The Use of Adsorbent Materials of Improving the Characteristics of Polluted Soils, Part 1 Phytoremediation of Soils Polluted with Oil Products, Cultivated with Technical Plants

Smaranda Mâşu[1], Maria Popa[2], Florica Morariu[3]

[1]National R & D Institute for Industrial Ecology, Branch of Timisoara, 300004-Timisoara, Regina Maria 1, Romania
[2]"1 Decembrie 1918" University of Alba Iulia, Science Faculty, 510009-Alba Iulia, N. Iorga 11-13, Romania
[3]Banat's University of Agricultural Sciences and Veterinary Medicine "King Michael I of Romania" from Timisoara, Faculty of Animal Science and Biotechnologies, 300645-Timisoara, Calea Aradului 119, Romania

Abstract

In this study are presented in pot experimental variants regarding alternatives to improve the characteristics of soils polluted with 74.12 ± 3.50 g kg^{-1} D.M. total petroleum hydrocarbon (TPH) in order to apply the phytoremediation process using technical plants from the common flax (*Linum usitatissimum*). The harmful effects of TPH polluted soils to plants was reduced by using fly ash from thermal plant as temporary adsorbent of non-polar pollutants, petroleum products. The increase of water retention capacity of the soil was achieved by treatments with indigenous volcanic tuff. The lack of nutrients, based on N and P in soils contaminated with TPH rich in C compounds are completed using sewage sludge anaerobically stabilized. The use of appropriate amounts of fly ash and fertilizer agents in the presence of volcanic tuff caused the formation of strong networks of roots and rich harvests of plants, stems and seeds from the treated soil. The TPH reduction efficiency of TPH polluted soils treated with fly ash (TPH soil: fly ash ratio 12:1 wt./wt.) and anaerobically stabilized sewage sludge respectively indigenous volcanic tuff during one vegetative cycle of crops was in the range of 56.2-63.25%.

Keywords: fly ash, phytoremediation process, sewage sluge, total petroleum hydrocarbon.

1. Introduction

Many studies on the phytoremediation of soils contaminated with Total Petroleum Hydrocarbon (TPH) show conflicting results regarding the efficiencies and performance technologies to reduce pollutants in soils using plant crops. But it has been shown that for the successful implementation of this method, variants that take into account the specific location of the polluted sites: geographic position, hydrodynamic regime, pollution characteristics, etc. should be used [1-3]. The selection and use of plants adapted to the area has the advantage that they can adapt and tolerate high concentrations of pollutants in the soil and is actually the key to the success of the phytoremediation process [4-6]. Based on these considerations many studies investigating the effects of pollution with petroleum products on plant growth have been made. A major deficiency of soils contaminated with TPH is the large excess of carbon compounds detrimental to the nitrogen compounds. Fertilization with organic fertilizers can bring the polluted soils the nitrogen quantities needed for both plant growth and the development of microorganisms [7]. In these circumstances it

* Corresponding author: Smaranda Mâşu
Tel: +40720080559, Email: andamasu@yahoo.com

was reported that the metabolic activity of microorganisms and plants increased the efficiency of reduction of petroleum products in a soil sustaining an installed culture. The potential of phytoremediation of some studied plants on soils highly polluted with oil is also influenced by both the composition of petroleum products on the growth parameters of these plants as it is by the type of soil treatment. It was reported that additions were used: clean soil, peat, humus, mixtures of clean soils and fresh manure in these phytoremediation processes of soils contaminated with TPH [8-9]. The results reported in studies on phytoremediation of soils contaminated with 0.1–5% (w/w) of crude oil using plants such as sorghum, fescue, flax etc. show that flax showed a high tolerance to pollutants present in soils proposed for phytoremediation [8, 10]. The ability of some plants like common flax and tall fescue to grow in soils contaminated with crude oil, demonstrated their phytoremediation potential [10]. In the case of heavily polluted soils the TPH removal process takes a long time even if the selected plants show a high tolerance to this pollutant. In case that after the end of the vegetative cycle of the selected crop, residual soil pollution still shows, it can be further cultivated with plant species in order to continue the metabolic processes of TPH elimination. [8, 11]. This study followed the advantages of a phytoremediation process with industrial crops of the species the common flax (*Linum usitatissimum)* by monitoring: the amount of biomass from stalks and seeds harvested from the experimental variants of polluted soils fertilized with sewage sludge anaerobically stabilized. In addition, it was studied the reduction of the quantities of petroleum in the contaminated and cultivated soils compared to the amount of oil from the polluted soil on which these plants were not seeded.

2. Materials and methods

The experimental study is performed on polluted soils. The initial soil was polluted with 80.52±3.90 $g \cdot kg^{-1}$ DM of TPH, and was taken from an area related to oil extraction activities or a park of oil drilling probes. Soil pollution began with oil extraction activities in the area. The area was polluted because of accidental leaks, malfunctions etc. This soil was mixed with fly ash in a proportion of polluted soil with TPH: fly ash ratio 12:1 wt./wt. resulting in a polluted soil P with a content of 74.12±3.50 $g \cdot kg^{-1}$ DM. The increase of water retention capacity of soils contaminated with TPH was achieved by using indigenous tuff from the Mirsid quarry of 0.2-2.0 mm grain. Polluted soil fertilization was performed with anaerobically stabilized sewage sludge taken from a municipal wastewater treatment plant. Experimental variants of soil cultivated with flax were: Polluted soil P mixed with fly ash and fertilized with sewage sludge 0.5 kg per growth vessel, BI-1; Polluted soil P mixed with fly ash and fertilized with sewage sludge 0.25 kg per vessel, BI-2; Polluted soil P mixed with fly ash and fertilized with sewage sludge 0.05 kg/vessel, BI-3; Polluted soil P mixed with fly ash and fertilized with sewage sludge 0.05 kg per vessel and an added indigenous tuff amendment of 0.05 kg per vessel, BI-4. The quantities of fertilizer and amendment were thoroughly mixed with polluted soil. The control version was the arable soil cultivated with flax, M. Each experimental variant contains three replicas. The plants used for phytoremediation of soils heavily contaminated with TPH were from the common flax (*Linum usitatissimum)* species. In order to determine the variation of TPH in soils, their concentration is periodically determined, in the top layer of the vegetation pot (2 cm depth). The soil is dried and ground through a 5 mesh sieve. To determine the TPH from the soils an analysis is performed periodically of the concentration [8], in the upper level: 1) 0.5-1.0 g of dry soil are weighed (M), then add 5g Na_2SO_4 anhydrous and 25ml solvent, CCl_4 (Fluka Analytical); 2) 30 minutes stirring at 50 rotations/min and then filtered; 3) the glass and filter paper (Whatman No. 4 paper) are washed with solvent CCl_4, which is added to the filtrate; 4) the filtrate is evaporated on water bath; 5) the residue is dissolved in CCl_4, then passed through the chromatographic column filled with aluminium oxide. The elute was collected in a tarred capsule, m_1 [g]; 6) CCl_4 is evaporated at room temperature and weighed at constant mass, m_2 [g]; 7) the same is done for the control from 28 ml CCl_4 (m_3–mass of capsule without control residue [g], m_4–mass of capsule with control residue [g]); 8). Calculating TPH:

$$TPH\ [g \bullet kg^{-1}] = 1000 \bullet [(m_2 - m_1) - (m_4 - m_3)] \bullet M^{-1}$$

3. Results and discussion

TPH harmful effects of polluted soils on plants was reduced by using fly ash from thermal plants as a temporary adsorbent of non-polar pollutants like petroleum products. Plants grow and bear fruit on all the experimental variants. The harvest was conducted after 100 days of vegetation with the conclusion of the vegetative cycle, seed ripening. Table 1 presents in percentages the amounts of plant aerial parts (industrial strains) harvested from experimental variants of THP polluted soils treated with fly ash and fertilizer compared to the control variant, the harvest from an unpolluted agricultural soil. The amount of harvested flax stems in the BI-1 experimental variant fertilized with the highest amount of fertilizer was 58.8% vs. the amounts of stems obtained in the experimental variant of unpolluted agricultural soil. Decreasing the amount of fertilizer resulted in decreasing the amount of harvested flax stems. The addition of indigenous tuff to the experimental variant that used the least amount of fertilizing agent determined an increase in the amount of harvested stems of 12% vs. the quantity harvested from the variant untreated with volcanic tuff. The highest amount of flax seeds was harvested from the experimental version fertilized with an average amount of fertilizing agent. The quantity of harvested flax seeds was 47.7% vs. the amounts of flax seeds harvested from the experimental variant of unpolluted agricultural soil. Increasing the amount of fertilizer did not determine an increased harvested amount.

Table 1. The quantities of common flax harvested stems and seed from the experimental versions of treated, TPH polluted soils compared to the quantities harvested from the control, unpolluted version

No.	Experimental variants	Quantities of common flax aerial plant parts harvested from experimental variants, polluted untreated / treated vs. control sample [%]	
		Stems	Seeds
1	BI-1	58.6	34.6
2	BI-2	46.9	47.7
3	BI-3	33.7	20.0
4	BI-4	45.9	29.8

The addition of volcanic tuff to the variant that used the least amount of fertilizing agent determined an increase in the quantity of harvested seeds up to 10 % vs. the same variant in the absence of volcanic tuff. The quantities of plant roots of common flax in the experimental variants using THP polluted soils and treated with fertilizers and amendments, volcanic tuff and/or ash compared with quantities of roots from the unpolluted control version are presented in Table 2. It is seen from Table 2 that the common flax roots have grown where we used the highest amount of sludge. In this case an amount of $8.8 g\cdot kg^{-1}$ was collected, which is 69.3 % of unpolluted soil roots formed on the control variant. The lowest amount of roots was obtained from the variant fertilized with the least amount of sludge. In this case the amount of roots represents only 48.1 % of the amount formed on the control version.

Table 2. The amounts of common flax roots resulting from experimental variants unpolluted and THP polluted, untreated/treated

No.	Experimental variants	The quantities of harvested common flax roots from the studied experimental variants	
		$g\cdot kg^{-1}$ DM	% vs. control
1	BI-1	8.80	63.9
2	BI-2	6.55	51.9
3	BI-3	6.11	48.1
4	BI-4	9.75	78.0

Addition of tuff to this latest variant caused a 30 % increase to the amount of formed roots compared to the amount formed on the variant untreated with tuff. In conclusion, the largest amount of fertilizer caused the formation of a dense and rich network of roots and therefore a large amount of strains. However the highest amount of seeds was obtained from the variant that has a less-developed network of roots and strains. This case corresponds to the case where the overall quantity of fertilizer used was reduced by 50% compared to the amount where plants had the best development in the experiment. Analyzing the content of TPH from a 0-30cm soil layer showed that TPH content was considerably reduced compared to pollute soils as shown in Figure 1. It is observed from the figure that in the early stages of plant development i.e. 40 days from the formation of the vegetation cover, the reduction efficiencies of TPH in the soil were located in all the studied cases between 25.1-31.1%. At the end of the vegetative cycle, TPH reduction efficiencies were in the range of 56.2-63.25%. On these soils containing residual TPH is necessary to cultivate a plant species more sensitive to heavy soil pollution such as herbaceous plants. The residual TPH content in the soil after plant harvesting is of 27.0-32.5 $g \cdot kg^{-1}$ D.M. To obtain normal, unpolluted soils a new phase of phytoremediation is required. The next stage of phytoremediation can be achieved by growing a plant species susceptible to heavy TPH soil pollution such as grasses.

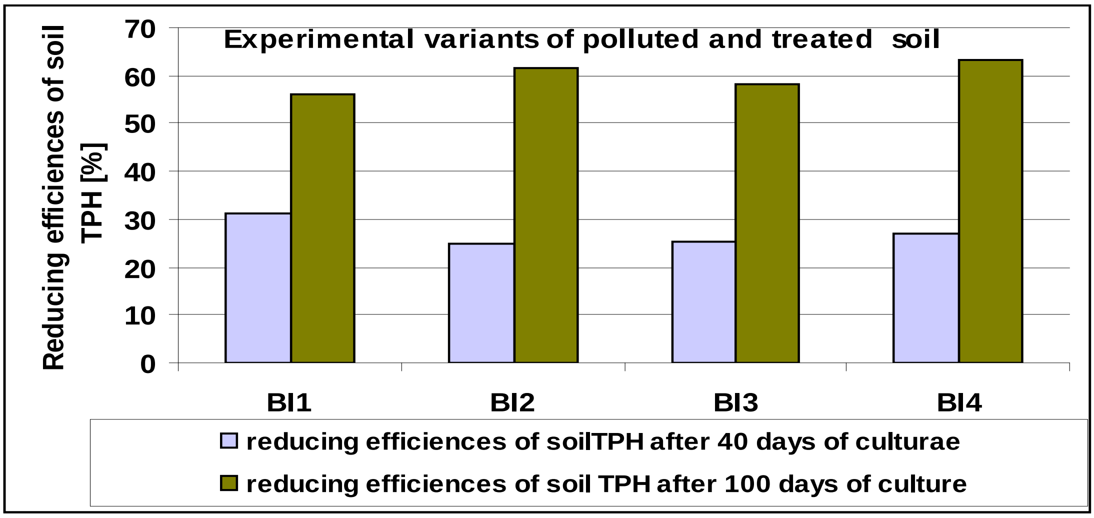

Figure 1. The efficiency for reducing oil content from polluted soils cultivated with flax, compared to the initial concentration

4. Conclusions

Soils contaminated with 74.12±3.50 $g \cdot kg^{-1}$ DM oil products can be phytoremediated in a first stage with plants tolerant to high levels of pollution, such as flax. TPH harmful effects of pollutants on plants grown on polluted soils was reduced by using fly ash from thermal stations as a temporary adsorbent of polar pollutants like petroleum products. (TPH polluted soil: fly ash ratio 12:1 wt./wt.). Soils contaminated with TPH compounds are rich in C, but with a high deficiency of nutrients based on N and P. The lack of these nutrients is solved by using urban sludge, anaerobically stabilized. The increase of water retention capacity of soils contaminated with predominantly non-polar petroleum products was done with the use of indigenous volcanic tuff. The use of appropriate amounts of fly ash and fertilizer agents in the absence/presence of volcanic tuff caused the formation of strong networks of roots and rich harvests of common flax (*Linum usitatissimum)*, stems and seeds from the treated soils. The TPH reduction efficiency of soils treated with fly ash during one vegetative cycle of flax crop was in the range of 56.20-63.25%. Residual TPH content in the soil after the plant harvest is of 27.0-32.5 $g \cdot kg^{-1}$ DM. In a first stage of phytoremediation, alterations to the characteristics of soils were made and their preparation for a subsequent stage of cultivation of plants that complete restoration was achieved. The next stage of phytoremediation can be achieved by cultivating plant species more sensitive to heavy TPH pollution such as herbaceous plants.

References

1. Hutchinson, S. L., Banks, N. K., Schwab, A. P., Phytoremediation of Aged Petroleum Sludge: Effect of Inorganic Fertilizer, J. Environ. Qual., 2001, 30, 395-403
2. Collins, C. D., Implementing Phytoremediation of Petroleum Hydrocarbons, Methods in Biotechnology vol. 23 Phytoremediation: Methods and Reviews, Eds. N. Wiley, Humana Press Inc., Totowa, New Jersey, USA, 2009
3. Pinedo, J., Ibáñez, R., Lijzen, J. P. A., Irabien, Á., Assessment of Soil Pollution Based on Total Petroleum Hydrocarbons and Individual Oil Substances, Journal of Environmental Management, 2013, 130, 72-79
4. Kaimi, E., Mukaidani, T., Tamaki, M., Screening of Twelve Plant Species for Phytoremediation of Petroleum Hydrocarbon Polluted Soil, Plant Product Sci., 2007, 10, 211-219
5. Muratova, A. Y., Golubev, D. N., Dobrovskaya, E. V., Pozdnyakova, N. N., Panchenko, L. V., Pleshakova, E. V., Chernyshova, M. P., Turkovskaya, O. V., Remediating Abilities of Different Plant Species Grown in Diesel-Fuel-Contaminated Leached Chernozem, Applied Soil Ecology, 2012, 56, 51-57
6. Sharonova, N., Breus, I., Tolerance of Cultivated and Wild Plants of Different Taxonomy to Soil Contamination by Kerosene, Science of the Total Environment, 2012, 424, 121-129
7. Ambroziak, B. C., Bowszys, T., Wierzbowska, J., Fungi Colonizing Soil Fertilized with Composted Sewage Sludge and Municipal Wase, J. Elemental, 2010, 15(1), 39-51
8. Shirdam, R., Zand, A. D., Bidhendi, G. N., Mehrdadi, N., Phytoremediation of Hydrocarbon-Contaminated Soils with Emphasis on the Effect of Petroleum Hydrocarbon on the Growth of Plant Species, Phytoprotection, 2008, 89(1), 21-29
9. Lau, S. S. S., Wong, J. W. C., Toxicity Evaluation of Weathered Coal Fly Ash Amended Manure Compost, Water, Air, Soil pollut., 2001, 128, 243-253
10. Khodaei, H. R., Rabrizi, A. M., Zand, A. D., Ability of Common Flax and Tall Fescue to Grow in Crude Oil Contaminated Soil and Their Phitoremediation Potential, Proceedings of the 12 International Conference on Environmental Science and Technology, Rhodes, Grecea, 8-10 sept. 2011
11. Inckot, R. C., De Olivera Santos, G., De Souza, L. A., Bona, C., Germination and Development of Mimisa Pilulifera in Petroleum Contaminated Soil and Bioremediation Soil, Flora, 2011, 206, 261-266
12. Mâșu, S., Dragomir, N., Popa, M., The Variation Oil Products in Contaminated Soil Cultivated with Leguminous Species, Journal of Environmental Protection and Ecology, 2013, 14(3), 901-906