



Low-temperature thermal desorption of diesel polluted soil: Influence of temperature and soil texture on contaminant removal kinetics

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ABSTRACT

Five soil size aggregate fractions, corresponding to coarse (500–840 μm), medium (200–350 μm), fine (75–200 μm) sand, silt (10–75 μm) and clay (<4 μm), were artificially contaminated with diesel, and thermally treated using a laboratory scale apparatus to investigate the effect of soil texture on contaminant adsorption and removal. Ex situ thermal process was simulated using helium as the carrier gas at a flow rate of 1.5 L min⁻¹, different temperatures (100–300 °C) and different treatment times (5–30 min). The amount of contaminant adsorbed on the soil and the residual amount after thermal treatment was determined by gas chromatography. Results showed that adsorption phenomena and desorption efficiency were affected by the soil texture and that temperature and time of treatment were key factors in remedial process. A temperature of 175 °C is sufficient to remedy diesel polluted sandy and silty soils, whereas a higher temperature (250 °C) is needed for clays. Thermal desorption of diesel polluted soil was shown to be governed by first-order kinetics. Results are of practical interest and may be used in scaling-up and designing desorption systems for preliminary cost and optimal condition assessment.

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1. Introduction

The occurrence of industrial sites contaminated by petroleum hydrocarbons is a widespread and relevant environmental problem. Among hydrocarbons, diesel fuel, a complex mixture of saturated (60–80% of n-alkanes and naphthenes) and aromatic hydrocarbons (20–40%), is widely used in the world and represents a permanent source of soil and water pollution [1,2]. Several technologies, such as chemical oxidation [3], biostimulation and bioaugmentation [4], or electrokinetic oxidation [5], can be used for the treatment of these specific polluted sites. Among them, thermal treatments are the most popular and versatile due to their removal efficiency, cost and required time [6,7]. According to their treatment temperatures, treatments can be classified as low-temperature (100–350 °C) and high-temperature (350–600 °C) thermal desorption, involving the physical separation of contaminants from the soil, and thermal destruction (600–1000 °C), involving the chemical modification of contaminants.

Several studies on thermal desorption treatment have been performed in order to understand the fundamentals of contaminant release [8–10] and to investigate the effects of process physical parameters on the remediation efficiency of hydrocarbon contam-

inants such as PCBs [11,12], PCPs [13], chlorinated solvents [14,15], and PAHs [16,17]. Temperature, treatment time and soil characteristics have been identified as key factors of remedial processes.

Specifically, it has been shown that the characteristics of soil influence contaminant-soil interaction, adsorption phenomena, and contaminant removal efficiency during the decontamination processes [18]. Amellal et al. [19] and Lee et al. [20] found that soil texture influences the bioavailability and the remediation of PAHs and BTEX within aggregates of polluted soil, whereas Stella et al. [21] showed that the influence of aggregate size on oil waste biodegradation is an effect of specific surface area available before the interaction of the compounds with the soil.

Limited research has been conducted on thermal remediation of diesel contaminated soils. Thermal treatment of soil artificially contaminated with fuel oil under rapid heating conditions and high temperatures was investigated by Bucalà et al. [22] assessing the effects of heating rate, final temperature and degree of contamination on removal efficiency calculated as weight loss. Piña et al. [23] also studied the effect of the final temperature on the weight loss of uncontaminated and diesel contaminated soil (2.5%, w/w) during thermal desorptive and destructive treatments (200–900 °C). Authors found that soil composition and temperature strongly influence the quantity and the composition of volatile compounds. Merino and Bucalà [6] assessed the influence of the treatment temperature on contaminant removal from a n-hexadecane artificially contaminated soil thermally treated at different final temperatures (150–800 °C) for 30 min. The analysis of the light gas released dur-

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Table 1
Properties of commercial diesel fuel used to artificially contaminate the soil.

Parameter	Value
Density at 25 °C (kg m ⁻³)	900.6
Flash point (°C)	55
Water content (mg kg ⁻¹)	200
Evaporation at 250 °C (% v/v)	64
Evaporation at 350 °C (% v/v)	85
Evaporation at 370 °C (% v/v)	95
n-Alkanes fraction C ₁₀ –C ₂₅ (%)	39.9
n-Alkanes fraction C ₁₀ –C ₁₃ /C ₁₀ –C ₂₅ (%)	37.1
n-Alkanes fraction C ₁₄ –C ₁₇ /C ₁₀ –C ₂₅ (%)	41.7
n-Alkanes fraction C ₁₈ –C ₂₁ /C ₁₀ –C ₂₅ (%)	16.7
n-Alkanes fraction C ₂₂ –C ₂₅ /C ₁₀ –C ₂₅ (%)	4.5

ing the treatment indicated that no pyrolysis reaction takes place, confirming that the evaporation-desorption of the contaminant is the process that governs the removal phenomena from the soil, and that at about 300 °C the contaminant can be removed almost completely from the soil matrix. Moreover, for fluidized thermal desorption treatment of diesel polluted soil, Lee et al. [24] studied the effects of temperature and heating time on contaminant removal efficiency. Results showed that the time to achieve the available efficiency depended on temperature and that maximum efficiency was achieved in 30 min.

The above-mentioned works were based on the assessment of removal efficiency by means of gravimetric analysis; moreover, kinetic phenomena, especially at low temperatures, have not been thoroughly investigated. Furthermore, the effects of soil texture on the diesel adsorption and thermal desorption processes are still unknown.

In the present work, low-temperature thermal desorption treatment of diesel contaminated soils with different soil textures, characterized by different particle size distributions, was studied using an experimental bench-scale apparatus. The main goals of the work were: (i) to test a bench-scale apparatus in order to predict optimum conditions for thermal treatment of organic contaminant polluted soils; (ii) to assess the effect of soil texture on the soil adsorption capability in order to predict the response of different soils to a contamination event; (iii) to assess the influence of the treatment temperature, heating time and soil texture on diesel residual contamination and thus removal efficiency; (iv) to model the experimental data in order to calculate the desorption parameters needed to optimize the treatment operating conditions and to guide the design and the scale-up of low-temperature desorption systems.

2. Materials and methods

2.1. Materials

Commercially available diesel fuel (Esso, Italy) (Table 1) was used to artificially contaminate the soils. All chemicals used in experiments were of analytical reagent quality. n-Hexane (C₆H₁₄, purity 99%) and anhydrous sodium sulphate (Na₂SO₄, purity 99%)

were purchased from Merck KGaA (Darmstadt, Germany). Activated carbons (RB1) used for the volatile compounds capture system of the experimental apparatus were supplied by Norit Italia S.p.A. (Ravenna, Italy). Since soil surface area (which increases with decreasing particle diameter) influences significantly the contaminant soil interaction in adsorption and desorption processes, model soils, free of anthropogenic contamination, with a wide range of specific surface areas were selected for the experiments. Specifically, five soil size aggregate fractions, corresponding to coarse (500–840 μm), medium (200–350 μm), fine (75–200 μm) silica sand, silt as silica flour (10–75 μm) and clay as kaolin (<4 μm) were used (Che.Mi.Fil. s.r.l., Verona, Italy). Soil properties are given in Table 2. Specific surface area was determined by the ethylene glycol monoethyl ether method [25].

2.2. Soil contamination

Selected soils were artificially contaminated by diesel fuel at different rates. The contamination procedure was performed by introducing a pollutant solution of diesel fuel (80 mL) in n-hexane (200 mL) into a 500 mL round-bottom flask containing the selected soil samples (120 g) to obtain a representative contaminant concentration for each type of soil [23,26,27]. Soil and pollutant solution were shaken for 48 h using an orbital shaker, then the n-hexane solvent was removed in 1 h, using a rotary evaporator, under slight vacuum, in order to obtain a homogeneous powdered soil. The contaminated soils were kept in a closed vessel and stored in a dark room at 4 °C for 5 days then analyzed by n-hexane extraction and subsequently gas chromatography for contaminant content before thermal treatment. Contamination procedure was carried out in triplicates and mean and standard deviation values of adsorbed contaminant concentration were calculated.

2.3. Experimental apparatus and procedures

Contaminated soil samples were treated simulating *ex situ* thermal process conditions using a bench scale apparatus (Fig. 1) which consisted of an input gas transport section under pressure (with flowmeter and pressure gauge), a tubular electric furnace (Carbolite MTF 12/38/400, maximum power 1.5 kW) that could reach a maximum temperature of 1200 °C, and a quartz cylindrical tube (inner diameter: 30 mm, length: 450 mm), where the polluted soil sample, inserted into an axially isothermal temperature region of the oven, was placed. The gas outlet section was connected to a volatile compounds capture system (n-hexane traps and activated carbon filters). A type-K thermocouple was axially inserted up to the middle of the soil sample and a type-K thermocouples system was used to measure the carrier gas temperatures in three different sections of the apparatus (inlet section, inside the quartz tube, and outlet section). Thermocouples were connected to a laptop for data recording.

In the experiments, once the electric oven reached the desired temperature (100, 150, 175, 250 or 300 °C), the quartz tube was purged with helium for 10 min maintaining the selected tempera-

Table 2
Properties and characteristics of selected soils.

Parameter	Coarse sand (500–840 μm)	Medium sand (200–350 μm)	Fine sand (75–200 μm)	Silt (10–75 μm)	Clay (<4 μm)
Soil mineral	Silica sand	Silica sand	Silica sand	Silica flower	Kaolin
pH	8.31	8.73	8.72	8.65	8.39
Bulk density (g cm ⁻³)	1.23	1.42	1.36	1.30	1.00
Porosity (%)	35.0	42.5	32.5	33.3	60.2
Specific surface area (m ² g ⁻¹)	0.6	2.11	3.45	12.7	20.01
Hydraulic conductivity (cm s ⁻¹)	0.67	1.2 × 10 ⁻²	5.0 × 10 ⁻²	2.1 × 10 ⁻⁴	10 ⁻⁶
Organic matter (g kg ⁻¹)	3.40	2.62	3.55	3.84	3.29
Moisture content (%)	0.9	1.0	1.2	1.8	2.1

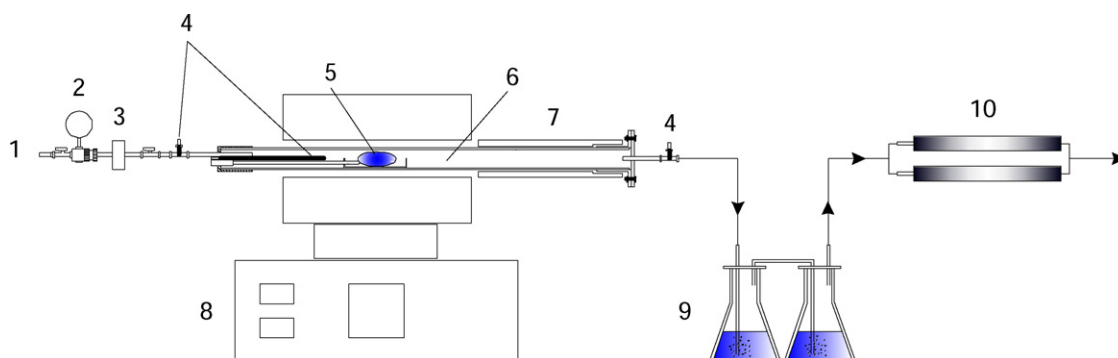


Fig. 1. Schematics of the experimental apparatus. (1) gas carrier inlet; (2) pressure gauge; (3) flowmeter; (4) gas type-K thermocouple; (5) soil sample; (6) quartz tube; (7) post-heater; (8) tubular electric furnace; (9) hexane traps; (10) activated carbon.

ture without cooling down the tube, then 5 g of polluted soil sample were placed inside the oven thus heated for a time of either 5, 10, 18 or 30 min. A constant helium flow of 1.5 L min^{-1} at a pressure of 1 atm was used.

After treatment, soil samples were removed from the apparatus, cooled at room temperature (20°C) and stored in a dark room at 4°C prior to analyzing. The thermal treatment procedure was carried out in triplicates and mean values of contaminant residual concentrations as a function of the treatment time were obtained for each selected temperature and soil.

Removal efficiency (R_e) was also calculated by the following expression:

$$R_e(\%) = \frac{C_0 - C}{C_0} \cdot 100 \quad (1)$$

where C_0 is the initial contaminant concentration in soil (mg kg^{-1}) and C is the residual concentration of contaminant in soil after the thermal treatment (mg kg^{-1}).

2.4. Kinetic data modelling

Residual hydrocarbon concentration curves as a function of the desorber residence time follow a first order kinetic [1,12,28], defining an exponential decay:

$$C = C_0 e^{-kt^n} \quad (2)$$

where C is the residual concentration in soil after a treatment time t , C_0 represents the initial contaminant concentration, k represents the decay rate of the function and n is the shape of the decay curve. k is temperature dependent and can be expressed as:

$$k = A e^{-E_A/RT} \quad (3)$$

where E_A is the activation energy of the system, A is a frequency term, R is the gas constant and T is the absolute temperature. Expressing Eq. (2) in a logarithmic form, and differentiating in terms of the time of treatment t , the desorption rate $-dC/dt$ can be expressed as:

$$-\frac{dC}{dt} = knC \left[-\frac{1}{k} \ln \frac{C}{C_0} \right]^{n-1/n} \quad (4)$$

Residual concentration results obtained during the experiments were fitted using the first order kinetic model expressed by Eq. (2). Desorption parameters k and n were calculated for each soil at different tested temperatures and the correlation was assessed as correlation coefficient R^2 .

Obtaining the experimental parameters k and n , Eqs. (2) and (4) could represent a valuable tool in calculating residual concentration C or desorption rate at any given initial contaminant concentration

in soil and in identifying the temperature and the time of treatment required to reach specific targeted levels of remediation.

2.5. Extraction and analysis

For each 5 g sample treated, a 2 g subsample was analyzed for hydrocarbon concentration. The subsample was mixed with *n*-hexane in a Soxhlet extractor for 6 h. 5 mL of effluent were mixed with 2 mL of *n*-hexane in a separate funnel, stirred for 2 min then left at rest for separation. The supernatant phase was mixed with internal standard (ISM-560 Ultra Scientific, USA) and analyzed by gas chromatography.

Due to their high proportion (40%) in diesel fuel, *n*-alkanes compounds (C_{10} – C_{25}) were chosen as representative components [1], and their total concentration in spiked and treated soil samples was taken as that of diesel fuel and expressed as $\text{mg/kg}_{\text{soil}}$.

The concentration of *n*-alkanes in soil samples was measured by gas chromatography (GC) (Agilent Technologies 6890N) equipped with a mass spectrometer (Agilent Technologies 5975) using the US-EPA 8270-C method. A capillary column (HP-5, 30 m length \times 0.32 mm ID \times 0.25 μm film thickness) was used. The GC was operated with a helium-carrier-gas flow rate of 1.5 mL min^{-1} and the oven temperature program starting at 40°C (held for 4 min) and increasing at a rate of $10^\circ\text{C min}^{-1}$ to a maximum temperature of 310°C . The temperature of the injector was 270°C .

3. Results and discussion

3.1. Contaminant adsorption capacity of soil

After the contamination procedure, adsorbed diesel on soil (C_0) as *n*-alkanes fractions (C_{10} – C_{25}) for all spiked soils was measured and the results are illustrated in Fig. 2. For the investigated soils, C_0 was in a wide range (from 689.2 mg kg^{-1} for coarse sand to $3989.4 \text{ mg kg}^{-1}$ for clay), and was strongly correlated with specific surface area and soil texture. The data suggest that C_0 increased linearly with increasing specific surface area values, while a logarithmic trend was observed for C_0 as a function of soil texture. Results are in agreement with Chiou and Shoup [29], Amellal et al. [19] and Sánchez-Martín et al. [30] who found that hydrocarbon compounds were much more concentrated in the soil fractions characterized by higher specific surface area. The presence of a fine-sized texture in soil is a main factor for the hydrophobic adsorption of organic matter on the surface of fine soil particles [31]. It seems important to emphasize the mechanism of this concentration phenomenon in order to define the behaviour and fate of contaminants in remediation processes.

Besides, since the same contamination procedure was used for all soils, the change of the final soil contamination indicated the

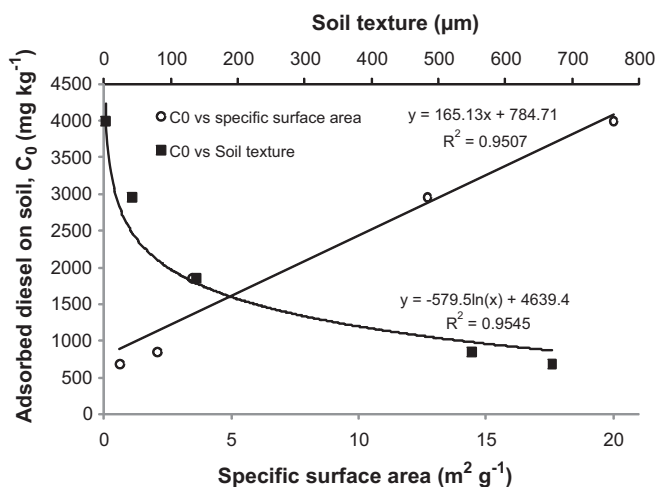


Fig. 2. Effect of soil texture and specific surface area on the concentration (C_0) of diesel fuel adsorbed in soil.

variation in the vulnerability of the selected soils to a contamination event. Specifically, an increase in vulnerability of about 6 times was observed for clay compared to coarse sand. Observed relationships could be useful to calculate the diesel adsorbed on soil and thus the vulnerability of any soil of which the characteristics are known and, consequently, appropriately planning a full scale intervention where a contaminant dynamic change might be needed.

Moreover, for all the investigated soils, the percentage distribution of single n-alkanes fractions (Table 3) (calculated as the ratio between the concentration of the single n-alkanes fraction C_n and the total concentration C_{10} – C_{25}) presented the highest percentage for the fractions ranging from C_{14} to C_{17} with a typical “Gauss distribution” shape, but it did not reflect the percentage composition of diesel used for the contamination procedure (C_{10} – C_{13} fraction was 37.1% for diesel while it ranged between 13.9% and 28.2% for soils). This indicated that all fractions did not similarly adsorb onto the different soil matrices and affinity was observed between specific n-alkanes fraction and soil. Specifically, C_{10} – C_{11} fraction was much more adsorbed in silty and clay soils compared to the sandy soils.

3.2. Kinetics of diesel removal

Figs. 3 and 4 show the dynamics of residual diesel concentration represented by C_{10} – C_{25} adsorbed on soil (C) with time, at temperatures of 100, 150, 175, 250 and 300 °C, respectively. As expected, contaminant concentration in soil after thermal treatment decreased with time for all soils, and the rate of diesel desorption increased with treatment temperature.

Most of the contaminant n-alkanes were removed during the first 18 min of thermal treatment, being the fastest in coarse sand (5 min). After that, further contaminant removal occurred at very low rates.

The change of slope in the kinetic curves is possibly due to the sequence of two distinct phases in thermal removal processes of porous media. At the first step a rapid evaporation of contaminant occurs from the soil particle surface while, at the second one, the evaporation rate is limited by internal diffusion phenomena [10]. Additionally, at a desorber temperature of 250 °C, a minimal residual diesel concentration (less than 10 mg kg⁻¹) was reached in just 5 min for all soils except for clay, which required a higher temperature of 300 °C or a longer treatment time at 250 °C. However, very low residual concentrations (about 100 mg kg⁻¹) can be reached only for sandy (coarse, medium and fine sand) and silty soil, using a lower temperature of 175 °C and times longer than 18 min.

Table 3
Distribution of adsorbed diesel as n-alkanes fractions in all soils.

n-Alkanes fraction	Coarse sand ^b (500–840 µm)		Medium sand ^a (200–350 µm)		Fine sand ^a (75–200 µm)		Silt ^a (10–75 µm)		Clay ^a (<4 µm)	
	mg kg ⁻¹	%	mg kg ⁻¹	%	mg kg ⁻¹	%	mg kg ⁻¹	%	mg kg ⁻¹	%
C ₁₀	0.0 ± 0.0	0.0	0.0 ± 0.0	0.0	16.7 ± 4.7	0.9	180.5 ± 9.7	6.1	295.2 ± 47.6	7.4
C ₁₁	19.3 ± 2.1	2.8	9.3 ± 0.7	1.1	63.2 ± 14.0	3.4	168.7 ± 6.1	5.7	239.3 ± 32.3	6.0
C ₁₂	42.0 ± 3.2	6.1	39.8 ± 3.8	4.7	113.4 ± 24.6	6.1	207.1 ± 4.4	7.0	279.2 ± 36.0	7.0
C ₁₃	57.9 ± 4.5	8.4	68.5 ± 2.9	8.1	150.6 ± 28.6	8.1	233.8 ± 1.7	7.9	311.1 ± 38.1	7.8
C ₁₄	75.8 ± 6.0	11.0	93.9 ± 6.5	11.1	198.9 ± 37.1	10.7	295.9 ± 16.0	10.0	398.9 ± 45.9	10.0
C ₁₅	83.4 ± 5.1	12.1	101.5 ± 5.1	12.0	223.6 ± 40.2	12.0	319.6 ± 7.2	10.8	434.8 ± 54.3	10.9
C ₁₆	77.2 ± 2.9	11.2	96.4 ± 4.8	11.4	206.3 ± 32.6	11.1	298.9 ± 7.5	10.1	398.9 ± 48.5	10.0
C ₁₇	66.8 ± 2.9	9.7	87.1 ± 5.4	10.3	182.2 ± 30.4	9.8	254.5 ± 10.2	8.6	335.5 ± 37.6	8.4
C ₁₈	57.2 ± 5.0	8.3	73.7 ± 4.2	8.7	154.3 ± 24.5	8.3	216.0 ± 14.4	7.3	287.2 ± 38.0	7.2
C ₁₉	49.6 ± 2.3	7.2	65.1 ± 2.2	7.7	133.8 ± 19.4	7.2	189.4 ± 6.8	6.4	247.3 ± 27.8	6.2
C ₂₀	45.7 ± 3.1	6.6	60.1 ± 5.1	7.1	119.0 ± 17.2	6.4	171.6 ± 11.5	5.8	223.4 ± 37.9	5.6
C ₂₁	37.2 ± 2.3	5.4	49.1 ± 3.9	5.8	96.7 ± 13.3	5.2	139.1 ± 8.4	4.7	179.5 ± 26.5	4.5
C ₂₂	29.6 ± 1.6	4.3	39.8 ± 3.1	4.7	78.1 ± 10.2	4.2	112.4 ± 5.8	3.8	139.6 ± 16.0	3.5
C ₂₃	22.7 ± 1.2	3.3	29.6 ± 1.6	3.5	61.3 ± 8.6	3.3	85.8 ± 4.4	2.9	107.7 ± 10.8	2.7
C ₂₄	15.2 ± 1.2	2.2	20.3 ± 0.9	2.4	39.0 ± 3.5	2.1	53.4 ± 2.4	1.8	67.8 ± 6.2	1.7
C ₂₅	9.6 ± 0.9	1.4	11.8 ± 0.6	1.4	22.3 ± 2.6	1.2	32.5 ± 1.7	1.1	39.9 ± 3.5	1.0
C ₁₀ –C ₂₅	689.2	100.0	846.1	100.0	1859.5	100.0	2959.1	100.0	3989.4	100.0

^a ±Standard deviation based on triplicate experiments.

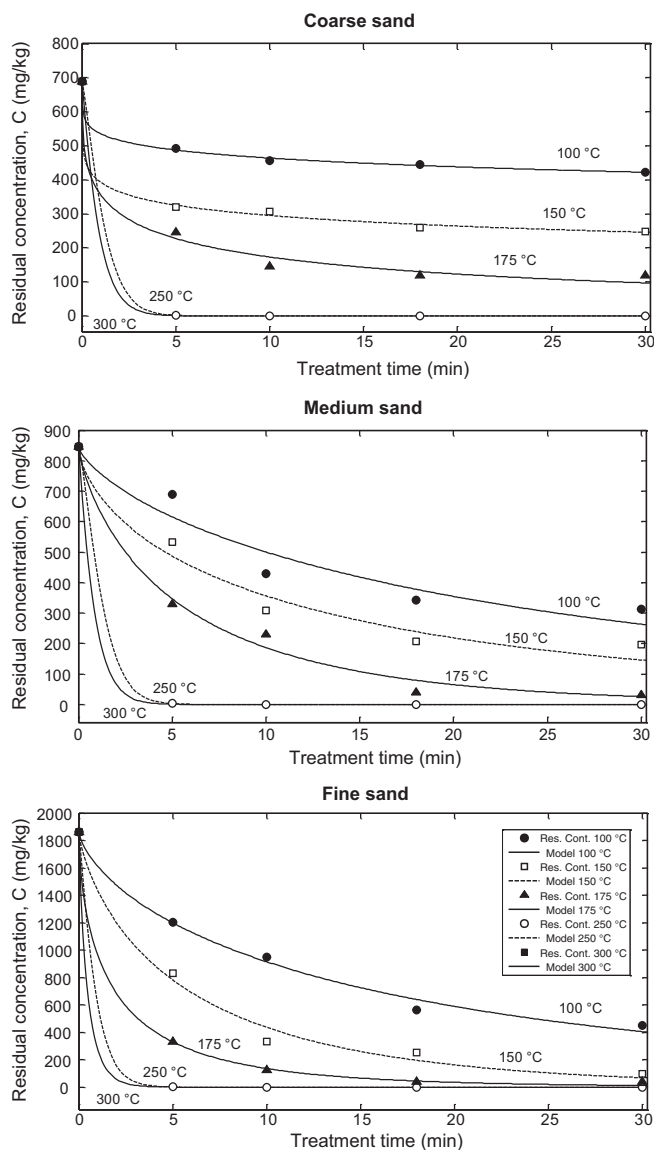


Fig. 3. Residual contaminant concentrations (C) and first order kinetic model curves for coarse sand, medium sand and fine sand at treatment temperature of 100, 125, 150, 175, 250 and 300 °C.

This is in agreement with Merino and Bucalà [4] and Lee et al. [24] who showed that at about 300 °C n-hexadecane and diesel can be removed completely from a fine sandy soil. Our results clearly indicated that contaminant removal depends on treatment time and that a very low temperature (about 175 °C) is sufficient to remedy diesel polluted sandy and silty soils, whereas a slightly higher temperature (250 °C) is needed for fine grains soils such as clay.

The comparison of obtained kinetic results with the literature findings, indicates that much more time (up to about 200 times) is required to successfully treat recalcitrant contaminants such as PCBs [12] or PAHs [28] compared to diesel.

Residual concentration data were fitted to Eq. (2), and values for the correlation coefficient (R^2) were calculated. Model parameters (rate of contaminant decay k and shape of the curve n) and R^2 values are shown in Table 4. The first order kinetic model showed an excellent correlation with the experimental data according to the very high R^2 values. Decay rates (k) are strongly correlated to treatment temperature (Fig. 5) with R^2 values higher than 0.96 for all tested soils and, as expected, k values increase with increasing

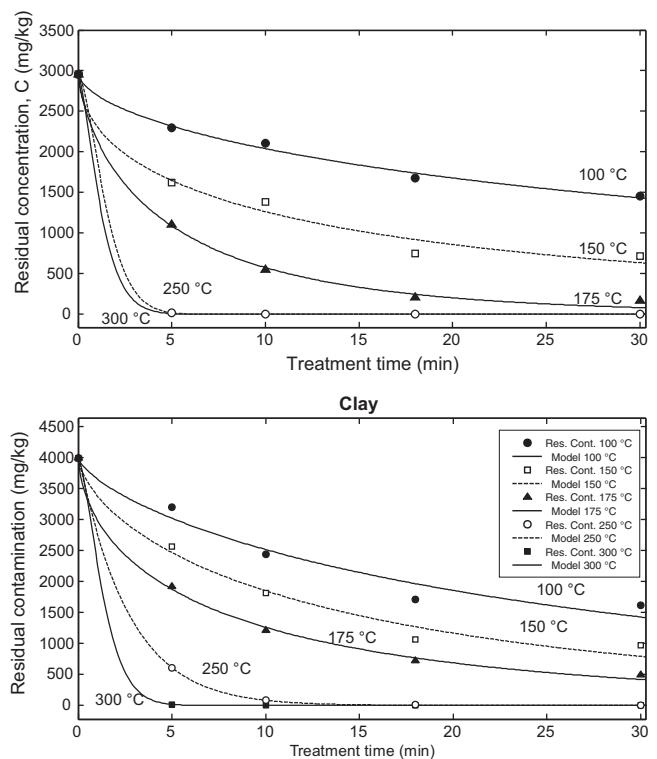


Fig. 4. Residual contaminant concentrations (C) and first order kinetic model curves for silt and clay at treatment temperature of 100, 125, 150, 175, 250 and 300 °C.

temperature for all soils due to the nature of the process [8–10]. Linear correlation between k and T was also observed by Smith et al. [28] and by Tse and Lo [13] who investigated the effect of temperature on decay rate for PAHs and PCPs polluted soils respectively, whereas an exponential relationship was observed by Uzgiris et al. [12] who studied the removal process of PCBs contaminants from the soils.

The slopes of the decay rates were different, implying that the activation energy is correlated with the nature of the soils. Specifically, the lowest activation energy is required for sandy soils while the highest is required for clayey soil. This is due to the adsorption capacity of the selected soils because of the specific surface area, lowest for sandy soil and highest for clayey soil (Fig. 2). Moreover, for clayey soil, the presence of inter-crystalline layers (ranging from 1 to larger than 10 nm in thickness) able to trap contaminants that penetrate into the layers [18] and high porosity values [32]

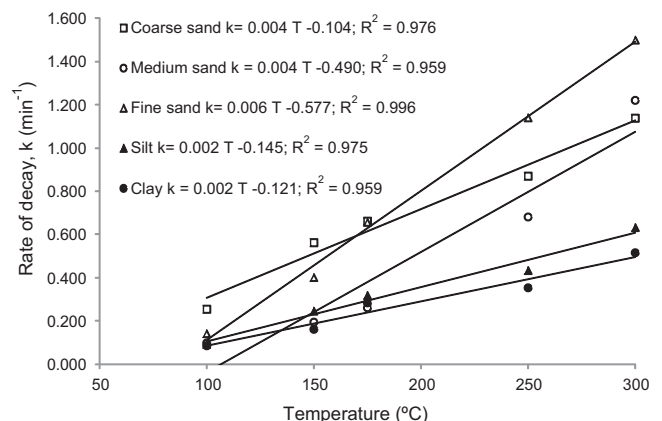


Fig. 5. Rate of decay (k) as a function of treatment temperature for all tested soils.

Table 4Desorption parameters (k , n) and correlation coefficient (R^2) of first-order kinetic model at temperature of 100, 150, 175, 250 and 350 °C for all tested soils.

T (°C)	Coarse sand (500–840 μm)			Medium sand (200–350 μm)			Fine sand (75–200 μm)			Silt (10–75 μm)			Clay (<4 μm)		
	k	n	R^2	k	n	R^2	k	n	R^2	k	n	R^2	k	n	R^2
100	0.253	0.195	0.998	0.098	0.727	0.914	0.14	0.696	0.993	0.092	0.607	0.993	0.086	0.730	0.996
150	0.563	0.177	0.998	0.195	0.647	0.974	0.401	0.748	0.992	0.246	0.539	0.984	0.161	0.677	0.982
175	0.662	0.319	0.992	0.261	0.763	0.989	0.656	0.600	0.997	0.319	0.711	0.998	0.283	0.609	0.998
250	0.870	1.251	0.999	0.681	1.314	0.999	1.140	1.120	0.999	0.434	1.518	0.999	0.354	1.037	0.999
300	1.140	1.085	0.999	1.213	1.066	0.999	1.499	0.852	0.999	0.633	1.375	0.999	0.515	1.441	0.999

that increased the contaminant diffusion phenomena, represent limiting factors in desorption processes.

Knowing of the residual concentration values as a function of treatment temperature and treatment time could be significant in assessing the change in energy efficiency and cost of a thermal remedial process. Based on available technical data on thermal desorption treatment [33] and considering a typical 20 tons h^{-1} rotary kiln system supplied by diesel fuel, an average specific savings of $0.2\text{€}^\circ\text{C}^{-1}\text{min}^{-1}$ was assessed. Therefore, also a minimal change of the treatment temperature could significantly influence the remedial costs. For instance, a temperature change of 10°C could result in a saving of €30,000 for the remediation of average-size polluted sites. This amount could increase up to about 20 million euro for the treatment of extremely large sites ($300,000\text{m}^3$).

3.3. Diesel removal efficiency

Fig. 6 shows the diesel removal efficiency vs. treatment time at the five treatment temperatures. At all tested temperatures, removal efficiency maximum values were observed for sandy soils

with the exception of coarse sand. The highest differences of removal efficiency between the five soils were observed at the lowest treatment temperature.

For fine sand, excellent efficiency was reached also at lower temperatures (i.e., 76% at 100°C and 95% at 150°C), whereas the lowest removal efficiency was observed for fine soils (silt and clay) and for coarse sand. For coarse sand, this specific behaviour could be due to high hydraulic conductivity (10^{-2}cm s^{-1}) that influenced significantly the cooling process of the soil sample during the thermal treatment, resulting in a limitation of the heat transfer and, consequently, a decrease in the soil temperature. In fact, temperature profiles (Fig. 7) obtained by the monitoring system showed that the lowest temperature values were recorded for coarse sand, while the highest were for clay at every temperature of treatment, with a difference up to 20°C being observed during the pre-equilibrium phase where none of the soils reached the temperature of the oven. Thus removal efficiency is not directly proportional to the soil area surface and soil texture.

The influence of soil texture on organic contaminant removal efficiency observed for the performed experiment is in the same range as that reported by previous literature findings on biologi-

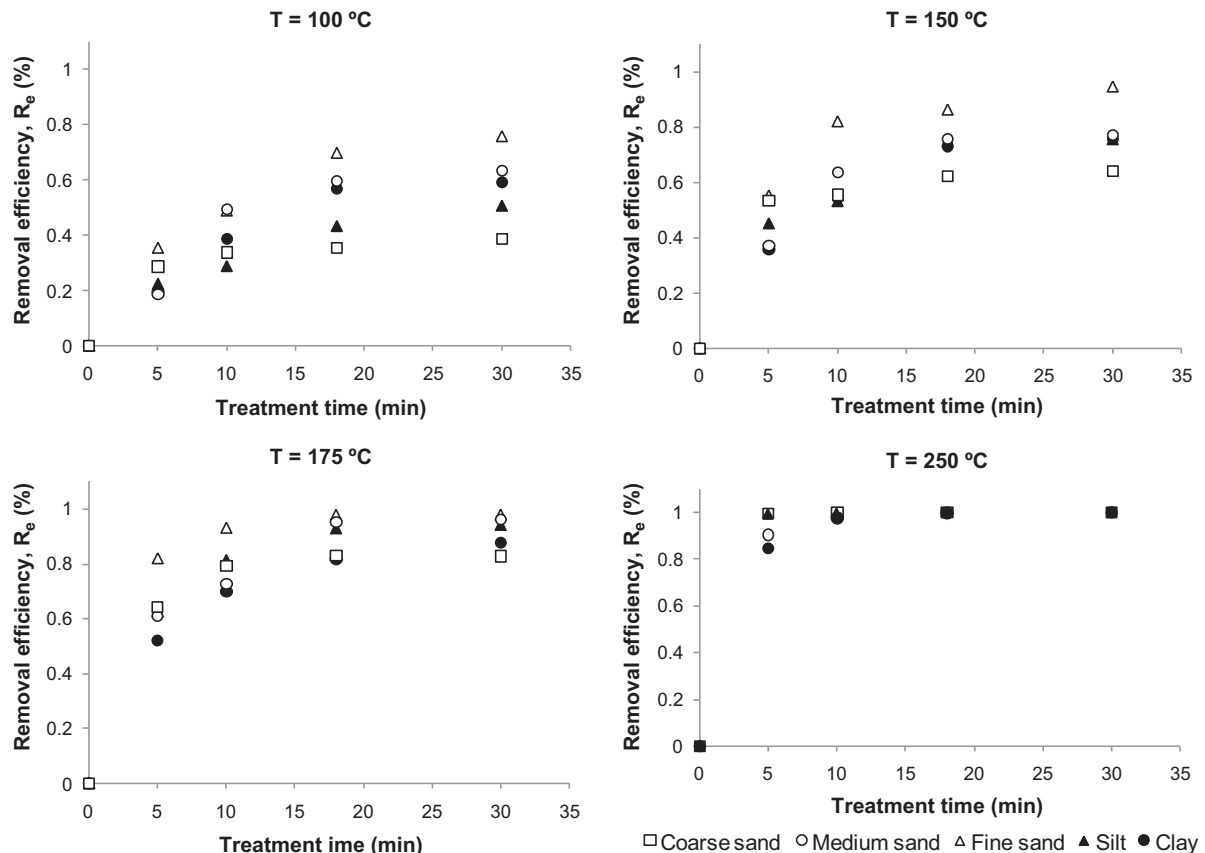


Fig. 6. Removal efficiency (R_e) as a function of time for a temperature of treatment of 100, 150, 175 and 250 °C for all tested soils.

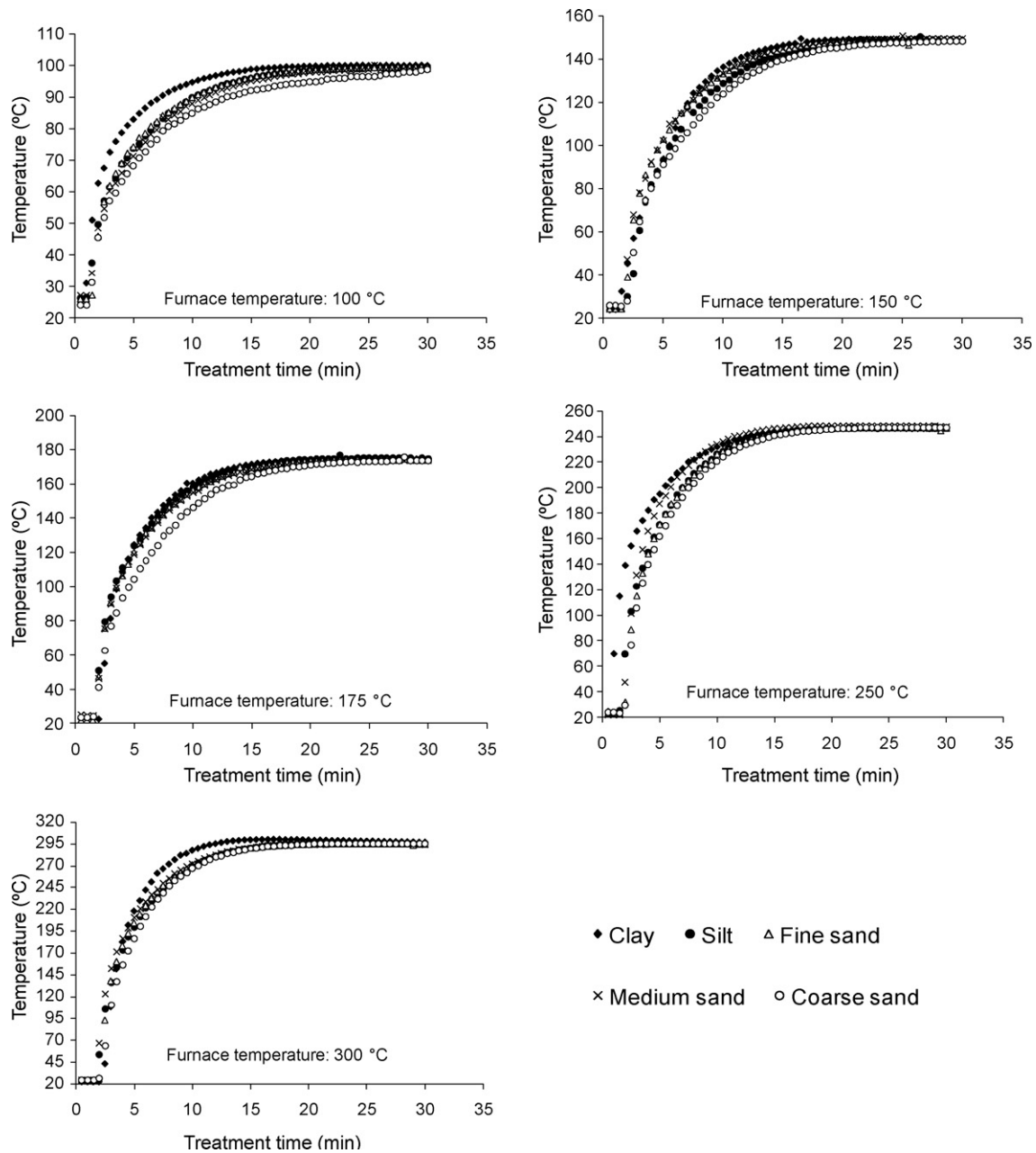


Fig. 7. Temperature profiles of the selected soils for 100, 150, 175, 250 and 300 °C oven treatment temperatures.

cal treatments. Lee et al. [20] demonstrated that the remediation efficiency for clayey soil polluted by toluene or TCB was about 30% lower than for sandy soil, while Jung et al. [34] reported a variation in n-hexadecane removal efficiency of about 40% between sandy and clayey soils for an integrated ozonation and biodegradation treatment. Moreover, Aelion [35] observed that in a natural biodegradation process of benzene and toluene, the soil texture induced a low variation (6%) in the removal efficiency.

High diesel removal efficiencies observed for thermal desorption are hardly achievable using other economical treatments such as natural biodegradation or even using more expensive treatments such as oxidation with chemical agents or ozone. However, high removal efficiencies comparable to thermal desorption can be reached by using soil washing with surfactants [1], or by using remediation treatments such as electrokinetic-Fenton oxidation [5] or microwave thermal remediation [36] which require a higher

energy consumption and consequently a higher cost. Li et al. [37] reported that for a sandy soil spiked with diesel fuel at different rates (ranging from 500 to 50,000 mg kg⁻¹), the TPHs natural biodegradation, for an incubation period of 110 d, reached a maximum value of about 73% for the lowest contamination levels, whereas it was less than 70% for the 5000 mg kg⁻¹ samples. Minimal percentages, not higher than 37%, were observed for the highest contaminated samples. Do et al. [3] showed that an in situ chemical oxidation treatment of a diesel polluted soil at 5000 mg kg⁻¹, using peroxydisulphate/cobalt (PMS/CoII), was characterized by a maximum contaminant degradation of approximately 47% and that a sequential injection treatment using a large quantity of chemicals was needed to reach a contaminant degradation of 88%. Moreover, Lee et al. [26] found that a diesel removal efficiency of 40% was obtainable by oxidation with ozone of a heavily contaminated sandy soil.

In terms of costs, with reference to treatment of VOC hydrocarbon polluted soils, the US Environmental Protection Agency [38] reported costs from 24 US\$ ton⁻¹ to 380 for ex situ bioremediation and from 75 US\$ ton⁻¹ to 560 for thermal desorption. Costs in the same range of thermal desorption are needed for oxidation treatments [39]. Moreover, for these treatments, treatment times and environmental impacts are comparable to those for thermal desorption and, based on our findings, energy required and environmental impact could be minimized. Therefore, low temperature thermal desorption appears to be a better choice for remediation of any type of diesel polluted soils especially due to their excellent cost effectiveness.

4. Conclusions

The following conclusions have been drawn based on experimental results and discussion:

- Soil texture significantly influences the diesel adsorption phenomenon and, consequently, the vulnerability of soils to a contamination event. This vulnerability is six times higher for clayey soils than for coarse sandy soil. Specific relationships observed between soil contaminant concentration and soil specific surface area or soil texture (linear and exponential respectively) could be useful in calculating the amount of diesel adsorbed on soil and thus to predict the vulnerability of any soil of which the characteristics are known, and consequently in appropriately planning an intervention where a contaminant dynamic change might be needed.
- In thermal desorption processes, the nature of the soil significantly influences temperature and remediation time, and very low temperature (175 °C) and times longer than 18 min could be used to successfully remediate diesel polluted sandy and silty soils, while a slightly higher temperature (250 °C) is needed for clayey soils.
- The first order kinetic model showed an excellent correlation ($R^2 > 0.99$) with the experimental data for residual concentration at all temperatures of treatment and for all tested soils. Experimental parameters k and n assessed for the different experimental conditions and tested bench-scale equipment are of practical interest and could represent a valuable tool in calculating residual concentration or desorption rate at any given initial soil concentration and in identifying the temperature and the time of treatment required to reach specific targeted levels of remediation. This is fundamental in designing and scaling-up desorption systems and then in assessing the change in energy efficiency and cost of a thermal remedial process.
- Low temperature thermal desorption appears to be a better choice for remediation of diesel polluted sandy and silty soils due to their excellent removal efficiency and costs that may be limited by low temperatures and times required.

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