

Atmospheric pressure dielectric barrier discharge for the remediation of soil contaminated by organic pollutants

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Abstract The remediation of soil, contaminated by organic pollutants, in a cylinder-to-plane dielectric barrier discharge reactor at atmospheric air pressure was reported. Two model organic pollutants were selected; a solid pollutant (2,6-dichloropyridine) and a liquid pollutant (*n*-dodecane). The effects of the contaminant's initial concentration and state, the energy consumption, and the soil type on the pollutant removal efficiency were investigated. To that scope, various contaminated samples of both quartz sand and loamy sandy soil were treated by plasma for various treatment times and initial 2,6-dichloropyridine/*n*-dodecane concentrations. The results revealed that (1) the removal efficiency of 2,6-dichloropyridine was higher compared to that of *n*-dodecane at a given plasma treatment time and (2) the removal efficiency increased with the energy density increasing, but decreased as the soil heterogeneity, organic matter and pollutant concentration were enhanced. The main removal mechanism proposed is the evaporation of pollutant molecules coupled with their oxidation by plasma species in the gas and solid/liquid phase.

Keywords Active species · Degradation efficiency · Non-thermal plasma · Pollutant oxidation · Soil remediation

Introduction

Soil contamination by organic pollutants such as pesticides, pharmaceuticals, poly-aromatic hydrocarbons (PAHs), chlorinated solvents and total petroleum hydrocarbons (TPHs) is strongly related to social, economic and environmental sustainability, and it is considered as a significant threat for human health through the food chain. Soil pollution by organic pollutants typically arises from the extensive use of pesticides, direct discharge of chemical and industrial wastes to the soil, leaching of wastes from landfills and leakages due to the rupture of underground storage tanks (Mirsal 2008).

Soil contaminated with organic pollutants is commonly treated by conventional technologies, such as incineration, steam injection (Triplett Kingston et al. 2010; Tzovolou et al. 2011), soil vapor extraction and bioremediation (Lladó et al. 2013) where oxygen or nutrient amendments are injected through the soil. Most of these methods are highly energy-consuming (e.g., incineration) or have low removal efficiency in low permeability zones (e.g., soil vapor extraction, steam injection) (Nilsson et al. 2011; Carroll et al. 2012). The latter is due to the high permeability fluctuation of mineral soils (sand/clay/silt) that leads to preferential flow of the flushing remedial fluids through the high permeability soil layers (Aggelopoulos and Tsakiroglou 2008, 2009). On the other hand, bioremediation is a time-consuming process and the activity of the microorganisms is strongly related to several parameters, such as soil humidity, soil

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temperature and pollutant toxicity. Alternative remediation techniques such as smoldering combustion, electrokinetic remediation (Pironi et al. 2011; López-Vizcaíno et al. 2014; Bocos et al. 2015) and chemical oxidation (e.g., ozonation, H_2O_2 , Fenton's reagent) have also been proposed (Yu et al. 2007; Cai et al. 2012; Pardo et al. 2015). However, these techniques are not only energy-consuming but also in some cases expensive chemical reagents are needed. Therefore, the development of efficient, cost-effective, rapid and environmental friendly methods for the removal of organic pollutants from soils is crucial.

Non-thermal plasmas (NTPs) are regarded as promising advanced oxidation processes (AOPs) for the sustainable and efficient removal of organic pollutants from wastewater (Ognier et al. 2009; Hijosa-Valsero et al. 2013; Iya-Sou et al. 2013; Jamróz et al. 2014; Magureanu et al. 2015; Stratton et al. 2015) and polluted gas (Ostapczuk et al. 2008; Malik et al. 2011; Jolibois et al. 2012; Bao et al. 2014; Zhang et al. 2015). During the last few years, they have started to be examined for soil remediation (Wang et al. 2010; Lou et al. 2012; Ognier et al. 2014; Aggelopoulos et al. 2015a). During NTP discharge at atmospheric pressure, high-energy electrons are produced, providing thus space charge and highly reactive oxidative species including active radicals (O, OH, H radicals) and active molecules (O_3 , NO_x , H_2O_2). All these species, due to their high oxidation potentials, along with the physical energies generated from plasma discharge (e.g., UV radiation and heating) are capable of oxidizing organic compounds with extremely high reaction rates (Locke et al. 2006). Regarding soil remediation studies, pulsed corona and dielectric barrier discharge (DBD) plasma have been used for the removal of solid or liquid organic pollutants at atmospheric pressure (Redolfi et al. 2010; Wang et al. 2011a, b; Lu et al. 2014; Aggelopoulos et al. 2015b), but no attention has been paid on the comparison of the removal efficiency between solid and liquid pollutants.

In this paper, the remediation of soil layers contaminated with one solid (i.e., 2,6-dichloropyridine) and one liquid organic pollutant (i.e., *n*-dodecane) was studied in a cylinder-to-plane DBD reactor, under atmospheric air pressure. 2,6-Dichloropyridine ($\text{C}_5\text{H}_3\text{Cl}_2\text{N}$) is widely used as an intermediate for manufacturing synthetic organics, pharmaceuticals, fungicides, herbicides and as a catalyst for phase transfer; *n*-dodecane (*n*- C_{12}) is a liquid alkane hydrocarbon which is found in kerosene-based fuels, and is also used as a solvent and distillation chaser. The plasma

discharge experiments were conducted at various treatment times and initial pollutant concentrations on two soil types differing with respect to the degree of micro-heterogeneity. In this manner, the removal efficiency of solid and liquid organic pollutants, which have the same boiling point, was compared and correlated with the energy consumption, initial pollutant concentration and soil type. Finally, the main mechanisms of organic pollutant degradation were discussed.

Materials and methods

Materials

2,6-Dichloropyridine (purity >98 %) and *n*- C_{12} (purity >95 %) were purchased from Sigma Aldrich and Merck, respectively (Table 1). Several soil samples were artificially polluted by 2,6-dichloropyridine or *n*- C_{12} . The contamination of the soil samples at various pollutant initial concentrations (i.e., 0.5, 5, 50 g/kg-soil) was carried out by mixing pre-weighted soil samples with pollutant solutions in acetone as described in a previous study (Aggelopoulos et al. 2015a).

Two different soil types were examined; a commercial quartz sand with narrow grain size distribution (homogeneous sand) and a loamy sandy soil with broad grain size distribution collected from the region of Western Greece. The latter had a content of 83 % sand, 4 % silt and 13 % clay. The main properties of these two porous media are presented in Table 2.

Dielectric barrier discharge (DBD) plasma reactor for soil treatment

The experimental setup along with the cylinder-to-plane DBD reactor used for the plasma treatment of contaminated soil samples is depicted in Fig. 1. The alternating (AC) driving voltage was supplied by a high voltage power supply (40 kHz, 0–20 kV peak-to-peak), and it was ranged from 12 to 14 kV for all experiments. The applied high voltage was measured with a Tektronix P6015 probe, and the circuit current was calculated by measuring the voltage between the ground electrode and an equivalent resistance of 50 Ω . Their waveforms were continuously monitored by a LeCroy LT 342, 500 MHz digital oscilloscope (Fig. 1a), and the discharge power P was calculated approximately by integrating the instantaneous voltage and current over two periods of the applied voltage.

Table 1 Pollutant properties

Pollutant	Molecular weight (g/mol)	Boiling point (°C)	Vapor pressure
C ₅ H ₃ Cl ₂ N	147.99	211	Not available
<i>n</i> -C ₁₂	170.34	214–218	18 Pa (25 °C)

Table 2 Soil properties

Soil	Grain size distribution	Porosity	Permeability (m ²)
Quartz sand	125–250 (μm)	0.40	25 × 10 ^{−12}
Loamy sandy soil	<2 μm–2 mm ^a	0.45	385 × 10 ^{−15}

^a 50 μm < *d_g* < 2 mm: 83 %; 2 μm < *d_g* < 50 μm: 4 %; *d_g* < 2 μm: 13 %

The biased electrode of the DBD reactor (Fig. 1b) was a stainless steel cylinder (80 mm length and 13 mm diameter) covered by a 4-mm-thick alumina tube acting as the dielectric barrier of the discharge. The grounded electrode was a stainless steel plate (97 mm × 85 mm, thickness: 10 mm) where 4 g of contaminated soil samples, about 1 mm thick, were spread uniformly. The grounded electrode was supported on a belt conveyor which was induced to motion by a motor at a constant velocity of 40 mm/min and therefore the time needed to treat the soil covering the grounded electrode was 2.5 min. In the present study, the distance between the alumina dielectric and the grounded electrode was kept constant at 2 mm. Bottled dry air was injected at atmospheric pressure in the reactor at a constant flow rate 1 l/min which was controlled by a gas flow meter (Fig. 1a).

The soil treatment time was controlled by adjusting the number of times the whole surface of the soil was treated (the belt conveyor completed a round) and varied from 2.5 to 34 min. Control experiments (i.e., ventilation without plasma) were also performed, confirming that no pollutant was removed due to air ventilation. All experiments were conducted in duplicates with the standard deviation of experimental data being negligible.

Chemical analysis of soils

After the plasma treatment, the remaining 2,6-dichloropyridine and *n*-C₁₂ were extracted from the soil samples using methanol and dichloromethane as extraction solvents, respectively. Each soil sample (4 g) was added to 10 ml of solvent, and the mixture was shaken for 24 h on an overhead shaker at a speed of 12 rpm. After filtration through 0.45 μm PTFE filters, the soil extracts were injected in a Shimadzu GC-FID (GC 2014) equipped with a fused silica capillary column (50 m × 0.2 mm i.d × 0.5 μm film thickness, PETROCOL, Supelco) to quantify the residual

concentration of organic pollutants (2,6-dichloropyridine and *n*-C₁₂) in the soil.

For the 2,6-dichloropyridine analysis, high-purity helium was used as a carrier gas at a constant flow rate of 29.2 ml/min. The sample injection volume was 1 μl, and the split ratio was fixed at 1:20. The injector and detector temperature were set to 270 and 300 °C, respectively. The oven temperature was kept at 100 °C for 1 min, ramped up at a rate of 30 °C/min to 180 °C and subsequently ramped up at a rate of 40 °C/min to 210 °C where it was kept constant for 1 min. For *n*-C₁₂ analysis, the flow rate of helium was 15.9 ml/min and the split ratio was fixed at 1:15. The injector and detector temperature were set to 250 and 280 °C, respectively. The oven temperature was kept at 40 °C for 10 min, ramped up at a rate of 1.1 °C/min to 114 °C and subsequently ramped up at a rate of 1.7 °C/min to 250 °C where it was kept constant for 15 min. Control experiments in untreated soil samples showed that the 2,6-dichloropyridine and *n*-C₁₂ recovery from soil was greater than 95 and 99 %, respectively.

Results and discussion

Effects of energy density and initial pollutant concentration on degradation efficiency

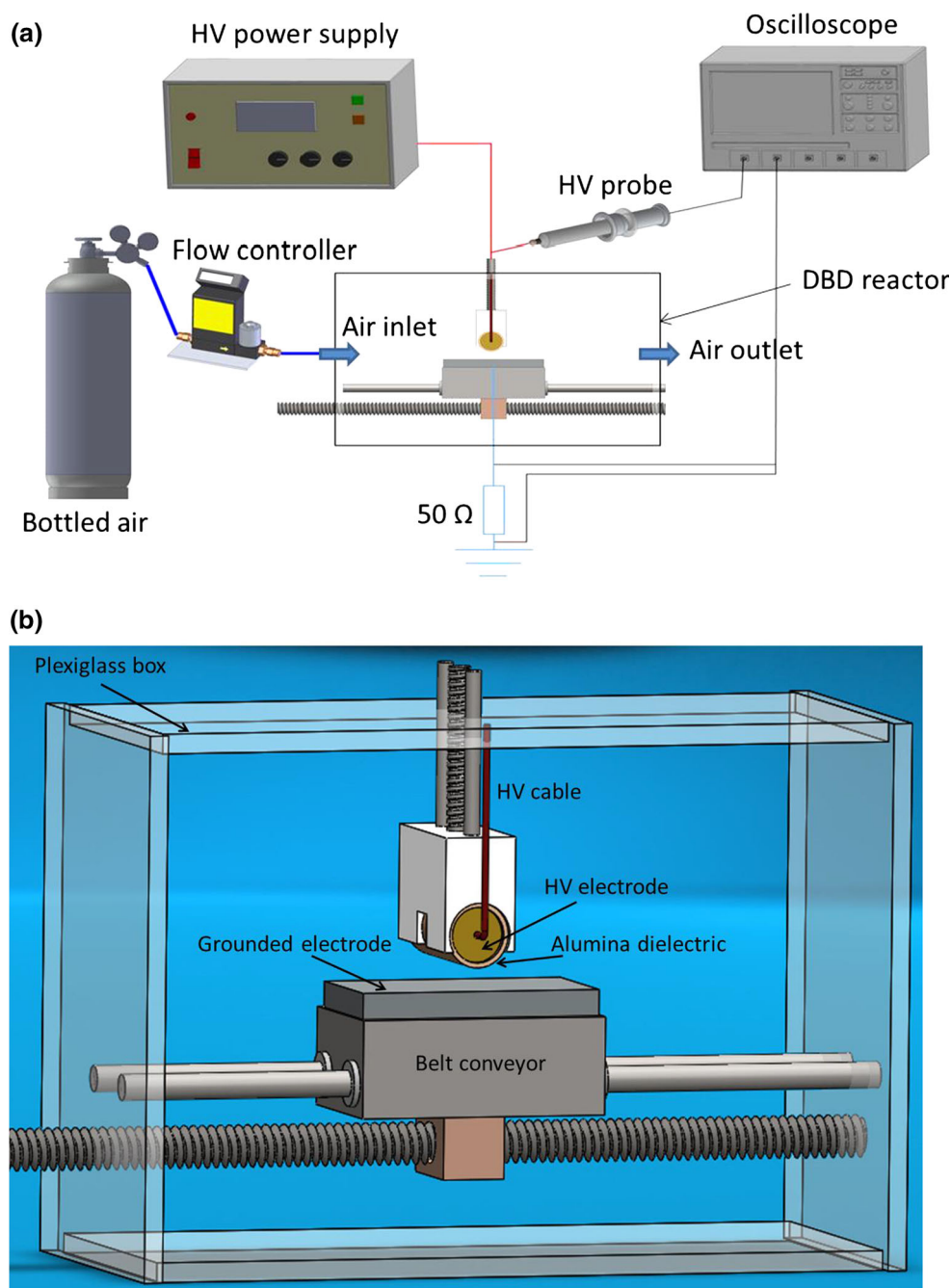
Plasma discharge experiments were performed at various treatment times ranged from ~2.5 to ~34 min with the corresponding energy density, *E_D*, ranging from 840 to 12650 J/g-soil, depending on the mass of the soil treated and the power of the DBD according to Eq. (1):

$$E_D = P_{\text{mean}} \times t/m \quad (1)$$

where *P_{mean}* is the calculated mean power of the DBD (~25 W in this study), *t* is the treatment time (s), and *m* is the mass of the soil sample (g).



Fig. 1 Schematic diagram of
a the experimental setup used to
 treat the contaminated soils;
b details of the DBD reactor



In Fig. 2, the 2,6-dichloropyridine removal efficiency is shown as a function of the treatment time and energy density for a loamy sandy soil sample at various initial pollutant concentrations. The 2,6-dichloropyridine removal efficiency was increased rapidly at shorter treatment times which correspond to low energy densities. However, the

removal rate becomes gradually slower tending asymptotically to reach a constant value, in agreement with recently published results (Lou et al. 2012; Aggelopoulos et al. 2015a; Aggelopoulos et al. 2015b). At shorter treatment times, where the 2,6-dichloropyridine concentration in the soil is high, the produced plasma reactive species reacted



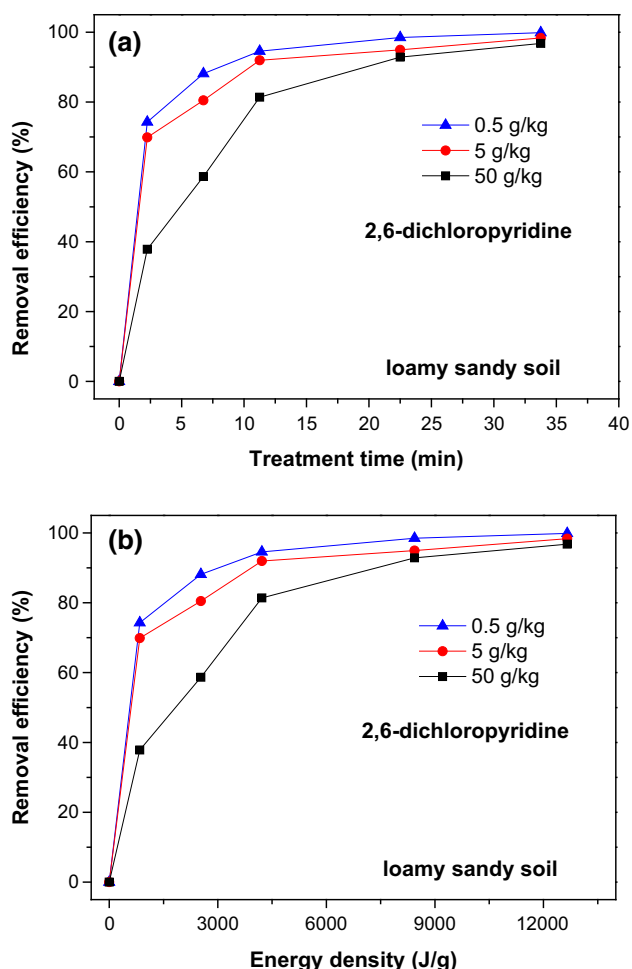


Fig. 2 The 2,6-dichloropyridine removal efficiency as a function of the **a** plasma treatment time and **b** plasma energy density for various initial 2,6-dichloropyridine concentrations

highly with the 2,6-dichloropyridine molecules and the reaction was fast. At longer treatment times, the plasma active species reacted less frequently with the 2,6-dichloropyridine molecules resulting to a slower reaction. This observation is consistent, considering that (1) a sufficient amount of 2,6-dichloropyridine molecules had already been removed and (2) intermediate products produced during the 2,6-dichloropyridine oxidation compete with the 2,6-dichloropyridine molecules for reactions with the plasma active species (Wang et al. 2014; Aggelopoulos et al. 2015b).

Regarding the effect of initial pollutant concentration, it becomes apparent that the 2,6-dichloropyridine removal

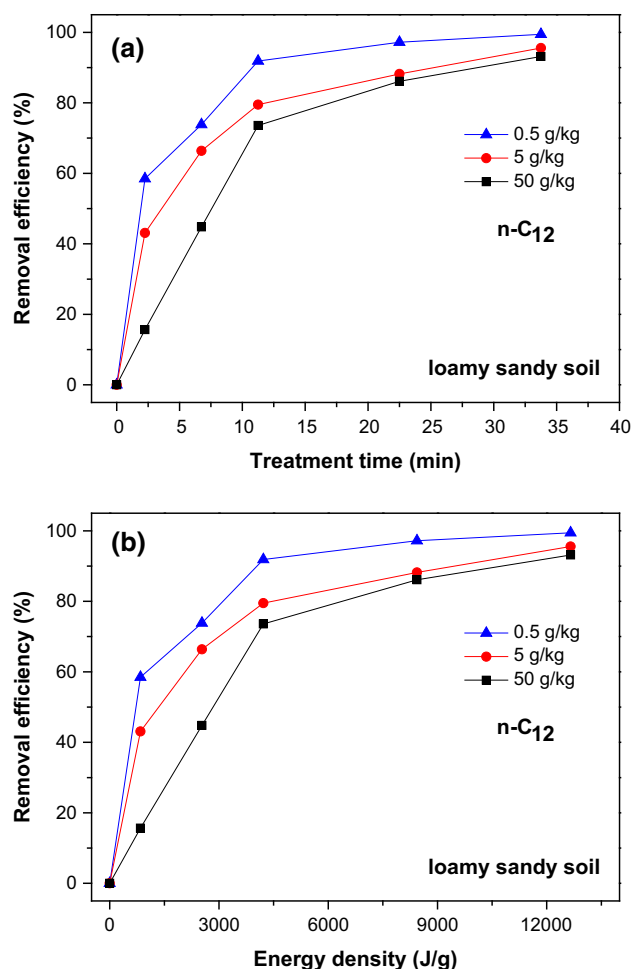


Fig. 3 The *n*-dodecane removal efficiency as a function of the **a** plasma treatment time and **b** plasma energy density for various initial *n*-dodecane concentrations

efficiency decreased as the initial 2,6-dichloropyridine concentration increased (Fig. 2) in agreement with published data in the literature (Lou et al. 2012; Aggelopoulos et al. 2015a). After 7 min of plasma treatment, 88, 80 and 59 % of 2,6-dichloropyridine was removed at initial concentrations of 0.5, 5 and 50 g/kg, respectively (Fig. 2a). It should be mentioned, however, that the 2,6-dichloropyridine degradation was almost complete after 34 min of plasma treatment, regardless of its initial concentration (Fig. 2a).

In Fig. 3, the *n*-C₁₂ removal efficiency is presented as a function of the treatment time and energy density for a loamy sandy soil sample at various initial pollutant con-



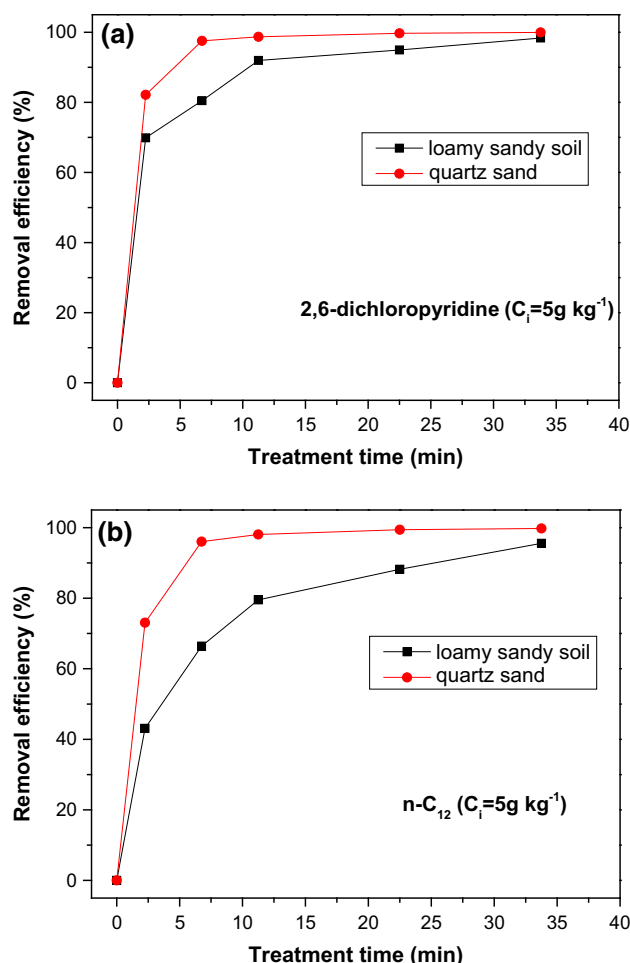


Fig. 4 Effect of soil type on the pollutant removal efficiency **a** 2,6-dichloropyridine; **b** n -dodecane

centrations. The same behavior (as in the case of 2,6-dichloropyridine) was observed regarding the effect of both treatment time and energy density on the $n\text{-C}_{12}$ removal efficiency. In particular, the removal efficiency of $n\text{-C}_{12}$ increased more rapidly over short treatment periods (low energy densities) than in long treatment periods (high energy densities). Furthermore, the effect of the initial pollutant concentration on the pollutant removal efficiency was confirmed, since it is apparent that the $n\text{-C}_{12}$ degradation efficiency decreased as its initial concentration in soil was increased from 0.5 to 50 g/kg (Fig. 3).

Effect of soil type on pollutant degradation

The effect of soil characteristics on the pollutants (2,6-dichloropyridine/ $n\text{-C}_{12}$) degradation efficiency is depicted

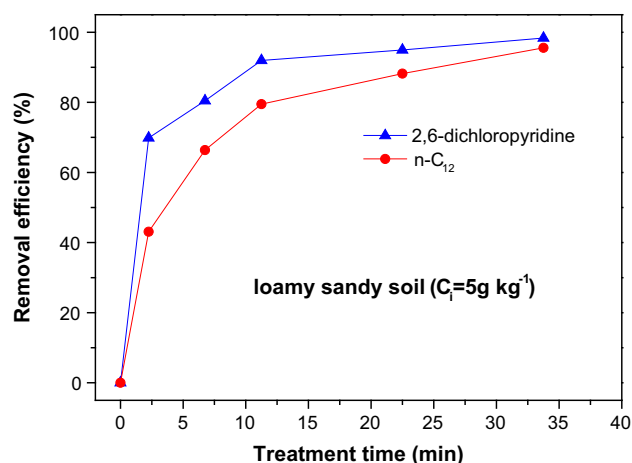


Fig. 5 The comparison between the removal efficiency of 2,6-dichloropyridine and n -dodecane

in Fig. 4. For an initial pollutant concentration 5 g/kg-soil, the pollutant removal efficiency was increased more rapidly for the quartz sand compared to the loamy sandy soil in agreement with published results (Wang et al. 2014). After 7 min of treatment, the 2,6-dichloropyridine removal efficiency for quartz sand and loamy sandy soil was 98 and 80 %, respectively (Fig. 4a). Similarly, the $n\text{-C}_{12}$ removal efficiency for quartz sand and loamy sandy soil was 96 and 66 %, respectively (Fig. 4b). It is noteworthy, that after 34 min of treatment, the removal efficiency of both pollutants was almost complete and independent of soil type (Fig. 4).

The variance of the pollutant removal efficiency between the quartz sand and the loamy sandy soil could be attributed to the different properties of the two soil types. These two soil types varied in terms of the organic matter and the particle/pore sizes, given that (1) there is no organic matter in the commercial quartz sand unlike the loamy sandy soil collected from the region of Western Greece and (2) the quartz sand has a narrower grain/pore size distribution compared to the loamy sandy soil. The loamy sandy soil organic matter not only could compete with the pollutants for reactions with the active species produced by plasma, but could also adsorb the organic pollutants slowing thus the reactions between the active species and the latter (Wang et al. 2014). Moreover, the penetration of the produced active plasma species and the pollutant transfer in the quartz sand is expected to proceed uniformly in accordance with its narrow pore size distribution, as opposed to the loamy sandy soil, where the smaller air/pollutant interfacial area of pollutant-occupied pores may lead to weaker pollutant removal rates and



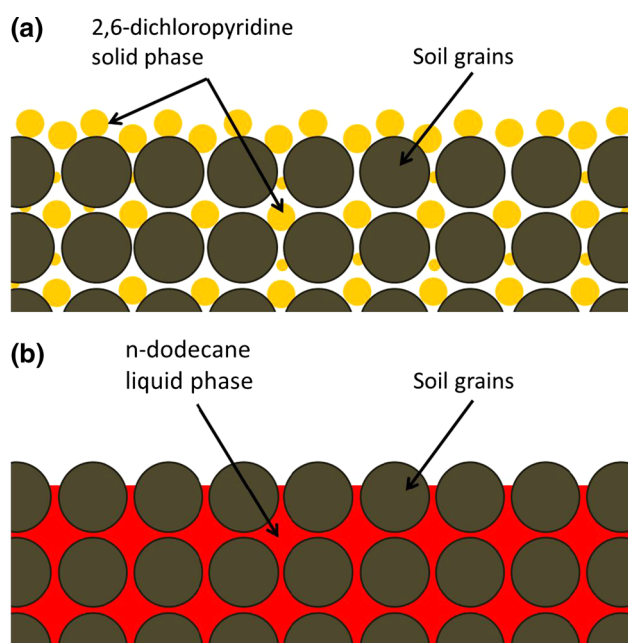


Fig. 6 Contaminated soil by **a** 2,6-dichloropyridine (solid pollutant); **b** *n*-dodecane (liquid pollutant)

subsequently to lower pollutant removal efficiency (Aggelopoulos et al. 2015a).

Effect of the pollutant state on the pollutant degradation

After ~ 2.5 min of plasma treatment, the removal efficiencies of 2,6-dichloropyridine and *n*-C₁₂ were 70 and 43 %, respectively (Fig. 5), whereas after ~ 7 min of treatment they were 80 and 66 % accordingly. It is therefore evident that the removal efficiency of 2,6-dichloropyridine was always higher compared to that of *n*-C₁₂ at a given plasma treatment time. Given that the vapor pressure of 2,6-dichloropyridine is not available (see Table 1), this difference could be attributed to the following reasons. Assuming higher vapor pressure of 2,6-dichloropyridine compared to that of *n*-C₁₂, the evaporation percentage, due to plasma temperature, would be also higher (see discussion below), leading to faster 2,6-dichloropyridine removal from soil layers. Conversely, in the case of similar or lower 2,6-dichloropyridine vapor pressure compared to that of *n*-C₁₂, the higher 2,6-dichloropyridine oxidation rate could be attributed either to its lower molecular mass (Table 1) leading to lower energy requirements for the corresponding oxidation reactions or to the solid state of 2,6-dichloropyridine molecules. In

particular, after acetone evaporation (it is reminded that soil contamination was carried out by mixing soil samples with pollutant solutions in acetone), a fraction of the initial solid 2,6-dichloropyridine molecules remained on the soil surface (confirmed by naked-eye observations) in contrast to the liquid *n*-C₁₂ molecules entirely placed into soil pores (Fig. 6). Plasma active species come in contact faster with the fraction of initial 2,6-dichloropyridine spread on the soil surface increasing thus its overall degradation rate. Furthermore, the air flow and the subsequent penetration of the active species inside the soil pores were hindered in the *n*-C₁₂-contaminated soil, since the volume of each *n*-C₁₂-polluted pore was completely occupied by the liquid pollutant (Fig. 6b), whereas each 2,6-dichloropyridine-polluted pore was partially occupied by the solid pollutant (Fig. 6a).

Pollutant degradation mechanism

During plasma treatment, the temperature of the sand could reach more than 200 °C (Ognier et al. 2014), due to the high-energy electron impacts with the background gas molecules. At such temperatures, a significant amount of the pollutant evaporates, allowing thus its subsequent oxidation in the gas phase by the active plasma species. Given that the boiling points of 2,6-dichloropyridine and *n*-C₁₂ are 211 and 218 °C, respectively, a high percentage of both pollutants is expected to evaporate.

In addition, some intermediate products were generated directly from the initial pollutant oxidation in the soil, given that new peaks were detected from GC-FID for both pollutants after ~ 7 min of plasma treatment (data not shown here). Regarding the *n*-C₁₂ oxidation by DBD plasma, the intermediates in soil have been identified as alcohols and ketones of the same number of carbon atoms (i.e., 6-dodecanol, 6-dodecanone, 3-dodecanol, 2-dodecanol, 3-dodecanone, 2-dodecanone, etc.) (Aggelopoulos et al. 2015b), whereas intermediates of 2,6-dichloropyridine oxidation are not available. It has been reported that the intermediates produced from the ozonation or plasma oxidation of chlorinated molecules (e.g., PCP) were less toxic than the initial pollutant (Anotai et al. 2007; Wang et al. 2010). However, a detailed intermediates identification and toxicity tests is needed to be further study. It is noteworthy that at the end of the plasma treatment, the produced intermediates of both pollutants were almost completely removed through evaporation and/or successive oxidation to CO and CO₂, given that the new peaks detected from GC-FID (after 7 min of plasma treatment)



were almost completely disappeared after 34 min of plasma treatment.

In order to estimate the percentage of pollutant evaporating, the carbon content of the intermediates, produced from n -C₁₂ oxidation in soil after 7 min of plasma treatment, was measured using a semi-quantitative approach (Redolfi et al. 2010) and found to be ~20 % of the carbon content of the initial pollutant, in agreement with recent published results (Aggelopoulos et al. 2015a). It is noteworthy that this percentage may be higher, since no soil samples were collected and analyzed in the time range 2.5–7 min, where the carbon content of intermediates could be >20 %. In other words, less than 80 % of the initial n -C₁₂ was evaporated with the rest >20 % being oxidized inside the soil pores. 2,6-Dichloropyridine evaporation percentage cannot be estimated due to unknown identity of its intermediates in soil. In order to measure the percentage of evaporation, a thorough on-line analysis of the exhaust gases is required. Based on the former calculations, it is suggested that the main pollutant degradation mechanism is evaporation coupled with the pollutants' oxidation in the gas and liquid/solid phase.

Implications for soil remediation

The cost to remediate soil contaminated by organic pollutants varies between different countries, but some estimates are: bioventing ~100 €/tn, soil vapor extraction ~100 €/tn, in situ thermal desorption ~100–150 €/tn, in situ oxidation ~100–150 €/tn, ex situ bioremediation ~100 €/tn, ex situ incineration cost ~500–1000 €/tn (Khan et al. 2004). In the present study, a cylinder-to-plane DBD reactor operating at atmospheric air pressure was used for the remediation of soil contaminated by liquid and solid organic pollutants. The experimental results revealed that the organic pollutants removal efficiency becomes respectable (~95 %) at energy densities ranging from 4000 to 10000 J/g-soil, depending on the pollutants initial concentration (Figs. 2b, 3b). At very high initial pollutant concentration (i.e., 50 g/kg-soil) the energy density required is ~10000 J/g-soil, which means that 1 kW h is required to remediate ~0.4 kg of polluted soil. At lower initial and more realistic pollutant concentration (i.e., 0.5 g/kg-soil), the energy density required is ~4000 J/g-soil which means that 1 kW h is required to remediate ~1.0 kg of polluted soil. In other words, the cost of soil remediation in a cylinder-to-plane DBD reactor ranges from 100 to 250 €/tn, depending on the pollutant initial concentration, indicating that DBD-based plasma could be a cost-

effective oxidation technology for the treatment of soil contaminated by solid and liquid organic pollutants. Recently, a plane-to-grid DBD reactor has been tested for the removal of NAPL (i.e., mixture of n -decane, n -dodecane and n -hexadecane) from soil layers (Aggelopoulos et al. 2015b) where the cost was ~20 €/tn (~6.0 kg-soil/kW h).

It is very important to point out that the reactor used in this study it is rather easy to be engineered despite its multidisciplinary character. Furthermore, this type of reactor can be very easily being up-scaled in order to be used for ex situ soil remediation. On the other hand, the penetration length of the produced active plasma species is normally short (up to 1–2 cm) (Lu et al. 2014) and this factor has to be taken into account when DBD plasma is used for ex situ soil remediation. For in situ plasma-based soil remediation, other configurations have to be developed, where appropriately designed electrodes will be inserted in the soil so that the discharge will be ignited within the pore space and propagate in a multi-jet like form within the soil.

Conclusion

The removal of both 2,6 dichloropyridine and n -dodecane from soil layers in a cylinder-to-plane dielectric barrier discharge reactor, which operated at atmospheric air pressure, was investigated. As energy density risen, the removal efficiency increased, whereas when the initial pollutant concentration increased the removal efficiency dropped. The variance between the degradation rates of 2,6-dichloropyridine (solid pollutant) and n -C₁₂ (liquid pollutant) reflected the effect of pollutant state (solid or liquid) on removal efficiency. The remediation efficiency of both pollutants was lower for the loamy sandy soil than that of quartz sand, revealing the effect of soil heterogeneity and organic matter on removal efficiency. Finally, both pollutants were completely removed after 34 min of plasma treatment regardless of initial pollutant concentration and soil type, indicating that DBD-based plasma could be a well-promising oxidation technology for the ex situ treatment of soil contaminated by solid and liquid organic pollutants.

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