as a function of plasma treatment time for different values of (a) pulse frequency and (b) soil type (conditions: pulse frequency 100 Hz, air flow rate 0.075 l/min, initial trifluralin concentration 200 mg/kg, mass of contaminated soil 6.1 g).

4. Conclusions

A novel nsp-DBD system with a cylinder-to-cylindrical grid reactor, which generates in situ plasma micro-discharges within soil pores, was examined for the removal of herbicide trifluralin in sandy and loam soil. Results have shown that this system achieved an extremely high-efficient degradation of trifluralin in soil. Within a few minutes, a complete removal of the pollutant can be achieved, with high energy efficiency in sandy soil. Field loam soil was studied at pulse voltage 26.8 kV. In this case, results have shown that removal efficiency decreased in comparison with sandy soil. The present study is a preliminary effort to develop an up-scaled in-situ cold plasma-based remediation solution for trifluralin contaminated soil.

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