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For a sustainable development: Phytoremediation of oil-polluted soils by using birdsfoot trefoil crops

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Abstract

Sustainable development requires a series of actions to be taken for environmental recovery and protection. Regulating the activity through ecologic-economic decisions justifies the balance between the two, the normality of natural and economic factors. While attempting to maintain and improve the existing potential of nature, a thorny problem is posed by soils polluted with oil residues. Increasingly intense anthropogenic activities lead to a growing amount of chemicals in the environment. The remediation of polluted soils through physicochemical methods involves large investments and additional operating costs. Versions of biotechnologies applied in recovering polluted soils such as phytoremediation involve crops able to metabolize pollutants. The method requires minimal investment and low maintenance costs compared to other methods. By using trefoil crop to reduce pollution caused by large amounts of crude oil (i.e. 113.5 ± 3.90 g/kg d.m.), one reached an effective reduction of TPH (Total Petroleum Hydrocarbons) of 80.0-91.8% during a growing period of 490 days. The content of nutrients in polluted soil has been supplemented with an appropriate quantity of sewage sludge. The stress caused on plants by the large amount of petroleum pollutants in soil was alleviated by the use of optimal amounts of fly ash coming from power plant. The results show that compared to conventional methods of remediation, phytoremediation is achieved at much less cost.

Keywords:crude oil, *soils*, phytoremediation, *costs.*

1. Introduction

In the recent decades, a broad research experience against pollution has developed. Now there were introduced the concepts of environmental goods and environmental services, a number of ecological models were also developed and the environmental issues have become a natural incorporation of the general economical equilibrium theory (the models of Pareto, Arrow, Samuelson, Solow etc.). There has also been an attempt to integrate economic and ecological models to highlight the fact that production involves flows from nature to economy and in reverse, flows which require taking into consideration the interdependencies and appropriate consequences.Quantitative, traditional economic growth models are aiming towards maximizing profits at an optimal satisfying of human needs. However, the material and energetic support provided by the economic environment was outbid, along with the tank role of emissions and waste, without taking into account the environmental needs. Apart from this, the most important environmental function has been neglected: maintaining life on earth.

Making an eco-development involves building a relationship between the economic development, on one hand, and the natural environment, on the other hand, this having to be represented by all natural resources which need to be managed sustainably through the ecological processes that support life on the planet, by respecting the production of ecosystems on which they depend: fisheries, forests, pastures and farmland.Acute soil pollution with petroleum products is the immediate consequence of leaks occurring during specific stages of oil extraction and processing. Transport and tapping of crude oil and its end products also contribute to this type of soil pollution. The importance of chemical polluting phenomena is closely linked to the industrialization level and intensity of use of these chemicals. Dozens and even hundreds of new polluted sites are added to the category of soils polluted with oil products annually. At the same time, concerns for remediation of oil-polluted soil result in new fast and effective remediation strategies. These concerns began several decades ago, but have intensified in the past 20 years (D.M. HAMBY [1], M. M.AMRO [2], P.F.Wich& al. [3], J. OTAVAKU & al. [4], M. DIPHARE & E. MUZENDA. [5]).The methods applied for decontamination are physicochemical and biological. Among the studied physicochemical methods are thermal treatments, stripping, soil washing, even capturing volatile elements (D.M. HAMBY [1]), fluid extraction, mixture of organic solvents, alcohol and water mixture, acetate-acetone-water mixture, critical fluids, steam at high temperatures and pressures, water mixed with surfactants and biosurfactants (M. DIPHARE and E. MUZENDA. [5], K. URUM & al. [6]), chemical oxidation with various oxidizing agents, chlorine compounds, potassium permanganate, sodium persulfate, Fenton reactive, ozone or air (D.M. HAMBY [1], P.F. WICH & al. [3], C.L.YAP & al.[7]). In most cases these methods are complex, difficult to apply and to maintain, they involve installations or expensive reagents and significant energy consumption. The scope is reduced to heavily polluted areas and the benefits are limited by scale and technology cost: many of these methods can be applied only at pilot scale (D.M.HAMBY [1]).

Table 1. Operating costs of the various remediation methods for soils contaminated with oil (F.I.KHAN & al. [8])

No	Remediation method	Costs
1	Soil washing	170 USD/t
2	Soil vapour extraction	20-50 USD/t *
3	Land farming	30-60 USD/t *
4	Soil flushing	25-250 USD/t *
5	Solidification/ stabilization	80-330USD/m^3 *
6	Thermal desorption	50-330 USD/m^3 *
7	Biopiles	130-260 USD/t
8	Phytoremediation	145000-250000 USD/ha
9	Bioslurry systems	130- 200 USD/ m^3
10	Bioventing	30- 90 USD/t *
11	Aeration	14000 USD/t

*These costs may be associated with some fixed costs related to the acquisition of equipment

Among the studied biological methods are biodegradation using microorganisms, biostimulation, bioaugmentation performed with microorganisms stimulated by the presence of nutrients, composting (biodegradation by microorganisms in controlled confined spaces) land farming and phytoremediation (P. F. WICH & al.[3], S. JALA and D. GOYAL [9], L. WESSELS PERELO [10], H. I. GOMES & al.[11], L. PASSATORE & al. [12]).

Phytoremediation is based on the potential of certain plants to detoxify environments. This potential of plants has been highlighted since the eighteenth century by the experiments conducted by A. Lavoisier, J. Presley, K. Scheele, and others. In recent decades, the concept of phytoremediation has been assimilated into some new technologies. Thus, some crops are used for the detoxification of soils contaminated with different chemicals (J. BURKEN [13]). In the here analysed phytoremediation case both fly ash and sewage sludge were used. Many researchers have shown that applying fly ash to the soil helped achieving improved crops (S.S.S. LAU, J.W.C. WONG [14], S.M, PATHAN & al. [15]; C. CARLILE & al. [16]) and also an improved reforestation of areas destroyed by human activities. The agronomic benefits of fly ash may be associated with improved physicochemical and biological soil characteristics (V.C. PANDAY and N. SINGH [17], L.C. RAM and R.E. MASTO [18], Z.T. YAO. & al. [19]).Essential micronutrients present in ash will result in plant and crop growth. Generally, the negative pressure exerted by fly ashes on crops is due to the transfer of heavy metals between soil and plant, a very complex process governed by some natural and anthropogenic factors. Using quantities of 40.80 and 120 fly ash tons / ha on sandy and loamy soils with increased amount of Si, P and K did not result in an excessive take-over of metals (H. LEE & al. [20]). Sewage sludge is a source of essential elements as N, P, S, Mg, of microelements such as Cu, Zn, Fe, Mo, etc., and of carbon-based organic matter and important microorganisms which have been identified as suitable for the biodegradation of some oil products, Alcaligenes, Arthrobacter Mycobacterium Pseudomonas, etc. (P.F.WICH & al.[3]). Sewage sludge can improve the physical, chemical and biological soil properties, but may also introduce into soil significant quantities of heavy metals and bacteria. Due to the physicochemical parameters of the mixture ash and sludge, soil treatment with this mixture is a convenient alternative (D. FYTILI and A. ZABANIOTOU [21], E.K. DZANTOR & al. [22], S.S. LAU & al. [23]).The starting assumption is that phytoremediation of soils polluted with petroleum products is an attractive method because it involves low cost and traditional plant cultivation strategies. Considering this issue, the present paper is structured as following: firstly, there is a short debate regarding the versions of biotechnologies applied in recovering polluted soils such as phytoremediation, which make crops able to metabolize pollutants, and secondly, an investigation on the impact of using phytoremediation of oil-polluted soils. Following, we provide the discussion and implications for research and practice (variations of Total Petroleum Hydrocarbons content in the studied soil variants not cultivated / cultivated with birdsfoot trefoil during the monitored period of 490 days). In the end, the paper presents the conclusions and recommendations for future studies.

2. Materials and Methods

The study was done in the experimental block, therefore having included some experimental variants of polluted soil mixed with fly ash in a proportion of 113.5 ± 3.90 g/kg d.m.TPH. Experimental variants of soil were: variant PS - polluted soil not cultivated (bare soil); variant PB - polluted soil fertilized with sewage sludge, with frail plants showing major suffering and beginning to turn yellow starting at the base; variant PC1 - polluted soil treated with 500g fly ash, with frail plants showing suffering, but the plants grow, the leaves turn yellow starting at the base; variant PC2 - polluted soil fertilized with sewage sludge and 500g fly ash; variant BC1 - polluted soil fertilized with sewage sludge and 250g fly ash; variant BC2 - polluted soil fertilized with sewage sludge and 50g fly ash. Tested soil (6.5 kg) was added in each pot. A paper filter was placed at the bottom of each pot to prevent the dry soil from escaping out through the drainage holes. The soil polluted with TPH was taken from an area related to oil extraction activities or a park of oil drilling probes. The device used for testing probes was the atomic absorption spectrophotometer AAS AVANTA. Soil pollution appeared due to oil extraction activities in the area. The area was polluted because of accidental leaks, malfunctions, etc. Stress due to pollutants for sprouting seed and seedling was diminished through the addition of fly ash from power plant. The fly ash used had a pH 6.5 ± 0.3 (ISO 10390: 2005), a moisture content of 26.43% (SR EN 12880/2002), and loss on ignition were 7.42% (SR EN 12879-02). Also, through test method SR ISO 11047-99, it was discovered that the fly ash presented a content of heavy metals in g/kg d.m. of Cd 1.16±0.5, Cr 123.2±0.5, Cu 59.6±0.5, Ni 37.6±0.5, Pb 78.9±0.5, Zn 157.4±0.5, Mn 276.3±0.5. At the same time, through test method SR ISO 11466: 1999 a content of Fe of 3012.4±0.5 g/kg d.m. was identified in the ash. Polluted soil fertilization was performed with anaerobically stabilized sewage sludge taken from a municipal wastewater treatment plant. The values in table 2 have been obtained as follows: the moisture percentage has been calculated according to SR EN 12880/2002, the organic matter percentage according to SR EN 12878/2002, the nitrogen content according to ASTM D 5291/2010 in fluids and the phosphorus content, according to SR EN 14672/2006.

Table 2. The nutrient content from sewage sludge fertilizer agent

Sewage sludge: Physicochemical characteristics	Moisture [%]	Organic matter [%]	Total Nitrogen [%]	Total Phosphorus [g/kg d.m.]
	91.5	59.78	1.138	1107

Experimental variants of soil were cultivated with birdsfoot trefoil. The control variant was the TPH contaminated soil, untreated and uncultivated. Each experimental variant contains three replicates. The plants used for phytoremediation of soils heavily contaminated with TPH were from the Lotus corniculatus species. To determine the TPH from the soils an analysis of the concentration is performed periodically [8], in the upper level: 1) 3–5 g of dry soil are weighed (M), then 5 g Na2SO4 anhydrous and 25 ml petroleum ether per annum are added, 2) 30 minutes stirring at 50 rotations / min and then filtered, 3) The glass and filter paper are washed with petroleum ether, which is added to the filtrate, 4) The filtrate is evaporated on water bath, 5) The residue is dissolved in petroleum ether, then passed through the chromatographic column filled with aluminium oxide. The eluate collected into the tarred capsules; m1 [g], 6) Petroleum ether is evaporated at room temperature and weighed at constant mass m2 [g], 7) The same is done for the control from 28 ml petroleum ether (m3 – mass of capsule without control residue [g], m4 – mass of capsule with control residue [g]), 8) Calculating TPH: TPH [g/kg] =1000•[(m2– m1)–(m4– m3)]•M-1.

3. Results

From the comparative study of the quantities of TPH lost from soil during the monitored period was found that the soil is losing different amounts of oil depending on the performed treatment of contaminated soil and the development degree of trefoil crop. The main phenomena through which oil products are eliminated from polluted soil are the volatilization of light components present in the initial mixture or resulted along the way under the action of natural thermal conditions, the bacterial metabolism due to the biocenosis which comes with sewer sludge and metabolism associated to rhizosphere (consortium plant - local biocoenosis).Tables 3 and 4 show that in the case of untreated contaminated soil TPH losses may be due only to volatilization phenomena. If sewage sludge was introduced in the soil, the plants did not survive in the heavily polluted soil and dried out in 2-3 weeks after sprouting. TPH loss in this soil is due to phenomena of volatilization and bacterial metabolism. Loss of TPH in polluted soil fertilized with sewage sludge increased by 25.3% in the monitored period vs. TPH loss in not fertilized polluted soil.

Table 3. Variations of TPH content in the studied soil variants not cultivated / cultivated with birdsfoot trefoil during the monitored period of 490 days

No Crt	Monitored period	TPH content in soils after certain periods of vegetation (g/kg d.m.)					
		PS*	PB**	PC1***	PC2 Sewage sludge and 500g fly ash	BC1 Sewage sludge and 250g fly ash	BC2 Sewage sludge and 50g fly ash
1	60 days	98.8± 3.5	95.4± 3.5	109.4± 4.5	94.5 ± 6.6	85.2 ± 4.5	89.6 ± 3.5
2	270 days	88.35± 4.2	74.81±2.8	113.05± 3.5	73.53± 4.5	68.93± 3.5	46.88± 2.5
3	360 days	80.6± 2.5	74.0± 2.4	106.2± 4.8	59.5 ± 1.4	49.9 ± 1.8	38.8 ± 1.8
4	420 days	65.5± 1.9	40.0± 1.5	56.2± 2.7	34.9 ± 1.4	28.2 ± 1.3	13.6 ± 1.1
5	490 days	58.6± 2.1	40.0± 1.4	40.2± 1.5	35.9 ± 1.4	22.3 ± 1.2	9.3± 1.0

* variant of polluted soil not cultivated (bare soil); ** variant of polluted soil, fertilized with sewage sludge, with frail plants showing major suffering and beginning to turn yellow starting at the base; *** variant of polluted soil, treated with 500g fly ash, with frail plants showing suffering, but the plants grow, the leaves turn yellow starting at the base. The plants dry out slowly.

Table 4. Quantities of TPH lost from soil variants not cultivated / cultivated with birdsfoot trefoil during the monitored period of 490 days in the experimental variant. The soil had an initial content of 113.5 g/kg d.m. TPH

	TPH lost from soils in 490 days (g/kg d.m.)					
	PS* V	PB** V+ M	PC1*** V+ M+ P	PC2 V+ M+ P	BC1 V+ M+ P	BC2 V+ M+ P
	54.9±3.2	73.5±2.2	73.3±2.7	77.4± 4.2	90.7± 3.2	104.2±1.2
%	48.4	64.7	64.6	68.1	80.0	91.8

*, **, *** See table 3, V – volatilization, M – bacterial metabolism, P – plant metabolism

Applying a complex treatment with sewage sludge and ash to polluted soil prompted the formation of crops that developed to full maturity. The optimal amount of ash that has led to a culture with maximum efficiency in metabolizing TPH components was 50g/kg d.m. TPH. In this case, cumulated phenomena of volatilization and metabolization of TPH components resulted in a two times higher loss of TPH during monitored period vs. losses in untreated polluted soil with no cultivated plants. Trefoil crops reach maturity in July when they bloom. First harvest was performed in accordance with specific agricultural norms for this crop. The table 5 presents the amounts of roots harvested at the end of August and the cumulated quantities of aerial part ofLotus corniculatus plants from the two harvests in July and August.

Table 5. Total green mass quantities harvested in 2015 (Harvest I and II), corresponding quantity of roots and the ratio aerial part of plants / roots quantities

No crt	Harvested plants	Experimental variants Min. – max. amount of plant tissue g / pot			
		PC1	PC2	BC1	BC2
1	Aerial part of crop I and II	30-40	50-60	60-70	70-90
2	Roots part	7.4-8.2	10.5-11.6	25.3-40.2	26.0-55.3
3	Ratio aerial part of plants / roots quantities	4.0-4.9	4.8-5.2	1.7-2.4	1.6-2.7

Table 5 shows that the harvested plants from the experimental variants fertilized with 500 g fly ash / pot and 250 g respectively 50 g fly ash / pot, i.e. variants BC 1 and BC 2, had the largest quantities of green mass and roots. This large amount of roots confirms also the high degree of TPH components metabolization in soil as presented in tables 3 and 4. The tables 6 and 7 bellow show the amount of bioaccumulated heavy metals in plant tissue from green mass harvested in 2015, Harvest I (July) and Harvest II (August).

Table 6. Amount of bioaccumulated heavy metals of green mass harvested 2015, Harvest I (July), from variants in experimental block

No crt	Metals	Amount of metals (g/kg d.m.)			
		PC1*	PC2	BC1	BC2
1	Cd	-	-	-	-
2	Cu	8.39	8.22	7.98	8.0
3	Cr	-	-	-	-
3	Fe	420.4	453.8	418.6	410.13
5	Mn	48.01	47.11	37.38	45.0
5	Ni	3.81	3.98	2.49	3.01
6	Pb	-	-	-	-
7	Zn	46.6	43.65	42.53	44.7

*sewage sludge and fly ash are provided free of charge by wastewater treatment plants respectively by power plants

Table 7. Amount of bioaccumulated heavy metals of green mass harvested 2015, Harvest II (August), from variants in experimental block

No crt	Metals	Amount of metals (g/kg d.m)			
		PC1**	PC2	BC1	BC2
1	Cd	-	-	-	-
2	Cu	9.69	6.51	4.97	7.88
3	Cr	-	-	-	-
3	Fe	121.69	141.89	121.11	194.65
5	Mn	34.8	34.7	29.2	66.7
5	Ni	5.05	4.75	2.57	3.12
6	Pb	-	-	-	-
7	Zn	78.5	65.49	49.43	50.8

** A medium transport per km was taken into consideration

Tables 6 and 7 show that:

- Bioaccumulation of toxic metals was not recorded in trefoil crops over the legally admissible limits in Romania i.e. for Cd, Cr and Pb (R. LACATUSU & al.[24]).
- There was in the plant tissue from harvest II a 65.9% lower bioaccumulated amount of iron compared to plant tissue of aerial parts from harvest I.

The bioaccumulated amounts of Cu, Mn, Ni, Zn in aerial tissues were not excessive. The amount of Cu in the plants was in the range 4.97-9.69 g/kg d.m., the amount of Mn in the range 29.2-66.7 g/kg d.m., the amount of Ni between 2.49-5.05 g/kg d.m., and the amount of Zn was in the range 42.53-78.5 g/kg d.m. (thepermited amount of Zn is 100 g/kg d.m.).The biomass resulting from these cultures for phytoremediation of oil-contaminated soil may be used as the cellulose addition in the process of composting. Table 8 summarizes the cost of the researched phytoremediation process.

Table 8. Costs for the phytoremediation with trefoil of oil-polluted soils

Agricultural work	Cost
Plowing	400 RON / ha
Sowing the trefoil seed	320 RON / ha
Watering	50 RON / ha
Herbicide treatment	50 RON / ha
Mowing and raking	260 RON / ha

** A medium transport per km was taken into consideration

The calculation for phytoremediation in this case indicates a cost of about EUR 75-85 / t polluted soil / year for greatly polluted soils (more than 10% TPH).

4. Conclusions

During 490 days, the oil-polluted soils exposed to alternating natural hydroclimatic conditions lost up to 48.4% TPH. Similar effective reduction of 64.6-64.7% TPH was obtained either by inducing microbial metabolism activity due to content of sewage sludge or by using an optimum amount of ash in the absence of sludge, which can reduce the strong stress caused by this pollution and enables metabolic activities in the rhizosphere of trefoil. Addition of ash in the case of soil variants polluted with 113.5 g/kg d.m. and treated with 500 g / pot sewage sludge led to a normal development of trefoil plants during growth, maturation and fruiting until the harvest stage. Reducing oil content in soil was determined by weather conditions (alternation of seasons) and the stage of plant development. The use of optimal amounts of ash caused the formation of vigorous crops capable of complex metabolic processes of petroleum products. The efficiency in reducing TPH during the period of 490 days reached up 80-91.8%. The bioaccumulation of toxic metals recorded in the trefoil crops were not over the limits currently admitted by Romanian legislation for Cd, Cr and Pb. The allowed amount of Zn in fodder is 100 g/kg d.m.. Varying the amount of ash did not affect the amount of bioaccumulated metals. The resulted trefoil crops can be used as additives suitable for nontoxic waste composting. From a technical standpoint, this method can be used in any situation, but the cost-benefit analysis involves taking into account all costs and benefits, whether they are free or not. Prevention costs are sometimes included in direct costs, but the cost-benefit analysis must show future benefits that are obtainable from a project. The cost for phytoremediation of oil-polluted soils is lower than the one of conventional methods. After phytoremediation, the soil can be used as the agricultural soil.

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