

ADVANCED METHODOLOGIES FOR THE TREATMENT OF HYDROCARBON CONTAMINATED SLUDGES FROM SOIL WASHING PROCESSES

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Abstract

Fine products (silt-clay fractions) from soil washing plants are normally highly contaminated due the great capacity to sorption the contaminants. The usual destination of these fractions is its disposal in dump or thermal destruction (in case of organic contaminants) with the consequential environmental impact. Preliminary physical-chemical and bioremediation treatability tests carried out on a sludge sample contaminated with hydrocarbons proceeding from a soil washing plant are presented in this paper. Until now best results were obtained in two bioremediation process tested at lab scale: landfarming and bioreactors, in which it have reached reduction hydrocarbon rates higher than 50% in two months and one month respectively.

Keywords: *sludges, hydrocarbon, soil washing, remediation technologies.*

INTRODUCTION

In soil treatments, fine products (silt-clay fractions) are normally highly contaminated due the great capacity to sorption the contaminants. The usual destination of these fractions is its disposal in dump or thermal destruction (in case of organic contaminants) with the consequential environmental impact. It is necessary to study alternative treatments friendly with the environment for these fractions with the aim to be reused in the same site.

Different remediation techniques are able to destruct or degrade organic contaminants as bioremediation that can be directed toward stimulating the microorganisms to grow and use the

contaminants as a food and energy source by creating a favourable environment for the microorganisms. Although not all organic compounds are amenable to biodegradation, bioremediation techniques have been successfully used to remediate soils, sludges, and ground water contaminated by petroleum hydrocarbons, solvents, pesticides, wood preservatives, and other organic chemicals.

Treatability or feasibility studies are used to determine whether remediation would be effective in a given situation. The extent of the study can vary depending on the nature of the contaminants and the characteristics of the site. For sites contaminated with common petroleum hydrocarbons (e.g., gasoline and/or other readily degradable compounds), it is usually sufficient to examine representative samples for the presence and level of an indigenous population of microbes, nutrient levels, presence of microbial toxicants, and sample characteristics such as pH, porosity, and moisture.

The objectives of remediation processes are usually based on threshold levels of soil contaminants. However, during remediation processes, changes in bioavailability and obtaining of metabolites can occur. Consequently, it is necessary to incorporate ecotoxicity assessment to estimate the risk to ecological receptors.

The possibilities of treatment of sludges (fine fraction) proceeding from a soil washing plant on a site contaminated by hydrocarbons were studied and the preliminary results are shown in this paper.

EXPERIMENTAL

Sample characterisation

The sample studied is the sludge fraction of a soil washing plant from a site contaminated by hydrocarbons. Sample collected from the plant, was mixed, air dried and thoroughly disaggregated, homogenised and stored at 4°C until its use.

The physical properties of the sample were performed according the standard procedures [2]. The grain size characterisation was carried out by elutriation using a Cyclosizer equipment.

The hydrocarbon content was determined by GC-FID chromatography determining aliphatic and aromatic hydrocarbons fractions in the range C10-C40. Also total petroleum hydrocarbon (TPHs) was determined by IR using the portable InfraCal analyzer.

The ecotoxicological effects of the sample was tested by using a multi-species-soil system (MS-3), which consisted of a terrestrial microcosm in soil columns [1].

Control soil for ecotoxicity test was collected from a surface layer of a field located near Madrid (Spain). Soil was air dried and sieved (2-mm mesh). Main physicochemical characteristics of this soil were: clay 7.8%, silt 18.8%, sand 73.4 %; pH 7.27 and organic C 1.09%. Samples of hydrocarbon contaminated sludges were homogeneously mixed with control soil at different concentrations (100, 90, 50, 25 and 12.5 test soil, w/w). Toxicity to soil and aquatic organisms was tested as described in [1].

Treatability study

Two different treatments: physical-chemical and biotreatment were studied. Within the first category, it was studied the possibilities of flotation technique aimed to pre-cleaning the sample trying to remove materials associated with hydrocarbons.

The flotation was carried out in a conventional Denver cell flotation of 2.5 L.

Also, the possibilities to oxidise the hydrocarbons by leaching with Fenton reagent were studied. The tests were carried out at lab scale using stirred reactors studying the different parameters of the process: pulp density, pH, concentration of Fenton reagent and time. In second category, at lab scales the processes of landfarming and bioreactors on initial sample were studied. Lanfarming simulation

tests were carried by respirometry at different conditions in microcosms following the oxygen consumption and carbon dioxide production by the respirometer Micro-Oxymax of Columbus Instruments equipped with an I.R. sensor of CO₂ and paramagnetic sensor of O₂ (Figure 1).



Figure 1. Respirometry with Micro-Oxymax respirometer

The respirometer is provided of 20 independent chambers being possible study the oxygen consumption and carbon dioxide production in each chamber in a simultaneous way. The chambers are ISO flask of 250 mL containing 20 g of sample at conditions to study.

Optima conditions of: moisture respecting water holding capacity of sample, addition of nutrients to establish an adequate C:N:P ratio and time of treatment , were studied .

Due to very fine texture of sample, the material was amended with barley straw to facilitate its aeration and handling. Amended assay (with nutrients) were compared with control assay (without nutrients). All samples were rolling over weekly to facilitate aeration. All tests were carried out by triplicate.

Test lasted 61 days and samples at different times were sacrificed analysing the hydrocarbon content to evaluate contaminant biodegradability and biodegradation rate.

Biotreatment simulating with bioreactors was carried out at lab scale using Erlenmeyer flasks of 1 L magnetic stirred at different pulp density. It was tested the addition of nutrients and time of treatment.

According with results obtained at lab scale, the optima conditions would be applied at pilot scale: a landfarming of 4000 kg of sample and in a BioEIMCO air-lift plant with three reactors of 60 L.

RESULTS AND DISCUSSION

The main physical parameters of the sample studied are in Table 1.

Table 1: Physical characteristics of initial sample.

Physical characteristics	
Parameter	Value
pH	8.2
Conductivity ($\mu\text{S}/\text{cm}$)	1002
Moisture content (%)	45.33
WHC (%)	61.02
Total C (%)	2.6
Total Inorganic C (%)	1.3
Black C (%)	0.3
Total organic C (%)	1.0
Oxidable organic carbon (%)	0.8
Total Nitrogen (%)	0.09

In Table 2 appears the hydrocarbon characterisation of the sample. The TPHs content obtained by IR was of 2262 mg/Kg. The results of the particle size analysis and its TPHs distribution have shown that higher than 80% of hydrocarbons are in particles less than 11 μm . The ecotoxicological characterisation of initial sludge sample showed toxicity to all soil organisms. Earthworms were the least sensitive organisms. Adult earthworms survival was only adversely affected at the highest sludge concentrations (100%), with a 10 ± 0 % of mortality.

Table 2. Hydrocarbon composition of initial sample and optimised treated sample.

Content (mg/Kg)	Initial sample	Treated sample	TPHs Reduction (%)
Aliphatic hydrocarbons			
C10-C12	5.4	4.1	24
C12-C16	396.2	89.1	77
C16-C21	837.7	476.2	43
C21-C35	446.0	395.2	11
C35-C40	18.3	12.8	30
Total aliphatic hydrocarbons	1703.6	977.4	43
Aromatic hydrocarbons			
C10-C12	< 3.0	< 3.0	
C12-C16	90.3	3.4	96
C16-C21	274.6	34.4	87
C21-C35	163.6	72.4	56
C35-C40	11.3	6.2	45
Total aromatic hydrocarbons	539.8	116.4	78
Total C10-C40	2243.4	1094	51.2

Exposure-concentration response relationships were described for plants and microorganisms. In the plant assays, sludge contaminants affected the emergence of

seedlings and the plant growth with EC50 values ranging from 43 to 71 % (w/w). No differences were observed between different plant species. Toxicity to microorganisms was determined using three parameters: mineralization rate induced by glucose and two enzymatic activities: deshydrogenase activity and phosphatase activity. Carbon mineralization significantly decreased respect to control soil, although effects on microorganisms were less than in plants (EC50 >100%, w/w). However, an increase of enzymatic activity was observed for both phosphatase activity ($213 \pm 28\%$) and deshydrogenase activity ($110 \pm 25\%$) at 100% of sludge concentration.

Leachates obtained from the sludge did not showed toxicity to aquatic organisms: algae, daphnia and fish cell lines. The lack of toxicity of the leachates indicated a very low transfer of contaminants from soil to water, which was confirmed by chemical analyses.

Preliminary flotation tests showed the difficulty to segregate adequately a fraction where hydrocarbons were mainly concentrated. The tests carried out until now by Fenton process have shown that is possible to oxidize around 30% of hydrocarbons in 24 hours at 15% of pulp density (w/v) but it is necessary work at pH 3 with the consequent sulphuric acid consumption.

Treatability test simulating landfarming, in which three moistures (60%, 70% and 80% of WHC) and nutrients additions (Control, CNP 100/10/1 and CNP 100/10/0.5) were studied, showed that best results were obtained at 70%WHC and CNP 100/10/1. In the Figure 2 are represented the evolution of oxygen consumption during time for these tests.

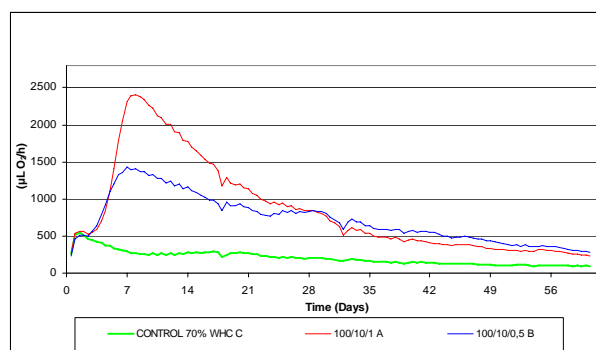


Figure 2. Oxygen consumption rate for control and amended samples.

Figure 3 shows the TPHs reduction obtained in these conditions comparatively with control test during assay time. Table 2 compares the hydrocarbon content and its fractionation after treatment respect to the initial sample. A TPHs reduction of 51% was obtained in two months.

Treatability test simulating a bioreactor process carried out until now, have studied the influence of pulp density from 1 to 20 % w/v and nutrients addition. The best results were obtained at 1% with nutrients addition with a

reduction rate of 72% in 28 days, but obviously this is not feasible. However promising results were obtained at higher pulp density. In Figure 4 are represented the evolution of TPHs reduction during time in tests carried out at 10% pulp density with nutrients addition.

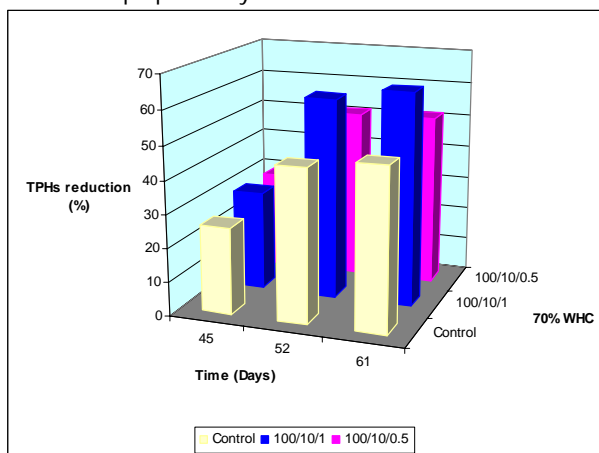


Figure 3. Evolution of TPHs reduction (%) comparatively for control and amended samples.

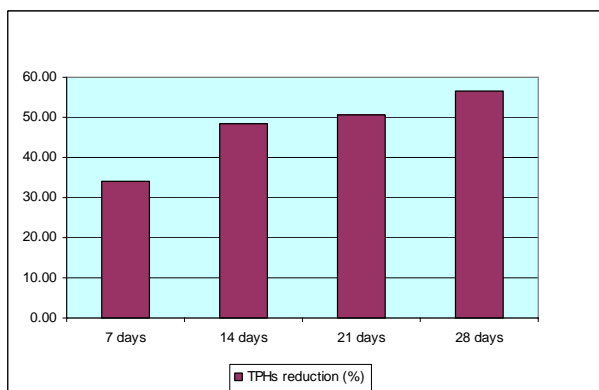


Figure 4. Evolution of TPHs reduction (%) at 10% of pulp density.

A TPHs reduction of 57% was obtained in 28 days of treatment. In Figure 5 we can observe the hydrocarbon degradation suffered after biotreatment comparatively with initial sample.

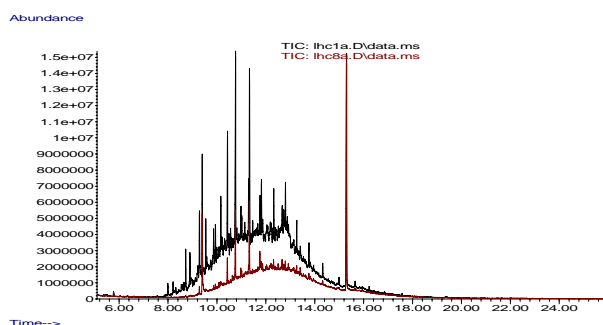


Figure 5. GC-MS Total ions Chromatograms of initial sample and biotreated sample (red).

From these preliminary results, tests programmed are landfarming at pilot scale on contaminated site and air-lift bioreactor pilot plant at IGME.

CONCLUSIONS

The conclusions obtained with preliminary treatability tests carried out until now are the next:

- The main problem that presents the material to treat is the fine texture and the association of hydrocarbons in these particles.
- Physical-chemical treatments studied until now have not got good results, with Fenton process the hydrocarbon oxidation was of 30%.
- By change, in biotreatments studied at lab scale, landfarming and bioreactors simulation, the total hydrocarbon reduction rates are higher than 50%, been more effective to aromatic hydrocarbons, around 80%.

Taking into account these preliminary results, tests on pilot scale will be carried out checking the feasibility of the processes not only in terms of on threshold levels of hydrocarbon contaminants but incorporating ecotoxicity assessment to estimate the risk to ecological receptors.

REFERENCES

- [1] Fernández, MD; Cagigal, E; Vega, MM; Urzelai, A; Babín, M; Pro, J; Tarazona, JV. (2005) Ecological risk assessment of contaminated soils through direct toxicity assessment. *Ecotoxicology and Environmental Safety*, 62, 174-184.
- [2] Guitián-Ojea, F. and Carballas, T. *Técnicas de análisis de suelos*. Pico Sacro, Santiago de Compostela, Spain. (1976).
- [3] Kukor, J, J y col. Remediation of contaminates including low bioavailability hydrocarbons. United States Patent 20020034421 (2002).
- [4] Lorch, H.J., Benckieser, G., Ottow, J.C.G.(1995). Basic method for counting microorganisms in soil and water. In: *Methods in Applied Soil Microbiology and Biochemistry*. pp 146-161. (Alef, K. and Nannipieri, P. Eds.). Academic Press, New York.
- [5] Soni y col. Secuencial biological / chemical / biological treatment of organic waste. United States Patent. 5,955,350 (1999).
- [6] Stieber, M., Haeseler, F., Werner, P. and Frimmel, F.H. (1994) A Rapid Screening Method for Micro-organisms Degrading Polycyclic Aromatic Hydrocarbons in Microplates. *Applied Microbiology and Biotechnology* 40, 753-755.
- [7] Swedish Environmental Protection Agency. 1993. Guidelines. Soil biological variables in environmental hazard assessment. Report 4262. Torstenson L, ed. Solna, Sweden.

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