

Extraction of Hydrophobic Organic Compounds from Soils Contaminated with Crude Oil

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The paper presents the results of the study regarding the influence of some factors over the extraction with solvents of hydrophobic organic compounds from soil ($K_{ow} > 10$), from accidental oil leaks. Hydrocarbons was quantified by a gravimetric method, using different solvents (trichlorethylene, petroleum ether and hexane) on contaminated soil samples with different crude oils in terms of chemical composition. To indicate the influence of soil moisture on the extraction of TPH (total petroleum hydrocarbons), the results from dry soil samples were compared with those of wet samples. The results give a wide range of values for TPH concentration, influenced by the type of solvent, crude oil type which infested the area and the soil moisture. Regardless of the type of solvent used in the saturated crude oil contaminated soil, the extraction of hydrocarbons is higher for dry soil samples, and in case of aromatic crude oil contaminated soil, the extraction is higher for the wet soil samples. From all solvents, trichlorethylene extracted the greatest amount of oil regardless of the type of oil that has infested the area and regardless of soil condition (dry, wet). This solvent can be recommended for the extraction of hydrocarbons from oil leaks with a high percentage of aromatic hydrocarbons.

Keywords: total petroleum hydrocarbons, sorbent, hydrophobic organic compound, contaminated soil

The objective of this study is to determine certain factors dependent on the type of solvent, the properties of the chemical pollutant and soil humidity, which can influence the extraction of the non-volatile hydrocarbons from the sorbent (soil).

The paper is timely because for any study investigating soil pollution it is necessary that soil studies are carried out by the territorial pedological studies office. In all these laboratories the concentration of hydrocarbons in soil is estimated by gravimetric method without specifying the standard use.

Nowadays in Romania there is no standard provided to assess hydrocarbons in soil, which one could use in all laboratories so that results are comparable and more realistic

Environmental legislation, according to Order 756/97, sets the normal values for TPH in soil below 100 mg/kg d.m. (dry matter), between 200-1000 mg/kg d.m. for alert levels and between 500-2000 mg/kg d.m. for intervention levels.

The extraction involves the usage of different solvents, where the contaminants are dissociated from the soil, dissolved or suspended in the solvents [1-3]. The efficiency of chemical extraction of crude oil from contaminated soil requires information about the crude oil composition and the type of contaminated soil [4-6].

The sorbent has some physical characteristics that may influence the chemical extraction due to the forces of association between hydrocarbons and the organic matter from the soil which also determines the retention capacity of hydrocarbons in soil [7-9].

Crude oil contains also aromatic hydrocarbons and non-hydrocarbons, such as asphaltenes, which have some solubility in water. Aromatics are toxic compounds and

asphaltenes are non-toxic, but they have the capacity to adsorb on mineral surface, altering the surface from water-wet to oil-wet [10].

The effect of wettability, which is the tendency of one fluid to spread on or adhere to a solid surface in presence of other immiscible fluids, is an important factor to study in the chemical extraction [11-12].

Experimental part

The concentration of TPH was determined of soil samples contaminated with a known chemical composition of crude oil - pollutant, by using a classic gravimetric method, with a Soxhlet apparatus. This study has focused on the influence of the soil humidity and the chemical composition of the oil, that infested the soil, on the degree of extraction of hydrocarbons. In order to carry out the experiments for ascertain the influence of the chemical composition and the soil moisture on the extraction of hydrocarbons from the chemical drain, soil samples were taken from two different areas which are known to be polluted with crude oils of different chemical composition. To determine the physical characteristics of soil samples, individual samples have been taken in the natural settlement. The concentration of TPH was determined on average samples collected from a treated settlement. For each studied area, samples of soil have been collected, from which 4 average samples were obtained by mechanically homogenization.

Each sample has a code number depending on sampling area (area infested with saturated crude oil-zone 1 and area infested with aromatic crude oil - zone 2). For the average sample composition were mixed all individual samples taken in the same conditions (depth, area), the samples were homogenized to clean debris plants (roots,

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stems, leaves) and it was retained for analyses a quantity of 1 kg.

Number of experimental determinations for each average sample was $N = 5$, so that from the processing of statistical data, the confidence factor to be below 5%. Each sample of each soil set was analyzed to determine the overall concentration of TPH using different solvents and work conditions. The two types of crude oil were taken from the petroleum tanks close to infested areas. The classification saturated hydrocarbons, aromatic hydrocarbons, resins, asphaltenes (SARA) divides the crude oil in four different classes by polarity and solubility. The chemical composition of the crude oil samples were determined using Thin-Layer Chromatography with Flame Ionisation Detector (TLC-FID) method on IATROSCAN MK-6s apparatus. Stationary phase was a chromarod (a quartz rod coated with a thin layer of silica on which the sample is developed and separated). Mobile phase was: heptane for saturated hydrocarbons, heptane and toluene (90:10) for aromatic hydrocarbons, dichloromethane and methanol (90:10) for resins and asphaltenes.

To study the influence of water on the degree of extraction of hydrocarbons from the soil, the chemical extraction of hydrocarbons from moist soils was compared with the results obtained from dry soil samples. Different solvents have been used as extraction agents: trichloroethylene, petroleum ether, *n*-hexane (hot), *n*-hexane (cold). Extraction time was 5-6 h.

Results and discussion

The soil used in these experiments has a porosity which ranged between 43 and 48% and a permeability between 1.1×10^{-3} and 4.6×10^{-4} m/s. Figure 1 presents the granulometric diagram for the soil sample characteristic to zone 1, while zone 2 has similar characteristics.

Figure 2 presents graphically the SARA chemical compositions (concentration of saturated hydrocarbons (S), aromatic hydrocarbons (Ar), resins (R) and asphaltenes (As) for the two crude oils taken from the FPF (Field Production Facility) related to the two infested areas. It can be noted that crude oil which infested zone 1 has a high concentration of saturates (68.3%), while crude oil which infested zone 2 has a high concentration of aromatics (41.2%).

Table 1 shows the concentrations of TPH identified on the samples taken from zone 1 which was infested with saturated oil, depending on the degree of extraction of each solvent and the soil condition (dry, wet).

A statistical analysis has been conducted and experimental data were analysed for each average sample of each set of samples according to the number of experimental determinations ($N = 5$), standard deviation and Student variable for a probability $P = 95\%$.

Concentrations of TPH for samples taken from zone 2, infested with aromatic crude oil, depending on the degree of extraction of each solvent and soil condition (dry, wet), are shown in table 2.

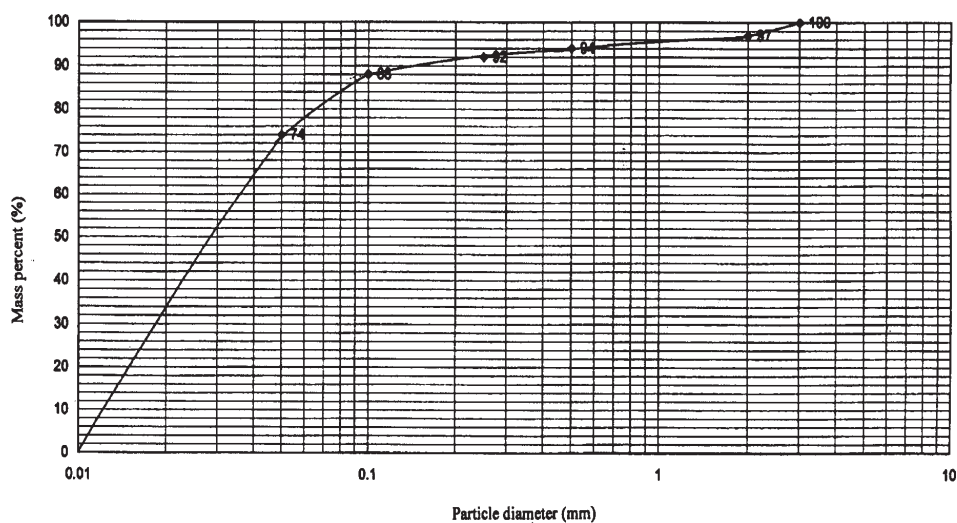


Fig. 1. Grain size distribution chart

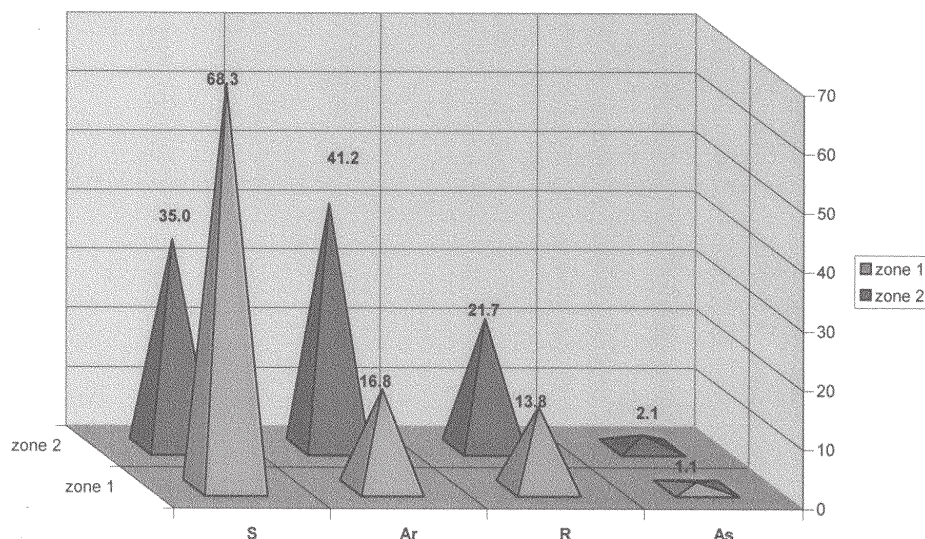


Fig. 2. Concentration of saturated hydrocarbons (S), aromatic hydrocarbons (Ar), resins (R) and asphaltenes (As) for the two crude oils which infested the soil from the two areas analyzed

Code sample	The amount of TPH extracted (mg /Kg d.m)		Solvent	Method extraction of hydrocarbons
	Dry soil	Wet soil		
(P 1-1) 1	22271±423,1	12200±253,7	Trichlorethylene	Gravimetric method, Soxhlet apparatus
(P 1-2) 1	13378±280	7249±137,7	Petroleum ether	
(P 1-3) 1	3008±75,2	1151±20,71	n-Hexane (hot)	
(P 1-4) 1	3564±78,4	1468±36,7	n-Hexane (cold)	

Note: (1-1/ set no-sample average no.) 1-no.zone, d.m.=dry matter

Table 1
CONCENTRATION OF TPH FOR ZONE 1 INFESTED WITH SATURATED CRUDE OIL

Code sample	The amount of TPH extracted (mg /Kg d.m)		Solvent	Extraction method of hydrocarbons
	Dry soil	Wet soil		
(P 2-1) 2	13422±241,5	17303±230,12	Trichlorethylene	Gravimetric method, Soxhlet apparatus
(P 2-2) 2	8847±159,2	10213±135,8	Petroleum ether	
(P 2-3) 2	2379±35,6	3473±86,8	n-hexane (hot)	
(P 2-4) 2	2943±44,14	4504±95,48	n-hexane (cold)	

Note: (1-1/ set No-sample average no.) 2-no.zone, d.m.=dry matter

Table 2
CONCENTRATION OF THE TPH FOR ZONE INFESTED WITH AROMATIC CRUDE OIL

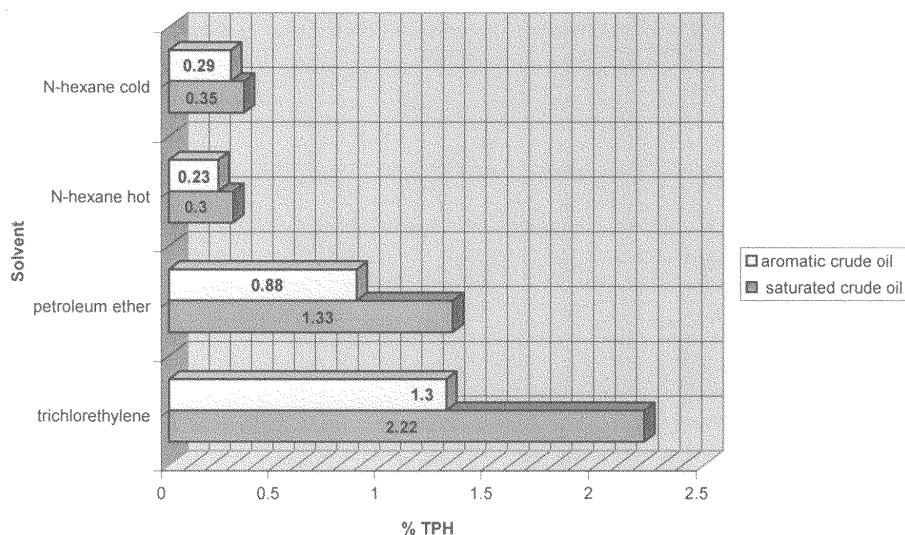


Fig. 3. Variation of the degree of extraction of hydrocarbons (mass % of TPH) on dry soils

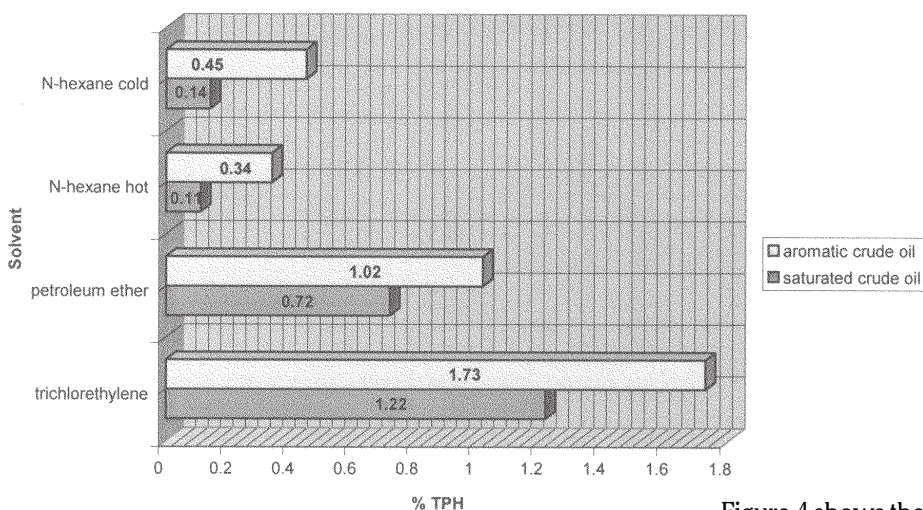


Fig. 4. Variation of the degree of extraction of hydrocarbons (mass % of TPH) on wet soils

Figure 3 shows the quantities of hydrocarbons extracted (mass % of TPH), depending on the type of solvent used and the type of crude oil that has infested the area, for dry soils.

Figure 4 shows the quantities of hydrocarbons extracted (mass % of TPH) depending on the type of solvent used and the type of crude oil that has infested the area, for wet soils.

The analysis of the experimental results shows the following aspects:

- regardless of the type of crude oil that has infested the area, the solvents that generally extracted the most hydrocarbons quantified as a TPH were trichlorethylene and petroleum ether.;

- for the soils infested with saturated oil, the presence of water has led to a reduction of extraction of hydrocarbons from moist soils, probably due to the non-polar (saturated) components which are insoluble in water.;

- for soils infested with aromatic oil, the presence of water led to a higher degree of extraction of hydrocarbons, probably due to aromatic hydrocarbons which have polarity higher than saturated hydrocarbons. The presence of water in wet soils favors the formation of a thin film that can reduce the adsorption of polar compounds on the mineral surface.

Conclusions

The determination of the concentration of TPH from the accidental leakage of crude oil is influenced by the chemical composition of the crude oil that infested the soil, soil humidity and the type of solvent used for obtaining the organic extract.

The quantifying TPH for contaminated sites with crude oil requires information about the composition of crude oil and soil conditions. The appropriate solvents can be

selected depending on the compounds in the crude oil which pollute soil.

Trichlorethylene is recommended as a solvent to quantify the TPH concentration by gravimetric method for soil polluted with aromatic crude oil.

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