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REMEDIATION OF SOIL CONTAMINATED WITH HYDROCARBON USING THE SUCCESIVE EXTRACTION METHOD WITH SOLVENTS

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ABSTRACT

Soils can be accidentally polluted with liquid hydrocarbons. The penetration of the pollutant into the soil structure will always be both vertical and horizontal. It is very important to act immediately to stop this migration. The choice of the depollution method is the most difficult action to be chosen by specialists.

The paper deals with the method of successive solvent extraction, the solvents used being, in order of use: petroleum ether, benzene and toluene. Two soil types were chosen: garden soil from Romania and red soil from Greece. The degree of depollution (%) is calculated for each of the two soil types.

KEYWORDS: soil properties, extraction, pollutant, diesel oil

1. Introduction

When, accidentally or not, a soil is polluted with liquid hydrocarbons, they migrate into the soil structure in different ways. This is influenced by the soil properties (density, capillarity, particle size and permeability) as well as the properties of the pollutant (density and viscosity).

When the nature of the pollutant is known, it is easier to choose the extraction solvents. If there is insufficient information on the composition of the pollutant, the choice of solvents comprises a longer list [1-4].

In this paper, two types of soils were chosen which were polluted under laboratory-controlled conditions with 5% of the same pollutant – diesel oil.

The studies carried out on this topic were based on the analysis of soils and their behavior in successive solvent extractions. The method of depollution by successive extractions has high costs, but pollutant recovery can be a gain [1].

There are many recent studies on accidental pollution, soil being the most affected environmental factor [5-9].

2. Material and methods

2.1. Soil analysis

Two soil types were chosen for the experiments: garden soil and red soil.

The garden soil used in the experiments had not been treated in the last 20 years with chemicals that could have altered its physical properties and nutrient content in any way.

The red soil is soil taken from a swampy, vegetated area that is undisturbed by human action.

The two soil types were characterized by: density, capillarity, permeability and grain size.

Soil density is a property that depends on several factors (depth, degree of subsidence, moisture content, organic and inorganic matter content) [10].

Two types of density are defined and can be calculated:

Apparent density:

$$\rho_{apparent} = \frac{m_{soil}}{V_{soil\ layer}},\ \text{g/cm}^3 \qquad (1)$$

Real density:

$$\rho_{real} = \frac{m_{soil}}{V_{soil}} = \frac{m_{soil}}{V_{soil\ layer} - V_{voids}},\ \text{g/cm}^3 \qquad (2)$$

Knowing these densities can also determine the porosity of the soil:

$$\varepsilon = 1 - \frac{\rho_{apparent\ soil}}{\rho_{real\ soil}} \qquad (3)$$

The determinations were made in a glass ampoule as shown in Figure 1.

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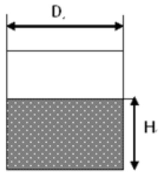

Fig. 1. *Glass ampoule with soil sample* [10]

Capillarity is the property that represents the phenomenon of a liquid penetrating the soil structure from bottom to top. This penetration occurs through the spaces between solid aggregates. In order to establish this penetration into the soil structure, it is necessary to moisten the soil samples, since it is necessary to imitate the horizons of soils [1, 2].

The device used in the laboratory consists of a glass tube (L > 50 cm, di = 2 cm) into which the moistened soil is introduced over a length of 50 cm.

The tube is protected at the base with gauze to prevent loss of sample. It is immersed in a vessel containing the liquid to be analysed (water and diesel oil).

Due to the capillarity of the soil layer the liquid will move ascending and form a moving moisture front, characterized by the height $H_{humidity}$ (H).

The value of the wet height will be measured every 10 minutes for one hour. Finally, the variation of the height of the moisture front with time will be graphically plotted.

The experimental scheme is shown in Figure 2.

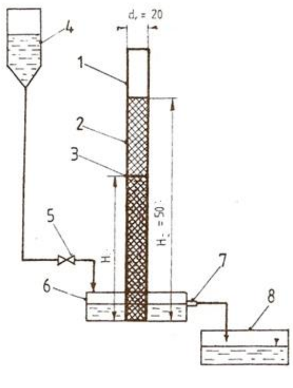

Fig. 2. *The experimental scheme for capillarity* [10]. *1-glass tube, 2-soil layer, 3-moisture front, 4-liquid supply vessel, 5-holding, 6- constant liquid level vessel, 7-pre-fill zone, 8-collecting*

Permeability is the property of soil that allows a fluid to flow through its structure. It is dependent on the clearances between soil aggregates. In the case of a pollutant, this property will influence the infiltration rate in the event of an accidental spill. The movement of the pollutant front leaves behind a soil saturated with the pollutant.

After the fluid permeates through the soil layer and begins to drip into the graduated cylinder 6 start measuring the time, noting the amounts filtered, at 15-minute intervals for one hour. After one hour, stop the flow of fluid and wait until all the fluid above the soil layer has passed through the soil volume and no more drops are flowing into the graduated cylinder 6 at the bottom.

The amount of liquid product embedded in the soil structure represents the retention capacity of that soil (kg liquid/m^3 dry soil). The retention capacity varies inversely with permeability [10].

The values measured and calculated during operation of the module to determine the permeability and retention capacity are:

$$V_{soil} = \frac{\pi \cdot d_{soil}^2}{4} \cdot H_{soil}, \text{ cm}^3 \quad (4)$$

- H_{soil} - soil layer height, cm;
- d_{soil} - soil layer diameter, cm;
- V_{soil} - soil layer volume, cm^3.

$$P_\tau = V_\tau \cdot \frac{60}{\tau}, \text{ cm}^3/\text{h} \quad (5)$$

- Pτ - average permeability for time τ, cm^3/h;
- Vτ - the volume of liquid filtered through the layer during τ = 15, 30, 45, 60 minutes.

$$P_a = \frac{P_{15} + P_{30} + P_{45} + P_{60}}{4}, \text{ cm}^3/\text{h} \quad (6)$$

P_a - average total permeability, cm^3/h.

$$C_R = \frac{(m_f - m_o) \cdot 10^3}{V_{soil}}, \text{ kg liquid/m}^3\text{soil} \quad (7)$$

- C_R - retention capacity, kg liquid/m^{3}soil;
- m_i the initial mass of the dry soil layer, g;
- m_f the final mass of the dry soil layer, g.

The experimental scheme is shown in Figure 3.

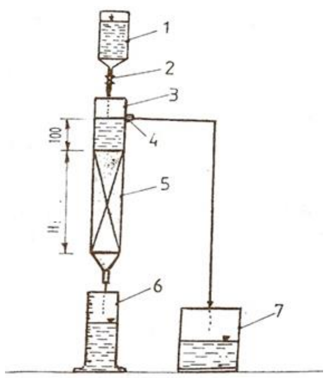

Fig. 3. *The experimental scheme for permeability* [10]. *1-liquid feed vessel, 2-holding, 3-glass tube Wolff, 4-strainer, 5-soil layer, 6-graduated cylinder, 7-collector vessel*

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Granulometry is the percentage distribution of soil particle size. In general, soil with a larger particle size will be more permeable to liquids. This property will be determined by the sieving method. The experimental assembly is shown in Figure 4.

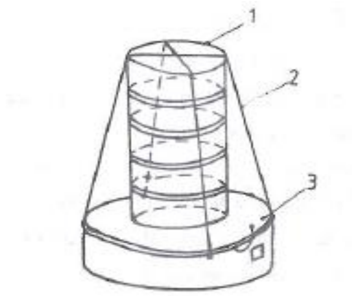

Fig. 4. *The experimental assembly for granulometry* [10]. *1-sifting sieves with different holes, 2-elastic support ropes, 3- vibrating system for the sieves*

2.2. Pollutant analysis

The controlled pollution product (5%) was characterized by density and viscosity, properties that will influence the penetration of the pollutant into the soil structure. These determinations were made at three different temperatures (20, 40 and 60 Celsius degree).

2.3. Extractive depollution method

Based on solubility differences, the separation of components from the soil pollutant can be realized by extraction. The solid-liquid extraction is done using the Soxhlet apparatus, as shown in Figure 5. The successive solvent extraction method involves the use of several solvents without removing the sample from the apparatus. Different solvents are used which will extract different components of the pollutant. These were, in order of use: petroleum ether, benzene, toluene. For each solvent used over the polluted sample cartridge, the extraction takes until the solvent is 'clean'. With a single solvent, extraction can take several hours. In each case, the solvent used can be recovered and the test sample will be oven dried at a temperature slightly above the boiling temperature of the solvent. The sample remaining after drying is weighed.

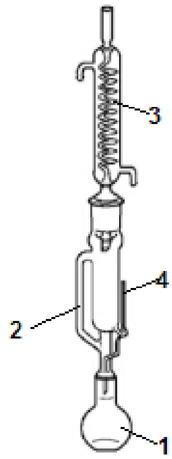

Fig. 5. *Soxhlet apparatus* [10]. *1-distilling ball, 2-side tube, 3-cooler, 4-siphon apparatus*

3. Results and discussions

The densities for the two soil samples are shown in Table 1.

Table 2 shows the measured values for the layer wetted with the two liquids: water and diesel oil.

Figure 6 shows the variation of the wetted layer height with time.

Table 3 shows the results for the average permeability and the retention capacity.

Table 4 shows the granulometric variation and Figure 7 shows the histogram corresponding to this variation.

The density and viscosity of diesel oil are given in the Table 5 for three temperatures.

Table 1. *Calculated values for density and porosity*

No. crt.	Calculated sizes	UM	Type of soil	
			Garden soil	Red soil
1.	m_{soil}	g	43	50.4
2.	$V_{soil\ layer}$	cm^3	52.8	52.8
3.	V_{voids}	cm^3	24.7	19.5
4.	Apparent density, $\rho_{apparent}$	g/cm^3	0.814	0.955
5.	Real density, ρ_{real}	g/cm^3	1.53	1.51
6.	Porosity, ε	-	0.468	0.368

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Table 2. *Wetted layer heights for two types of soil*

No. crt.		Type of soil			
		Garden soil		Red soil	
		Water	Diesel oil	Water	Diesel oil
1.	$H_{10\ min}$, mm	28	36	39	49
2.	$H_{20\ min}$, mm	35	54	45	62
3.	$H_{30\ min}$, mm	42	67	51	62
4.	$H_{40\ min}$, mm	50	82	55	62
5.	$H_{50\ min}$, mm	56	89	57	64
6.	$H_{60\ min}$, mm	62	98	62	69

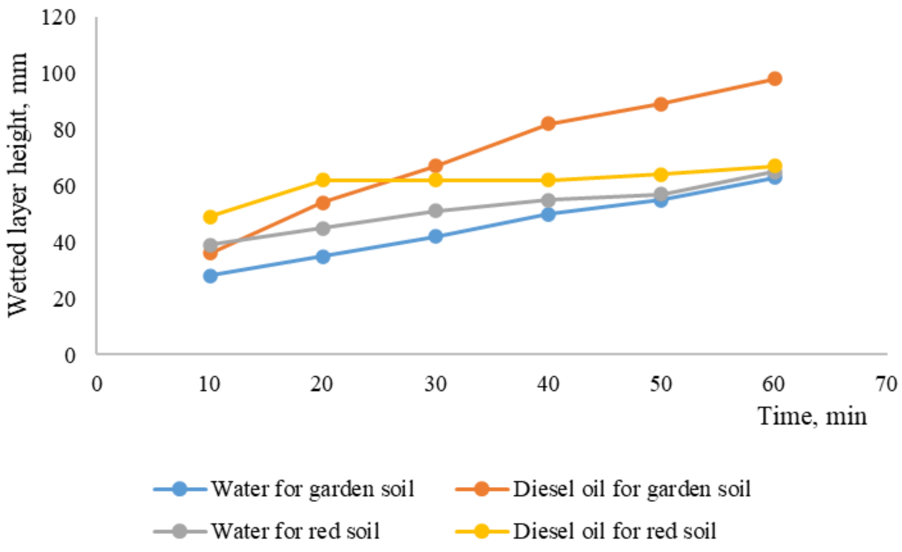

Fig. 6. *Variation in the height of the wetted layer with time*

Table 3. *Sizes measured and calculated for permeability and retention capacity*

No. crt.	Measured sizes	Type of soil			
		Garden soil		Red soil	
		Water	Diesel oil	Water	Diesel oil
1.	m_0, g	348.4	375.2	364.6	364.6
2.	H_{soil}, cm	12	13.8	14.5	14.5
3.	d_{soil}, cm	4.1	4.1	4.1	4.1
4.	V_{soil}, cm^3	158.4	182.2	191.4	191.4
5.	V_{15}, cm^3	300	22.5	410	715
6.	V_{30}, cm^3	546	45.4	710	1340
7.	V_{45}, cm^3	774	68.6	960	1920
8.	V_{60}, cm^3	924	92.5	1185	2410
9.	m_f, g	424	436.2	424.8	404.4
10.	P_{15}, cm^3/h	1200	90	1640	2860
11.	P_{30}, cm^3/h	1092	90.8	1420	2680
12.	P_{45}, cm^3/h	1032	91.47	1280	2560
13.	P_{60}, cm^3/h	924	92.5	1185	2410
14.	P_a, cm^3/h	1062	48.6	1381.25	2627.5
15.	C_R, kg/m^3	477	335	314.5	206

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Table 4. *Granulometric variation*

Type of soil		Sieve 1 1.5 mm	Sieve 2 0.49 mm	Sieve 3 0.2 mm	Sieve 4 0.12 mm	Sieve 5 0.088 mm	Sieve 6 0.06 mm	Σm_i	Sieve 7 Losses
Garden soil	m_i, g	49.6	32.8	8	2.4	1.6	0.8	95.2	4.8
	%	49.6	32.8	8	2.4	1.6	0.8	95.2	4.8
Red soil	m_i, g	55.4	30.6	8	3.4	0.2	0.1	97.6	2.4
	%	55.4	30.6	8	3.4	0.2	0.1	97.6	2.4

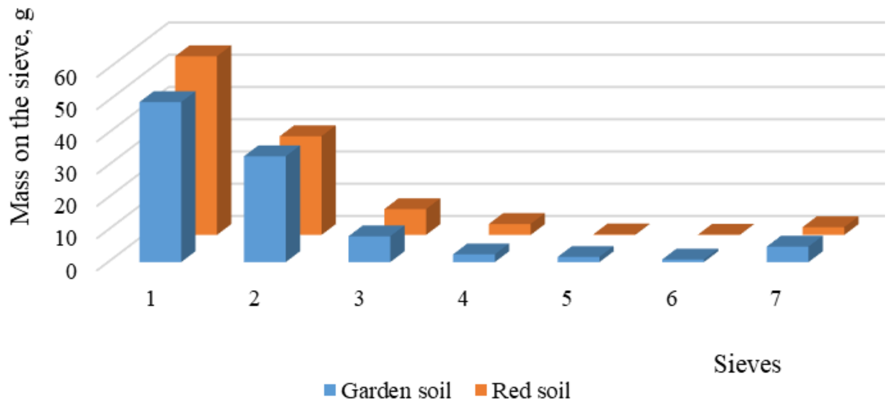

Fig. 7. *The histogram corresponding for granulometric variation*

Table 5. *The density and the viscosity values for diesel oil for three temperature*

No. crt.	Temperature, °C	Diesel oil	
		Density, kg/m³	Viscosity, kg/ms
1.	20	836.2	$5.2 \cdot 10^{-6}$
2.	40	819.6	$4.07 \cdot 10^{-6}$
3.	60	813.2	$3.23 \cdot 10^{-6}$

Table 6. *Results of successive solvent extraction for garden soil*

Clean garden soil			
	Petroleum ether	Benzene	Toluene
Organic material extracted with, g	0.0193	0.0287	0.0146
Total mass organic extracted, g	0.0626		
Polluted garden soil with 5% diesel oil			
	Petroleum ether	Benzene	Toluene
Total mass organic extracted + diesel oil with, g	0.5701	0.0184	0.0372
Total mass organic extracted + diesel oil, g	0.6252		
Total diesel oil extracted, g	0.563		
Depollution degree, %	56.3		

It was necessary for this study to know the physical properties of both soils and pollutants. This information helps to analyse the penetration of the pollutant into the soil structure.

When an environmental accident occurs, you need to act quickly. It is difficult to choose an optimal method for depollution of soils contaminated with hydrocarbons.

The successive extraction method with solvents can be one of these options.

The advantage of this method is that, although solvents are very expensive, they can be recovered in the successive extraction method. The pollutant can also be recovered.

Table 7. *Results of successive solvent extraction for red soil*

Clean red soil			
	Petroleum ether	**Benzene**	**Toluene**
Organic material extracted with, g	0.0253	0.0413	0.03
Total mass organic extracted, g	0.0966		
Polluted red soil with 5% diesel oil			
	Petroleum ether	**Benzene**	**Toluene**
Total mass organic extracted + diesel oil with, g	0.9870	0.0692	0.0397
Total mass organic extracted + diesel oil, g	1.0959		
Total diesel oil extracted, g	0.9993		
Depollution degree, %	99.93		

4. Conclusions

The choice of soil types was not accidental. Garden soil has a high humus content (indicated by colour). The presence of this component has a great influence on the behavior of liquids (water and diesel oil).

The higher porosity of the garden soil (0.468) will influence the penetration and stagnation of liquids in voids.

The maximum wetted layer is 98 cm for diesel oil in garden soil compared to 69 cm for red soil.

The pollutant retention capacity in the soil is higher for garden soil (335 kg/m^3) than for red soil (206 kg/m^3). This aspect explains why the degree of depollution for red soil is higher (99.93%).

For successive extraction with solvents, when comparing results for different soils it is easy to determine the number of solvents. There is a possibility that for the lower degree of depollution, there may be another solvent to extract other components remaining in the soil structure. A proposed option for future studies would be a mixture of alcohol: benzene (1:1).

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