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Effective decontamination of low dielectric hydrocarbon-polluted soils using microwave heating: Experimental investigation and modelling for in situ treatment

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A B S T R A C T

This work aims to obtain essential data for the in situ application of microwave (MW) heating for hydrocarbon-polluted soil remediation. For this purpose, lab-scale experiments were performed and a dedicated computer code was developed and applied to simulate the phenomena induced by a MW treatment. MW process was modelled by means of the mono-dimensional transient equations of energy taking into account the interaction between the electromagnetic field and soil and conductivity phenomena. The model was validated by comparison with results from lab-scale experiments.

Main results indicate that, after a MW irradiation of 6 days, the electric field was reduced by about one third of its initial value at a distance of 60 cm and, as a consequence, soil temperatures equal to and lower than 180 °C were observed. Overall, the thermal effect of the MW treatment was observed to affect a maximum distance of about 120 cm, and this allows the achievement of the contaminant removal in the range 50–99% for a maximum distance of 80 cm from MW source.

Results are of scientific and practical interest and can be used to guide the design of in situ MW treatments. The proposed model provides good prediction of the experimental data and it can be applied to investigate further operating conditions (soil types, incident electric field applied, remediation time). It represents a powerful and suitable tool to predict the effectiveness of the MW techniques.

1. Introduction

The distribution of petroleum products such as diesel–fuel involves several transportation and storage modalities, during which large volumes of contaminants are released into the environment, causing hydrocarbon contamination of soils and groundwater, one of the most prevalent environmental concerns worldwide due to economic, environmental and human health impacts [1–3]. In recent years, a number of chemical–physical or biologic treatments have been investigated to remediate diesel-polluted soils [4–8]. However, these alternatives may be ineffective, expensive or too lengthy [9]. Literature has demonstrated that thermal treatments could be successfully used to remedy hydrocarbon-polluted soils or rocks due to their versatility, removal efficiency and required time [10–15]. On the other hand, conventional ex-situ thermal techniques may be expensive due to excavation, transport and fuel costs, making in situ treatments an option strongly desired. The need for conventional fuels represents another crucial point in remediation operations.

Recently, thermal remediation using microwave (MW) irradiation has attracted great attention in the environmental field representing a potential remedial alternative for contaminated soils, sludge or wastes [16–19]. MW and enhanced-MW treatments were shown to be efficient in a short time for the remediation of soils contaminated with polychlorobiphenyls (PCBs) [20], polycyclic aromatic hydrocarbons (PAHs) [21], polychlorophenols (PCPs) [22], crude oil [23], diesel–fuel [24], hexachlorobenzene (HCB) [25] or antibiotics [26]. The major driving force, which generated a great interest in MW technologies, is its higher ability than conventional thermal remediation to heat the soil rapidly. In fact, heating time is three orders of magnitude lower than with conventional heating as reported [21]. Other merits that should make in situ MW application desirable are [19]:

- homogeneous heating of the contaminated materials;
- low energy consumption linked to short remediation times;
- high flexibility with possibility of instantaneously controlling the power-temperature response;

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- selective heating (in the presence of polar contaminants).

However, despite these advantages, at the moment, full-scale in situ MW application for the decontamination of hydrocarbon-polluted soils is inhibited by a lack of information especially regarding the influence of time and distance of the MW irradiation, the electromagnetic and temperature variation in the soil and their effects on contaminant removal. A potential scheme of in situ-MW treatment includes the irradiation of the contaminated soil by means of specific antennas connected to a MW generator and a power supply. The heat generated by the interaction of the electric field with the soil results in a separation through vaporization of the hydrocarbon contaminants from the solid matrix. The irradiation system must be coupled with conventional extraction for volatile compound (VOC) capture and treatment.

With the exception of very few studies [27,28] where short times or low irradiation distances were investigated, literature addressed soil decontamination by MW only at bench-scale that was reported as not applicable for scale-up processes [29]. In fact, bench-scale MW irradiation generates electric field values in a range that can be representative up to a maximum distance from the irradiation source that at the moment is unknown. In addition, bench-scale experiments are usually performed using small size samples and this makes unassessable both the spatial effects and the heating conductive phenomena.

The internal electric field (E) generated by MW irradiation as a function of the distance from the irradiating source d (m), can be evaluate by Eq. (1) assuming that the microwaves are partially absorbed by the medium according to the law of Lambert and Beer [17,30]:

$$E_d = E_0 \cdot e^{-\frac{d}{D_p}} \tag{1}$$

where E_0 is the incident electric field (V m^{-1}) and D_p is the penetration depth (m) that represents the ability of the electromagnetic waves to penetrate into the medium.

For low loss dielectric materials (i.e.: soils), D_p is given by the simplified form expressed in Eq. (2):

$$D_p = \frac{\lambda_0}{2\pi} \cdot \frac{\sqrt{\varepsilon'}}{\varepsilon''} \tag{2}$$

where λ_0 is the wavelength of the irradiation (m), whereas ε' (–) and ε'' (–) are the real part (dielectric constant) and the imaginary parts (dielectric loss factor) of the complex permittivity, respectively. The electric power $\dot{Q}$ dissipated into heat per unit of volume during the MW irradiation depends on the frequency of the applied electromagnetic field and the dielectric and thermal properties of the medium. The dissipation is quantified by Eq. (3), which is derived from Maxwell's equations [31]:

$$\dot{Q} = \frac{1}{2}\omega\epsilon_0\varepsilon''|E^2_{\max}| = \omega\epsilon_0\varepsilon''|E^2| \tag{3}$$

where ω is the angular frequency ($\omega = 2\pi f$), ε_0 is the permittivity of free space ($8.85 \cdot 10^{-12}$ F m^{-1}), E_{max} is the electromagnetic field peak value (V m^{-1}) and E is electromagnetic field effective value (V m^{-1}). Specifically, the dielectric constant ε' denotes the electric energy storage capacity of the medium, while the dielectric loss factor ε'' can be considered as the ability of the medium to convert electromagnetic energy into heat due to the dielectric polarization of the particles in an alternating electric field. Substances which exhibit a large value of loss factor are good microwave absorbers, whereas substances whose loss factor is close to zero can be considered to be microwave transparent [24]. For most hydrocarbon contaminants, for example diesel–fuel, which are classified as semi-polar compounds having dielectric properties similar to those of soils, the key factor of the remediation process is not represented by a selective heating/desorption of the contaminant alone but by the final temperature of the contaminated soil. In addition, as the amount of water in soil (as soil moisture) increases, so does MW removal efficiency due to water high dielectric properties and, consequently, high MW absorbing features [24].

In the present study the equation of energy has been considered in the simplified form [17]:

$$\rho c_p \frac{\partial T}{\partial t} = -k\nabla^2 T + \dot{Q} \tag{4}$$

where ρ is the density of the medium (kg m^{-3}), c_p is the heat capacity (kJ kg^{-1} °C^{-1}) and k is the thermal conductivity (W m^{-1} °C^{-1}). Eq. (4) is justified as in the present case the dissipation due to viscosity is negligible and the pressure derivative is zero. The term $\dot{Q}$ is the heat generated due to MW irradiation and it is computed by means of Eq. (3).

Based on the above equations, it is clear that, for an effective remediation treatment, the selection of the correct radiation frequency is fundamental. As a matter of fact, in order to achieve the most effective and rapid heating, the highest possible frequency should be applied, but with increased frequency, the radiation range decreases, and for values too high, the radiation effect is not noticeable.

The frequency (f) of 2.45 GHz is generally adopted for remedial purposes being the better compromise ensuring a noticeable heating effect [24]. However, considering soil dielectric parameters in a typical range (ε' = 3.2–7–2; ε'' = 0.6–0.8) [32], calculations from Eqs. (1) and (2) show that the generated electric field (E) drops into the soil rapidly, making the MW radiation effects noticeable only within a few centimetres from the emission point. On the other hand, this limitation could be overridden because soil dielectric properties are temperature-dependent [29]. Long-term MW irradiation, in fact, generates an increase in the soil temperature progressively modifying the temporal and spatial variation of the electric field which has a direct effect on the final soil temperature and consequently on the overall effectiveness of the decontamination process. However, the variation of these fundamental physical parameters is unknown at the moment. The lack of crucial data such as the electric field penetration, the generated soil temperature profiles and the contaminant removals as a function of the irradiation time and the distance from the MW source, makes the limits of the treatment unclear and its full-scale applicability not permissible. This work has been carried out in order to fill those gaps.

The objectives of the present paper are: (i) the experimental evaluation of the temporal and spatial effects of the application of a diesel-contaminated MW irradiation on the electric field penetration, temperature profiles and contaminant removal; (ii) the formulation and the application of a dedicated equation based-process computer code able to simulate the MW heating phenomena and predict its effects at different conditions. Experimental results will define the limits of the MW treatment and will allow its in situ real applicability. The model will represent a suitable tool to predict the impact of operating conditions on the effectiveness of the MW heating and, consequently, for the design of full-scale decontamination treatment in different cases.

2. Materials and methods

2.1. Materials

Commercially available diesel fuel (Esso, Italy) [32] was used for the artificial contamination procedure. All chemicals used in the experiments were of analytical reagent quality. n-Hexane (C_6H_{14}, purity 99%) was purchased from Merck KGaA (Darmstadt,

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