Dielectric barrier discharge plasma used as a means for the remediation of soils contaminated by non-aqueous phase liquids

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HIGHLIGHTS

- Soil remediation by DBD plasma resulted in the fast and complete removal of NAPL.
- The plasma species were identified and gas temperature was determined.
- High-throughput organic profiling analysis by GC–MS to identify the intermediates.
- Ketones and alcohols were identified as intermediate products of alkane oxidation.
- The energy consumed by DBD plasma is low and almost independent of soil thickness.

ARTICLE INFO

ABSTRACT

A plane-to-grid dielectric barrier discharge (DBD) reactor operating with air at atmospheric pressure was used to investigate the removal of non-aqueous phase liquids (NAPLs) from soil layers. A mixture of n-C_{10}, n-C_{12} and n-C_{16} was used as a model NAPL that polluted the soil at a very high initial concentration (100,000 mg/kg-soil). The effect of treatment time, energy consumption, and soil thickness on the NAPL removal efficiency was investigated, the plasma active species were identified, and the macroscopic gas temperature was determined. The NAPL remediation efficiency found to be as high as 99.9% after 60–120 s of plasma treatment, depending on soil thickness. The energy density required to remediate completely the NAPL was about 600 J/g-soil and was practically independent of the soil thickness, indicating that the DBD-based plasma has the potential to become a highly cost-effective technology for the remediation of NAPL-contaminated soils. N_2^+, N_2^*, NO_x and O_3 were identified as plasma-induced reactive species, a maximum gas temperature close to 300 °C was recorded, and the total carbon detected in exhaust gases, in the form of CO and CO_2, was ca 40% of that contained in the NAPL removed from the soil. The main mechanisms of NAPL removal by plasma found to be the evaporation of organic compounds coupled with their oxidation in liquid and gas phase. Using ATR-FTIR in combination with high-throughput organic profiling analysis by GC–MS, ketones and alcohols were identified as the main intermediate products of alkanes oxidation in soil matrix.

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1. Introduction

Soil contamination by non-aqueous phase liquids (NAPLs) could, seriously, affect human health through direct contact with soil, food chain, and contaminants in water resources. Soil pollution is often caused by industrial activity and urbanization, improper disposal of chemical and industrial waste, leakages from

underground storage tank rupturing, downward migration of leachates from landfills, oil spills from accidents and fuel dumping. The most common NAPLs involved in subsurface contamination include poly-aromatic hydrocarbons (PAHs), pesticides, chlorinated solvents (e.g. PCBs) and petroleum cuts (gasoline, diesel oil, kerosene) containing alkanes of high molecular mass [1].

For the abatement of soil pollution by NAPLs, various soil remediation methods have been proposed: thermal desorption, bioremediation, chemical flushing and soil vapor extraction [2–7]. The efficiency of these methods is commonly controlled by a broad

variety of parameters related with the pore space properties of soils (e.g. local permeability, effective gas diffusivity, moisture), the NAPL composition and concentration and the biological activity of micro florae. For instance, due to the existence of strong heterogeneities in the pore space of mineral soils (sand/clay/silt), the pore length scales span five-to-six orders of magnitude [8], the local permeability fluctuates over a broad range [9,10], the fluid transport within soils is controlled by preferential flow pathways, and the efficiency of the conventional remediation techniques based on the flushing of fluids through the porous media becomes very low [11,12]. In addition, due to certain drawbacks of the conventional remediation technologies, such as energy/time requirements, and secondary pollution, it becomes widely accepted that the development of cost-effective, rapid and highly efficient methods for soil remediation is crucial.

Recently, it has been shown that the advanced oxidation processes (AOPs) constitute well-promising technologies for the pollution control [13,14]. Among the AOPs, the non-thermal plasmas (NTPs) are regarded as highly competitive technologies for the removal of organic pollutants [15]. During the plasma production, high energy electrons are generated, providing space charge and highly reactive species, such as O, OH, and H radicals, and O_3, H_2O_2 molecules [16]. All these species along with the physical energies involved (e.g. the UV radiation) converge to oxidize the pollutants, increasing thus the energetic efficiency of AOPs compared to the conventional methods [17,18].

Non-thermal plasmas have been used for the treatment of wastewater [15,17,19–23] and polluted gas [24–27], whereas during the last few years they have started to be examined as eco-innovative methods of soil remediation. In these few studies, emphasis was placed on the removal of solid pollutants from soils by corona [28–31] or dielectric barrier discharge (DBD) [32,33], while only a little attention has been paid on the NAPL removal [34,35].

In this paper, a new plane-to-grid DBD reactor operating with air at atmospheric pressure was used to remove a model NAPL (i.e. a mixture of n-C_{10}, n-C_{12} and n-C_{16}) of high initial concentration (100,000 mg/kg-soil) from soil layers with thickness ranging from 1.3 to 4.0 mm. The effect of the treatment time, energy consumption and soil thickness on the NAPL removal efficiency was investigated. The chemically active species, produced by the discharge, were identified, the macroscopic gas temperature was estimated, and the gaseous byproducts were analysed. Furthermore, the main intermediates of the NAPL degradation in the soil were identified by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy in combination with high-throughput organic molecule profiling of gas chromatography–mass spectrometry (GC–MS).

2. Experimental section

2.1. Materials

The NAPL was a mixture of n-decane, n-dodecane, and n-hexadecane mixed at equal mass concentrations (w/w). All reagents were purchased from Merck (purity > 95%). The soil used was a well-sorted silicate sand with narrow grain size distribution (125–250 μm). The contamination of the soil samples was carried out as previously described [34]. The initial NAPL concentration in contaminated soil was very high and equal to 100 g/kg-soil.

2.2. Plasma setup and diagnostics

The schematic diagram of the experimental setup, along with a detailed representation of the DBD reactor, used for the treatment of the NAPL-contaminated soils, is shown in Fig. 1. The driving

voltage was supplied by a custom-made AC high voltage power supply (10 kHz, 0–30 kV peak-to-peak, less than 1% total harmonic distortion on a linear load) and it was set at 28 kV peak-to-peak for all experiments, unless otherwise stated. Its waveform during soil treatment (see Fig. 2a for a typical example) was continuously monitored on a digital oscilloscope (LeCroy WaveRunner 44Xi-A, 400 MHz, 5 GSamples/s) with a Tektronix P6015A probe (0–75 MHz). The waveform of the circuit current (see Fig. 2a for a typical example) was also recorded on this oscilloscope by means of a wideband current transformer (Pearson electronics 6585, 40 Hz–250 MHz) clamped on the grounded lead (Fig. 1a). The electric mean power consumed by the plasma, P_{mean}, was calculated approximately by averaging the instantaneous power, $p(t)$ (see Fig. 2b for a typical example produced by the signals of Fig. 2a), over two periods (2T, for better approximation) of the applied voltage, namely

$$P_{mean} = \frac{1}{2T} \int_0^{2T} p(t)dt = \frac{1}{2T} \int_0^{2T} u_{meas}(t) \ i_{meas}(t)dt \qquad (1)$$

where $u_{meas}(t)$ and $i_{meas}(t)$ are the time varying voltage and current waveforms, respectively (like those in Fig. 2a).

The reactor (Fig. 1b) was a cylindrical vessel made of borosilicate glass (Pyrex™) with PTFE flanges (top and bottom), both sealed with Viton™ O-ring gaskets due to shaft-glad assemblies. The vessel inner diameter and height were 124 mm and 100 mm, respectively. The biased electrode was a stainless steel disc of diameter 50 mm and thickness 5 mm. This electrode was housed in a quartz cylinder and connected to the high voltage cable. The wall of this cylinder was 5 mm thick, while its bottom had a thickness of 2 mm forming thus the dielectric barrier of the discharge. The grounded electrode was a stainless steel grid of diameter 46 mm where samples of contaminated soil, 1–4 mm thick, were spread uniformly. The grounded electrode was supported on a hollow PTFE cylinder able to move vertically due to a thread along its periphery, facilitating thus the inter-electrode gap adjustment. In the present study, the distance between the quartz and grid surfaces was kept constant at 5 mm. Soil samples of different thickness were confined on the grid by using exchangeable PTFE rings of different heights mounted on the top of the hollow cylinder. Bottled dry air (Respal™) was injected in the reactor at a constant flow rate equal to 2 standard liters per minute (slm) controlled by an Aalborg GFC17 gas flow controller. Four (4) gas inlets were symmetrically distributed on the top flange of the reactor and a hole was drilled on the bottom of the hollow cylinder acting as the only gas outlet (Fig. 1b). In this manner, the gas phase was forced to pass through the soil.

The soil treatment times varied from 10 s to 3 min. Control experiments (i.e. ventilation without plasma) were also performed in some soil samples, confirming that no NAPL was removed due to air ventilation. All experiments of remediation were conducted in duplicates with the standard deviation of experimental data being negligible.

2.3. Chemical analysis of soils

After the soil treatment by plasma, the NAPL was extracted from the soil sample and the extracts were analyzed by gas chromatography-flame ionization detection (GC-FID), gas chromatography–mass spectrometry (GC–MS) and Fourier transform infrared spectroscopy (ATR-FTIR), in order to quantify the composition of residual NAPL in soil and identify the intermediates of reactive processes in liquid/solid phase. Dichloromethane (DCM, Sigma Aldrich) was used as extraction solvent, whereas the methods used for the extraction and chemical analysis of residual NAPL in soil by GC-FID and ATR-FTIR have been described in detail