# USE OF CRUDE COFFEE GRAIN FOR TREATMENT OF PETROLEUM HYDROCARBON-CONTAMINATED SOIL

***G. A. Roldán-Martín, R. Rodríguez-Vázquez***
*Centro de Investigación y Estudios Avanzados del IPN (CINVESTAV) Av. Instituto Politécnico Nacional 2508 Col. San Pedro Zacatenco, 07360 Apartado postal 14-740, 07000 México, D.F.*
*aroldanm@iingen.unam.mx, rrodrig@mail.cinvestav.mx*

## ABSTRACT

The environmental pollution caused by toxic compounds is a global problem. In Mexico, a number of diverse technological options in biological processes have been tested for the restoration of sites contaminated with hydrocarbons. One of these processes is the addition of organic bulking agents to improve the characteristics of soil and to enhance the removal of the contaminant. The present research was designed to evaluate the crude coffee grain as a bulking agent in biopiles and to increase the biodegradation of petroleum hydrocarbons in contaminated soil. The first part of the work consisted in designing the biopile and the second, in the evaluation of the biopile. Sampling were done every week during the first month, every fifteen days during the second, and every month during the third stage. Along the treatment; humidity, pH, organic matter, phosphorus, nitrogen and Total Petroleum Hydrocarbons (TPH) were determined. The conditions of the tests were: humidity, 30%; soil/agro-industrial waste ratio, 98:2 and C:N:P ratio, 100:10:1. The process consisted on placing the biopile (23 kg) in a rectangular glass container and mixing the contaminated soil with the required nutrients and humidity. The nitrogen source was $(NH_4)_2SO_4$ and the phosphorus, $K_2HPO_4$ .The initial concentration of soil contaminant was 58 000 ppm of TPH. The highest degree of TPH's removal (65%) was attained at 90 days.

## INTRODUCTION

Composting is a biological aerobic decomposition of organic materials in which conditions are strictly controlled in order to help the thermophilic microorganisms to transform organic materials into a stable, soil like product. (Miller, 1993; Rymk, 1992). In order to increase these transformation rates and use compost for industrial purposes, it is necessary to optimize microbial growth. This means optimizing oxygen concentration, pH, moisture content, carbon to nitrogen ratio(C:N) and particle size (Miller, 1993; Rymk, 1992). There are a variety of composting systems including; in-ground trenches, rotary drums, circular tanks, open bins, silos, windrows and open piles. Aerobic composting gives a higher degree of decomposition for many compounds. Thus, most composting systems utilize bulking agents (such as bark chips, straw and chopped sugar beet), which increase the porosity and, therefore, aerobicity of the medium under treatment and decrease the moisture levels

There are numerous examples about employing bioremediation against pollutants. to remove and/or transform pollutants (Bollag & bollag, 1995). Among the specific methods used for bioremediating contaminated soil and water.

The use of composting strategies in biodegradation/bioremediation of organic pollutants have been seriously adopted; as a result, there is a lack of general information as well as a limited number of pollutant/pollutant mixtures treated. Pollutants investigated include petroleum hydrocarbons, monoaromatics (benzene and toluene), explosives [2,4,6-trinitrotoluene (TNT)], chlorophenols [pentachlorophenol (PCP)], pesticides [2, 4-dichlorophenoxyacetic acid (2,4-D) and diazinon] and polycyclic aromatic hydrocarbons (PAH's) (anthracene, phenanthrene, benz[a]anthracene and benzo[a]pyrene). (Sample, 2001) PAH's are perhaps the most studied of these contaminants.

With the previous antecedents it is possible to say that the bulking agents (agroindustrial waste) help the removal of pollutants and that with small ratios of soil:bulking agents the removal is greater.

## MATERIAL AND METHODS

**Characterization of soil and coffee grain samples.** Soil and coffee grain were analyzed for moisture content, pH, organic matter, total nitrogen, assimilable phosphorus, total carbon. The moisture content was determined by a gravimetric method, by a weight difference (Gardner and Klute, 1982). The assimilable phosphorus was analyzed by the method of Bray and Kurtz (Olsen, 1982). The organic matter was determined by the method of Walkley and Black (Nelson and Sommers, 1982), and total nitrogen by the Kjeldahl method (Bremner, 1982). The pH was determined in a 1:1 sample to water mixture (Mc Lean, 1982), using a potentiometer OAKATON. In addition, the field capacity, real and apparent density, particle-size distribution and TPH content of the experimental soil and ash, cellulose and lignin content of coffe grain also were determined

**Desing and Building of Biopile.** Factors as geometry, aeration system, addition of nutrients and the construction process were evaluated, The biopiles were designed in the laboratory for a volume of 0,02977 $m^3$ and 23 kg, with a concentration of 58 000 mg TPH $Kg^{-1}$ of soil., the conditions of nutrients C:N:P were 100:10:1, and a soil:coffee grain ratio of 98:2. The mixture was made manualy, to assure homogenous mixing. In this case, the biopiles were built with a moisture content in soil of 30,3 %. The aeration system was by injecting air using perforated glass tubes. For the biopile in field, the volume were 1$m^3$ and 1,200 kg of soil, the concentration of TPH's and condition of treatment were the same as in laboratory. The mixture was made using a shovel. The aeration system was passive by difussing oxygen through perforated tubes crossing the narrowest part of biopile.

**Biopiles Monitoring.** Monitoring of biopile consisted on sampling four different points from the laboratory biopiles. On the other hand, for biopile in field, 16 points of sampling at two heights were selected to cover significantly the whole bulk. The points were separated 50 cm horizontally. Sampling were done every week during the first month, every fifteen days during the second month and every month during the third stage for both biopile systems. During the treatment, humidity, pH, organic matter, phosphorus, nitrogen and TPH were determined.

**Determination of total petroleum hydrocarbons.** Hydrocarbons were extracted by agitation-centrifugation as reported by Schwab (1999). One gram of dry or humid soil, 2 g of $Na_2SO_4$ and 5 ml of dichloromethane were placed in a conical centrifuge tube. The mixture was shaken in a vortex for approximately 45 seconds and then it was put in a centrifuge at 6,000 rpm for 15 minutes this procedure was repeated three times. The three supernatant was kept for further use, 5 ml of dichloromethane were added. The dissolvent was evaporated from the extract in a rotaevaporator at 740 mbar and 40°C until 2 ml of volume were obtained. Once concentrated, the extract was analyzed by infrared spectroscopy by a Nicolet 470 FT-IR (EPA 418.1 method).

**Statistical analysis.** Analysis of correlation was performed using a software program SAS® 6.0. A comparison of means was made by using a LSD test at 0.05 of confidence

## RESULTS AND DISCUSSION

For the biopile in laboratory, the moisture content was 30,3%, which represents 90% of the field capacity, the texture of the soil was clay with a content of organic matter of 7,86%, pH 7.5, total Nitrogen 0.173(%), and 5,767 ppm of available. According to requirements of nutrients, previously calculated, it was necessary to add; as nitrogen source, 79.96g of ammonium sulphate; 342.05g of potassium phosphate as source of phosphorus and 460 g of coffee grain. In the case of biopile in field it was necessary to add 1,896.8g ammonium sulphate as nitrogen source; 6,349 g of sodium phosphate as source of phosphorus and 20 kg of coffee grain.

The removal of TPH's was evaluated after 7, 14, 21, 30, 45, 60 and 90 days of treatment. The percentage of removal in all the points of sampling in laboratory biopiles was similar at 7 days of treatment average of 40,600 ppm of TPH's was found by 14 days a 34,800 ppm of TPH's was obtained, at 21 days a 29,000 ppm, finnaly at the $90^{th}$ day the concentration had decresed to 23,200 ppm. For the case of biopile in field the final percentage of removal was 57% with small variability in all the biopile. For day 0 an average of 52,334 ppm of TPH's was found, to 14 days the concentration had decreased to 43,463 ppm, at 28 days to 35,791 ppm, at 42 days to 30,364 ppm, at 56 days to 23,687 ppm, at 70 days to 17,566 ppm, at the end of 84 days TPH decreased to 22, 578 ppm.

The nitrogen consumption was high in both biopiles (Laboratory and field) This could be a result of the high solubility of nitrogen added as $(NH_4)_2SO_4$ (Atlas and Bartha, 1998), which can easily be assimilated by plants and microorganisms (Sylvia *et al.*, 1999), unlike nitrogen from agro-industrial residues. The highest rate of phosphorus consumption was observed at the beginning of treatments. The consumption was high, because phosphorus is as necessary for cell maintenance as for microbial growth. In addition, low levels of phosphorus may not have been available to the microorganisms, due to adsorption into the soil (Liebeg *et al.,* 1999).

In the statistical correlation, we can observed that in both cases (laboratory and field) exist a correlation between TPH degradation and the other variables, (moisture content, phosphorus, nitrogen, pH and organic material), and it is particularily significant in the case of phosphorus and nitrogen.

## CONCLUSIONS

With the previous results it is possible conclude that the coffee grain can be used in the bioremediation of contaminated soil with hydrocarbons as a bulking agent and the treatment is cheaper than others technologies, also the time of treatment is shorter than treatment without coffee grain and the concentration residual of TPH's was lower that treatments without coffee grain (Data not show), finally the results obtained in biopiles in field and laboratory were similar.

## REFERENCES

Atlas, R.M., Bartha, R. 1998. *Microbial ecology: Fundamentals and Applications.* 4th edition. Benjamin/ Commings Publishing Company. Inc., California, USA.

Bremner, J.M. 1982. Total nitrogen. In: *Methods of Soil Analysis, Part 2* Page, A.L., Miller, R.H. & Keeney, D.R. (eds) American Society of Agronomy, pp. 1162-1165. Madison, WI

Gardner, H. W, Klute, A. 1982. Total water content and water capacity. In: *Methods of Soil Analysis, Part 2* Page, A. L., Miller, R.H. & Keeney, D. R. (eds) American Society of Agronomy. pp. 273-278. Madison, WI

Liebeg, E.W., Cutright, T.J. 1999. The investigation of enhanced bioremediation through the addition of

macro- and micronutrients in a PAH contaminated soil. Int. Biodeter. Biodegr., 44: 55-64.
McLean, E.O. 1982. Soil pH and lime requirement. In: *Methods of Soil Analysis, Part 2* Page, A.L., Miller, R.H., Keeney, D.R. (eds). American Society of Agronomy, pp. 199-224. Madison, WI.
Miller, F.C. 1993. Composting as process based on the control of ecologically selective factors. In *Soil microbial ecology*, F. B. Metting, Marcel Dekker (ed.). pp 515-544. USA
Nelson, D.W., Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. In: *Methods of Soil Analysis, Part 2* Page, A.L., Miller, R.H., Keeney, D.R. (eds). American Society of Agronomy, pp. 539-580. Madison, WI.
Olsen, S.R. 1982. Phosphorus. In: *Methods of Soil Analysis, Part 2* Page, A.L., Miller, R. H., Keeney, D. R. (eds). American Society of Agronomy, Madison, WI. pp. 1040-1042.
Rynk, R. 1992. Composting methods. In: *On-Farm composting handbook*. Ithaca: Northeast Regional Engineering Service, Cooperative Extension. pp 24-42.
Sample, K.T., Reid, B.J., Fermor, T.R. 2001. Review of composting strategies to treat organic pollutants in contaminated soils. Environ. Pollut., 112: 269-283.
Schwab, A.P., Su, J., Wetzel, S., Pekarek, S., Banks, M.K.1999. Extraction of petroleum hydrocarbons from soil by mechanical shaking. Environ. Sci. Technol., 33: 1940-1945.
Sylvia, D., Fuhrman, J., Hartel, P., Zuberer, D. 1999. *Principles and applications of soil microbiology*. Prentice Hall, USA.