

An experimental study of in-situ remediation of NAPL-polluted soils by ozonation

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Abstract. The effectiveness of ozonation as a method for the in situ remediation of non-aqueous phase liquid (NAPL)-polluted soils is examined. Soils were polluted artificially with a model NAPL consisting of equal mass fractions of n-decane, n-dodecane and n-hexadecane at two concentrations 1g/kg-soil, and 10g/kg-soil. The polluted soils were placed inside a stainless steel column and treated with the injection of ozone-rich gas, produced from oxygen by a corona discharge ozone generator, controlled by a gas mass flow controller, and monitored by an ozone analyzer. Soil samples collected from the soil column were used after pre-treatment to measure the concentrations of the total organic carbon (TOC), and total petroleum hydrocarbons (TPH) as function of time. The concentrations of carbon dioxide (CO₂), carbon monoxide (CO), nitrogen oxides (NO_x), and volatile organic compounds (VOCs) were detected on-line by a multi-sensor and portable gas analyzer.

1 Introduction

Non-aqueous phase liquids (NAPLs) represent a significant environmental challenge due to their persistence and detrimental effects on soil and groundwater quality. Conventional remediation techniques often face limitations in effectively addressing NAPL-contaminated soils, so that innovative and sustainable approaches are needed. Technologies based on the injection of steam, oxygen, or remedial solutions, such as permanganate, dithionate, or nutrient supplements for bioremediation, are frequently used to treat contaminated soil [1], [2], [3], [4]. In recent years, ozonation has emerged as a promising in-situ remediation technology with the potential to treat efficiently and comprehensively NAPL-polluted soil systems. Significant progress has been achieved on ozone delivery techniques, including the flushing of high-concentration acetic acid containing high-level dissolved ozone [5], sparging with mixed surfactant and dissolved ozone [6], and the injection of micro- and nano-sized bubbles (MNBs) containing ozone [7], [8]. Ozonation, involving the production and injection of ozone (O₃) in contaminated matrices, has given prominence to its strong oxidative properties, as an advanced oxidation technique. Ozone readily reacts with a wide range of organic contaminants, initiating a cascade of chemical reactions that lead to the degradation of target pollutants [9]. Unlike other remediation approaches, ozonation offers several advantages, such as the direct treatment of soils, the minimal generation of harmful by-products, and the

compatibility with diverse NAPL compounds [10]. Previous studies have demonstrated the effectiveness of ozonation for the in situ remediation of NAPL-polluted soils, and highlighted the importance of reaction kinetics on the optimization of ozonation processes and enhancement of treatment efficiency [11]. In the present work, an in-depth analysis of the in-situ remediation of NAPL-polluted soils by ozonation, as a primary treatment method, is carried out. Specifically, laboratory-scale experiments are conducted in soil columns to evaluate the ability of ozonation to degrade NAPLs in soil. The long-term goal is to design effective site-specific remediation strategies, promoting the sustainable restoration of contaminated sites and ensuring a healthier environment.

2 Methods and materials

2.1 Preparation of soils

The selected model NAPL was a mixture of three n-alkanes with different number of carbon atoms (n-decane, n-dodecane, n-hexadecane) at equal mass concentrations (w/w). All NAPL compounds were purchased from Sigma-Aldrich. Commercial silicate sand (Merck) was polluted artificially by stirring it with NAPL dissolved in acetone. Then the polluted sand was left under a fume hood until the acetone evaporating. In this way, soils polluted at two concentrations of NAPL were obtained. (10 g/kg-soil, 1 g/kg-soil)

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2.2 Experimental setup

The flow sheet of the experimental setup is shown in Figure 1. All experiments were conducted in semi-batch mode in a stainless steel cylindrical column of 3 cm inner diameter and 50 cm height. A mass of 200 grams from the polluted soil was packed in the column. The ozone was produced by injecting in an ozone generator (LAB2B, Suez) pure oxygen at flow rate ranging from 0.5 to 0.9L/min, regulated by a mass gas flow controller (SmartTrack 50, SIERRA). To confirm the absence of moisture and dust the oxygen passed through a HEPA filter (Sigma) and a silica gel column. The ozone rich gas was injected in the column through a porous cylindrical diffuser adapted at the bottom of the column. The ozone concentration in injected and exhausted gases was monitored on-line with a PC-controlled ozone analyzer BMT 965 (BMT MesstechnikGmbH). During the experiment, the inlet and outlet gas pressures (Model P1, Analysis Ltd, Greece) along with the soil temperature (Autosen, AT011-AT014) were monitored with sensors, and transmitted to PC for storage via a data-acquisition system (ADAM 4561 & ADAM 4117, Advantech). The entire system was placed under a fume hood for safety reasons (Figure 1). Soil samples of 10 gr were collected from several sampling ports placed across the side of the column every 30 minutes.

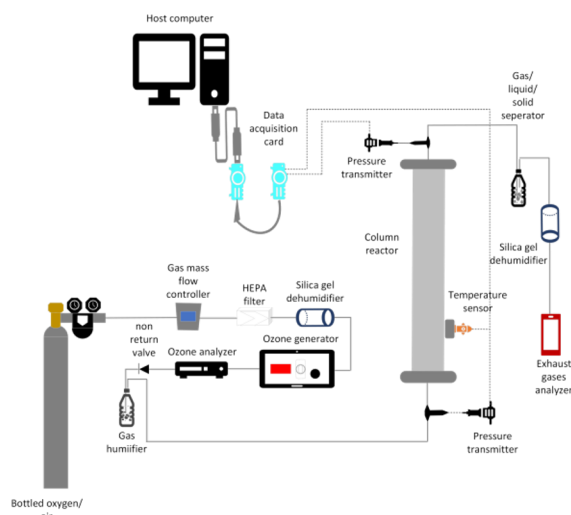


Fig. 1. Flow chart of experimental setup.

2.3 Measurement of Total Organic Carbon

In order to quantify the residual TOC in the samples, 1500 mg of soil was weighed each time and the total organic carbon was measured in a TOC analyzer (multi N/C 2100S, Analytik Jena GmbH).

2.4 Total Petroleum Hydrocarbons

For the extraction of hydrocarbons in organic solvents, 4 g of sample was mixed with 16 mL of acetone and 8 mL of hexane and sonicated for 30 min at 30°C in an ultrasonic bath. After sonication, the supernatant was placed in a separation funnel and rinsed with 3DW

twice. The extract was mixed with 0.6 g of florisil in a SPE syringe and filtered. The organic solution was analysed with a gas chromatographer (Shimadzu, GC-2014) equipped with an flame ionization detector (FID) and auto sampler.

2.4 Analysis of exhaust gas

To assess the potential for NAPL degradation, the exhaust gases was analysed on-line every 30 min by using an Optima 7 gas analyser equipped with sensors able to detect the concentration of CO₂, CO, NO_x, VOCs, and connected with the host computer for data transfer and storage.

3 Results and Discussion

3.1. TOC removal efficiency by ozonation treatment

The concentration of organic carbon in prepared soils was measured and found ~8g/kg and ~0.7g/kg, respectively. The transient response of the TOC removal efficiency during ozonation is shown in Figure 2. It seems that ~80% of the TOC removal was achieved after 90 min of treatment, whereas the TOC removal tended to a plateau after 150 min, and was almost completed after 4 hrs (Figure 2). The final TOC removal efficiency was higher in the soil of low NAPL concentration (1g/kg) (~99%) compared to that (~96%) of the high NAPL concentration soil (10g/kg). Eventually, a reaction mechanism for the degradation of saturated hydrocarbons (NAPL) is that the ozone attacks directly the saturated compounds by 1, 3-dipolar insertion, with this insertion leading to an intermediate ROOOH that was then decomposed into R and OH radicals [12]. The 1, 3-dipolar insertion procedure frequently involves a cycloaddition reaction, in which the dipolar species combines with the chemical to produce a cyclic product. The Huisgen cycloaddition, a 1, 3-dipolar cycloaddition of an azide with an alkyne, is one of the best-known instances of 1, 3-dipolar insertion.

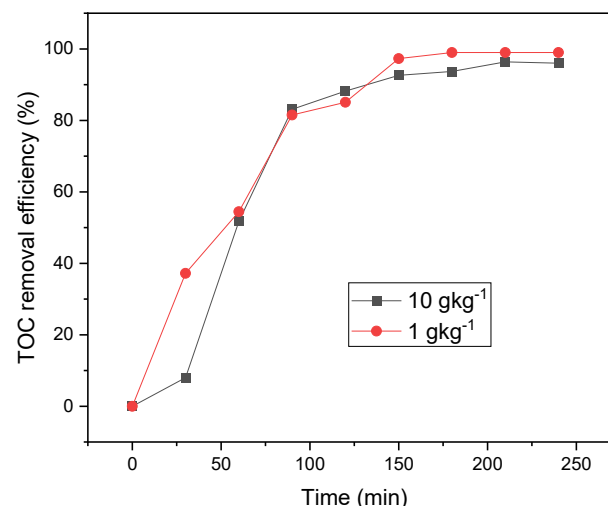


Fig. 2. Transient changes of the total organic carbon (TOC) during soil ozonation

3.2. Effects of ozone in NAPL concentration

The NAPL removal efficiency as a function of time for two different initial NAPL concentrations is shown in Figure 3. Concerning the soil of low initial concentration (1g/kg), the NAPL removal efficiency was maximized (~100%) at early treatment times. In soil of high initial concentration (10g/kg), the NAPL removal efficiency became quite high after 90 min of treatment.

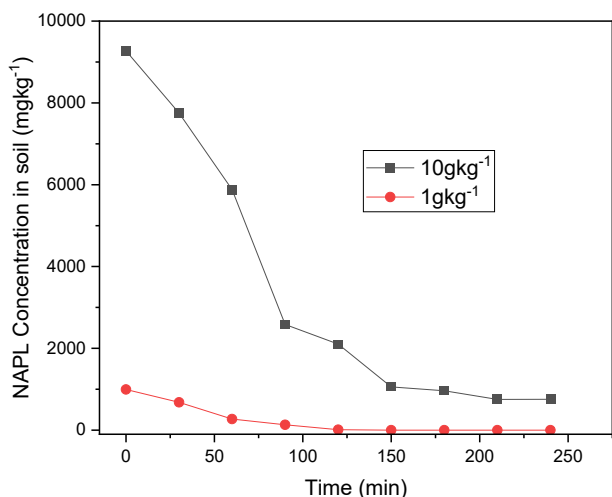


Fig. 3. Effect of NAPL concentration on NAPL removal efficiency

Figure 4 shows the chromatograms of NAPLs before and after ozonation for both concentrations. It is evident that the lower the number of carbon atoms the faster the degradation of hydrocarbon (Figure 4).

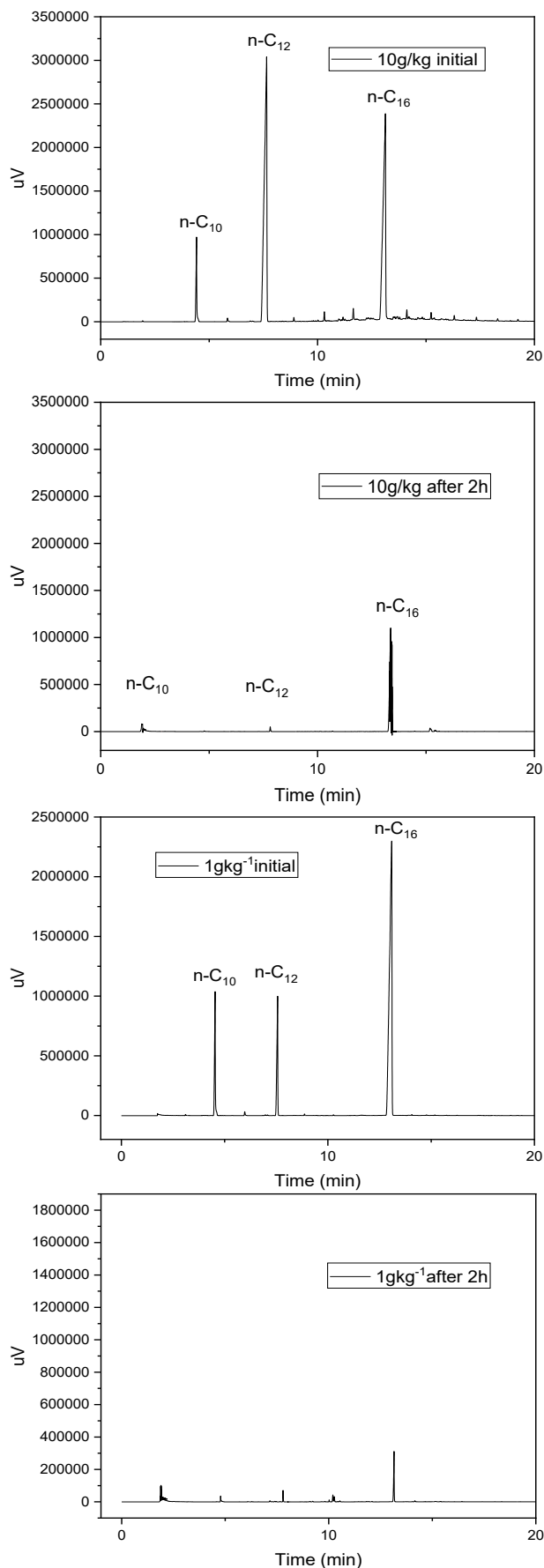


Fig. 4. GC-FID chromatograms of untreated and treated sand extracts

3.3. Analysis of gaseous by-products

The ozone reacts with the organic compounds present in NAPL, leading to their partial or complete oxidation and degradation. The specific reaction products can vary, depending on the composition of NAPL and the conditions of ozonation. However, the breakdown of organic compounds in NAPLs is gradual and first results in the generation of smaller and oxygen-containing molecules, such as aldehydes, ketones, and carboxylic acids. Figure 5 (a) and (b) shows the transient emission of carbon dioxide in exhaust gas, corresponding to the treatment periods during which the highest removal efficiency (~33% and ~86.9 % respectively) was observed. Figure 5 (c) shows the ratio of cumulative concentration of CO to cumulative concentration of CO₂. In the case of high concentration (10g/kg) the low value of the ratio indicates the efficiency of the combustion process. In the case of the lower concentration of NAPLs (1g/kg) the values of ratio shows that CO has been emitted relative to CO₂. Figure 5 (d) shows that 16.75 % of the total carbon content in the case of higher concentration and 34.3%, in the case of high concentration respectively was completely oxidized directly in soil.

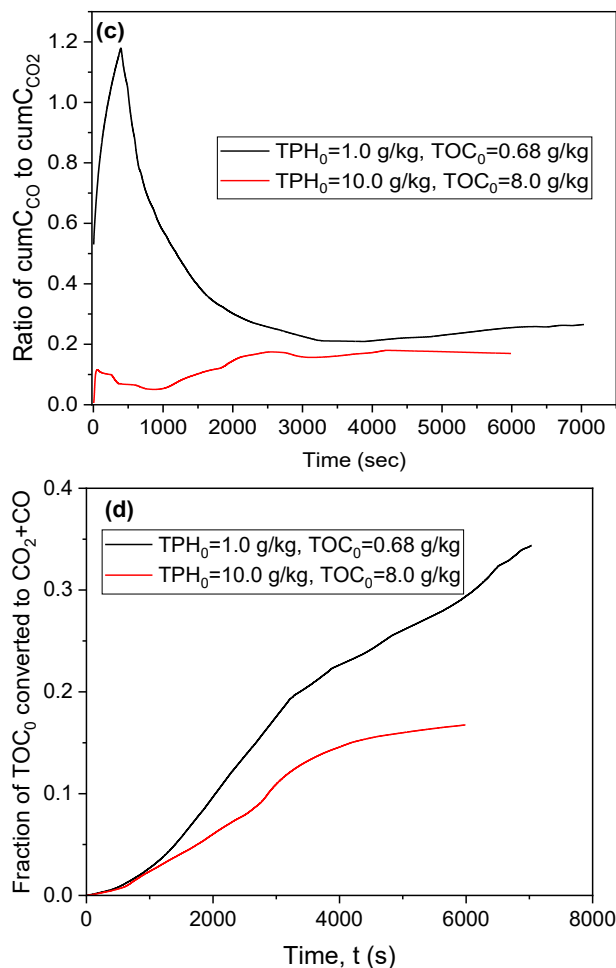
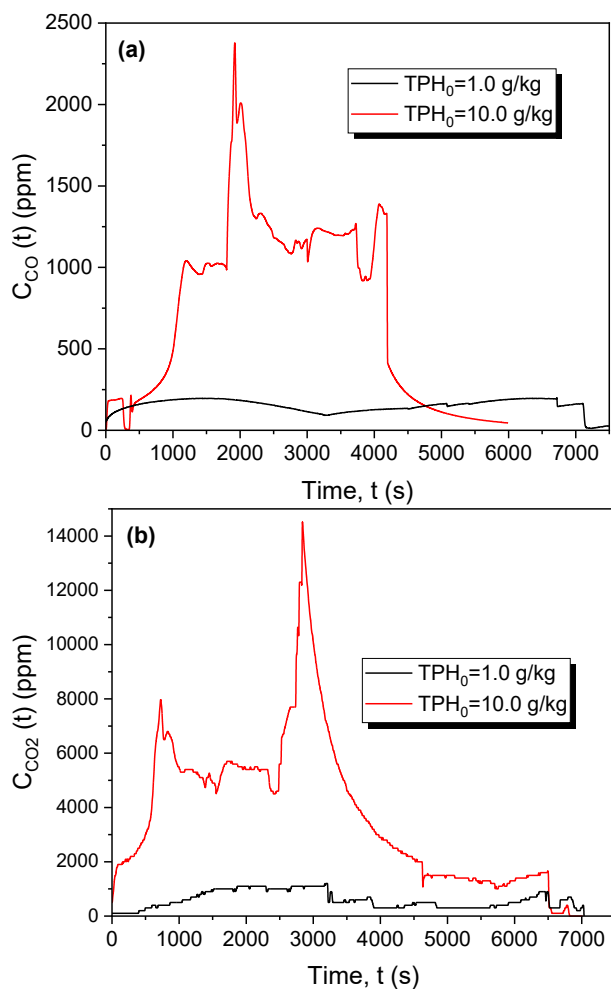


Fig. 5. (a), (b) Transient evolution of CO₂, CO concentration in exhaust gas during the highest level of NAPLs removal, (c) Ratio between cumulative CO₂ and cumulative CO, (d) Fraction of TOC converted to CO₂ and CO

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