Wat. Sci. Tech. Vol. 20, No. 10, pp. 231–236, 1988.
Printed in Great Britain.

0273–1223/88 $0·00+·50

THE DEVELOPMENT OF ASSESSMENT TECHNIQUES TO EVALUATE THE BIODEGRADATION OF OILY SLUDGE IN A LANDFARMING SYSTEM

D. C. P. Casarini*, R. M. de Macedo*,
R. C. de A. Cunha** and J. C. O. Mauger***

**Divisão de Solos, Águas Subterrâneas e Vegetação; **Gerência de Estudos e Pesquisas Ambientais, CETESB, Av. Prof. Frederico Hermann Jr. 345, 05459, São Paulo, Brazil*
****CRA — Centro de Recursos Ambientais, Ruo São Francisco No. 1, Monte Serrat, 40.000, Salvador, Bahia, Brazil*

ABSTRACT

A respirometer assay was developed with the intention of defining a standard methodology to identify the major mechanisms related to biodegradation of oily sludge in a landfarming system. The oily sludge is characterized as a biological sludge produced in an activated sludge wastewater treatment plant which treats industrial and domestic wastewater from a petroleum refinery. The effects of soil pH control, nutrient balance, and sludge application rates were investigated. It was concluded that the methodology is acceptable as a procedure to qualify waste for land treatment. The soil with pH control (pH about 7.0) was shown to be more effective in oily sludge biodegradation than without pH control. Under these experimental conditions, the best application rate for the oily sludge on soil was 1% (w/w) of its hydrocarbon content. Soil pH control, sludge nutrient balance, and sludge application rate are all of importance to optimize the system, to avoid leaching, and to protect the groundwater. The landfarming system has been used by several refineries.

KEYWORDS

Soil biodegradation; refinery oily sludge; landfarming; environmental parameters.

INTRODUCTION

Petroleum refining unavoidably generates considerable volumes of oily sludges. Common sources of sludges are the bottoms of storage tanks, water-oil separation systems, flotation and biological wastewater treatment units, cleaning of process equipment, and domestic sewage. Unlike the carbohydrates found in municipal and industrial wastewaters, the hydrocarbon compounds in oily sludge are difficult to decompose by microorganisms in classical biological treatment systems. Such systems usually work at low levels of efficiency and require land disposal as an alternative to complete the decomposition of the waste.

Soil disposal for wastes and effluents, known as landfarming, has been used as an alternative method to complete the petroleum refinery waste treatment, since the soil provides a wide spectrum of bacteria and a large surface area on which bacterial reactions may take place. However, the mechanisms of oily waste treatment using soil systems are not clearly understood, and various mechanisms may occur simultaneously. Some of the constituent substances of petroleum oil wastes are volatile and unstable under normal conditions. When disposed of in a landfarming system, they may be subject to evaporation, photodecomposition, adsorption, percolation, and biodegradation. Although these processes are known to occur, there exists a generally accepted belief that microbial decomposition is the primary cause of the reduction of oily sludge (Hutton and Zobell, 1949).

Microorganisms such as Pseudomonas and Candida are capable of decomposing hydrocarbons (McKenna and Kallio, 1964; Vanloocke et al., 1975), but the studies on the ways in which environmental factors affect the microbial reduction of oil in soils are inconclusive and controversial. Loynachan (1978) observed that mixing the soil may improve the transfer rate of oxygen, which is needed by the microorganisms, and thus it may also enhance the oil reduction rate. In contrast, Odu (1978) reported that there is no apparent difference in reduction of oil whether the soil is disturbed or not. It is a well known fact that balanced nutrients, such as nitrogen and phosphorus, are needed for the microbial degradation of organic matter. Regarding this, some researchers have found that the addition of fertilizers enhances the oil decomposition rate (Kincannon, 1972; Westlake et al., 1978), but the results of other workers (Raymond et al., 1976) have refuted this conclusion. Raymond et al. (1976) conducted a careful and extensive field study on the biodegradation of oily sludge in soil under local weather and precipitation conditions. Dibble and Bartha (1979) conducted a laboratory study with the aim of evaluating and optimizing the environmental parameters of oily sludge landfarming.

In the project reported in this paper, the objective was the standardization of the respirometer methodology, in order to control some environmental parameters related to the biodegradation of oily sludge constituents in soil. Once these parameters are established, the operational conditions of landfarming in the field can be defined. Suitable management practices and adequate monitoring of the landfarming system can be developed, the treatment system can be optimized, and the groundwater protected.

MATERIALS AND METHODS

The method adopted was that developed by Bartha and Pramer (1965). A respirometer flask was used to verify oily sludge biodegradability in soil. The soil sample and the oily sludge used in this assay were collected from the landfarming site of a petroleum refinery (São Paulo). The soil was air dried and passed through a 2 mm sieve.

The chemical characterization of the soil was undertaken. The water holding capacity of the soil was determined by the Hildegard ring method (Pramer and Schmidt, 1966), and soil moisture and pH were also determined (EMBRAPA, 1979). The normal pH of this soil sample was acid, around 5.0, and it was corrected to 7.0 using calcium hydroxide.

The oily sludge came from an activated sludge wastewater treatment plant which treats industrial and domestic wastewater from a petroleum refinery. This oily sludge was characterized regarding its contents of oil and grease, total solids, moisture, and heavy metals, using Standard Methods (APHA, 1985).

The respirometer flask used and described by Bartha and Pramer (1965) measures the evolution of carbon dioxide from soil samples in an enclosed system. It consists of a 250 ml Erlenmeyer flask modified with a side-arm addition which serves as an alkali reservoir (KOH, 0.2 N) to trap the carbon dioxide. A septum in the side-arm allows for the removal of samples of the alkali. This septum contains an ascarite trap to maintain CO_2-free aerobic conditions within the flask.

Each respirometer flask was filled with 10 g of soil, and oily sludge was added at the application rates shown in Table 1, with duplicates of each application rate. For each treatment, a control flask containing soil without oily sludge was prepared, to determine the soil CO_2 evolution which must be deducted from the CO_2 evolution of the treatment respirometer flasks. The soil moisture level used was 50% of its water holding capacity. The flasks received addition of the following complementary nutrients: NH_4NO_3 to provide nitrogen at a C:N ratio of 60:1; and, K_2HPO_4 to provide phosphorus at a C:P ratio of 300:1. The water required to attain the correct moisture level was added to the flasks in the nutrient solution. The flasks were incubated at a temperature of 25°C ± 1.

The carbon dioxide produced by microbial respiration was quantified by titration of the alkaline solution with HCl (0.1 N) every 24 hours during the first week, and every subsequent week, always with aeration of the system.

TABLE 1 The Different Treatments in the Respirometer Flasks

Treatment number	Description of treatment
1	10 g of soil at normal pH + 1 g of oily sludge
1	10 g of soil at normal pH + 1 g of oily sludge
Control 1	10 g of soil at normal pH
2	10 g of soil at pH 7.0 + 1 g of oily sludge
2	10 g of soil at pH 7.0 + 1 g of oily sludge
Control 2/3	10 g of soil at pH 7.0
3	10 g of soil at pH 7.0 + 2 g of oily sludge
3	10 g of soil at pH 7.0 + 2 g of oily sludge

RESULTS

Samples were collected from the landfarming site, and Table 2 shows the results of the chemical characterization of the soil at two depths, 20 and 40 cm.

TABLE 2 Chemical Characterization of the Soil

Parameter	Soil depth, cm 0 - 20	20 - 40	Parameter	Soil depth, cm 0 - 20	20 - 40
pH, H_2O	4.50	4.60	Al^{3+}, meq/100 g	2.80	2.40
pH, KCl	4.10	4.10	H^+, meq/100 g	9.60	5.60
C, %	1.39	0.92	Fe, mg/g	1684	962
N, %	0.07	0.04	Cu, mg/g	1.08	0.62
Na^+, meq/100 g	1.00	1.00	Zn, mg/g	1.04	0.22
K^+, meq/100 g	2.00	1.70	Mn, mg/g	1.52	1.92
Ca^{2+}, meq/100 g	0.20	0.20	Oil and grease, %	0.03	0.02
Mg^{2+}, meq/100 g	0.10	0.25			

The soil sample used in the respirometer assay had a pH around 5.0 which was corrected to 7.0 with calcium hydroxide. The water holding capacity of the soil was 42%, and water was added to fill 50% of this capacity.

The oily sludge was characterized as regards its contents of oil and grease (hydrocarbons), total solids and moisture (Table 3). In addition, it contained a small percentage of organic compounds such as carboxylic acids, aldehydes and ketones.

TABLE 3 Chemical Characterization of the Oily Sludge

Oil and grease, %	Total solids, %	Volatile solids, %	Fixed solids, %	Moisture, %	Cd, µg/g	Pb, µg/g	Hg, µg/g	Zn, µg/g	Ni, µg/g	V, µg/g
10.80	18.90	15.60	3.30	81.30	0.84	26.80	0.50	500	41.9	44.8

The experiment was conducted for a period of 107 days. Table 4 shows the cumulative amount of carbon dioxide produced by biodegradation in the control flasks and in the treatment flasks. The amount of CO_2 produced in the control flasks represents the oxidation of the carbon content of the soil. The CO_2 evolution of the normal pH control was subtracted from the CO_2 evolution of the pH 7 sample to show the net effect of pH on soil sludge biodegradation. Figure 1 shows the cumulative amount of CO_2 (µmol) produced by the controls (1, 2, and 3) and the cumulative amount of CO_2 produced by the biodegradation of the oily sludge in treatments 1, 2, and 3. At the end of the experimental period, the soil pH was measured in each respirometer (Table 5), and the soil content of oil and grease was determined (these values are not shown because we did not have sufficient soil to get a significant result).

In order to determine the microbiological status of the soil, counts of bacteria, fungi, and actinomycetes were made using two samples of soil from the landfarming site, one with oily sludge and one without (Table 6).

TABLE 4 Cumulative Amount of Carbon Dioxide

Time from start, d	Amount of carbon dioxide, µmol				
	Control 1	Treatment 1*	Control 2/3	Treatment 2*	Treatment 3*
1	135	177	150	190	237
2	150	215	185	242	282
3	175	260	225	310	375
4	195	280	275	350	450
6	250	370	350	445	590
8	250	377	355	487	730
10	265	462	400	617	1065
12	265	452	405	710	1267
14	265	515	410	777	1477
19	265	627	410	942	1782
21	265	647	410	960	1822
25	285	745	425	1077	1967
34	320	965	485	1307	2110
41	325	1075	510	1390	2175
50	375	1210	555	1500	2257
56	415	1322	575	1605	2330
64	420	1372	580	1675	2365
78	440	1427	590	1710	2395
92	475	1472	600	1790	2425
107	540	1509	615	1872	2475

*Average of two duplicates

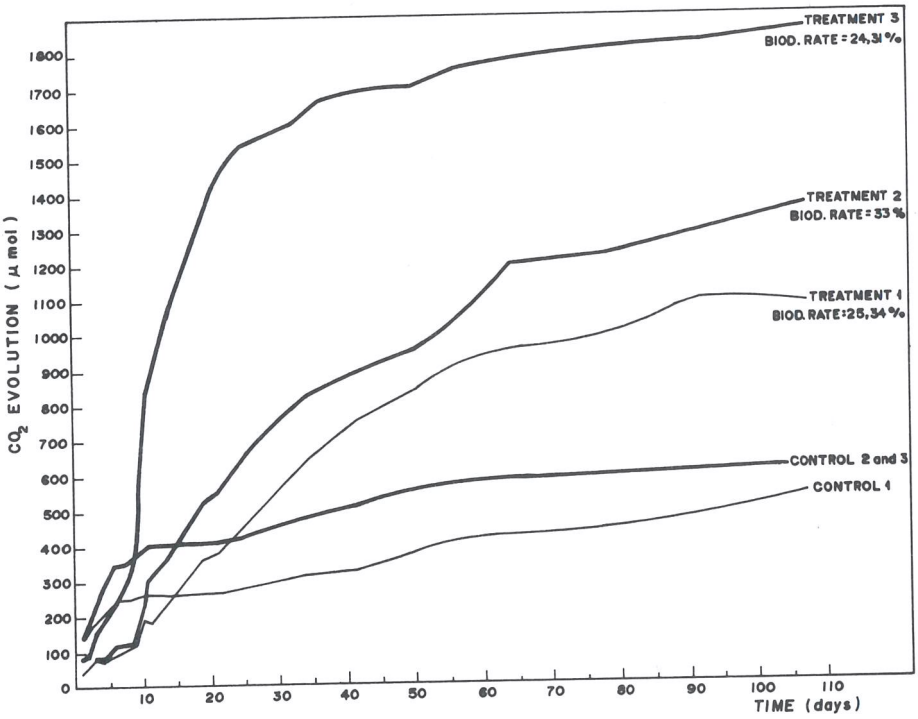

Fig. 1. Cumulative production of CO_2 (µmol) by the treatments and the controls

TABLE 5 Soil pH in the Respirometers at the End of the Assays

	Control 1	Control 2/3	Treatment 1	Treatment 2	Treatment 3
pH	5.5	6.8	5.6	5.9	5.4

TABLE 6 Soil Microbiological Counts

Soil sample	pH	Moisture, %	Microbiological count, No./g of soil dry wt		
			Bacteria	Fungi	Actinomycetes
Landfarming cell with sludge	2.6	10.1	7.8×10^4	3.8×10^3	2.22×10^2
Landfarming cell without sludge	5.1	3.5	1.5×10^5	1.8×10^4	5.4×10^3

DISCUSSION AND CONCLUSIONS

The increase in the soil pH from the addition of CaOH had a marked positive effect on oily sludge biodegradation (Fig. 1, treatments 1 and 2). The evolution of CO_2 by the controls which did not receive oily sludge showed a similar trend, but the increases were smaller (Fig. 1, controls 1 and 2/3).

The liming of the soil by the addition of calcium hydroxide instead of calcium carbonate as suggested by Dibble and Bartha (1979), is possible, since calcium carbonate also acts as a buffer. This procedure could optimize the biodegradation of the oily sludge even more.

From Table 5 it can be seen that the biodegradation of oily sludge induces soil acidification, since the initial soil pH in the assay was 7.1 in treatments 2 and 3, and the final pH had decreased to 5.9 and 5.4, respectively. In part, this may be due to the acidity of the sludge, since the untreated control flask showed a final pH of 6.8, and also, to the fact that the buffer compound calcium carbonate was not used to lime the soil.

The biodegradation rate of the treatments was calculated using the method of Bartha (personal communication), who assumes that 85% of the total amount of oil and grease present in the oily sludge is carbon, and that 50% of this carbon is converted into biomass and humus in the soil. Considering that the content of oil and grease in the sludge was 10.8% (Table 3), 1 g of oily sludge contained 108 mg of oil and grease. From this, it can be calculated that for each gram of oily sludge applied to the soil, 91.8 mg or 7 650 µmol of carbon are applied.

In treatment 1, where 1 g of sludge was applied and the soil pH was not corrected, the final amount of CO_2 produced was 969 µmol plus 50% which was converted into biomass with a total production of 1 938 µmol of CO_2. Comparing this value to the amount of carbon applied, the rate of biodegradation of this treatment was 25.34% (Fig. 1). In treatment 2, where 1 g of sludge was applied and the soil pH was corrected to 7.1, the final amount of CO_2 produced was 1 257 µmol plus 50% which was converted into biomass with a total production of 2 514 µmol of CO_2. This gives a biodegradation rate of 33% (Fig. 1). In treatment 3, the amount of sludge was doubled to 2 g, which corresponds to 15 300 µmol of carbon applied. The total amount of CO_2 produced by this treatment was 1 860 µmol plus 50% which was converted into biomass with a total production of 3 720 µmol. Considering the percentage of carbon assimilated by the biomass, the biodegradation rate for this treatment was 24.31% (Fig. 1).

From Fig. 1 it can be seen that although in treatment 3 the production of CO_2 was higher than in treatment 2, the biodegradation rate was lower. This is because the biodegradation rate is calculated considering only the amount of hydrocarbons in the oily sludge, although other organic compounds, such as aldehydes, organic acids, and ketones, may be present and may also be oxidized to CO_2. Under these experimental conditions, it can be concluded that the best application rate was 1% (wt/wt) of oily sludge hydrocarbon content to 10 g of soil. At this application rate, as discussed above, the biodegradation rate was 33% of the hydrocarbons applied.

Dibble and Bartha (1979), in their experiments, achieved a biodegradation rate of 1.0 g hydrocarbons in 20 g of sandy soil. These authors also considered that a biodegradation rate above 30% (minimum) was high enough for the waste (in this case the oily sludge) to be a good candidate for landtreatment. Considering the upper 15 cm soil layer (the plough layer or furrow slice), which has a density of 1.4 g/cm^3, for 1 hectare of land this gives 2.10×10^6 kg of soil in the furrow slice. Bearing in mind that for this experiment the best application rate for the oily sludge was 1.0 g of oily sludge in 10 g of soil, it can be

calculated that the field application rate of this sludge should be 210 tons of oily sludge per hectare of soil, if the soil pH is adjusted to between 7.0 and 8.0 and nutrients are added at the ratios of C:N of 60:1 and C:P of 300:1.

In this experiment, the oily sludge applied was a biological sludge classified as a sludge with a low content of oil and grease, and its biodegradation rate was too low. These results can be explained by considering the low microbiological potential of this soil. This can be seen in Table 6, which shows the microbiological counts of a soil sample collected at the landfarming site. One soil sample came from a landfarming cell with oily sludge addition, and the other came from a cell with no previous history of oily sludge addition.

It can be seen that the soil pH in the cell where oily sludge had been applied was strongly acidic, and this could significantly inhibit the development of microorganisms responsible for biodegradation. Even in the cell with no addition of oily sludge, the quantity of bacteria, which are the most important microorganisms regarding the biodegradation of hydrocarbons, was well below the normal level (around 10^8 per g of soil, dry weight), because of the low pH.

The landfarming system for oily sludges has been adopted by several refineries. However, it can be seen from the parameters measured in the initial phase of this experiment that management of the environmental parameters at the site has not been adequate for optimization of the process. Of the major parameters which should be controlled, the most important appear to be soil pH, nutrient balance, and sludge application rate.

Regarding the laboratory methodology used, this was shown to be acceptable with a satisfactory level of response for the oily sludge. It may be possible to also use this method for other wastes. However, there are limitations with such studies in reproducing field situations. Important parameters, such as tillage and soil texture, could not be tested in this laboratory system. Nevertheless, this laboratory study will simplify field experiments by providing pilot data that can be used to predict future field tests.

REFERENCES

APHA (1985). Standard Methods for the Examination of Water and Wastewater. APHA-AWWA, 16th edn, Washington, 1268 pp.

Bartha, R. and Pramer, D. (1985). Features of a flask and method for measuring the persistence and biological effects of pesticides in soil. Soil Science, 100 (1), 68-70.

Catani, R.A. and Jacintho, A.O. (1974). Análise química para avaliar a fertilidade do solo. Boletim Técnico No. 27, 7 pp., Piracicaba, ESALQ, USP.

Dibble, J.T. and Bartha, R. (1979). Effect of environmental parameters on the biodegradation of oily sludge. App. and Envi. Microbiol., 37 (4), 729-739.

EMBRAPA (1979). Manual de Métodos de Análise de Solo. Rio de Janeiro.

Hutton, W.E. and Zobell, C.E. (1949). The occurrence and characteristics of methane-oxidizing bacteria in marine sediments. J. Bacteriology, 58, 463-473.

Kincannon, C.B (1972). Oily waste disposal by soil cultivation process. US EPA, R2-72-110.

Loynachan, T.E. (1978). Low temperature mineralization of crude oil in soil. J. Envi. Qual., 7, 494-500.

McKenna, E.J. and Kallio, R.E. (1964). Principles and Application of Aquatic Microbiology, John Wiley and Sons, New York, NY.

Odu, C.T.I. (1978). The effect of nutrient application and aeration on oil degradation in soil. Envi. Poll., 15, 235-239.

Pramer, D. and Schmidt, E.L. (1966). Experimental Soil Microbiology. Burgess Pub. Co., Minneapolis.

Raymond, R.L., Hudson, J.O. and Jamison, V.W. (1976). Oil degradation in soil. App. and Envi. Microbiol., 31, 522-535.

Vanloocke, R., de Borger, R., Voets, J.P. and Verstraete, W. (1975). Soil and groundwater contamination by oil spills; problems and remedies. Intern. J. Envi. Studies, 8, 99-111.

Westlake, D.W.S., Jobson, A.M. and Cool, F.D. (1978). In situ degradation of oil in a soil of the boreal region of the Northwest Territories. Can. J. Microbiol., 24, 254-260.