AN EVALUATION ON THE EFFECTIVENESS OF A BIODEGRADABLE NATURAL SORBENT USED IN THE REMEDIATION OF PETROLEUM HYDROCARBONS POLLUTED SOIL

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This paper presents the results of an experimental laboratory study on treatment of an artificially polluted soil with engine oil. A natural biodegradable, peat-based sorbent is used for soil remediation. The aim of this study is to evaluate the effectiveness of the applied soil remediation method.

Keywords: polluted soil, engine oil, total petroleum hydrocarbons, soil remediation, natural sorbent

1. Introduction

Soil pollution with crude-oil and/or oil products generates a series of significant negative consequences, both environmentally and economically. So, hydrocarbons polluted soil contributes to air and water pollution and has undesired effects on plants and animal species. The health of the population can also be influenced by the toxicity of soil pollutants, directly or through soil-plant-human and/or soil-plant-animal-human circuits.

Soil pollution with petroleum hydrocarbons is a phenomenon of an increased incidence. Pollution can occur accidentally (due to an unforeseen event) or may result from accumulations of pollutants over time (“historical pollution”).

The literature provides various remediation solutions for the sites polluted with petroleum products [1-4]. Selecting the soil depollution method depends on the following factors: type of hydrocarbons, site features; the desired depollution degree; sensitivity of the area and the subsequent use of the land; duration of the action; by-products and their elimination costs; total cost of depollution.

In recent years, biotechnologies are preferred [5-12], due to their advantages: they are relatively easy to apply; they have lower costs than other remediation techniques; they are considered safe from the point of view of environmental protection.

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This paper presents the results of an experimental laboratory study on treatment of an artificially polluted soil (under controlled conditions) with a petroleum product (engine oil). A natural biodegradable, peat-based sorbent is used for soil depollution. The purpose of this study is to assess the effectiveness of the applied soil remediation method, based on the following criteria:

- the removal rate of total petroleum hydrocarbons content from the studied soil;
- the estimated time required to reach allowed/normal limits of hydrocarbons concentration in the treated polluted soil.

2. Materials and method. Description of the experiment

The remediation method applied in the experiment consists in spreading a natural sorbent (dehydrated peat moss) onto artificially polluted soil with a motor oil. It is a technique for *in situ* treatment of polluted soils and it is recommended for accidental oil products spills. The sorbent material has the property of adsorbing/absorbing the petroleum product, thus creating a favorable growth media for microorganisms that break down petroleum fractions. Therefore, this technique allows the fixation of pollutants and prevents their infiltration into the soil, in depth. At the same time, the method favors the development of biodegradation processes for pollutants.

To carry out the experiment, 2 kg of reddish-brown soil was taken from an area - with no previous history of hydrocarbons pollution - in southern Bucharest, and placed in a container. The soil sampling depth was 10 cm (after the vegetation layer was removed). The average soil temperature at the time of sampling was 13°C. The soil moisture was determined in the laboratory at 15,65% (w/w). (Soil sampling was carried out in compliance with provisions of STAS 7184/1-84 [13]).

Atmospheric conditions (according to the National Meteorological Administration data) at the time of soil sampling were: temperature - 16°C; atmospheric humidity - 69%; rainfall on the day of sampling - Ø; dew point - 11°.
The soil was artificially polluted (under controlled conditions) by mixing with an engine oil (100 cm^3), ensuring the uniform spread of the pollutant throughout the soil. The resulting mixture was allowed 7 days for acclimation between the oil and the soil, and then was divided into two equal quantities, placed in identical containers, marked 1 and 2.

Polluted soil from the first container was not treated during the experiment; it served as the control sample. The second container holds the working sample. The polluted soil from the working sample was subjected to a remedial treatment by applying a peat-based natural sorbent (absorbent): dehydrated peat moss.

Engine oil (petroleum product) used as a pollutant has the following characteristics (according to the datasheet [14]):

- it is a mixture of refined mineral oil, with additives and chlorine-free. It contains about 75% of hydrotreated base oils and highly refined paraffin oils; the remaining approximately 25% are additives;
- relative density at 15°C, ρ_{oil} = 0,850 g/cm^3;
- kinematic viscosity at 100°C, ν = 12,5 cSt;
- auto-ignition temperature, min. 450°C;
- boiling range, 420÷550°C;
- vapor pressure is negligible at room temperature;
- it is not soluble in water; it dissolves well in organic solvents;
- the product is stable; it does not hydrolyze; it does not polymerize;
- in the event of accidental spill, forms film at the top of surface water, bioaccumulates in soil and contaminates groundwater; it is toxic to aquatic organisms.

The sorbent used in the experiment is a biodegradable, hydrophobic, non-toxic, insoluble organic material capable of absorbing a quantity of hydrocarbons more than 10 times its mass. It is easy to handle, does not require special storage conditions and does not generate waste that requires further treatment. Other properties of the sorbent are: humidity - 7%; density, ρ_{abs} = 0.08 g/cm^3; pH = 4÷6.

The minimum quantity of sorbent required was calculated taking into account its hydrocarbon absorption capacity and the amount of pollutant used in the experiment. The absorbent was mixed with the polluted soil to allow both the aeration and the increase of the soil-sorbent contact surface.

The experiment was carried out for 182 days (six months). The evolution of the TPH-total petroleum hydrocarbons was monitored in both treated and untreated soil polluted with 4,25% (w/w) motor oil. For this purpose, treated soil samples (working sample) and untreated soil samples (control sample) were collected and analyzed according to the following schedule:

Stage I - the beginning of the experimental period, (t_I= 0 days);

Stage II- after 56 days (t_{II}= 56 days);

Stage III- after 119 days (t_{III}= 119 days);

Stage IV- the end of the experimental period (t_{IV}= 182 days).

The remediation treatment is applied immediately after taking the first sample of polluted soil, in stage I.

The total petroleum hydrocarbons content (both in the untreated and the treated soil samples) was determined by gravimetric method, according to SR 13511:2007 [15]. The working principle of the method consists in determination of TPH content from polluted soil after extraction with methylene chloride (CH_2Cl_2) and the separation of polar substances on the column with neutral alumina (Al_2O_3). The solvent is removed by distillation and the residue is gravimetrically determined against the control sample.

Laboratory equipment used: water bath, analytical balance, glass capsule, oven, extraction plant, glass column filled with alumina, distillation plant. For soil moisture determination (according to SR ISO 11465: 1998 [16], drying to constant mass) a desiccator was required.

3. Experimental results. Processing and interpretation of experimental results

Results of experimental tests are presented in Table 1 and Figs. 1-3 respectively.

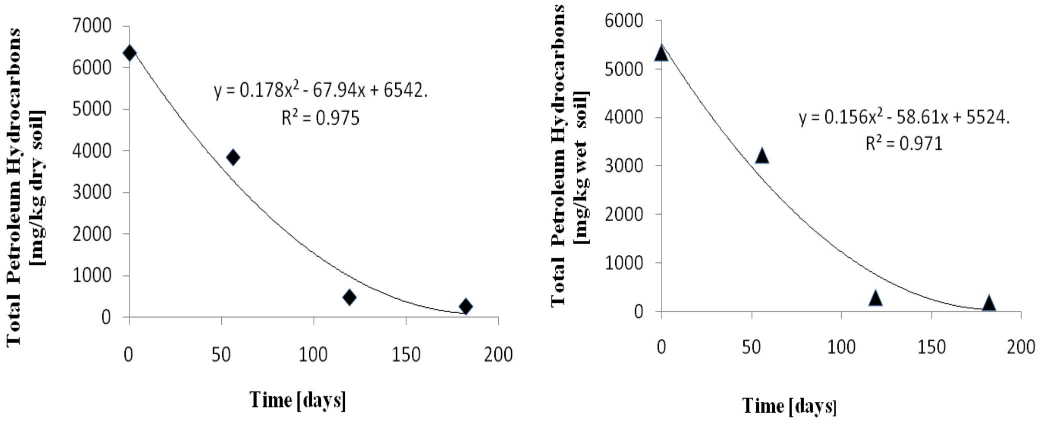
Table 1

Water content in untreated and treated polluted soil samples, at the different stages of experiment

Stage of experiment/ No. of days	Untreated polluted soil (Control sample)	Treated polluted soil (Working sample)
	U [% w/w]	**U** [% w/w]
I/ t_I = 0 days	15,650	15,650
II/ t_{II} = 56 days	32,160	29,330
III/ t_{III} =119 days	34,255	37,714
IV/ t_{IV} =182 days	24,370	28,273

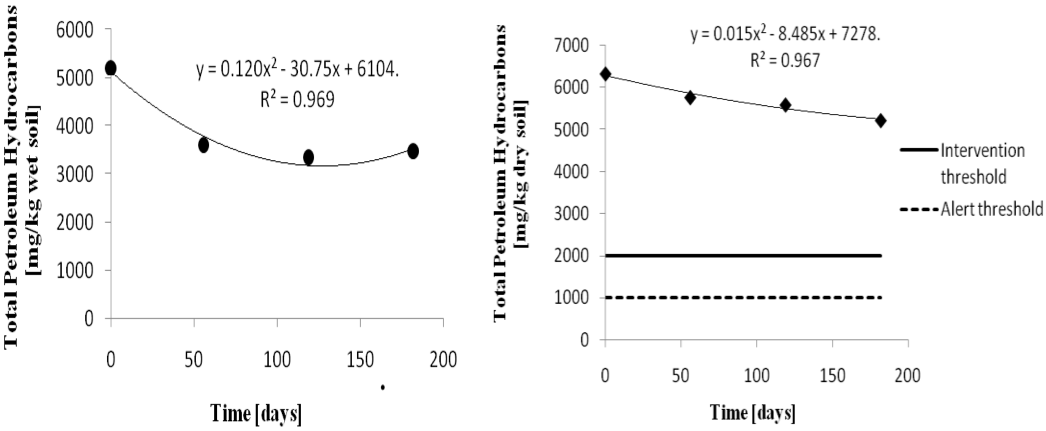
Key:
U [% w/w] - Water content in the polluted soil, expressed in percent mass;
I,II,III,IV- Sequence of sampling and analyzing soil samples during the experiment.

Figs. 1 and 2 show graphic representations of the values obtained experimentally (throughout the 182 days) for petroleum hydrocarbons concentrations – relative to wet and dry soil, respectively - corresponding to the treated soil (working sample) and untreated soil (control sample). The theoretical models resulting from processing experimental data by regression analysis are found on the same graphs (fig.1, 2).



(a) *(b)*

Fig.1. Time evolution of total hydrocarbons TPH content in treated soil (working sample). Regression models.
a- relative to dry soil; *b*- relative to wet soil;



(a) *(b)*

Fig.2. Time evolution of total hydrocarbons TPH content in untreated soil (control sample). Regression models
a- relative to wet soil; *b*- relative to dry soil
Alert threshold value (for less sensitive land use): THP =1000 mg/kg dry soil;
Intervention threshold value (for less sensitive land use): THP =2000 mg/kg dry soil.

Values of R^2 (R-squared or coefficient of determination), indicated in Figs. 1 and 2, prove the fit of the polynomial regression models to the experimental data in all cases. Thus the polynomial regression models are considered to make a good approximation of the time evolution of hydrocarbons content in the studied soils (treated and untreated).

Fig. 3 illustrates the comparative evolution of petroleum hydrocarbons content - in the untreated soil, and in the treated soil, respectively - during the experiment.

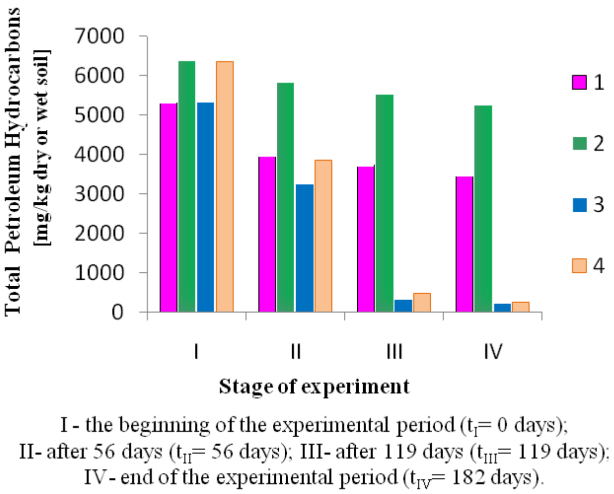


Fig.3. The comparative evolution of total petroleum hydrocarbons (TPH) content - in the untreated soil (control sample), and in the treated soil (working sample), respectively- at the different stages of experiment
1- TPH relative to wet soil, in the control sample; 2- TPH relative to dry soil, in the control sample; 3- TPH relative to wet soil, in the working sample; 4- TPH relative to dry soil, in the working sample.
Alert threshold value (for less sensitive land use): THP =1000 mg/kg dry soil [17];
Intervention threshold value (for less sensitive land use): THP =2000 mg/kg dry soil [17].

For each measurement performed, the removal rate, η, of total petroleum hydrocarbons, TPH, was calculated by the relationship:

$$\eta_j = \frac{TPH_I - TPH_j}{TPH_I} \cdot 100 \ \left[\%\right], \qquad (1)$$

where:

j – the serial number of the experiment stage, j = II, III, IV;

TPH_I – the initial concentration of hydrocarbons, determined at the beginning of the experiment (stage I).

Residual total petroleum hydrocarbons TPH (relative to dry soil) remaining in treated soil at the different stages of experiment and regression model of hydrocarbons removal rate (η) are graphically represented in Fig. 4. The coefficient of determination (R^2) indicates the accuracy of the mathematical model.

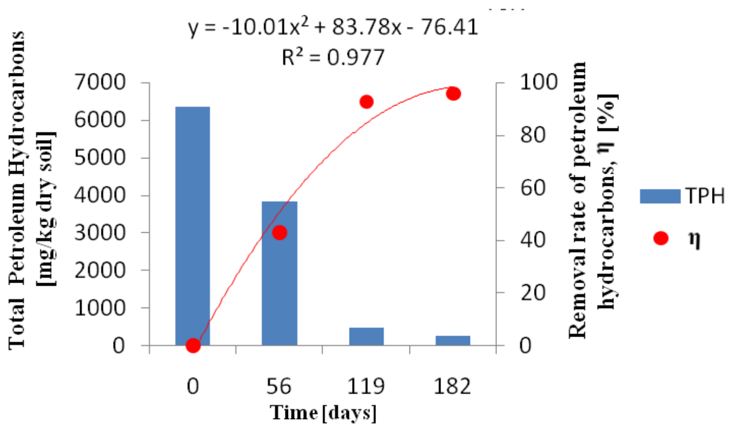


Fig.4. Residual total petroleum hydrocarbons TPH (relative to dry soil) remaining in treated soil at the different stages of experiment and regression model of hydrocarbons removal rate, η.

The regression models (Figs.1, 2 and 4) resulting from processing experimental data were used to do the following:

- evaluate the ability of the untreated polluted soil to self-treat. In this regard, it was attempted to estimate the required time to reach intervention threshold values of the hydrocarbons' concentrations in the untreated soil. The solutions obtained by solving the corresponding equations are complex numbers, that do not have physical sense. The conclusion is: the natural attenuation of pollution in the case of untreated soil has insignificant effects and cannot be an alternative to the known remediation methods.
- estimate the time required to reach normal limits of hydrocarbons concentration (according to Order 756/1997 [17]), in the treated polluted soil. This time is considered a measure of the effectiveness of the soil remediation method applied. The normal values of hydrocarbons concentration in the soil are lower than 100 mg/kg dry soil (according to Order 756/1997 [17]). Solving the corresponding equation has led to the following result: $t \approx 273$ days.

Analysis of experimental data and graphic representations in Figs. 1-4, show the following:

- Initial concentrations of total petroleum hydrocarbons (TPH) in the studied soil exceed the intervention threshold value (2000 mg/kg dry soil) for less *sensitive land* use, according to Order 756/1997 [17];
- In each stage of the experiment, measured values of hydrocarbons concentrations relative to the wet soil are lower than those relative to the dry soil, both in the treated and untreated soil;

- The dynamic of the TPH content during the experiment reveals major differences between the treated and untreated soil. Hydrocarbons concentration decreases in both cases, but untreated soil fails to reach the intervention threshold through its own cleaning mechanisms in the 6 months of monitoring and after that. Hydrocarbons removal rate at the end of the monitoring period is only 18,15% in the case of untreated soil. Conversely, in the case of treated soil by applying the natural sorbent, hydrocarbons removal rate at the end of the experimental time is 95,92%;
- Monitoring the time evolution of TPH content in the treated soil reveals the acceleration of the hydrocarbons content decrease process after the first 56 days. It is the result of development of microorganisms capable to degrade petroleum hydrocarbons. Basically, the natural absorbent used (peat moss), soaked in the engine oil, creates favorable conditions for these organisms. Thus, a fertile soil results at the end of the remediation process. This is one of the major advantages of this technique applied to the soil depollution.
- The effectiveness of the method for treating polluted soil can be assessed based on the following criteria:
  - ✓ the TPH removal rate at the end of the experiment (after 182 days): η=95.92%;
  - ✓ the estimated time periods to reduce hydrocarbons concentration down to the values corresponding to the normal limit: $t \approx 273$ days.

4. Conclusions

Remediation of oil polluted soils by using a biodegradable natural sorbent - dehydrated peat moss - is an efficient technique, recommended in the case of accidental oil spill.

The relatively long time required for site depollution may be considered a disadvantage of the method applied. However, benefits of this technique must be taken into account as well, namely:

- the final TPH (total petroleum hydrocarbons) removal rate is over 95%;
- it is a simple and quick method, applicable *in situ*;
- total costs are reduced; it does not generate waste that require elimination at the end of the remediation process;
- the resulting treated soil is fertile (this technique can be an alternative to conventional solutions for thermal treatment of polluted site, because the soil treated by thermal methods is lacking nutrients).

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