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The study on the possibility of using sewage sludge in the ecological reconstruction of contaminated sites from the petroleum industry

Cristian Mugurel Iorga[1], Maria Cătălina Ţopa[1],
Mihaela Marilena Stancu[2]

[1]"Dunarea de Jos" University of Galati, Faculty of Sciences and Environment, European Centre of Excellence for the Environment, Domneasca Street, no. 111, 80020, e-mail:cristian.iorga@ugal.ro; catalina.topa@ugal.ro

[2]Institute of Biology Bucharest of Romanian Academy, 296 Splaiul Independentei, 060031 Bucharest, Romania, email: mihaela.stancu@ibiol.ro

Corresponding author email: cristian.iorga@ugal.ro

Abstract
One field of activity that pollutes important land surfaces with hydrocarbons is the petroleum industry. In the ecological reconstruction of contaminated sites from the petroleum industry, natural geological resources are used to fill the excavations resulting from the decommissioning of some equipment and installations. Increasing amounts of sewage sludge are generated by the growing number of municipal wastewater treatment plants. For this reason, solutions are being sought for the elimination or utilization of sewage sludge. For the decontamination of soils polluted with petroleum hydrocarbons, bioremediation technologies with the help of microorganisms, especially bacteria are used on a large scale. From the results carried out in the present study, it appears that sewage sludge has microbiological, agrochemical, and geotechnical characteristics, which could make possible their utilization for the ecological reconstruction of sites contaminated with petroleum hydrocarbon. Thus, it would be possible to capitalize on the sewage sludge in the petroleum industry.

Keywords: contaminated site, ecological reconstruction, decontamination, sewage sludge**.**

1. INTRODUCTION

Petroleum has been discovered since ancient times, but the development of the oil industry began at the end of the 19th century and experienced an accelerated development after the discovery of the internal combustion engine. Gradually, in addition to the indisputable qualities of petroleum, possibilities of capitalization as a raw material for various industries were identified. Along with the increase in the world demand for petroleum, the petroleum industry is developing which occupies significant areas of land [1]. In addition to the benefits brought to mankind, both petroleum production and activities related to the petroleum industry have also negative effects on both ecosystems and human health. By spilling petroleum and petroleum products into the environment, large areas of soil can no longer be used [2]. In the last decades, petroleum pollution has become a global problem for mankind. Soil decontamination and ecological reconstruction of sites polluted with petroleum products are a priority for reducing the negative effects on the environment, as on human health. Currently, in the activity of the petroleum industry, measures are taken to prevent accidents and intervene as soon as such problems appear, to limit the negative effects on the environment [3-5]. There are soils that have been affected by petroleum pollution over time, on which it is necessary to intervene in order to return them to the natural fund. The spill over a long period of time made it possible to accumulate important quantities of petroleum products in the soil, underground up to the groundwater level. Soil pollution affects their fertility by destroying microbial activity. It could be observed that over time the petroleum products that reached the basement underwent a degradation process due to the consortia of bacteria that metabolize petroleum hydrocarbons [6]. The spilling of petroleum and petroleum products into the soil results in a numerical increase in bacterial populations that use hydrocarbons as a carbon source, with a concomitant reduction in bacterial diversity and the predominance of species that tolerate and/or degrade hydrocarbons [7-11].

Bioremediation technologies have been developed for soil polluted with petroleum hydrocarbons [4,5]. In many cases, for the bioremediation of soil contaminated with petroleum hydrocarbons, it is necessary to excavate the contaminated soil, followed by the inoculation of microorganisms and ensuring the conditions for their development with the help of nutrients and the necessary carbon sources. As part of the ecological reconstruction works of the sites affected by the activity of the petroleum industry, important quantities of filling material are needed to cover the excavations and systematize the land. The increasing need and the difficulty of obtaining filling materials led to finding solutions regarding the identification of sources. An important source of filling materials is the dehydrated sewage sludge resulting from municipal wastewater treatment plants [12]. Along with the increase in investments in new urban wastewater treatment plants, the quantities of sewage sludge that require proper management have also increased [12,13]. Therefore, eliminating increasing amounts of sludge is a challenge for sewage treatment plants. Due to the content of organic matter and micronutrients, sewage sludge can be used in agriculture, but with caution due to the content of chemical contaminants and pathogens [14-18].

The present study identifies the possibility of using the dehydrated sludge resulting from the sewage treatment plants, in the ecological reconstruction of the sites contaminated with petroleum products. The use of the sewage sludge could solve both the need for filling material and the valorization of the sewage sludge in the bioremediation of the terrestrial sites contaminated with petroleum hydrocarbons.

2. EXPERIMENTAL

Sampling. The dehydrated sludge sample was taken from a municipal sewage treatment plant (Galați County, Romania), and the soil sample contaminated with petroleum hydrocarbons was taken from an old former petroleum product storage (Constanța County, Romania, Fig. 1). The sewage sludge and soil mixture was made by mixing the two samples in equal proportions (1:1 v/v). The samples were collected in a sterilized glass jar using a sterilized ceramic spatula. The samples were transported at 4^0C to the laboratory for further analysis.

a b

Fig. 1. The sewage sludge and soil samples used in this study
a - dehydrated sewage sludge; b - old contamination of soil with petroleum products

Determination of heavy metal content. The concentration of heavy metals in sewage sludge was determined using the ICP-OES technique - a combined technique of inductively coupled plasma and optical emission spectrometry.

The sample was dried at room temperature, then subjected to a process of grinding and progressive sifting through a sieve with a mesh size between 2 mm and 0.25 mm. The extract was obtained with a mixture of hydrochloric acid HCL and nitric acid HNO3 after maintaining for 16 hours at room temperature, and a slow heating up to the boiling temperature at which it was maintained for 2 hours. After cooling, the extract was clarified and brought to constant volume with nitric acid. The measurement solution was analyzed using the Agilent 5110VDV Inductively Coupled Plasma Optical Emission Spectrophotometer.

Determination of the total petroleum hydrocarbons (TPH).

The TPH was determined for the contaminated soil sample and for the sewage sludge and soil mixture. After 68 hours, a new TPH determination was done for the sewage sludge and soil mixture. The petroleum hydrocarbons from the samples were extracted with S-316 solvent and then analyzed by infrared (IR) detection. Briefly, 3 g of anhydrous sodium sulfate and 2 g of activated aluminum oxide were used to dry 5 g of the sample. The organic compounds were extracted by using 20 ml of S316 solvent. After the extraction (30 min on the horizontal shaker) the organic phase was recovered from the samples through filtration. Record and measure the absorbance of the organic extracts at 2930 cm^{-1} by the baseline method. The amount of petroleum products is read on the calibration curve.

Microbiological analysis of the samples.

To determine the number of heterotrophic, hydrocarbon-tolerant, hydrocarbon-degrading bacteria, and enterobacteria that exist in the analyzed samples the plate culture method was used [7]. From the samples, serial dilutions (10^{-1}-10^{-6}) were made in phosphate saline buffer, which were then inoculated in Petri dishes with solid LB nutrient medium [10], to determine the total number of heterotrophic bacteria, solid LB nutrient medium supplemented with diesel fuel (5% v/v) for determining the number of hydrocarbon-tolerant bacteria, solid mineral medium [11] supplemented with diesel fuel (5% v/v) for determining the number of hydrocarbon-degrading bacteria, and solid EMB medium for determining the total number of enterobacteria. For each dilution, 2 repetitions were done. The plates were incubated at 30°C for 1-5 days. Then, the number of bacteria present in a g of the sample was determined (CFU g^{-1}).

Geotechnical analysis of dehydrated sewage sludge.

In order for the sewage sludge to be used as a filling material, it must meet certain geotechnical characteristics that are determined through various tests. First, it must be identified and described according to the rules of SR EN ISO 14688-1 which correlates with ISO 14688-2, which includes the principles of classification of soils for engineering purposes of the most used characteristics. In order to be able to apply the standardized testing methods in order to determine the geotechnical characteristics, it is very important to frame and describe it. From the standardized definitions, sewage sludge does not strictly fit one of the criteria. For this reason, a detailed description and research of the geotechnical characteristics is important. A description "in the field" can be made according to the criteria described in SR EN ISO 14688-1 as follows: Fine soil, having clay as the primary fraction, anthropogenic soil, can also include natural soils, can be considered a fine composite soil (Clay soil or dusty clay), having a high plasticity, with a soft consistency, gray to black, which indicates that it has a significant content of organic matter.

To determine the degree of **compaction** of soil, granulometric characterization is necessary, in order to establish the test methods. The granularity represents the percentage distribution by size of the component grains of the solid phase of soils (SR EN ISO 14688-1).

In order to determine **the granularity** of sewage sludge, it was necessary to dry it in an oven at 80^0C for 24 hours using the sieving method. The separation of the granules according to their size (into granular fractions) is done by sieving on sieves and sieves. Due to the cohesion of the particles, the sample was covered with drinking water to which 0.2 g of lithium carbonate was added and kept for 24 hours. The soil in the capsule was washed with water until the binder was removed, then it was heated to constant mass. Sifting was done manually, on several sieves with smaller and smaller mesh diameters, until the material was exhausted. The percentage distribution by the fraction of the grains is plotted on a grain size distribution [19].

The determination of **the limits of plasticity** applies to soils made of particles with sizes below 2 mm with organic matter content. The **lower limit** of w_P **plasticity** was achieved by the soil cylinder method, which consists in determining the minimum moisture at which the soil can be modeled in the form of cylinders. Cylinders of approximately 4 mm in diameter and 30 to 50 mm in length are obtained from the test paste by rolling with the palm of the hand on the glass plate as it loses water. When soil cylinders show cracks, moisture is determined. A minimum of three determinations are made. The lower limit of plasticity is expressed by the arithmetic mean of the determined humidity [19].

The **upper limit of plasticity** was achieved by the cup method, which consists in determining the humidity at which a slot made in the soil paste closes over a length of 12 mm after 25 drops of the cup from a height of 10 mm. Moisture is determined on a sample of pulp from the cup, taken from the immediate vicinity of the slot. The determination is repeated by adding paste and water until two moisture tests for more than 25 cup drops and two moisture tests for less than 25 cup drops are obtained. The recorded data are entered in a graph where the ordinate represents the number of drops in the cup, and the abscissa represents the determined humidity. The upper limit of plasticity is the moisture corresponding to the number of 25 drops of the cup and is obtained by interpolation [19].

Soil moisture represents the mass of water lost by a soil sample by drying at 105 ±2^{0}C relative to its dry mass. For soils containing organic substances, drying is done at 80^{0}C. Considering that the soil subjected to the determinations is cohesive, the total mass of the sample is approximately 75g. The sample was dried for 24 hours at a temperature of 80^{0}C. The expression of the results is based on the determined values and is calculated as follows:

$$w(\%) = \frac{m_u - m_d}{m_d - m_c}$$

m_u – mass of the container with the material to be tested immediately after harvesting;
m_c – mass of container with lid;
m_d – mass of the container with the dry specimen.

The units of measure for the determined masses were in expressed in grams (g) [19].

3. RESULTS AND DISCUSSION

The sewage sludge was tested chemically, microbiologically, and geotechnically to verify the fulfillment of the conditions of use in the ecological reconstruction of contaminated sites from the oil industry. The values of heavy metal concentrations obtained from the sludge sample are presented in Table 1. These concentrations of chemical elements are obtained from a sludge sample taken at a certain time and do not represent the average of periodic monitoring. Heavy metal concentrations may vary in different samples that will be taken from the dehydrated sludge. Previous studies have shown that sewage sludge can be used in agriculture [14] and the results of the present chemical analyses indicate values that fall within the limit values for use in the ecological reconstruction of contaminated sites from the petroleum industry. A parameter that characterizes the contamination with oil hydrocarbons of a site in the petroleum industry is total petroleum hydrocarbons (THP). Just like other chemical contaminants, this parameter must fall within certain limit values in order not to affect the environment and human health.

Table 1 Heavy metals content in the sewage sludge, dry substance (d.s.)

Heavy metals (mg/kg d.s.)	Mn	Zn	As	Mo	Pb	Cr	Cd	Cu	Ni	Ag	Co	Hg
	229	220	5	6	38	15	<1	17	15	<1	11	<1

The decrease in the concentration of the THP parameter was observed in a mixture of sewage sludge and soil. The initial value of the THP parameter from the soil sample contaminated with petroleum products was 3650 mg/kg d.s. By mixing in equal proportions (1:1 v/v) the sludge and soil resulted in a concentration of the THP parameter of 3060 mg/kg d.s. for the mixture formed. The mixture made was kept in the free atmosphere of the laboratory without being preserved, and after an interval of 68 hours, the concentration of the THP parameter was determined again. A decrease in the THP parameter was found to the value of 2650 mg/kg d.s. The results of the previously described tests are presented in Table 2.

Table 2 Total petroleum hydrocarbons content in soil and mixture of soil and sewage sludge

Samples	Total petroleum hydrocarbons (TPH mg/kg s.u)
Soil	3650
Sewage sludge - soil mixture (1:1 v/v)	3060
Sewage sludge - soil mixture (1:1 v/v) after 68 hours	2650

Table 3 The number of bacteria in the sewage sludge and soil

Samples	Number of bacteria (CFU g^{-1})			
	Heterotrophic bacteria	Hydrocarbon-tolerant bacteria	Hydrocarbon-degrading bacteria	Enterobacteria
Sewage sludge	$2.5x10^7$	$1.9x10^5$	diffuse growth	$1.8x10^7$
Soil	$6.8x10^7$	$6.5x10^7$	diffuse growth	$5.1x10^6$

As could be observed (Table 3, Fig. 2), four groups of bacteria, such as heterotrophic, hydrocarbon-tolerant, hydrocarbon-degrading, and enterobacteria were detected in the sewage sludge sample, as well as in the soil sample polluted with petroleum hydrocarbons. The number of these bacteria varied from one sample to another (10^5-10^7 CFU g^{-1}). In the case of the hydrocarbon-degrading bacteria, due to the presence of diesel fuel in the minimal solid medium, we observed diffuse growth of these bacteria. The presence of both hydrocarbon-degrading and hydrocarbon-tolerant bacteria in the sewage sludge leads to the hypothesis that the sewage sludge could contain petroleum hydrocarbons.

a b c d

Fig. 2. Microbiological analysis of the sewage sludge and soil samples
a - heterotrophic bacteria; b - hydrocarbon-tolerant; c - hydrocarbon-degrading; d - enterobacteria

The existence of enterobacteria (e.g., *Escherichia coli*, *Clostridium prefringens*) in sewage sludge led to the idea to see what happened with these bacteria in the mixture of sewage sludge and soil (Table 4). Not all the bacteria present in the sewage sludge can tolerate and grow in the presence of toxic hydrocarbons which exist in the contaminated soil. As expected, we observed that the number of enterobacteria slowly decrease (10^5 CFU g^{-1}) after 68 hours in the sewage sludge and soil mixture, as compared with their initial values (10^6 CFU g^{-1}).

Table 4 The number of enterobacteria in the soil and mixture of sewage sludge and soil

Samples	Number of bacteria (CFU g^{-1})
Sewage sludge - soil mixture (1:1 v/v)	$2.9x10^6$
Sewage sludge - soil mixture (1:1 v/v) after 68 hours	$1.0x10^5$

The results of the chemical and biological tests highlighted the potential of using sewage sludge in ecological reconstruction. For use as a filling material, the sewage sludge must be able to be compacted. Soil compaction is, in general, a technique for improving the main geotechnical characteristics of soil, in the context in which it does not have a sufficient bearing capacity to create a certain foundation under safe conditions. Also, the compaction process is useful when you want to make certain fillings, generally called compacted earth pillows. Through this process, an increase in the resistance of the respective earth is obtained, both to axial and transverse stresses, by reducing its compressibility. There are two main problems that arise when compacting a certain type of soil is desired, namely: either the soil is dry with a low moisture content and compaction is almost impossible due to the friction between the particles that make up the soil in question, or the soil is wet with a significant amount of water and compaction is difficult due to the incompressibility of water. Therefore, there is optimum moisture by means of which a maximum degree of compaction of the soil in question is ensured (w_{opt} - %). This moisture is reached for a certain volume weight of the soil in the dry state ($\gamma_{d,max}$). These two parameters (w_{opt} and $\gamma_{d,max}$) represent the optimum compaction parameters and can be determined in the laboratory using the Proctor test. After determining these parameters, proceed to the actual compaction on the site. After compaction is completed, samples are taken from the compacted soil in order to determine the bulk density in the dry state $\gamma_{d,şantier}$. [20]. This value $\gamma_{d,max}$ refers to $\gamma_{d,opt}$ and thus the degree of compaction is obtained, which cannot be less than 90%. If it is less than 90%, the effective compaction on site must be redone until a degree of 98-99% is reached (Fig.4, Table 5) Carrying out the Proctor test for the sewage sludge was not possible due to the fact that the sewage sludge (clay dust) contains a large amount of organic matter, has a high water content (45%) and high plasticity.

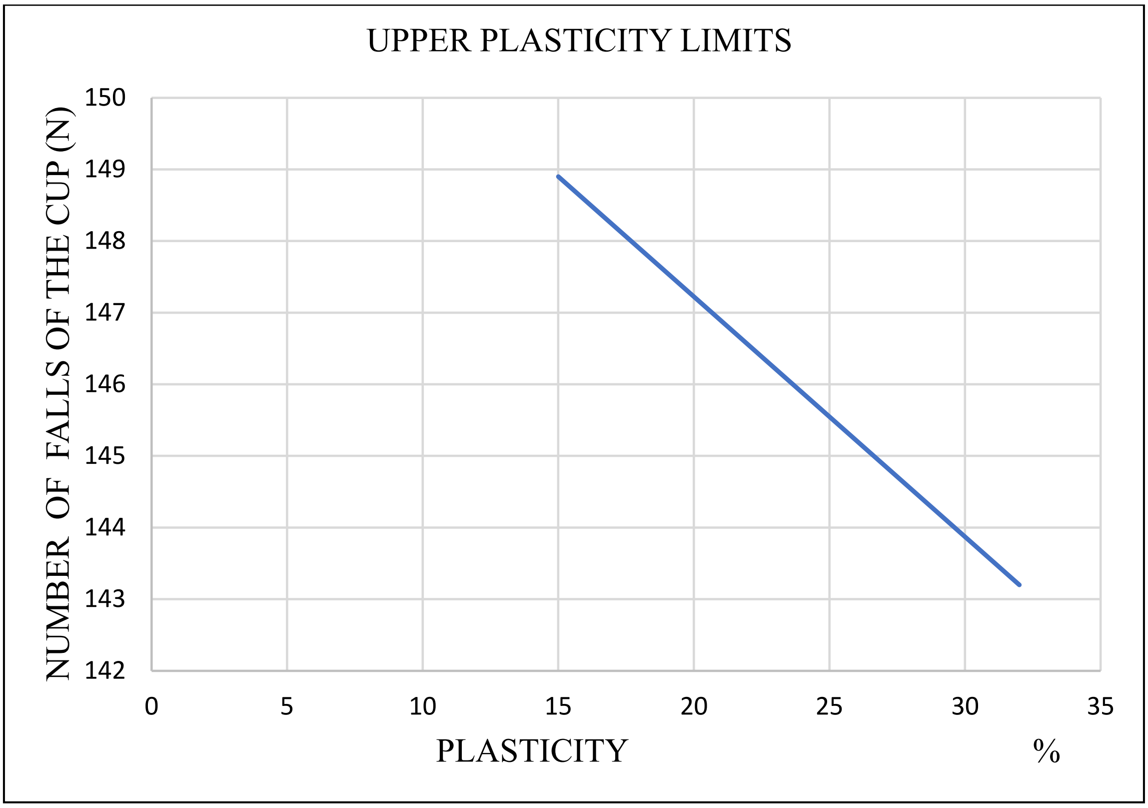

Figure 4 The upper limit of plasticity

Table 5 Plasticity limits and natural humidity

Plasticity limits - natural humidity					
Course of determination	Natural humidity	Upper plasticity limit		Lower plasticity limit	
Glass no.	20	21	22	23	24
Number of falls N of the cup		32	15		
Wet sample + tare A(g)	150.00	35.47	29.30	32.57	24.15
Dry sample + tare B(g)	117.10	31.78	25.18	31.79	23.38
Tare C(g)	43.10	29.21	22.41	28.87	20.32
A-B (g)	32.90				
B-C (g)	74.00				
$w = \frac{A-B}{B-C} 100$ (%)	44.50	143.20	148.90	26.40	25
$w_{medie(\%)}$	44.50				

4. CONCLUSIONS

The results obtained in the present study are preliminary and constitute the basis of future research for the use of sewage sludge in the ecological reconstruction of sites contaminated with petroleum products. The concentrations of heavy metals in sewage sludge have values that fall within the legal limits for use in the ecological reconstruction of oil-contaminated sites, but careful monitoring on representative batches is necessary for use.

In the two analyzed samples, sewage sludge and soil, we highlighted the presence of the following groups of bacteria: heterotrophic bacteria, hydrocarbon-tolerant bacteria, hydrocarbon-oxidizing bacteria and enterobacteria, and their number varied from one sample to another. Further studies will be carried out for the purpose of bioremediation of environments contaminated with petroleum products.

Carrying out the proctor test for sewage sludge was not possible because it contains a large amount of organic matter, has a high water content (45%) and extremely high plasticity, which prevents optimal compaction. Detailed geotechnical studies are needed regarding the possibility of using it as a filling material mixed with natural soils from each contaminated site.

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