Petroleum Products Removal from Contaminated Soils using Microwave Heating

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The purpose of this work is to analyze the influence of dielectric properties of polluting compounds and moisture content on the efficiency of microwave treatment of soil contaminated by hydrocarbons. Temperature, residual moisture and amount of pollutants removed during the time were investigated. The presence of water is essential in order to completely remove the most amount of the volatile substances. The optimal condition resulted 0.15 kg water/kg dry soil to remove all the more volatile components of kerosene and up to the 99% of the heavier compounds in short times. In conclusion microwave heating has resulted applicable to enhance the petroleum hydrocarbons extraction from the soil. In addition moisture content and dielectric properties of the contaminants significantly affected the decontamination efficiency.

1. Introduction

Petroleum products, such as mixtures of volatile hydrocarbons, represent some of the main sources of soil pollution, especially when resulting from petroleum spill, out-of-service oil distribution, leaking from underground storage tank or other industrial wastes (Dror et al., 2002). Consequently there is the need to develop new decontamination technologies that are quick, low cost and suitable to a wide range of physical and chemical conditions (Khan et al., 2004). Low temperature thermal treatments represent suitable alternative treatments to soil incineration and offer the advantage of very short remediation time and the possibility to remove a wide range of polluting substances. To this aim microwave (MW) heating is a promising technique to thermally treat soils contaminated by organic volatile compounds (VOCs), providing rapid and energy-efficient heating (Jones et al., 2002). Both electrical heating and radio-frequency radiation have already been applied in the 1970's in order to remove bitumen from tar sand deposit. MW heating was then applied to decontaminate airfield soils contaminated with petroleum products (Downey and Elliott, 1990). Li et al. (2008) and Acierno et al. (2003) have published results from laboratory-scale experiments on MW treatment of soil contaminated with polychlorinated biphenyls aromatic hydrocarbons (PCBs) obtaining an efficiency greater than 98%.
In this work hydrocarbons were removed from soils using MW heating in a laboratory-scale apparatus. The water resulted the contaminant carrier and, at the same time, it improved the soil dielectric properties allowing the removal of the most part of the volatile pollutants.

2. Experimental Section

2.1 Sample Preparation

Soil was collected from the University Campus in Pisa. It was ground and filtered through a 1-mm sieve to remove debris and stones and then extracted in a Soxhlet apparatus with dichloromethane for 24 h to remove extractable organic material. Soil samples were oven dried at 105 °C during 24 h to obtain constant weight and then its composition was analyzed. It had a particle size of 0.90 mm or less (composition: sand (0.90–0.05 mm) 55%; silt (0.05–0.002 mm) 29%; clay (<0.002 mm) 16%). The soil was then mixed with an amount of contaminants of 18 g for 1 kg of dry soil. Additionally, some samples were prepared with different amounts of deionised water (X_0=0.15–0.3 kg water/kg dry soil). The contaminants used in this work were: n-octane, n-decane, n-dodecane, t-butylbenzene, "synthetic kerosene" (n-octane 3.0%, xylene 2.6%, cumene 5.8%, t-butylbenzene 2.1%, n-decane 46.4%, n-dodecane 37.3% and n-tetradecane 2.8%), and commercial kerosene.

2.2 Pollutant Removal Procedure

The soil sample was placed inside a cylindrical holder made of Teflon® (10 cm internal diameter x 16 cm long with a 1 cm wall thickness) shielded on the side surface by a thin coat of aluminium in order to reproduce a portion of soil irradiated from the top. The sample was placed in vertical position in a PANASONIC NN-F623M multimode MW oven with maximum power supply of 1000 W working at 2450 MHz. The cavity size of the oven had the following measurements: 30 cm height, 34 cm width and 34.5 cm depth. The oven chamber was equipped with a "mode stirrer" in order to obtain a more homogeneous field distribution and heating process. The axial thermal profile of the sample was measured during the time. The top of the holder was connected to a condensing system, a manometer and a vacuum pump in order to allow the vapour extraction at low pressure (0.8 atm) without any alteration of the evaporation process. A scheme of the experimental apparatus is shown in Fig. 1. The nominal power setting was 1956W/kg dry soil. The vapour condensed was collected and analysed by a Thermo Quest TRACE gas chromatograph.
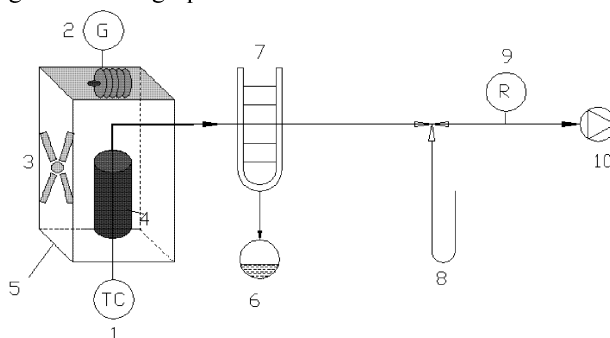

Fig. 1: Schematic of the laboratory-scale microwave apparatus: 1 Thermocouple probe – 2 Microwave generator – 3 Mode stirrer – 4 Soil sample – 5 MW chamber – 6 Condensate collector – 7 Condenser – 8 Manometer – 9 Pressure regulator – 10 Extraction pump.

3. Results and Discussion

3.1 Water Evaporation Tests

Water evaporation tests have the aim to evaluate the temperature profile with time and the water evaporation rate inside the soil sample. As reported in Table 1, a time of 2 min is needed for the sample with X_0=0.15 and 0.3 kg water/kg dry soil to reach 100 °C, while less time is necessary in case of X_0=0.2 kg water/kg dry soil. Then the soil temperature was practically constant during the time, when the water has begun to evaporate out of the soil. The sample with X_0=0.2 kg water/kg dry soil resulted the best compromise between the overall dielectric properties, which allows a rapid and efficiency heating, and the amount of energy required to evaporate the water content. As the temperature continues to increase, the unbound water at the surface of the soil particles and inside the soil pores begins to evaporate with rapid and constant evaporation rate. When the most quantity of the unbound water within the soil has evaporated and the residual water content is about 0.08 kg water/kg dry soil, the remaining water continues to evaporate, but the evaporation rate decreases. Finally when only a small quantity of water is inside the soil, the system can absorb energy difficulty and the heating process stops.

Table 1: Time needed to reach 100 °C for the water-soil system as varying the initial water content.

X_0 [kg water/kg dry soil]	time [min] needed to reach T=100 °C
0.15	2
0.20	1.6
0.30	2

The temperature of 100 °C reached in this system is ideal in the thermal treatment of soil, because it prevents too high temperatures, mainly in case of organic matter-rich soils where carbonisation of humic substances might occur (Kawala and Atamanczuk, 1998).

3.2 Decontamination runs

Decontamination profiles obtained from the MW treatments of soil contaminated by n-octane, n-decane and n-dodecane, are reported in Fig. 2 a) for the duration of 16 min. The results are reported in terms of overall percentage of pollutant that has removed after the irradiation. That is expressed (1) in terms of removal efficiency $\eta(\%)$.

$$\eta(\%) = \left(1 - \frac{C_e}{C_0}\right) \cdot 100 \qquad (1)$$

where: C_e is the pollutant concentration at the end of the MW treatment (g pollutant/kg dry soil) and C_0 is the initial concentration of the pollutant (18 g pollutant/kg dry soil). The removal efficiency shows the same trend in function of the water content in the three cases considered. A general decrease is observed respect to the percentage of

contaminant removal, when the number of carbon atoms and the molecular weight of the hydrocarbons increases. That may be attributable to the vapour pressure of these compounds that decreases with the increasing of the molecular weight (Fig. 2 b) at fixed temperatures. In fact the amount of n-octane in phase vapour is greater than the amount of heavier compounds (n-dodecane) thus allowing its faster removal.
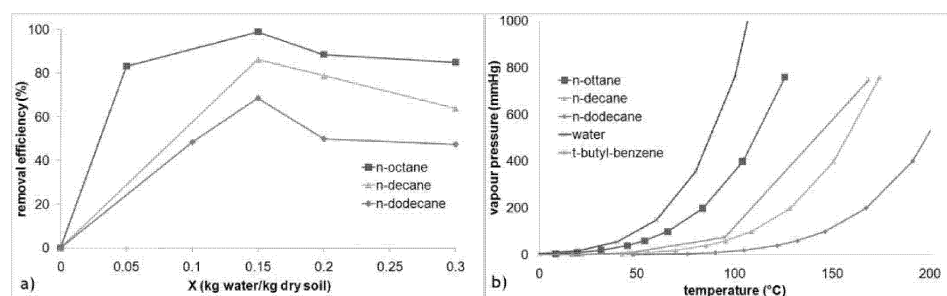

Fig. 2: Removal efficiency for n-octane (■), n-decane (▲) and n-dodecane (♦) by varying the initial amount of water (a) and vapour pressure of n-octane, n-decane, n-dodecane and water vs. temperature (b).

In this type of experiments the three aliphatic compounds present almost identical dielectric constants and however considerably inferior respect to those of the water. Therefore the dielectric constant of each single compound does not influence the extractive effectiveness particularly.

In case of contaminants the maximum in the removal efficiency curve was found for 0.15 kg water/kg dry soil. Actually X_0=0.2kg water/kg dry soil resulted the best compromise in case of soil-water mixture. In the presence of organic pollutants, the overall dielectric properties of the soil–water–organic compound mixture appreciably changed respect those of the soil-water mixture, as reported by Francisca and Rinaldi (2003). The increasing of the heating rate in case of 0.15 kg water/kg dry soil, in the presence of contaminants, may be due to the slightly increasing of the overall loss dielectric factor of the soil. So this value was chosen in the following experiments on MW assisted-decontamination.

To determine the influence of the dielectric properties of the contaminants on the remediation process, two experiments were performed at the same conditions of power, pressure, concentration of contaminants and moisture content. For each case, a portion of dry soil was contaminated respectively by t-butylbenzene and n-decane.

The contaminants have similar chemical-physical characteristics as boiling temperature, density, molecular weight and only slight different vapour pressure, but they have different dielectric properties ($\varepsilon'_{t\text{-butylbenzene}}$=2.4 and $\varepsilon'_{n\text{-decane}}$=2). In fact the induction of heat resulting from the MW radiation is influenced by the dielectric properties of the chemical compounds irradiated.

In the first minutes of the treatment the removal efficiency of t-butylbenzene is widely higher respect to n-decane. The removal efficiency is calculated as the rate between the amount of hydrocarbon at the beginning and the residual amount of hydrocarbon after

the MW treatment. After 15 minutes the residual concentration in soil of n-decane results 5 times greater than that of t-butylbenzene, but the removal efficiency is greater than 99% in both cases, due to the high amount of water which allowed easier the absorption of energy as consequence of its high loss factor.

This quite appreciable difference in the removal efficiency may be attributed both to the slight difference in volatility between n-decane and t-butylbenzene, both to the higher MW absorption by polar t-butylbenzene respect to non polar n-decane which determines an higher amount of energy absorbed by the more loss dielectric compounds.

In general the induction of heat resulting from the MW radiation is determined by the dielectric properties of the substance heated. T-butylbenzene exhibits good dielectric constant and loss factor, due to its polarity and asymmetric structure, while n-decane has lower permittivity because of its linear chemical formula and perfect symmetric structure. Then t-butylbenzene absorbed a higher amount of heat respect to n-decane, so decontamination from t-butylbenzene is easier.

The important result obtained in this work is that the removal efficiency is higher than 99% in both cases, with 15 min of treatment, while without MW heating, up to 90% of aromatic compounds were removed after 2 hr, but about 40% of the aliphatic still remained after 16 hr (Acher et al., 1989).

Experimental trials carried out on soil samples contaminated by mixture of hydrocarbons (simulating kerosene) indicated that most of the contaminants (n-octane, n-decane and aromatic compounds) evolved during approximately the first 5 min of the treatment and they reached the 100% of removal efficiency within 15 min (Fig. 3 a)). Same observations can be carried out for soils contaminated by kerosene, as reported in Fig. 3 b).
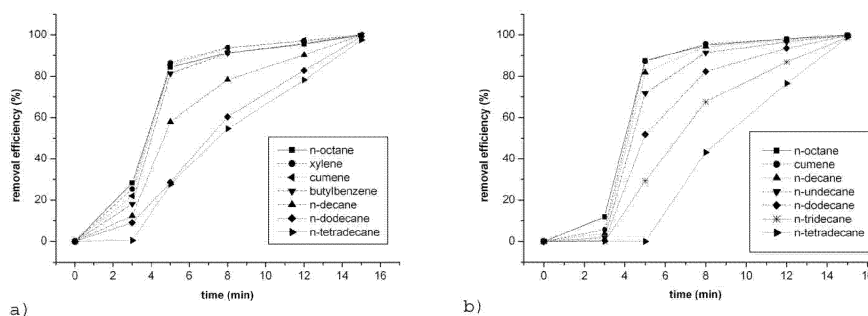

Fig. 3: Removal efficiency for a mixture of hydrocarbons during time (a) and removal efficiency for kerosene components during time (b).

In both cases, after a treatment time of 15 minutes on soil contaminated with a mixture of selected hydrocarbons and commercial kerosene, the efficiency of decontamination results almost 100% for the low boiling temperature compounds, and about 99% for the heavier hydrocarbons. So a decrease in the removal efficiencies is observed when the molecular weight increases, but if the molecular weight is the same, dielectric properties have high influence on the effectives of the process. This fact is evident by comparing

the removal efficiency after 5 min of t-butylbenzene (80%) and n-decane (60%). Respect to the previous study by Acher et al. (1989), even if with higher energetic consume associated to the use of MW irradiation, the removal time is sensibly decreased (from 16 hr to 15 min) and the efficiency of the decontamination is up to 100%.

4. Conclusions

In this work MW treatment of soils contaminated by hydrocarbons was carried out. The removal of hydrocarbons resulted greatly dependent on the water amount in the soil, because it influenced the dielectric properties of the overall system, enhancing the capacity of soil to be heated. Moreover dielectric properties of contaminants in the soil resulted important critical parameters at identical pressure, moisture content and temperature conditions. In fact pollutants with higher loss dielectric factor can be easily removed respect to other compounds with similar boiling temperature and molecular weight, but lower dielectric properties like aliphatic hydrocarbons. Experimental observations also indicated that most of the contaminants (99%) evolved during approximately the first 5 min of the treatment, which was completed within 15 minutes, using 0.15 kg water/kg soil. The final temperature reached by the soil resulted approximately 140 °C. This temperature is relatively low which is another advantage of the MW heating because the soil can maintain the integrity of the matrix and of its organic part, thus allowing its possibly reuse for agricultural purposes.

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