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INFLUENCE OF THE DEGREE OF CONTAMINATION ON THE EFFICIENCY OF THE DECONTAMINATION PROCESS THROUGH THERMAL DESORPTION OF SOILS CONTAMINATED WITH CRUDE OIL

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ABSTRACT. This paper presents the results of researches on the contamination and depollution of soil samples polluted with crude oil. The depollution was performed by repeatedly heating the soil samples at the constant temperature of 350 degrees C, and different times of keeping in the proposed installation: 5, 10 and 15 minutes. The initial quantity of the pollutant in the soil was 15321.6; 25113.6 and 79000 mg/kg of dried substance. At the end of these experiments, the results have revealed that the efficiency of thermal desorption was influenced by the duration of the treatment and the degree of contamination, obtaining a highly efficient decontamination process with efficiencies up to 99.85 %.

Key words: *thermal desorption, decontamination, pollution, crude oil*

INTRODUCTION

The problems of environment pollution due to oil exploitation require more precise knowledge on them, in order to implement the most adequate measures for preventing and fighting the toxicity.

Among the technologies of remediation of the soil available today for the decontamination of soils polluted with petroleum products, thermal desorption is one of the most efficient ones, from the point of view of the efficiency regarding the contaminant removal.

Thermal desorption consists of applying heat at approximately 600 °C, to extract volatile and semi-volatile pollutants from the soil, through volatilization. At this temperature, the volatile pollutants are evaporated and later eliminated from the evacuation gases, by condensing, filtering or destroying them at high temperatures. After the treatment, it is possible to reuse the soil, depending on the used temperatures and the concentration of residues of contaminants. Primary use of thermal desorption is treating organic contaminants, but it was also used in treating soils contaminated with mercury (Wood, 2001).

In the international practice, the solid material resulted after the thermal desorption process is used under two forms: in the activity of filling excavated areas and recover the former agricultural fields, of which the contaminated soil was excavated. Thus, it has been proved that the material has satisfying compacting features, and if this material is considered sterile, that field is recovered by covering the material with vegetative soil and adding nutrients (Petrom E&P, 2008).

The main advantage of ex situ desorption is the fact that they generally require shorter periods of time for treatment, and there is a greater certainty regarding the uniformity of the treatment, the soil becomes homogenous and is continuously mixed (Prodan, 2012).

The United States Environmental Protection Agency (U.S. EPA) has acknowledged thermal desorption as a technology that is being implemented for more than 10 years, being designated first of all, as remediation technology, in the Record of Decision (ROD) in 1985 (TR-2090-ENV, 1999).

MATERIAL AND METHOD

For performing the experimental researches of decontamination of soil samples polluted with various quantities of crude oil, the scheme of the research plan was elaborated, as shown in figure 1.

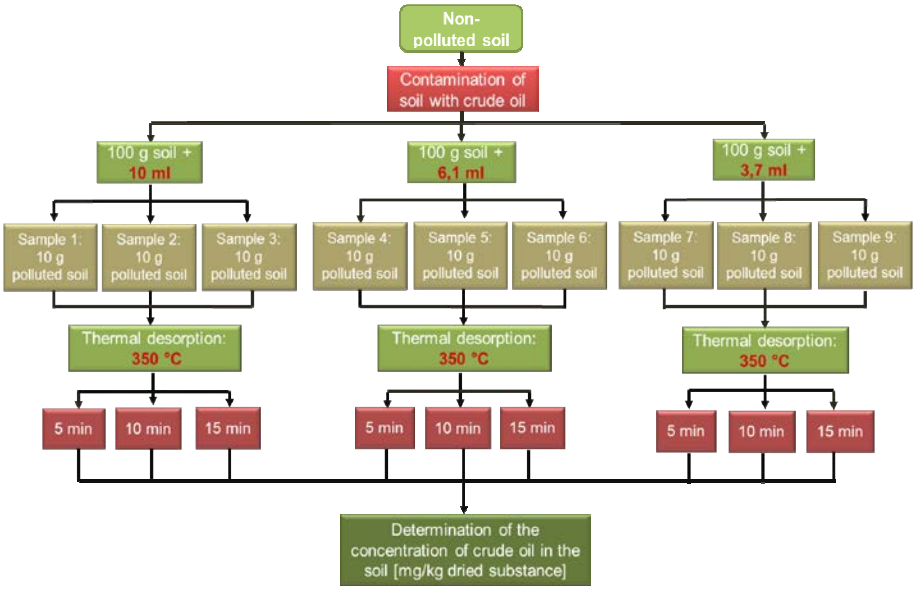

Fig. 1. *Scheme of the research plan*

The soil sample was taken at a depth within the interval 0 – 20 cm as per STAS 7184/1-75, (STAS 7184/1-75) in the commune of Bonţida, Cluj County (figure 2).

Fig. 2. *Map of the soil sampling area*

The equipment necessary to apply the technology of thermal desorption was the silicon carbide bars oven, available at the Technical University of Cluj-Napoca.

Experiments were performed as follows: 100 g of soil were weighted for each experiment, samples were polluted with three different quantities (3.7; 6.1 and 10 ml), they were subject to thermal desorption at 350 °C with three different amounts of time for treating (5, 10 and 15 minutes), then the quantity of crude oil from the soil was determined, in order to establish the efficiency of the decontamination process.

There was a total number of 9 experiments, with the purpose of determining the influence of thermal desorption on the soil polluted with various quantities of crude oil.

Due to the fact that the process of contaminating the soil samples took place in the laboratory, the analysis of the pollutant was necessary. The analysis of the crude oil sample was performed using a: Gas Chromatograph Mass Spectrometer, Shimadzu within the "Babeş–Bolyai University" Cluj-Napoca, Faculty of Chemistry and Chemical Engineering.

The quantitative determination of the crude oil content was performed as per STAS SR 13511/2007 (SR 13511, 2007) using the Soxhlet method (figure 3).

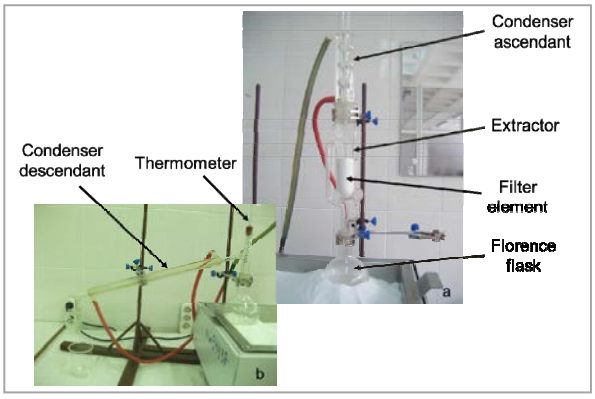

Fig. 3. *Scheme of lab equipment*
a) Soxhlet extractor, b) Distillation device

The evaluation of effectiveness of the extraction technology was performed by determining the final extraction efficiency, which is estimated on mixes or synthetic samples (in this case, the soil polluted in the lab), in which the quantity of the analyte added is known (control sample), $m_{analyte}$(sample). After determining the quantity of the analyte in the solvent used in the extraction, $m_{analyte}$(solvent), the extraction efficiency is given by the relation 1 below (http://cachescan.bcub.ro):

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

where: - **$m_{analyte}$(solvent)** – the concentration of pollutant extracted through thermal desorption at different temperatures and amounts of time for maintaining in the oven, in mg/kg;

- **$m_{analyte}$(sample)** – the initial concentration of pollutant existing in the soil (that can be extracted using the Soxhlet method), in mg/kg.

RESULTS AND DISCUSSIONS

Interpretation of results of the crude oil analysis

Following the analysis performed with the GC – MS, in the crude oil mix we identified the following compounds: n-octane, n-nonane, 9-octadecenamide, 3,12-diethyl-2,5,9-tetradecatriene (figure 4).

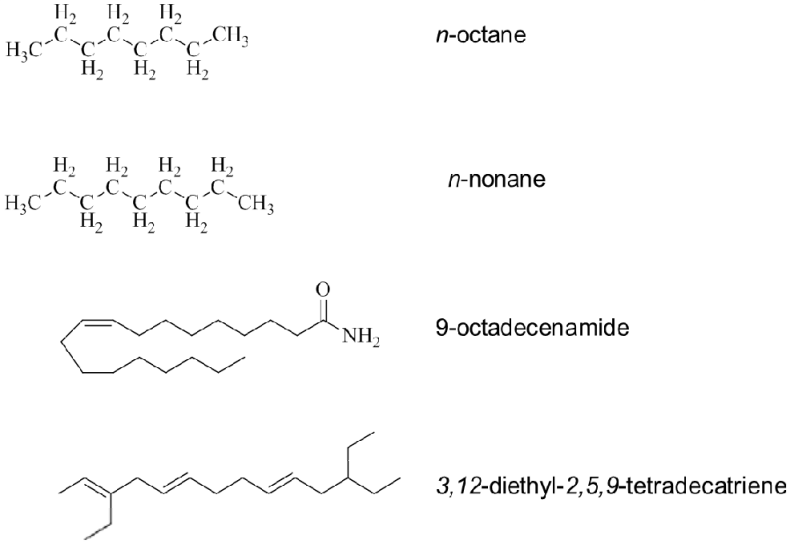

Fig. 4. *Formula of compounds identified in crude oil*

From the chromatogram of the crude oil (figure 5) we can observe that, as the structure of the compound is simpler and the chain of carbon atoms is shorter, the more the retention time (Rt) of each compound is smaller. **Rt** = retention time = indicates the time at which the compound emerges from the chromatographic column, being specific for each compound and each separation method.

Thus, for the n-octane the time is 2.3 min, for n-nonane 3.7 min, 9-octadecenamide 30 min and for 3,12-diethyl-2,5,9-tetradecatriene the time is approximately 38 min.

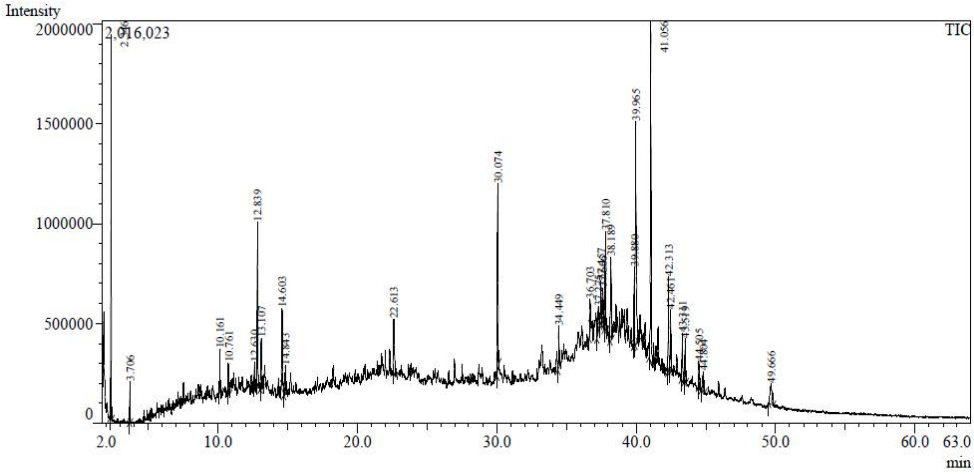

Fig. 5. *Chromatogram of rough crude oil – GC – MS*

Interpretation of the results of thermal desorption researches

The initial values of the crude oil content determined for the control samples were 15321.6 (PC_1); 25113.6 (PC_2) and 79000 (PC_3) mg/kg dry substance. By comparing the initial values with the values of alert thresholds (1000 mg/kg dried substance (d.s.)) and intervention thresholds (2000 mg/kg d.s.) according to Order no. 756 of 11/03/1997 (Order no. 756, 1997), it results that they exceed the legal limits (Table 1).

Table 1. *Results of the determination of crude oil quantity in the control samples*

Crt. No.	Sample	Quantity of pollutant [ml]	Initial experimental quantity [mg/kg]	Alert threshold [mg/kg dried substance]	Intervention threshold [mg/kg dried substance]
1.	PC_1	3.7	15321.6	1000	2000
2.	PC_2	6.1	25113.6		
3.	PC_3	10	79000		

❖ **Variation of the quantity of crude oil in the soil after thermal desorption**

By analyzing the graphs of the pollution values 15321.6 and 25113.6 mg/kg (Fig. 6 and 7), it can be observed that there is a decrease of the concentration of crude oil remaining in the soil, as the amount of time for maintaining in the oven increases. At the sample kept for 5 minutes, the value of the concentration is over the alert threshold (1000 mg/kg d.s.), being necessary to perform another decontamination. For the samples kept for 10 and 15 minutes, we could observe that the value of the concentration of crude oil is under the alert threshold, according to Order no. 756/1997.

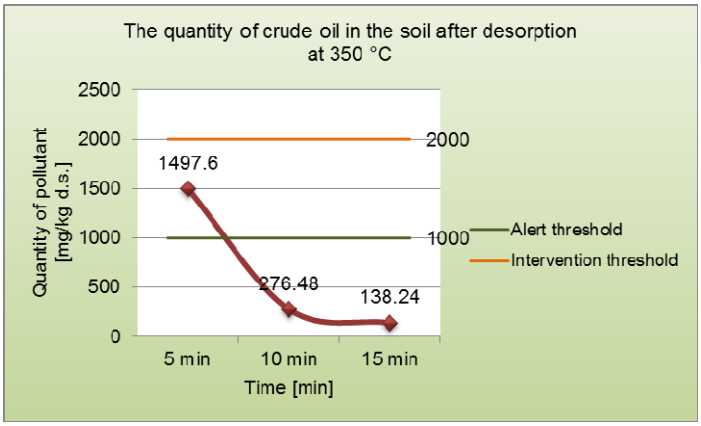

Fig. 6. *Variation of the quantity of crude oil in the soil after thermal desorption at 350 °C of soil samples polluted with* ***15321.6 mg/kg d.s.***

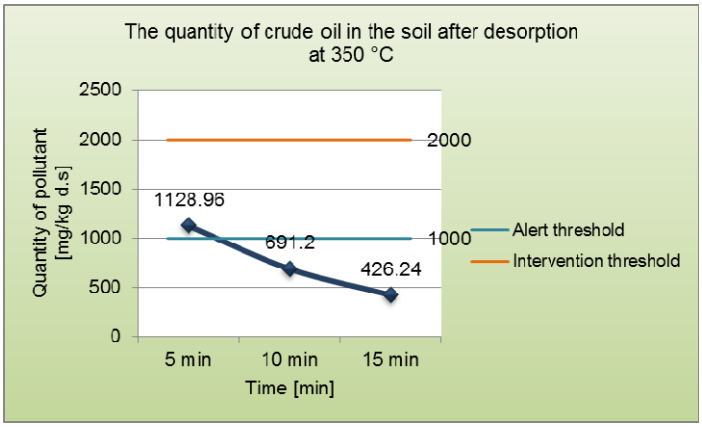

Fig. 7. *Variation of the quantity of crude oil in the soil after thermal desorption at 350 °C of soil samples polluted with* ***25113.6 mg/kg d.s.***

Figure 8 reveals that the pollutant observed has a good desorption only for treating the soil for 15 minutes, its concentration being under the alert threshold and the intervention threshold. Regarding the concentration remaining after a 5 minute treatment, it can be noticed that it exceeds the intervention threshold three times, and the sample subject to desorption for 10 minutes exceeds the alert threshold and is under the intervention threshold, according to Order no. 756 of 11/03/1997 (Order no. 756, 1997).

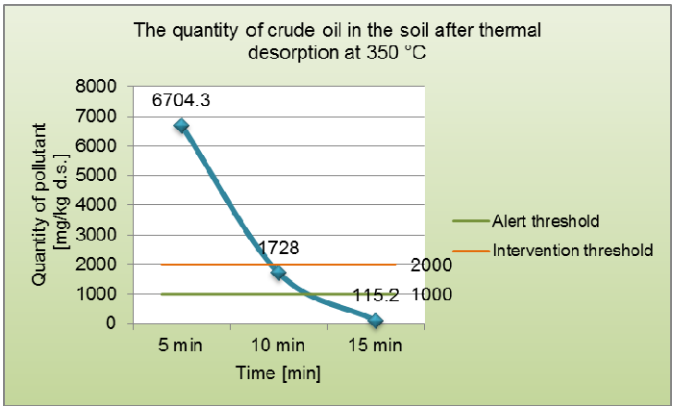

Fig. 8. *Variation of the quantity of crude oil in the soil after thermal desorption at 350 °C of soil samples polluted with* ***79000 mg/kg d.s.***

❖ Efficiency of the desorption at 350 °C

After these experiments, we calculated the efficiency of the extraction process of crude oil from the soil for the three stages of pollution, depending on the temperature and amounts of time for keeping the samples in the oven. Relating to the contamination level (figure 9), the pollutant was extracted from the soil, recording high value efficiencies, between 91.51 – 99.85 %.

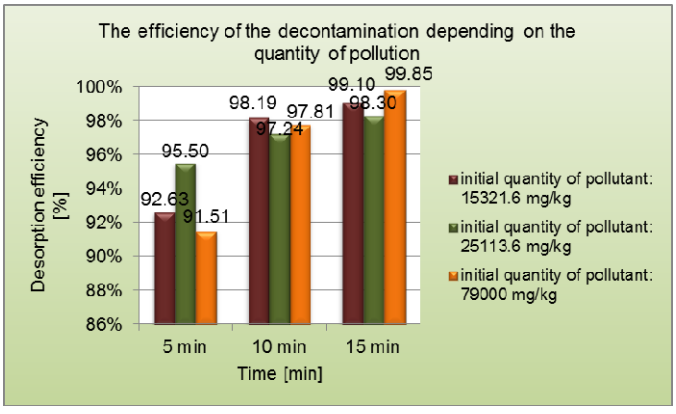

Fig. 9. *Variation of the efficiency depending on the quantity of pollution and the amount of time kept in the oven, at 350 °C*

As the amount of time for treating samples in the oven increases, the decontamination level is higher. The highest efficiency was obtained when keeping the sample polluted with 79000 mg/kg in the oven for 15 minutes.

CONCLUSIONS

❖ From the analysis of the contaminant it resulted that the following compounds were identified in its mixture: n-octane, n-nonane, 9-octadecenamide, 3,12-diethyl-2,5,9-tetradecatriene, influencing the results of the desorption process.

❖ While performing the analyses, we found that the temperature, the amount of time kept in the oven and the concentration of pollutant are the main factors influencing the process of thermal desorption.

❖ Experiments performed at 350 °C let to the conclusion that thermal desorption is very effective, the efficiencies obtained being between 91.51 ÷ 99.85 %.

❖ Analyzing the efficiencies obtained, depending on the quantity of pollution, we can observe that the sample polluted with 79000 mg/kg d.s. and kept in the thermal desorption process for 15 minutes has the highest efficiency, the obtained value being 99.85 %.

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