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Bioremediation by composting of heavy oil refinery sludge in semiarid conditions

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Abstract

The present work attempts to ascertain the efficacy of low cost technology (in our case, composting) as a bioremediation technique for reducing the hydrocarbon content of oil refinery sludge with a large total hydrocarbon content (250–300 g kg^{-1}), in semiarid conditions. The oil sludge was produced in a refinery sited in SE Spain The composting system designed, which involved open air piles turned periodically over a period of 3 months, proved to be inexpensive and reliable. The influence on hydrocarbon biodegradation of adding a bulking agent (wood shavings) and inoculation of the composting piles with pig slurry (a liquid organic fertiliser which adds nutrients and microbial biomass to the pile) was also studied. The most difficult part during the composting process was maintaining a suitable level of humidity in the piles. The most effective treatment was the one in which the bulking agent was added, where the initial hydrocarbon content was reduced by 60% in 3 months, compared with the 32% reduction achieved without the bulking agent. The introduction of the organic fertiliser did not significantly improve the degree of hydrocarbon degradation (56% hydrocarbon degraded). The composting process undoubtedly led to the biodegradation of toxic compounds, as was demonstrated by ecotoxicity tests using luminescent bacteria and tests on plants in Petri dishes.

Introduction

The petrochemical industry generates a series of liquid effluents during the petroleum-refining process and as the installations are cleaned. The sludges that result from this treatment process have a high content of petroleum-derived hydrocarbons, mainly alkanes and paraffins of 1–40 carbon atoms, along with cycloalkanes and aromatic compounds (Overcash & Pal 1979), making them a potentially dangerous waste product. Simply dumping these wastes or burning them with no previous treatment has serious environmental consequences and presents a risk to both ecosystems and human health (Baheri & Meysami 2001).

Due to economics and simplicity, landfarming has traditionally been the biological treatment method chosen to dispose of most oil sludge (Wilson & Jones 1993; Persson & Welander 1994). In this procedure, the hydrocarbon wastes are mixed with soil, being biodegraded with time. Due to the fact that landfarming often requires a large surface area, other bioremediation methods such as composting of petroleum wastes has therefore received increased attention as a potential substitute technology for landfarming (Williams & Keehan 1993; Kirchmann & Ewnetu 1998).

The composting process used to stabilise organic materials can be considered as a bioremediation process (Bollag & Bollag 1995). Organic residues constitute a medium in which the microbial population present can remedy the said sludge as long as the conditions support the microbial activity. In this way, some of the problems which may arise from the use of organic wastes (odour, pathogenic micro-organism content, excess of labile organic matter, undesirable organic compounds) may be mitigated by a bioremediation process such as composting (Epstein 1997). Such a process implies that different organic compounds can be used as substrates by microorganisms and thus be totally or partially eliminated through mineralisation. Although the most suitable criteria for optimising the composting process are known (careful control of temperature, moisture, aeration, particle size, macro and micronutrients in the mass to be composted, C/N ratio of the materials, etc., Alexander 1994) so that the microbial activity necessary for treating this organic matter can be encouraged, very few studies attempt to quantify such treatment in semiarid conditions.

For the specific case of refinery sludge containing large quantities of hydrocarbons, the intervening microorganisms must be able to accept hydrocarbons as substrate (Tabuchi et al. 1998). The microorganisms must be able to synthesise the enzymes that catalyse the reactions by which these contaminants are degraded to simpler, less toxic or even innocuous compounds, obtaining the nutrients and energy necessary for their survival in the process (Johnson & Scow 1999). The alkanes and cycloalkanes present in these wastes are the most easily biodegraded, while the aromatic compounds, asphaltenes and resins are much more recalcitrant and resistant to degradation (Eweis et al. 1999).

The main aim of this study was to evaluate the efficacy of a low cost technology (composting) as a bioremediation process for reducing the hydrocarbon content of oil-refinery sludges with a high hydrocarbon content in semiarid conditions. The addition of a carbon-rich bulking agent (wood shavings) to improve oxygen diffusion and to create suitable aerobic conditions within the piles was also assessed, as was the inoculation of the medium with a liquid organic fertiliser (pig slurry) with high nitrogen and microbial biomass content.

Materials and methods

Materials

The organic material consisted of a sludge resulting from the treatment of the effluents proceeding from cleaning of tanks of an oil-refinery in SE Spain. According to Oolman et al. (1992), the sludge generated in refineries are submitted to a process of centrifugation in order to eliminate some of the water, giving them a semi-solid consistency (700–800 g kg^{-1} moisture). The principal chemical-physical characteristics of the sludge used in our experiment are summarised in Table 1. The hydrocarbon content was very high (281 g kg^{-1}), as was the phenol content. The metal contents were under the limits established by the EU legislation for the use of sewage sludge in agriculture (CEC 1986), and no chlorinated solvents were detected.

As will be discussed below, one of the compost piles was inoculated with pig slurry, the analysis of this organic material pointed to a high mineral nitrogen content and high biological oxygen demand (BOD) value due to the complex organic material it contained (see Table 2).

Composting process

Piles of about 1 m wide × 2 m long × 1 m high (2 m^3) were prepared (in triplicate), corresponding to the following treatments: oil-refinery sludge (OS), oil refinery sludge plus the bulking agent of wood shavings (OS + W) and oil refinery sludge plus bulking agent plus pig slurry (OS + W + PS). The bulking agent was added to the oil refinery sludge in a proportion of 3/1 (w/w, wet weight) and mixed thoroughly, while the pig slurry was inocu-

Table 1. Characteristics of the oil refinery sludge

Total petroleum hydrocarbon content (g kg^{-1})	281.0
Total organic carbon C (g kg^{-1})	391.0
Cl^{-1} (g kg^{-1})	1.0
SO_4^{-2} (g kg^{-1})	23.0
NO_2^{-1} (mg kg^{-1})	22.0
Phenols (mg kg^{-1})	534.0
Fluoride (mg kg^{-1})	1.3
$NH4^+$ (mg kg^{-1})	82.1
Chlorinated Solvents (mg kg^{-1})	
1,2-Dichloroethane	< 1
Tetrachloromethane	< 1
Dichloromethane	< 1
Chloroform	< 1
Perchlorethylene	< 1
As (mg kg^{-1})	< 0.01
Pb (mg kg^{-1})	112.2
Hg (mg kg^{-1})	< 0.01
Cd (mg kg^{-1})	< 0.05
Ni (mg kg^{-1})	175.0
Zn (mg kg^{-1})	1299.0
Cu (mg kg^{-1})	115.0
Cr (mg kg^{-1})	121.0

Table 2. Characteristics of Pig slurry

PH	7.75
Electrical conductivity (dS m^{-1})	1.20
Total N (g kg^{-1})	2.60
Total P (mg kg^{-1})	0.30
Total K (mg kg^{-1})	2.90
Nitrate (mg kg^{-1})	7.6
Ammonium (mg kg^{-1})	17.4
Microbial biomass C (mg kg^{-1})	3260.0
Organic matter (g kg^{-1})	628.4
Total organic carbon (g kg^{-1})	364.5
Fe (mg kg^{-1})	233.7
Mn (mg kg^{-1})	18.6
Zn (mg kg^{-1})	105.5
Cu (mg kg^{-1})	38.6
Ni (mg kg^{-1})	< 5
Cr (mg kg^{-1})	7.9
Pb (mg kg^{-1})	21.2
Cd (mg kg^{-1})	< 5
BOD (mg O_2 l^{-1})	6750
Solid (g $100g^{-1}$)	3.7

lated in a proportion of 20 l m^{-3}. Water was added to the OS and OS + W piles to compensate the water input with pig slurry in OS + W + PS. The piles were set on a concrete base with a system for collecting the leachate and kept at 60% of their water holding capacity (WHC). The temperature of the interior (60 cm depth) and of the surface (10 cm depth) was monitored periodically with a digital thermometer equipped with a probe (638 PT, Crison, Spain). During composting, the piles were turned each week. Oxygen was periodically measured with a digital oxymeter (Oxi 330, Crison, Spain) supplied with a probe to carry out oxygen determination inside piles. The composting experiment was conducted from March to May 2003 and in this period of time the average temperature was 17 °C and 100 mm of rain was collected. Random samples were taken from within the piles and from the outer layer 1, 4, 8 and 12 weeks after the beginning of composting. Samples were sieved and air-dried for analysis.

Chemical parameters

In both oil sludge and pig slurry, the electrical conductivity (EC) and pH were measured in a 1/10 solid/liquid aqueous extract. Total P and Total K and heavy metal content were determined in the nitric-perchloric 1/1 digestion extract; P was determined by colorimetry following the Murphy & Riley (1962) method, and K and heavy metals by atomic absorption. Total organic carbon (TOC) and Total N, were determined by elemental analyser. In oil sludge, chloride, nitrites, sulphate, ammonium and fluor were measured by ion chromatography.

In addition, in the samples derived from the composting processes the organic matter content was determined by calcination at 750 °C for 4 h. Total petroleum hydrocarbon content (TPH) was measured by the infrared EPA method no 8440 (EPA 1996). Water-soluble carbon was measured in the 1/10 (solid/liquid) extract in an automatic TOC analyser. Water-soluble carbohydrates, in the same extract, were measured with antrhone by the Brink et al. (1960) method. All assays were carried out in triplicate.

Respiration experiment

The CO_2 released by the samples during biodegradation was determined by placing 30 g of each sample in 125 ml flasks and bringing the samples to 60% of their WHC. The flask were closed, incubated at 28 °C and the CO_2 was measured at given time intervals (1, 2, 3, 4, 7, 9, 12, 14, 17, and 21 days) with an infrared gas analyser (Toray PG-100). The flasks were opened for half an hour after each measurement in order to ensure aerobic conditions in the samples.

Germination experiment

The germination experiments (in quintuplicate) were carried out on filter paper in Petri dishes. The corresponding aqueous extract (2 ml) (1/10) from the wastes were introduced into the dishes, with distilled water used as control in other dishes. Ten seeds (*Lepidium sativum*) were then placed on the filter paper and the dishes placed in a germination chamber maintained at 28 °C in darkness. The germination percentages with respect to the control and root lengths were determined after 5 days.

The germination index (GI) was calculated according to the formula proposed by Zucconi et al. (1985).

$$IG = \%G \times L_e/L_c$$

where %G is the percentage of seeds germinated in each extract with respect to the control, L_e is the mean total root length of the germinated seeds in each extract and L_c is the mean root length of the control.

Ecotoxicity assay

A toxicity test was carried out using luminescent bacteria (Multitox), in which the inhibition of the luminescence of *Photobacterium phosphoreum* (ISO 11348-2) was measured after addition of the extracts of the samples, using a luminometer (Kapanen & Itävaara 2001).

Statistical analysis

ANOVA was carried out for each treatment to determine significant differences at $p < 0.05$ between the results obtained at each period of the composting process. Lower significant differences (LSD) were obtained by LSD multiple range test. All statistical analysis were performed using Statgraphic Plus 2.1 software.

Results and discussion

Physical factors in the composting process

The maximum temperatures reached in the composting process did not exceed 55 °C in any of the treatments (Figure 1). This temperature was maintained for several days during the thermophilic stage, suggesting that the organic matter was suitably treated (Garcia et al. 1991). It is of interest to note, the contrast with other composts, for example using sludges from urban wastewater treatment plants, when temperatures can easily exceed 65 °C (Garcia et al. 1991;Tseng et al. 1996). This difference would presumably be due to the differing capacity of the microorganisms to degrade the hydrocarbons and to accept them as substrate, since in organic sludges containing highly degradable material the easy access generates much activity, leading to the higher temperatures. Two types of thermal behaviour were observed in the different treatments. The composts containing bulking agent (OS + W and OS + W + PS), on the one hand and the OS with no additives on the other. The first two composts reached their thermophilic phase during the first week, while the third remained 3 weeks in its mesophilic phase before entering the thermophilic stage. It seems, then, that the bulking agent encourages the diffusion of oxygen inside the pile, facilitating microbial development and raising the temperature earlier. These findings concerning this delay in microbial activity agrees with those of Bengtsson et al. (1998), also in a composted oil-refinery sludge, in which, after a short mesophilic stage, maximum temperatures of 50–55 °C were reached and maintained for several days.

Oxygen content is known to be a key factor in composting (Zhou & Crawford 1995), which should progress in aerobiosis. In the piles containing bulking agent, the oxygen content remained at 10–14%, as measured with an oxymeter (the highest values always after turning), while in those not containing the agent it remained at 2–9%. These data demonstrate the effectiveness of a bulking agent for fostering microbial activity during the composting process. In our case, oxygenation was carried out by turning the piles periodically every 15 days during the first month and weekly thereafter.

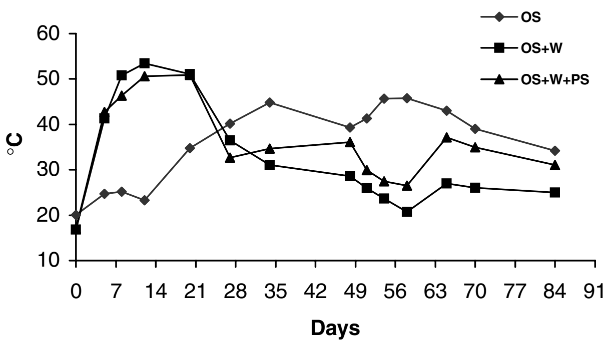

Figure 1. Temperature evolution during composting. OS: Oil refinery sludge; OS + W: Oil refinery sludge plus wood shavings; OS + W + PS: Oil refinery sludge plus wood shavings plus pig slurry.

Humidity of the piles must be kept at 40–60% for microbial activity to be adequate and for the biodegradation of the hydrocarbons (in our case) to proceed. Initially, the moisture level of the piles containing bulking agent was around 60–65% and higher (73%) in the OS piles since this is the moisture content of the material as it leaves the plant. This, together with the lower oxygen content, would explain the lower temperature reached by the piles containing only this material. As time progressed, the moisture content of all the piles fell and water had to be added; however, this proved to be difficult because the material would not readily absorb water due to the highly hydrophobic nature of compound such as hydrocarbons. This should always be borne in mind since it is one of the problems which always arise in bioremediation processes involving composting.

Evolution of the physical–chemical parameters

The pH of the piles at the beginning of composting was slightly basic (Table 3), since neither the wood shavings nor the liquid manure used as additives had a pH significantly different to modify that of the refinery sludge. In all the piles the pH fell slightly during the first 4 weeks of composting before recovering to their initial values (Table 3). The decrease recorded may have been due to the appearance of low molecular weight organic acids during the degradation of the carbon compounds (Garcia et al. 1991). The oxidation of alkanes (presumably a component of the added sludge) would also produce acids (Eweis et al. 1999).

As regards electrical conductivity (EC), this was lower at the beginning of composting in those piles incorporating bulking agent and inoculum (OS + W and OS + W + PS), which could be due to the diluting effect of adding the bulking agent. The EC of all three piles rose as composting progressed due to the accumulation of salts that are not expelled to the atmosphere by volatilisation (Table 3).

Hydrocarbon degradation

The total petroleum hydrocarbon (TPH) content of the piles at the beginning of composting was different because of the dilution effect of the bulking agent and organic fertiliser (Figure 2). The most effective treatment as regards TPH degradation was the OS + W (59% degraded in 3 months) followed by OS + W + PS (56%), although the difference was not significant. In the remaining pile (OS alone) only 32% of the initial TPH was degraded, emphasising the positive effect on bioremediation of the bulking agent and oxygenation The greatest decrease in TPH occurred in the first 8 weeks of composting, when the easily biodegraded hydrocarbons are used by the microorganisms as carbon source for growth. This initial degradation of the most labile hydrocarbons in a refinery sludge may be catalysed by mono and dioxygenase enzymes (Britton 1984; Singer & Finnerty 1984) probably synthesised by aerobic microorganisms, which clearly benefit from the addition of the bulking agent. In such a reaction, the enzymes gradually oxidise the alkanes to alcohols and aldehydes in the presence of oxygen, producing acids that finally follow a metabolic pathway to produce CO_2 and water. This idea is leant weight if we bear in mind the fact that

Table 3. Changes in pH and electrical conductivity (EC, dS m^{-1}) during composting (Mean values of three replicates)

Weeks	pH			EC		
	OS[a]	OS + W	OS + W + PS	OS	OS + W	OS + W + PS
1	7.81	7.88	7.83	1.79	0.82	0.83
4	7.65	7.08	7.01	3.05	3.07	3.14
8	8.04	7.52	7.50	2.69	2.86	2.99
12	7.78	7.46	7.26	2.63	2.62	2.93
LSD[b]	±0.06	±0.03	±0.01	±0.30	±0.06	±0.05

[a]OS: Oil refinery sludge; OS + W: Oil refinery sludge plus wood shavings; OS + W + PS: Oil refinery sludge plus wood shavings plus pig slurry.
[b]Least significative difference at $p < 0.05$ using ANOVA with the LSD multiple range test.

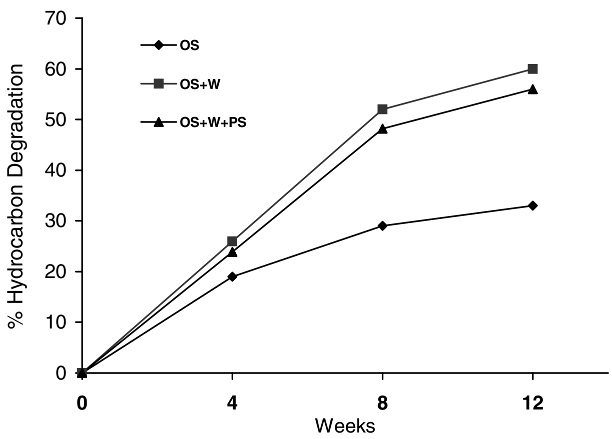

Figure 2. Hydrocarbon degradation (%) during composting (MSD +/- 6.1). For treatment nomenclature see Figure 1.

polynucleated aromatic hydrocarbons, polychlorinated biphenyls (PCBs), alkanes and alkenes (the last two products normally being the major components in products such as refinery sludges) are initially degraded by the catalytic action of the oxygenase, which needs the presence of molecular oxygen (Atlas 1991). The higher degree of hydrocarbon degradation in the piles containing bulking agent could be due to the dilution of the waste through the addition of the bulking material, which reduce the toxicity of the parent material. The lower degree of oxygen diffusion when bulking material is not incorporated can also be responsible of this different degradation. Kirchmann & Ewnetu (1998) reported 90% degradation of TPH in refinery sludge mixed with horse manure, although it should be pointed out that the sludge used by these authors contained 4–20 g kg^{-1} TPH compared with the 281 g kg^{-1} of the sludge used in our study.

It is equally clear that inoculation of the piles with an organic fertiliser (pig slurry), with a noticeable nutrient and microbial biomass content (Table 2), did not improve hydrocarbon degradation (Figure 2), despite the fact that some authors have pointed to the benefits of adding nutrients for better degradation (Beaudin et al. 1999; Margesin et al. 1999) when the hydrocarbons are added to the soil in landfarming. However, in our case, this did not apply, perhaps because refinery sludge contains sufficient nutrients to activate the microbial flora involved in the biodegradation process (Table 1). It seems, then, that it is more beneficial to introduce a bulking agent that will increase the porosity than an organic or inorganic fertiliser when the material to be composted is a refinery sludge rich in hydrocarbons.

It could be thought to think that a fraction of the TPH reduction was due to volatilisation, particularly in well aerated substrates and warm conditions. However the TPH content reduction by volatilisation in this case was minimum because the volatile compounds content in this heavy oil sludge was very low (Marín 2004).

Evolution of C fractions

The addition of wood shavings and pig slurry increased the TOC values compared with the piles without bulking agent (Table 4) due to the carbon they contained, especially the wood shavings with their lignocellulosic character. The TOC levels fell during composting, as is to be expected, due to the mineralisation of the carbon brought about by microbial activity, a decrease matched by that of the volatile organic material (Table 5). The carbon degradation seen in the piles containing the wood shavings would mainly be that of the C contained in the refinery sludge since the carbon content of the wood shavings (bulking agent) is more resistant to degradation by microbial attack during the first stages of composting. This trend of TOC was corroborated by the fact that the organic matter decreased in the OS was twice that in the treatments with additive (Table 5). On the other hand, wood shavings added in OS + W and OS + W + PS could contribute to fungal development and changes in both microbiota and degradation pathways

Table 4. Changes in water soluble carbon, total organic carbon and water soluble carbohydrates during composting

Weeks	Water soluble carbon(mg kg^{-1})			Total organic carbon (g kg^{-1})			Water soluble carbohydrates (mg kg^{-1})		
	OS	OS + W	OS + W + PS	OS	OS + W	OS + W + PS	OS	OS + W	OS + W + PS
1	4185.9	4037.4	6168.4	391.0	430.0	420.9	458.5	404.1	645.6
4	4996.3	4678.8	3144.6	371.0	392.4	394.6	433.5	368.6	244.4
8	4744.0	3492.6	4127.8	309.0	365.9	373.9	387.7	369.5	525.2
12	3782.4	3154.8	4042.4	304.5	349.0	357.3	345.8	356.9	303.4
LSD	±461.1	±292.7	±165.4	±16.4	±14.0	±9.9	±81.3	±32.8	±40.8

(Tang et al. 2004) could be established in these treatments with regards to the control.

The most labile carbon fractions, such as the water soluble fractions (Table 4), reflect the potential of the mass to make available to the microorganisms some carbonated materials that are readily degradable, thus maintaining a high level of microbial activity. This C fraction is much more dynamic than TOC since, during biooxidative processes such as composting, it is the water-soluble C structures that are generated and degraded by the microorganismss (Garcia et al. 1992). As can be seen from Table 4, the changes in the water-soluble C fractions (water soluble C and carbohydrates) during the different stages of composting confirm the above mentioned behaviour of the C fraction. When no pig slurry is incorporated, the water-soluble fraction at the beginning of composting is smaller.

Microbial activity

A biomarker that is generally considered to be an acurate measure of microbial activity in a given medium is the respiration of these microorganisms as represented by the CO_2–C release (Nannipieri et al. 1990). The respiration experiment of samples taken at different times of the composting process permit to assess the microbial activity changes and the kinetic of organic matter mineralisation as the composting process proceeds.

As can be seen from Figure 3, piles with additives (OS + W and OS + W + PS) showed at all composting times higher respiration rates than those without additives, pointing to their greater microbial activity. The porosity and improved aeration provided by the bulking agent to the compost mass benefit the microorganisms responsible for the degradation of the organic material (and, in our case, the hydrocarbon content in the oil sludge, and with time, a part of the bulking can also be mineralised). The toxicity reduction in the oil sludge due to the dilution effect of the bulking agent can do the sludge more biodegradable. The incorporation of a liquid manure, which provides very labile organic matter and microbial biomass to the composting mass, also induced greater activity, although, perhaps due to the low quantities used, this improvement was not significantly greater than that obtained with bulking agent alone.

Microbial metabolic activity, measured as CO_2 emission, varied with the compost age (1, 4, 8 or 12 weeks), piles with and without additives behaving in a different way. Curves representing cumu-

Table 5. Changes in organic matter and ash during composting

Weeks	Organic matter (g kg^{-1})			ASH (g kg^{-1})		
	OS	OS + W	OS + W + PS	OS	OS + W	OS + W + PS
1	532.4	814.0	813.8	465.2	186.0	186.7
4	507.9	774.0	768.8	486.8	226.0	237.9
8	484.3	768.6	758.7	514.0	231.4	241.3
12	425.8	736.9	758.7	574.0	259.5	277.6
LSD	±6.9	±8.9	±6.9	±7.1	±11.3	±5.8

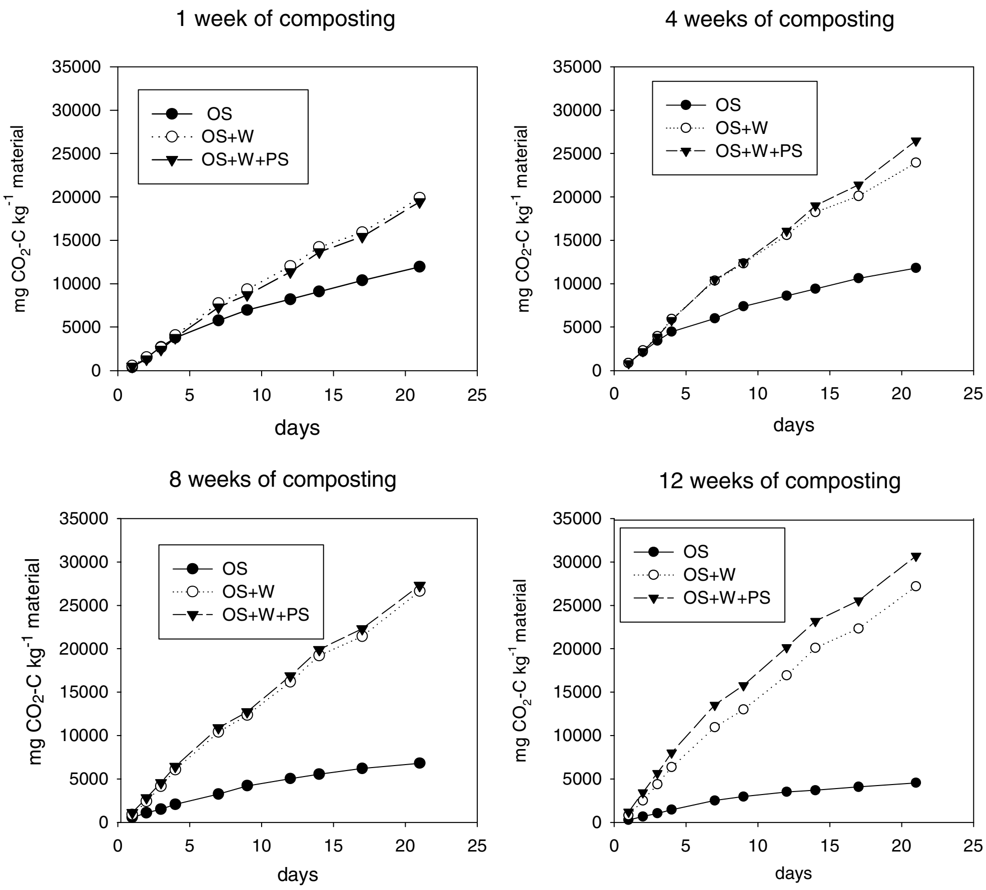

Figure 3. Accumulative C–CO_2 losses with time at different stages of the composting process. For treatment nomenclature see Figure 1.

lative CO_2–C with incubation time usually show two different kinetic phases of C mineralisation (Solano-Serena et al. 1999), the first part of the slope being steeper (1–7 days), reflecting the faster mineralisation rate as the microorganisms attack the large quantity of easily biodegradable C. As the carbon substrates are gradually used up and only the more difficult ones remain, a slower mineralisation kinetic becomes evident and the CO_2–C production stabilises. In our experiment, these two phases were only distinguishable in OS while the samples from composts containing bulking agent (OS + W and OS + W + PS) showed for all composting times (1, 4, 8 and 12 weeks) a maintained mineralisation rate during the 20 day incubation period, suggesting the presence of a great amount of mineralisable substrates in the medium.

OS samples showed a similar microbial metabolic activity after 1 week and 4 weeks of composting but this activity decreased after 8 weeks and even more after 12 weeks of composting, indicating that the more easily mineralizable substrates have been consumed, the remaining substrates being more difficult to be attacked by microorganisms.

In the piles with additives C mineralisation was slower in the 1 week compost samples than in the aged composts, suggesting that the microorganisms need a time of adaptation before using hydrocarbons as substrates.

Contrarily to the OS compost, microbial activity in the composts with additives did not decrease with the composting time but increased. This suggests that a continuos generation of the degradable compounds (likely at expense of recalcitrant compounds from the additives and hydrocarbons) occurs. The better aerobic conditions of the mixtures with bulking agent stimulates microbial activity meaning that microorganisms can degrade hydrocarbons better than in the OS compost; this bulking agent favours fungal development and the establishment of new microbial degradation pathways, all this leading to a higher respiration rates (Figure 3) and contributing to a higher hydrocarbon biodegradation (as observed in Figure 2).

Lysate toxicity tests

The germination assay using watercress seeds pointed to a gradual detoxification of the material as composting advanced in OS + W and OS + W + PS, while the same degree of phytotoxicity was observed at the end of composting in OS that at the beginning (Figure 4). The germination index (GI) in the extract of the OS samples after 8 weeks of composting decreased because the absence of a structuring agent provoked anaerobic conditions in which secondary metabolites of a phytotoxic nature were presumably produced. However, these metabolites would eventually be degraded, after 12 weeks, since the GI tended to rise at this stage of composting.

The increase in the GI in the two treatments containing bulking agent reflects the sharp decrease in ecotoxicity detected using luminescent bacteria in these extracts, which were practically free of toxicity after 4–8 weeks of composting (Figure 5). However the extracts of OS showed a decrease trend in the % of toxicity using luminescent bacteria but not an increase in the GI. This fact can be due to some compound, which inhibited the germination, but was not toxic for lumi-

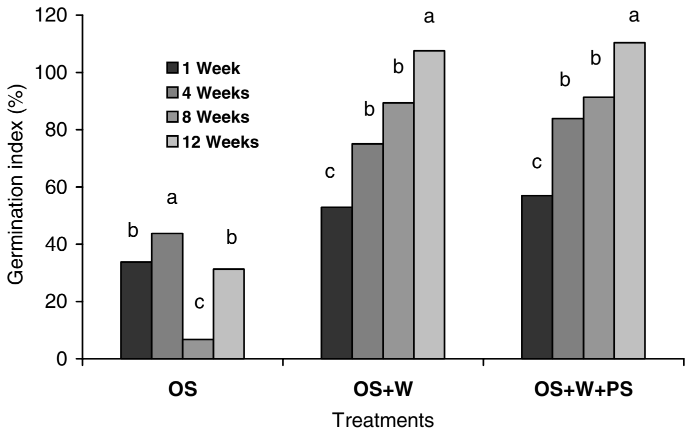

Figure 4. Changes in the Germination Index during composting (100% for Control). For each treatment, bar values with the same letter are not significantly different at the $p < 0.05$ probability level. For treatment nomenclature see Figure 1.

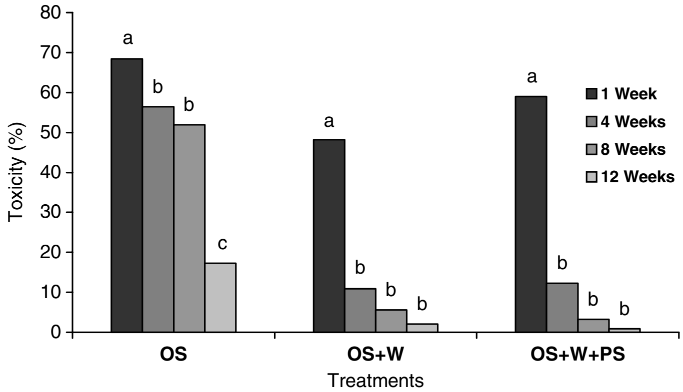

Figure 5. Changes in the % of inhibition measured by *phosphobacterium phosphoreum*, during composting. For treatment nomenclature see Figure 1.

nescent bacteria. Both the phytotoxicity and ecotoxicity indices, then, point to the detoxification of this hydrocarbon-contaminated sludge, perhaps due to the dilution of the oil sludge with the bulking agent. It should be emphasised that the indices were determined in aqueous lysates, so that they would only apply to those contaminants potentially present in these extracts. Phenolic compounds have been reported as toxic compounds to microorganisms and plants (Saviozzi 1997). The high content of phenolic compounds in the oil sludge at the beginning of compost (Table 1) could be considered lowered after 12 weeks of composting because the decrease of its ecotoxicity

Conclusion

In conclusion, it seems that the addition of a suitable bulking agent improves aeration of material and thus the performance of the composting process in an oil-refinery sludge since the total hydrocarbons present undergo a greater degree of biodegradation. The bioremediation process undertaken leads to the detoxification of the mass and the loss of toxic substances, as seen from the results of the phytotoxicity and ecotoxicity tests carried out. Inoculation of the mass with an organic fertiliser such as pig slurry does not significantly improve the results obtained with the bulking agent alone.

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