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"Gheorghe Asachi" Technical University of Iasi, Romania

OPTIMIZING THE PROCESS OF DEPOLLUTION THROUGH THERMAL ABSORPTION OF SOILS CONTAMINATED WITH CRUDE OIL

Dorina Pop*, **Valer Micle, Ioana Monica Sur**

Faculty of Materials and Environment Engineering, Departament: Environment Engineering and Entrepreneurship of Sustainable Development, Technical University of Cluj-Napoca, 103-105 Muncii Blvd., 400641 Cluj-Napoca, Romania

Abstract

This paper presents the results of experimental researches regarding the optimization of a decontamination process through thermal desorption of soils contaminated with crude oil. The optimization was performed for the following desorption parameters: heating temperature of the soil and the treatment duration, by increasing the temperature from 300°C to 350°C and decreasing the treatment duration from 10, 15 and 20 minutes to 5, 10 and 15 minutes. The economic calculation of the decontamination process was performed for emphasizing the efficiency of thermal desorption. The experiments were performed on soils with loamy sand texture, loamy texture and loamy clay texture.Iit was found that the contamination degree, the texture and the treatment duration influence the thermal desorption efficiency. The analysis of how the texture influences the process of depolluting soils contaminated with various concentrations of crude oil, reveals that the loamy-sand texture has a higher efficiency, as compared to the loamy and loamy-clay textures. Moreover, it was shown that the highest efficiency is obtained by treating the loamy-sand soil for 15 minutes at 350°C.

Key words: crude oil, pollution, soil, thermal desorption

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1. Introduction

The problems occurring during the process of depolluting sites contaminated with oil led to the necessity of developing remediation technologies that would be feasible, rapid and which could be applied to a wide variety of pollutants (Khan et al., 2004). The technology for treating soils through thermal desorption is used for organic pollutants, and it has the following advantages: quick and easy application; destruction of pollutant compounds and allows the reuse of the depolluted soils, depending on the temperature used and the residual concentration of the pollutants (Calamar et al., 2017; Tan et al., 2017; WORDPRESS, 2010). Meuser (2013), showed that in the case of decontaminating soils polluted with volatile halogenated hydrocarbons (VHH), the necessary temperature is approximately 90 - 320°C, in case of benzene, but it can be reduced to approximately 150°C, while in case of pesticides the treatment can be performed at temperatures ranging between 320 - 540°C for a high efficiency.

The experience acquired by the company S.C. SetCar S.A. Brăila in treatments using thermal desorption of soils contaminated with oil products, proves that, as the pollution degree increases, it can observed that the efficiency of the decontamination process is intensified (www.setcar-braila.ro/desorbtie-termică-directă _2_619_1.htm). The researchers from FRTR/USA show that the efficiency of the desorption

* Author to whom all correspondence should be addressed: e-mail: dddorinaa@yahoo.com; Phone: +40 0754617776

is > 91% for the decontamination of soils polluted with PCBs (FRTR, 2014). The results of applying this technology, following the researches performed by Araruna et al. (2004), show that the content of oil products significantly decreases as the temperature increases, while exposure to temperatures higher than 450°C practically eliminates any trace of organic substance residues (Araruna et al., 2004).

Regarding the decontamination of soils polluted with volatile/semivolatile compounds through *in situ* thermal desorption, the specialists of the Deep Green company/Belgium emphasized the main advantage of heating soil by conduction. The heat transfer does not depend on the type of soil, revealing that the evaporation of pollutants from the soils is influenced by the temperature, pressure and treatment duration (DEEP GREEN, 2010; Micle and Neag, 2009).

Falciglia et al. (2011) studied the influence of soil texture and temperature in the kinetic removal of pollutants through thermal desorption at low temperature for soils contaminated with diesel fuel. The results showed that for sandy soils and muddy soils polluted with diesel fuel, the necessary remediation temperature is 175°C and for clay soils a higher temperature is required (250°C). Also, they found that the main factors in the remediation process were temperature and treatment duration, while the thermal desorption efficiency was influenced by the soil texture (Falciglia et al., 2011).

A study performed by Chang and Yen (2006) was related to the use of the thermal desorption technology in treating soils contaminated with mercury, in the Southern part of Taipei city, in Taiwan. They reached the conclusion that removing the mercury from the contaminated soil using thermal methods is efficient when treating it at a temperature higher than 700°C and a retention time of at least 2 hours. After the desorption, the concentration of residues achieved was under 2 mg/kg and for some, even lower than 0.05 mg/kg (Chang and Yen, 2006).

The cost of remediation by thermal desorption of soils contaminated with oil products can vary from 50 to 330 $ per ton of soil. From this amount, between 20 $ and 35 $, is directed towards the costs of direct exploitation. These figures include the initial configuration and transportation costs per unit, the cost of excavation of contaminated soil and the replacement of the treated soil (Hunt and Troxler, 2005).A study performed by Pop et al. (2013a), after treatment through thermal desorption at low temperatures (200°C, 300°C) revealed that at 300°C for a certain treatment duration (10, 15 and 20 minutes respectively) the efficiencies are high (87.15 ÷ 98.51%). Regarding the influence of the texture on the depollution of soils using thermal desorption at different parameters: temperature (350°C) and time (5, 10, 15 minutes) the efficiencies obtained in this research were between 93.84 ÷ 98.30% (Pop and Micle, 2014).

The main purpose of the paper consists in optimizing the main parameters of thermal desorption (temperature and treatment duration), through economic calculation and investigating the influence of the contamination degree and texture on the efficiency of the decontamination process.

2. Material and methods

Soil sampling was performed in the village of Bonţida, Cluj County, according to STAS 7184, (1975), for the depth interval of 0–20 cm (Fig. 1). Experiments on the parameters influencing the process of decontamination through thermal desorption were performed in the laboratory. Experimental analyses were performed on soil samples of loamy sand texture (P1), loamy texture (P2) and loamy-clay texture (P3).

A set of analyses of the thermal desorption were performed at the temperature of 300°C with the treatment durations of 10, 15 and 20 minutes, for the concentration C of samples of loamy sand texture, followed by a set of analyses at 350°C (with treatment durations of 5, 10 and 15 minutes).

The experimental studies of decontamination at 350°C were performed as follows: 100 g of soil was weighed for each experiment, the samples were polluted with three different concentrations (3.7 mL – A, 6.1 mL – B and 10 mL – C), they were subject to thermal desorption for treatment during the time intervals of 5, 10 and 15 minutes, then we determined the concentration of crude oil remaining in the soil, in order to establish the efficiency of the decontamination process. The thermal desorption was performed using the electric oven with silicon carbide bars, owned by the Technical University of Cluj-Napoca.

For a simplified notation of the three textures polluted with various concentrations of crude oil in the experimental researches, we used the following form: X texture (P1, P2, P3) + pollutant (A, B, C). Each texture was polluted with the three concentrations of pollutant, resulting in the following coding: for the soil with loamy sand texture: P1A – samples polluted with 3.7 mL crude oil; P1B – samples polluted with 6.1 mL crude oil, and P1C – represent the samples polluted with 10 mL crude oil.

In the case of loamy and clay loam textures, we used the same notation, replacing only P1 by P2 and P3, thus resulting the following: for the loamy texture – P2A, P2B and P2C, and for the clay loam texture – P3A, P3B and P3C (Fig. 2). There was a total of 27 experiments, when we proved the influence of the contamination degree and of texture on the efficiency of thermal desorption. The plan of the experiments' methodology is presented in Fig. 2. The pollutant concentration was determined according to state standards STAS SR 13511/2007 (SR ISO, 2007), using the Soxhlet method.

Fig. 1. The map of the sampling area (Pop et al., 2013b)

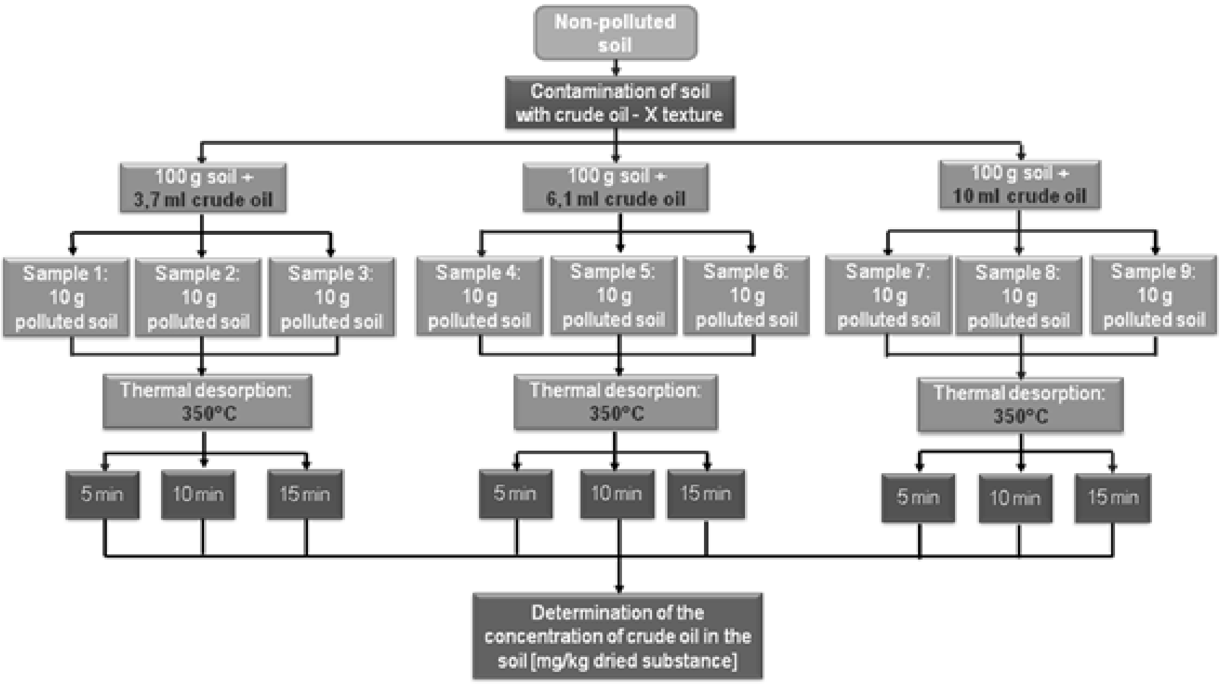


Fig. 2. Plan of the experiments' methodology

3. Experiments

The extraction of the concentration of pollutant from the soils, using the Soxhlet method is accomplished with the device presented in Fig. 3. The stages for determining the initial concentration of crude oil in the samples are shown in the diagram in Fig. 4.

The efficiency of extraction using the Soxhlet method, in this case, was influenced by: the size of the solid particles (polluted soil), the contact time between the sample and the solvent (eight hours), the temperature (40°C), the nature of the solvent and the nature of the interactions between the analyte and the matrix of the solid sample. In this case, the disadvantages are overcome due to the fact that we used methylene chloride, which has a very low boiling point, as compared to the pollutant used.

The concentration of pollutant determined before and after the decontamination process was compared to the values of the alert threshold and intervention threshold established by Order 756/1997 (GD, 1997), regarding soils with less sensible use.

The efficiency of decontaminating soils polluted with crude oil, using thermal desorption, was calculated with Eq. (1):

$$\eta = \frac{m_{analyte}(solvent)}{m_{analyte}(sample)} \cdot 100\,[\%] \qquad (1)$$

where:

- $m_{analyte}(solvent)$ – the concentration of pollutant removed through thermal desorption at different temperatures and treatment durations, in mg/kg;
- $m_{analyte}(sample)$ – the initial concentration of pollutant in the soil (that can be extracted using the Soxhlet method), in mg/kg.

4. Results and discussions

4.1. Process optimization

Analyzing the histogram of the variation of crude oil concentration in the soil (Fig. 5) we can observe a significant decrease for all the four extraction times established (5, 10, 15 and 20 minutes). The extraction of crude oil has a higher efficiency in case of samples used for desorption at the temperature of 350°C, as compared to 300°C (Fig. 6). In case of samples used for desorption at 350°C we observed that for the sample kept for 10 minutes at the value of the quantity of crude oil is under the intervention threshold, and the one kept for 15 minutes is under the alert threshold.

Regarding the samples treated at the temperature of 300°C, we observed that the value of the quantity of crude oil is under the intervention threshold only for the sample treated for 20 minutes. We can also see that during the decontamination at both 300°C and at 350°C, the quantity of contaminant in the soils decreases, as the treating duration increases. After analyzing chart 6 we can observe that the extraction efficiency has a linear increase at both samples, depending on the time.

Fig. 3. Soxhlet extraction device (Pop and Micle, 2014)

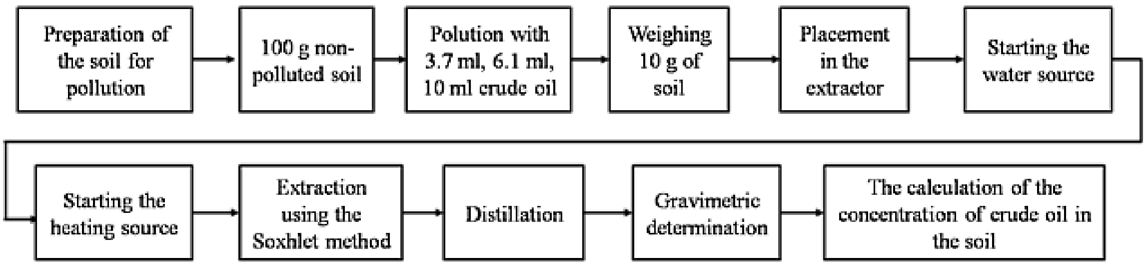


Fig. 4. The stages for determining the concentration of pollutant in the soil samples

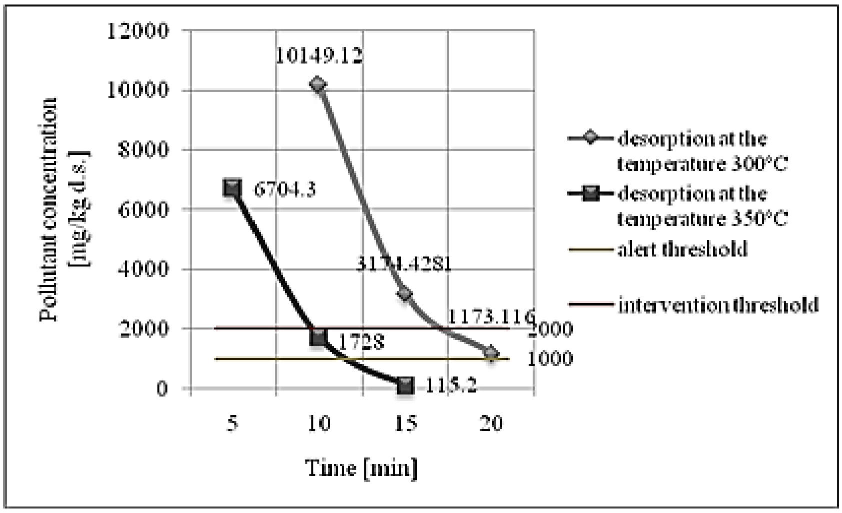


Fig. 5. Variation of the concentration of pollutant following the decontamination at 300°C and 350°C

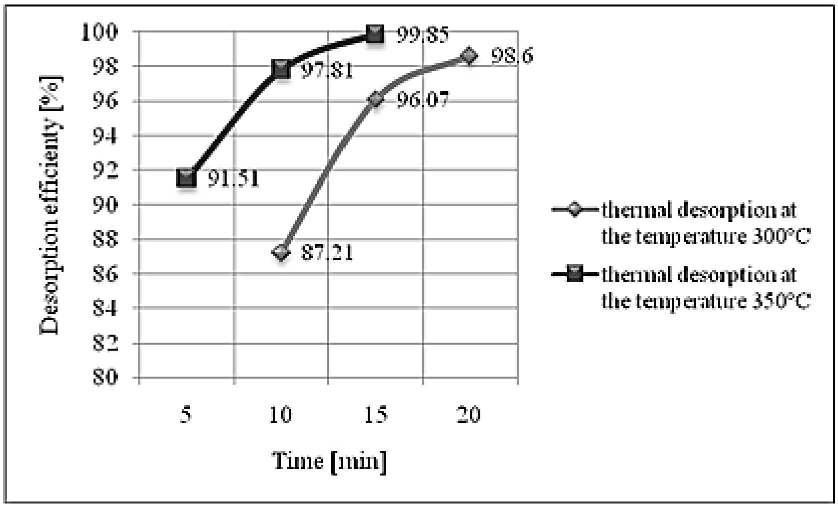


Fig. 6. The efficiency of thermal desorption at 300°C and 350°C

For the sample treated for 5 minutes at 350°C the desorption efficiency is higher than in the case of the sample treated for 10 minutes at 300°C. The highest efficiency was obtained for the sample kept for 15 minutes at the temperature of 350°C. The efficiency of thermal desorption was determined according to Eq. (1), being evaluated on mixes or synthetic samples (soil polluted in the lab), where the quantity of analyte added (initial concentration of the sample) is known, $m_{analyte}$*(sample)* and we determine the quantity of analyte from the solvent used in the extraction, $m_{analyte}$*(solvent)* (WORDPRESS, 2010).

4.2. Economic optimization

On the basis of the results obtained following the experiments, we performed the economic calculation for the optimization of the decontamination process. The electric oven with silicon carbide bars used in the process of thermal desorption works in alternating current, which is why it is important to measure the active and reactive power. In an alternating current circuit there are several categories of power. These categories of power are due to the fact that the two values, U and I, are variable in time and generally dephased (http://www.circuite-electrice.accounting-business.eu/puterile-in-circuitul-de-curent-alternativ.htmL). In order to perform the economic calculation of the electric energy consumed during the decontamination process, it was necessary to calculate the following types of powers: apparent power, active power, inductive reactive power, neutral inductive reactive power and the paid inductive reactive power. The detailed explanation of these types of powers is given below:

- **S** – apparent power (total) determined through the product between the actual value of the voltage at the circuit clamps and the actual intensity of the current established by the circuit, in VA;

- **P** – active power representing the average value of the instantaneous power, during a period of the alternating current, in W;

- **cosφ** – is called power factor and is defined as the proportion between the active power P and the apparent power S of the system;

- **sinφ –** phase angle;

- **Q** – inductive reactive power, which represents "the product between the actual values of the voltage and the intensity and the sinus of the phase angle between the instantaneous voltage at the clamps of the circuit and the instantaneous intensity of the current in the circuit", in VAr (http://www.circuite-electrice.accounting-business.eu/puterile-in-circuitul-de-curent-alternativ.htmL).

The results of the calculations made are shown in Table 1. After finalizing the calculations regarding the total expenses required for the desorption process, we can observe that, at the temperature of 350°C the costs and the energy consumed increase as the treatment interval increases, and for the temperature of 300°C the values decrease as the duration of keeping the samples in the oven increase (Fig. 7).

By comparing the results of the desorption efficiency depending on the costs, shown in Fig. 8, we find that the value of the decontamination cost is lower at 350°C for a treatment duration of samples for 5 minutes in the oven (the efficiency is higher), as opposed to the temperature of 300°C for 10 minutes treating time (the efficiency is lower).

4.3. Efficiency of the desorption depending on the degree of pollution, soil texture and treating duration

After the experimental researches, the efficiency of the depollution process was determined using Eq. (1). The chart representing the efficiency of the thermal desorption depending on the degree and the duration of treating the samples in the electric oven is presented in Fig. 9, where we can observe that as the degree of the contamination and the treating duration increase, the efficiency of the decontamination process increases as well (Fig. l0).

The efficiencies obtained record values between:
- loamy sand texture (P1A, P1B and P1C): 91.51 ÷ 99.85%;
- loamy texture (P2A, P2B and P2C): 93.84 ÷ 98.91%;
- clay loam texture (P3A, P3B and P3C): 88.69 ÷ 97.78%.

By analyzing chart 10 regarding the influence of the texture and treatment duration on the decontamination process, it is revealed that the loamy sand texture has higher efficiencies as opposed to the soils of loamy texture or loamy-clay texture. The results with the lowest efficiencies were obtained for the soil samples of loamy-clay texture.

5. Conclusions

The modification of the main parameters of thermal desorption led to the optimization of the decontamination process, because the treatment of the sample at 350°C for a duration of 5 minutes is more efficient than the decontamination at 300°C for a soil sample kept in the oven for 10 minutes. The economic calculation of the total expenses required for the decontamination process shows that at a higher temperature, the costs and the consumed energy increase as the treating interval increases, and at a lower temperature, they decrease as the duration for keeping the samples in the oven increase.

Table 1. The results of the powers calculations

Power [W]	***S [VA]***	***P [W]***	***cosφ***	***sinφ***	***Q [VAr]***	***$Q_{neutral}$ [VAr]***	***Paid inductive reactive power [VAr]***
3960	6600	3960	0.6	0.8	3168	1686,564	1481,436

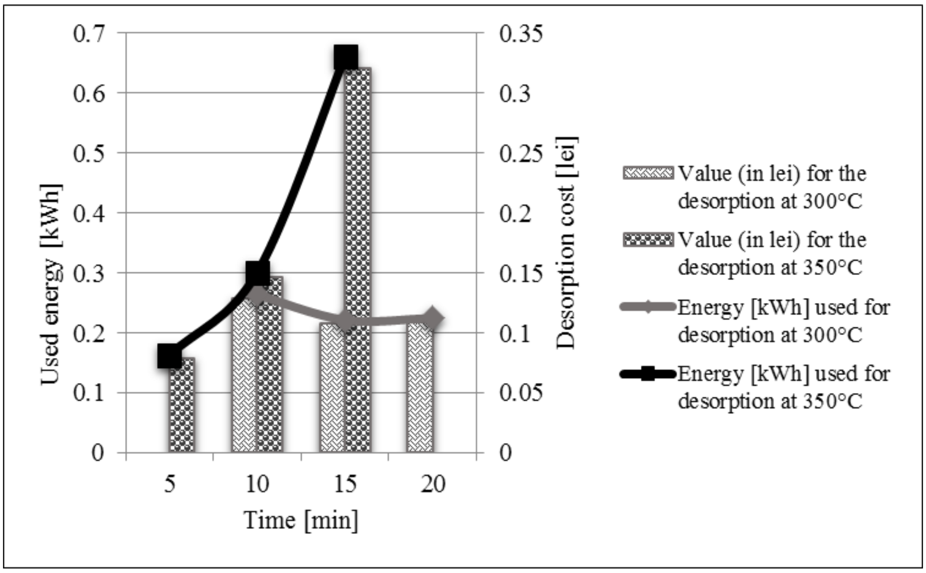


Fig. 7. Variation of the active electric energy and of the cost of the decontamination process depending on the parameters of thermal desorption

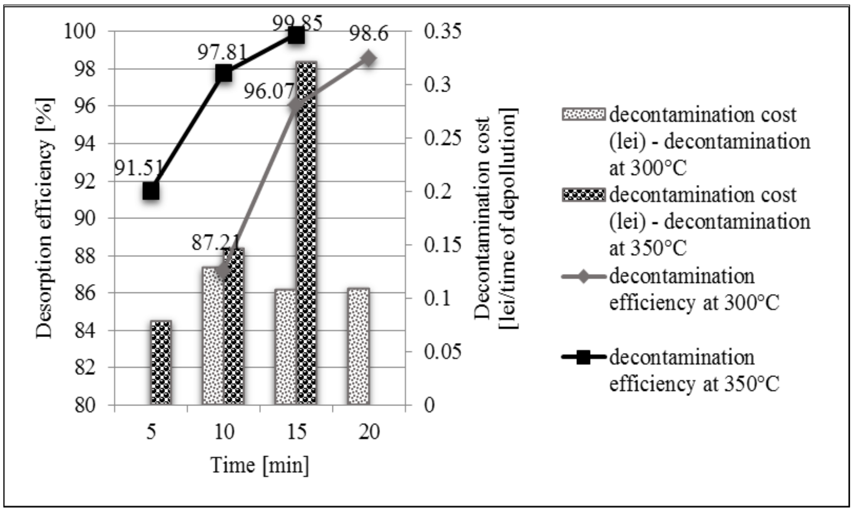
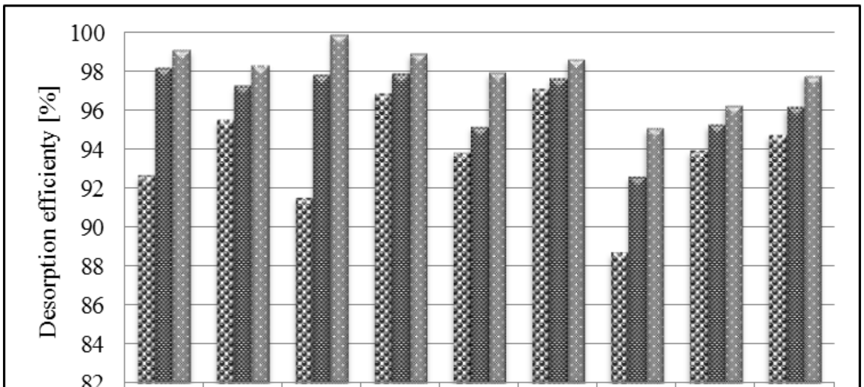
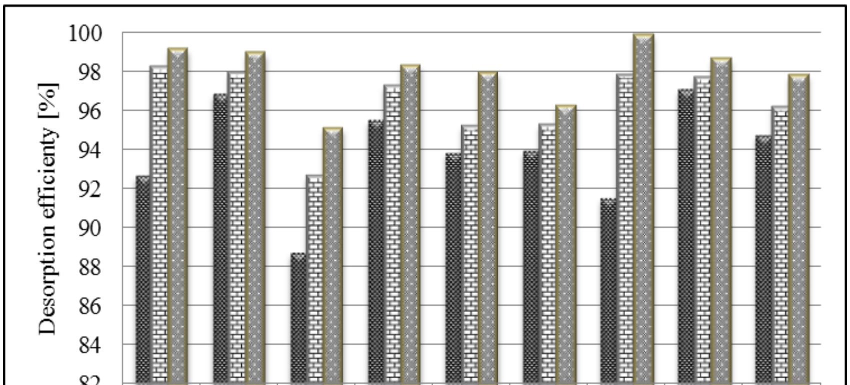


Fig. 8. Efficiency of thermal desorption compared to the value of its cost, depending on the treating duration



	P1A	P1B	P1C	P2A	P2B	P2C	P3A	P3B	P3C
5	92.63	95.5	91.51	96.82	93.84	97.06	88.69	93.92	94.73
10	98.19	97.24	97.81	97.9	95.17	97.65	92.6	95.26	96.15
15	99.1	98.3	99.85	98.91	97.93	98.61	95.06	96.23	97.78

Fig. 9. Desorption efficiency depending on the concentration of pollutant and treatment duration



	P1A	P2A	P3A	P1B	P2B	P3B	P1C	P2C	P3C
5	92.63	96.82	88.69	95.5	93.84	93.92	91.51	97.06	94.73
10	98.19	97.9	92.6	97.24	95.17	95.26	97.81	97.65	96.15
15	99.1	98.91	95.06	98.3	97.93	96.23	99.85	98.61	97.78

Fig. 10. Desorption efficiency depending on the texture of the soil samples and the treatment duration

Because in case of desorption at 300°C for 10 minutes treating duration the quantity of pollutant does not decrease under the alert threshold, the samples require repeating the thermal desorption, thus increasing the costs of the depollution process.

Following the experimental researches, we can observe that the contamination degree, the soil texture and the treating duration influence the process of thermal desorption. As it can be observed in the performed researches, the desorption of crude oil from the loamy sand texture has a higher efficiency as opposed to the soils of loamy and loamy-clay texture.

The results obtained in the laboratory are of practical interest and can be used at a high scale in projecting desorption systems for the purpose of determining preliminary costs and optimal evaluation conditions.

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