Aspects of bioremediation of polluted soils with hydrocarbons

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Abstract. Bioremediation is a process widely used for the treatment of soils contaminated with oil. This technology is based on the premise that a major part of the crude oil components can be used by the microorganisms existing in nature. The success of oil spill bioremediation depends on the ability to establish and maintain the conditions that favor the growth of oil biodegradation speed in a contaminated environment. This paper presents the results of the experimental research that identifies areas polluted with hydrocarbons, where must be taken remedial measures, and developing a remedial program based on laboratory test results. Were analyzed main indicators of polluted soil, after which settled the quantities of nutrients to be added for biodegradation to occur in good conditions.
Key Words: bioremediation, contaminated site, remedial program, nutrients, microorganisms.

Introduction. Bioremediation uses living microorganisms, primary microorganisms in order to degrade the environmental contaminants in less toxic forms. Microorganisms may be indigenous or from the contaminated area or can be isolated from elsewhere and brought to the contaminated area. For bioremediation to be effective, microorganisms must enzymatically attack the pollutants and convert them to less toxic products. This process often involves manipulating environmental parameters in order to allow microbial growth so that degradation to proceed with a greater speed.

There are two main approaches for bioremediation of the soils and of the subsoils contaminated with hydrocarbons:

- bioaugumentation, when bacteria known to the degradation of oil are added to supplement the microbial population;
- biostimulation, when is stimulated the growth of indigenous microorganisms that degrade the oil by the addition of nutrients and other materials. Recent studies in the field have shown that biostimulation is a more effective approach because the addition of microorganisms that degrade the hydrocarbons does not improve the oil degradation more than the mere addition of nutrients (Rocco 2000).

Bioremediation has more advantages comparing to conventional actual remediation technologies. First, its application is relatively inexpensive. It involves the possible degradation of the oil at mineral products (such as carbon dioxide and water), while the chemical methods, for example, usually transfer the contaminant from one environment compartment to another.

Bioremediation, like other technologies, has of course its limitations. Bioremediation involves very heterogeneous and complex processes. Bioremediation success depends on the presence of the suitable microorganisms in the area, in appropriate environmental conditions. At the same time, bioremediation using may be limited by the discharged oil composition.

The natural biodegradation process can take place more slowly or faster, depending on the type of oil (light oils degrade themselves faster than the heavier crude oils) (Dumitran & Onuţu 2010).

The main steps in selecting the bioremediation and of the response plan include:

- pre-treatment evaluation involves assessing whether bioremediation is a viable option based on the type of oil that was spilled, its concentration, the presence of microorganisms able to biodegrade hydrocarbons, the type of soil that has been affected and other factors environment (pH, temperature);
- establishing and monitoring the treatment plan involves selecting agents have speed limiters treatment (e.g. - nutrients) determine strategies for implementing agencies have speed limiters;

- evaluation and completion of treatment; after treatment is implemented according to plan, assess the effectiveness of treatment and to determine its endpoint is based on the analysis.

Bioremediation can be applied in-situ or ex-situ. In-situ techniques are defined as those that are applied to the soil pollution place with minimal disturbance. Ex-situ techniques are applied to the soil that has been removed from the pollution area by excavation (Pătraşcu et al 2008).

Factors to be taken into account when deciding on the type of soil remediation include: type of oil; total concentration of petroleum hydrocarbons in the soil; salinity; the existence of a microbial population capable of degrading the pollutants; soil type; pollution age; the pH; temperature; humidity; nutrients; the presence of oxygen; microelements.

Microbial growth and activity are affected by pH, temperature and humidity. Although microorganisms were isolated also in extreme conditions, most of them optimally grow in a narrow field, so that it is important to achieve optimal conditions (Stoica et al 2014).Thus, if the soil is too acidic, it is possible pH increase by the addition of lime.

Temperature affects the rate of biochemical reactions, for many of the sere actions, the rate doubles at every temperature increase with 10^oC. However, above a certain temperature, the cells die.

Available water is essential for all living organisms, irrigation being necessary to achieve an optimum level of moisture.

The amount of available oxygen shall determine if the system is aerobic or anaerobic. Hydrocarbons are easily degraded under aerobic conditions. Increasing the oxygen quantity in the soil is possible by plowing or air blowing (Riser-Roberts 1998).

Soil structure controls the efficiency of air supply, water and nutrients. In order to improve soil structure can be applied materials such as straw or sawdust. A less permeable soil may prevent the transport of water, nutrients and oxygen.

Material and method. The objectives of this study are to identify areas contaminated with petroleum products where remedial action must be taken and to develop a remedial program based on the laboratory test results.

Experiments aimed to highlight the effect of microorganisms to decontaminated soils polluted with oil products and also the time shortening for achieving the bioremediation process by adding nutrients, water, surfactant, gypsum, microelements in well established amounts.

Contamination has been occurred with a single type of oil and affected a forest area and a plum orchard.

From each point of the contaminated area has been taken a composed sample of soil (consisting of several single samples) and a sample of crude oil, resulting four samples (Table 1).

Table 1

The code of the soil samples that were taken

Ord. No.	*Soil sample name*	*Contaminant oil sample name*
1	Soil A, forest land	oil a
2	Soil B, forest land	oil a
3	Soil C, forest land	oil a
4	Soil D, plum orchard	oil a

The soil samples have been analyzed for several parameters determination. On the extract of saturated paste the following tests were conducted: pH, electric conductivity, Na, Ca, Mg, sodium adsorption ratio (SAR) particles TGR, Cl^-, SO_4^{2-}, TPH-IR (total petroleum hydrocarbons), Simdist Analysis on the soil extract, determination of the content of clay, determining the number of bacteria, determination of the available trace elements content (Cu, Zn, Fe, Mn).

Oil samples were analyzed for API density determination and by Simdist chromatographic method. After completing the tests, contaminated soils prepared as saturated paste have been put in plastic containers fo rbioremediation testing. In each container were added the following stimulating agents:

- nutrients - added monthly in equivalent amounts of N - 30g/m ^{2}, P_2O_5 - 12 g/m ^{2}, K - 7 g/m^2 until it will be obtained the optimum ratio C:N:P:K;
- water;
- loosening agents 5-10 kg/m^2;
- biodegradable surfactant 3 l/m ^{2} asa 10% solution ;
- trace elements (Cu, Zn, Fe, Mn, Mo, W, Se) ;
- gypsum - to improve saline soils - added after 6months in maximum dose of 1000g/m^2.

After every six months were checked TPH (total petroleum hydrocarbons content) and SAR (sodium ratioa dsorbed) and was recalculated the treatment time with nutrients and gypsum.

The most important factors for the biodegradation of crude oil are: the total petroleum hydrocarbons content (TPH), electrical conductivity (EC), the presence of microorganisms in an adequate number, clay content, oil density, pollution age, pH.

Results. Analyzed parameter values obtained by laboratory analysis are presented in Table 2.

Table 2

The parameters values of the soil samples

Ord No.	*Soil sample code*	*TPH-IR primary mg/kg*	*Bacteria ,MPN/ g soil*	*pH*	*Electrical conductivity μS/cm*	*Na, mg/ kg*	*Ca, mg/ kg*	*Mg, mg/ kg*	*PS, %*	*SAR*	*Cl, mg/ kg*	*SO_4 mg/kg*	*Clays <2μm*	*Particles <20 μm*
1	Soil A	13900	≥10^7	8.2	2060	230	74	24	78	6.6	375	7	1.9	22.5
2	Soil B	21000	≥10^7	8.31	2910	195	71	14	55	7.4	440	25	7.8	28.88
3	Soil C	119600	≥10^7	8.45	590	52	61	12	101	1.6	40	14	0.2	33
4	Soil D	100900	≥10^7	8.06	11200	1980	390	110	107	22	3900	270	0.4	36

Table 2 (continuation)

The parameters values of the soil samples

Ord No	*Soil Sample code*	*API Density of the contamina -ting oil*	*TPH-IR initial *10^{-2} mg/kg*	*Final TPH-IR *10^{-2} mg/kg*	*Primary TPH-GC, *10^{-2} mg/kg*	*Final TPH-GC, *10^{-2} mg/kg*	*C18/ Fitan oil*	*C18/ Fitan soil*	*Area peaks/ primary Squalan*	*Area peacks / final Squalan*	*Fe, mg/ kg*	*Cu, mg/k g*	*Zn, mg/ kg*	*Mn, mg/ kg*
1	Sol A	45	139	99	-	-	2.5	2.5	-	-	50	<1	0.3	280
2	Sol B	34	210	127	200	98	2.31	2.3	1.12	0.34	1000	2.2	5.9	360
3	Sol C	34	1196	839	800	239	2.31	1.68	0.55	0.33	2900	7.5	142	480
4	Sol D	34	1009	578	920	248	2.31	2.26	4.09	0.62	3200	15.8	54	270

Upon the test results were calculated the necessary nutrient quantities, amendments (gypsum - TGR), straw (Table 3), biodegradable surfactant and trace elements for each sampling point, in order to obtain optimal conditions for biodegradation of crude oil (Table 4).

Table 3

Necessary nutrients quantities

Ord. No.	*Soil Sample code*	*TPH-IR, mg/kg*	*mg N/ kg soil necessary*	*mg P/ kg sol necessary*	*mg K/ kg sol necessary*	*NPK treatment months*	*TGR, t/ha total*	*TGR, g/m^2 step I*	*TGR, g/m^2 step II*	*TGR, g/m^2 step III*
1	Soil A	13900	596	119	119	6	-	0	0	0
2	Soil B	21000	900	180	180	9	-	0	0	0
3	Soil C	119600	5126	1025	1025	51	-	0	0	0
4	Soil D	100900	4324	865	865	43	11.7	1000	170	0

For a proper aeration of the soil and for incorporating of nutrients, straw, trace elements, in order to improve the biodegradation of the crude oil were performed agricultural work (manual o rmechanized) periodically (monthly).

Table 4

Required trace elements and surfactant quantities

Ord. No.	*Soil Sample Code*	*Mo, g/m²*	*Se, g/m²*	*W, g/m²*	*Fe, g/m²*	*Cu, g/m²*	*Zn, g/m²*	*Straw, kg/m²*	*Biodegradable Surfactant Solution 10%, l/m²*
1	Soil A	0.3	0.15	0.06	0	0.45	1.5	10	3
2	Soil B	0.3	0.15	0.06	0	0	0	10	3
3	Soil C	0.3	0.15	0.06	0	0	0	10	3
4	Soil D	0.3	0.15	0.06	0	0	0	10	3

Discussion. For soil sample A used as forest land, it is proposed to realize the monthly nutrient application for 6 months. Under the proposed conditions, the soil can be remedied in 1-2 years. Because the primary TPH-IR of the soil is less than 3%, it can be cultivated with plants (willow, poplar), which by phytoremediation process accelerates the restoration of the soil properties.

On the soil sample B used as forest land it will be monthly applied nutrient for 9 months. Using the proposed treatment, the soil will be bioremediated in 1-2 years. Cultivating the land with plants (willow, poplar) accelerates the restoration of the soil properties through phytoremediation.

For soil sample C, used as forest land it is proposed to monthly apply nutrient for 51 months. Under the proposed conditions, the soil can be remedied within 4-7 years. After every six months it is necessary to determine TPH from soil in order to track progress of the bioremediation. When the TPH is below 1% for C10-C40 components (GC-SimDist analysis) or 3% for TPH-IR (whichever is obtained faster) soil can be cultivated with plants (willow, poplar), which in the phytoremediation process accelerates restoration of soil properties.

For soil sample D, used as a plum orchard it is proposed a monthly applying treatment for up to 43 months. Gypsum is used in the total amount of 1170 g/m^2 for correcting the balance between Na and Ca+Mg, and for eliminating the salted water. The gypsum should be applied in two stages:

- stage I: 1000 g/m^2;
- stage II: 170g/m^2 (applied 6 months after stage I).

For a good soil aeration and for nutrients raw, trace elements incorporation, in order to improve the biodegradation of crude oil it is necessary to perform agricultural work (plowing, disking) before the cultivation of plants.

The soil sample originally had a total petroleum hydrocarbons (TPH-IR) of 100.900 mg/kg and was affected by salt water pollution.

The estimated time for bioremediation process is about 6-8 years. After every six months it is necessary to determine TPH from soil in order to track the progress of the bioremediation process. When the TPH is below 1% for C10-C40 components (GC-SimDist) or 3% for TPH-IR (whichever is obtained faster), soil can be cultivated with plants (alfalfa, oats), which by the phytoremediation process accelerates the restoration of soil properties.

Conclusions. The most important factors for evaluating the biodegradability of oil are: the total petroleum hydrocarbons content (TPH), electrical conductivity (EC), the presence of microorganisms in an adequate number, content of clay, oil density, age pollution, pH.

Soil bioremediation using the appropriate type of pollutant treatment is effective. Biremediation may be an option if are known the parameters of the contaminated soil and the contaminant properties.

On the basis of the analysis of soil and of the contaminant can be achieved a treatment prescription and can be estimated the time required for bioremediation.

Bioremediation is a cheap method of decontamination that can be used successfully for the soil polluted with oil.

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