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Method of Remediation of Oil Contaminated Soil nearby a Petroleum Products Storage

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Abstract

This paper presents a method of remediation for Diesel and lubricating oil contaminated soil nearby a petroleum products storage of SNTFC Brasov, using ex-situ technics. The contaminated soil is removed and transported for treatment in special places and treated chemically and biologically, by using eco-friendly solvents and biodegrading products. Chemical composition of oil contaminated soil was analysed by GC-MS, thermogravimetry and solvent extraction and demonstrated that this methods made a decrease with about 65% in 30 days, in saturates, aromatics and resins concentration.

Key words: *contaminated soil, lubricating oil, eco-friendly solvents, biodegradation.*

Introduction

Aliphatic hydrocarbons make up a substantial portion of organic contamination in the terrestrial environment. However, most studies have focused on the fate and behavior of aromatic contaminants in soil. Despite structural differences between aromatic and aliphatic hydrocarbons, both classes of contaminants are subject to physicochemical processes, which affect the degree of loss, sequestration and interaction with soil microflora. Biodegradation by microbes is one of the key removal process of hydrocarbons in soils, controlled by hydrocarbon physico-chemistry, environmental conditions, bioavailability and the presence of active microbes.

Oil contamination is one of the common pollution incidents in Romania. During 2005, there were about 134 incidents reported about soil and water pollution with oil, but the number of these incidents is decreasing.

Aliphatic hydrocarbons are significant contaminants, in Romania oil pollution is dominated by crude oil, diesel and lubricating oil, containing about 88% of aliphatic hydrocarbons, dominated by C14-C20 alkanes. Research has centered on aromatic contaminants, particularly polycyclic aromatic hydrocarbons (PAHs), because of their toxic effects on land and human and animal health, despite this class is less than 6% in pollution incidents. [1]

Contaminated sites are usually those in which certain products have been used over a number of years or sites where major accidents have happened, leading to pollution of the soil.

Soil is composed of inorganic and organic components separated by pores containing air or water. Organic matter is very important in the fate and behavior or organic contaminants, including aliphatic hydrocarbons in soil. [2]

A bioavailable compound is defined as a compound which is freely available to cross an organisms membrane from the medium the organism inhabits at a given point in time. A bioaccesible compound is described as a compound which is available to cross an organisms membrane from the environment it inhabits, if the organism has access to it, however it may be either physically removed from the organism or only bioavailable after a period of time.[2]

The Objective and Methods of Research

The objective of this research was to develop environmentally acceptable land application for oil contaminated soils nearby rails and petroleum products storage of SNTFC Brasov.

The objective was accomplished by measurement of the rates of degradation of the oil wastes in soil at different waste concentrations, frequencies of application, pH and soil temperature under controlled conditions.

The contamination started from the begining of the railway activities in this area, during about 40 years. The contaminated soil is located between rails and nearby fuel storage, on areas between 1 and 6 sqm.

To establish the contamination rate of the soil there were made soil analysis, according to national standards *SR 7587:1996* and *SR 7877-1:1995*. The soil samples were collected according to national standard *STAS 7184/1-1984* and to *Minister's Order no 184/1997* at two different sampling depths: 5 cm and 30 cm. The number of soil samples depends on the perimeter of contaminated area. In this case, the polluted area is between 1 and 6 sqm, so there were made 18 soil samples and 2 blank samples.

The sampling was made in march-april 2008. Samples were received in plastic bags, therefore the integrity of the results may be compromised. The quantity was about 0,5 kg soil for each sample, enough to analyse the total extractable hydrocarbons (TEH) and pH. Each bag has a label with a numeric code, the place, the depth and data of sample.

According to Minister's Order no 756/1997, references values for chemical elements in soil are presented in table 1:

Table 1. References values for chemical elements in soil

Chemical element	**Normal Values**	**Alert Limit/ Soil Using Type (mg/Kg dry wt.)**		**Intervention Limit/ Soil Using Type (mg/Kg dry wt.)**	
		Sensibile Soil	**Less Sensibile Soil**	**Sensibile Soil**	**Less Sensibile Soil**
Total Extractable Hydrocarbons (TEH)	100	200	1000	500	2000

Soil samples must be analyzed for total extractable hydrocarbons for carbon ranges C11 to C30+ using appropriate solvent extraction methods (e.g. soxhlet extraction) followed by Gas Chromatography Flame Ionization Detector (GC/FID) or equivalent instrumentation. [4]

For the analysis of TEH we used the solvent extraction method which is based on extraction with a highly volatile solvent, the recovery of the solvent and gravimetrical precision weighing of the extract residue.

The analysis of TEH in soil indicates the level of contamination, but not indicates the concentration of each hydrocarbon in samples. The analysis of TEH it is not a good indicator

for historical pollution with oil products, because of their low concentrations in soil and of the properties similar with petroleum waxes, which are very resistent to degradation.[3]

For measuring the concentration of hydrocarbons, a gas-cromathographic with mass spectrophotometer is needed. The GC-MS analysis shown the composition of samples in Diesel (C8-C22) and lubricating Oil (C20-C40). Analytical results for each sample are presented in table 2.

Table 2. Analytical results for each sample

Sample	Depth, cm	pH, pH units	TEH (C11-C30+), mg/kg dry wt.	Limit values for less sensible soil (Ordin no. 756/1997)	
				Alert limit	Intervention limit
S1 blank	5	6,58	0	1000	2000
	30	6,43	0		
S2 blank	5	6,23	0	1000	2000
	30	6,18	0		
S3 between rail 1 and 2 S4	5	7,12	1187	1000	2000
	30	7,16	1069		
S5 between rail 2 and 3 S6	5	6,87	1243	1000	2000
	30	6,92	1192		
S7 Fuel feed area S8	5	7,08	1859	1000	2000
	30	7,14	1738		
S9 Remiza 2 area S10	5	7,25	1387	1000	2000
	30	7,42	1194		
S11 Lubricating oil discharge area S12	5	6,85	2147	1000	2000
	30	6,94	1973		
S13 Wagon revision area S14	5	7,19	1759	1000	2000
	30	7,24	1689		
S15 Fuel storage area S16	5	6,79	2235	1000	2000
	30	6,86	2437		
S17 Rail 2F S18	5	6,88	1356	1000	2000
	30	6,93	1284		

According to results presented in Table no 2, the TEH concentration in analysed soil is higher than 1000 mg/kg dry wt. for samples with code S1- S18 and higher than 2000 mg/kg dry wt. for samples with code S11, S15, S16. The pH values are in normal limits for soil which are between 6,5 and 8,5 pH units. [5]

A soil with a concentration over 1000 mg/kg dry wt. or over 0.01% TEH is contaminated and need remediation. So, the samples presented in tabel no 2 need a treatment process for decontamination and remediation.

The contaminated soil was removed and transported for treatment in a special place in the limited area of SNTFC, for treatment and decontamination.

The contaminated soil was treated chemically and biologically, by using eco-friendly solvents and biodegrading products. The eco-friendly solvents are produced by ICECHIM with their own patented technology and the composition is based on fat acids alchylic esters, from natural fats. After the treatment the solvent was collected in special basins and recovered.

The remain soil was treated by biodegradation using a mixed microbial consortia with a content of bacteria and fungi as Rhinocladiella sp., Aspergillus sp., Acremonium sp., and Penicillium sp., in special cells, with respect to the pH. Hydrocarbon-degrading bacteria had tendency to play the greatest role at the neutral-alkaline condition (pH: 7~7.8). When pH is acidic (pH: 2~4), the fungi took over to degrade oil products. [6]

The pH of the medium was adjusted to pH 7,5 using 1N NaOH solution. Culture were incubated for 30 days at room temperature (24 ^{O}C) at static conditions.

Conclusions

After 30 days, the chemical composition of soil was analysed by GC-MS, thermogravimetry and solvent extraction.

The results of the analyses are presented in table 3.

Table 3. Results of the analyses

Sample	Depth, cm	TEH (C11-C30+), mg/kg dry wt. before treatment	TEH (C11-C30+), mg/kg dry wt. after 30 days treatment	Limit values for less sensible soil (Ordin no. 756/1997)	
				Alert limit	Intervention limit
S1 blank	5	0	-	1000	2000
	30	0	-		
S2 blank	5	0	-	1000	2000
	30	0	-		
S3 between rail 1 and 2 S4	5	1187	416	1000	2000
	30	1069	342		
S5 between rail 2 and 3 S6	5	1243	386	1000	2000
	30	1192	394		
S7 Fuel feed area S8	5	1859	651	1000	2000
	30	1738	629		
S9 Remiza 2 area S10	5	1387	485	1000	2000
	30	1194	418		
S11 Lubricating oil discharge area S12	5	2147	783	1000	2000
	30	1973	752		
S13 Wagon revision area S14	5	1759	616	1000	2000
	30	1689	591		
S15 Fuel storage area S16	5	2235	843	1000	2000
	30	2437	964		
S17 Rail 2F S18	5	1356	475	1000	2000
	30	1284	467		

During this period of 30 days, the aliphatic hydrocarbons were reduced significantly, whereas the aromatic hydrocarbons were less reduced.

The decreasing of hydrocarbons concentration for analyzed samples is presented in figure 1.

The results of the analysis demonstrated that this combined methods made a decrease with about 65% in saturates, aromatics and resins concentration in 30 days of treatment. These results

suggest that both methods may contribute to the degradation of oil products from accidental spills.

The treated soil can be stored on the land in the courtyard of SNTFC Brasov, because the soil is no more contaminated and the concentration of TEH is less than 1000 mg/kg dry wt. or 0,01% TEH.

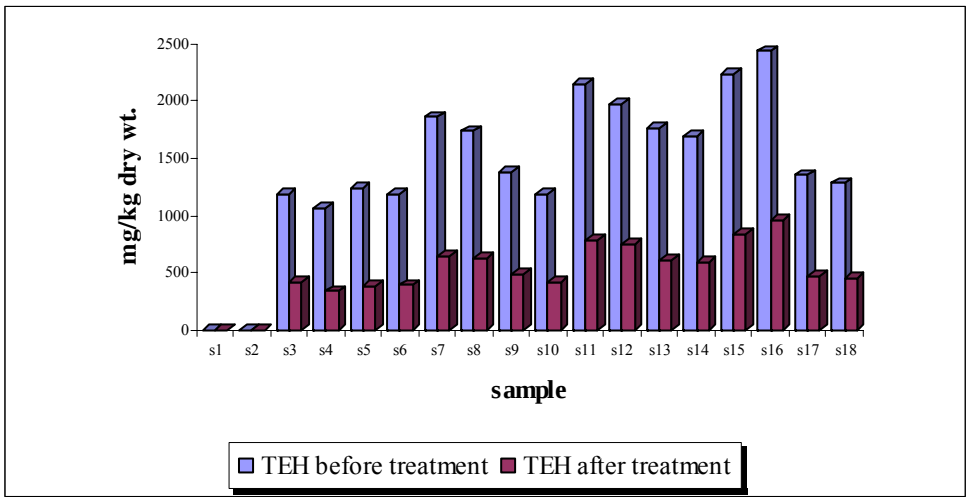

Fig. 1. TEH concentration in soil samples before and after treatment

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Metodă de remediere a solului contaminat cu țiței din vecinătatea unui depozit de produse petroliere

Rezumat

Lucrarea prezinta o metoda de remediere a solurilor contaminate cu motorina si uleiuri din vecinatatea unui depozit de produse petroliere apartinand SNTFC Brasov, utilizand tehnici ex-situ. Solul contaminat a fost indepartat si transportat intr-un loc special amenajat si tratat chimic si biologic, prin utilizarea de solventi ecologici si produsi biodegradabili. Compozitia solului contaminat a fost analizata prin GC-MS, termogravimetrie si extractie selectiva cu solventi si s-a demonstrat ca prin aplicarea acestor metode s-a inregistrat o scadere a concentratiei de hidrocarburi saturate, aromatice si rasini, cu aproximativ 65% in 30 de zile.