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Combined slurry and solid-phase bioremediation of diesel contaminated soils

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Abstract

This work investigates, at a laboratory and pilot-scale, the influence of various operating parameters on the combined slurry and solid-phase bioremediation technique for a diesel contaminated soil. For slurry-phase bioreactors (SPB), it has been found that, as far as famine conditions are attained at the end of the react cycle, a low hydraulic retention time and a low slurry recycle ratio allows for a better utilization of the reactor volume. A 7-day slurry-phase bioreactor treatment has been shown to provide enough contaminant removal allowing the soil drawn from the slurry-phase bioreactors to be fed effectively to the solid-phase bioreactors (SoPB) for completing the soil cleanup. However, an important improvement of the solid-phase bioreactor performance has been found using soil additives, namely sand and surfactants. While the first soil additive improves pile porosity and consequently oxygen diffusion, the latter increases contaminant bioavailability.

Keywords: Bioremediation; Bioreactors; Biopiles; Diesel fuel; Contaminated soil; Slurry

1. Introduction

Bioremediation technologies are today well-established techniques that can be used for the cleanup of chemically contaminated soils [1,2]. Among their advantages with respect to other widely used techniques, are simplicity, the possibility of being coupled with other physical or chemical treatment methods, cost-effectiveness and the capability of complete destruction of the pollutants [3]. Bioremediation can be carried out both in situ (without removing the soil) as well as ex situ (by excavating the contaminated soil). In both the cases,

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pollutant degradation is carried out in a bioreactor (which actually is the ground itself for in situ treatment), whose operating parameters have to be optimized in order to reduce costs and increase efficiency [4,5].

In this work, we have focused on ex situ treatment, with particular reference to slurry-phase bioreactors (SPB) and solid-phase bioreactors (SoPB). Both the reactors involve contacting the contaminated soil with water, nutrients, oxygen, biomass and occasionally cosubstrates or surfactants to enhance the biodegradation rate. However, while in a slurry-phase bioreactor the soil is suspended in water by utilizing a mechanical stirrer, in the solid-phase bioreactor water is just sprinkled over the soil to adjust the soil moisture content.

Slurry-phase bioreactors are well-stirred tanks in which soil and water are mixed with air, microbial cells and nutrients. Soil is sieved to produce a 2 mm particle (approximately) before feeding it to the reactor. This sieving is done to eliminate rocks, gravel and debris since they do not usually contain a significant amount of contaminant and are difficult to suspend in the slurry [6–8]. These reactors have been successfully used for the bioremediation of soils contaminated with several chemicals, including petroleum and its derivative, PAH, and explosives [6–13]. Moreover, they require a treatment time of the order of days or weeks, thus making unsteady processes more suitable for slurry-phase soil bioremediation. For instance, semi-batch processes, such as the sequencing batch reactor (SBR) technology, are widely used for wastewater treatment [14]. They have a good compromise between cost and performance. These periodic processes involve three main phases, namely:

(1) soil sieving, slurry preparation and feeding the reactor (*fill* step);
(2) mixing and aeration (*react* step);
(3) discharging and dewatering of a given amount of slurry (*draw* step).

Some amount of slurry is left in the reactor at the end of the draw period to seed the following reaction cycle.

Solid-phase bioreactors (also called biopiles) are piles of contaminated soil amended with nutrients. Ventilation is provided by pulling air through a network of slotted piping woven throughout the pile, while moisture is provided by spraying the soil with water until it is wet but does not have puddles [15]. Also, these reactors have been successfully used for the bioremediation of soils contaminated with various chemicals [2,16–18].

Clearly, the SPB is by far more effective than SoPB in contacting microbial cells with pollutants, nutrients and oxygen. This efficiency results in a significant enhancement of the rate of pollutant degradation (and consequently in a reduction of the treatment time), as well as of the uniformity of soil remediation with respect to SoPB. However, SPBs are more expensive than SoPBs because of the energy required keeping the solid particles in suspension. This advantage of the SPB results in it being competitive when the required treatment time is not too long. On the other hand, SoPBs are very inexpensive ex situ treatment methods for soil remediation. They require only a small amount of energy for forced aeration and this makes solid-phase bioremediation cost-effective even when long treatment times are required. However, non-uniform contaminant removal and low rates and extent of degradation often limit the effectiveness of solid-phase treatment. This limitation has been attributed to a lack of soil, nutrients and biomass homogenization [9,19].

Several SPB studies have shown that rates of contaminant biodegradation decrease significantly as the contaminant bioavailability becomes the rate limiting step [10,11,20,22]. This limitation occurs since the rate at which microbial cells can convert contaminants depends on the rate of contaminant uptake and metabolism as well as on the rate of mass transfer of the contaminant to the cells. At the beginning of the treatment a high mass transfer rate allows for the complete exploitation of the microbial conversion capabilities, while once consumed the most available contaminant mass transfer rate towards the degrading microbes becomes the rate limiting step, thus significantly reducing the overall rate of contaminant abatement. In the following we will refer to the initial high pollutant abatement rate as the "*first phase*" and to the following slower one as the "*second phase*" of SPB treatment.

The contaminant limitation that characterizes the second phase of SPB treatment leads to long treatment times when the contaminant bioavailability becomes limiting at a concentration value larger than the required cleanup level. In this case, the final long-time degradation phase can be more cost-effectively carried out in a SoPB rather than in a SPB. Moreover, the SPB breaks up the larger soil particles and homogenizes soil, nutrients and biomass. This advantage avoids non-uniform contaminant removal when the soil from the SPB is fed to the SoPB. In other words, slurrying followed by solid-phase bioremediation can combine the advantages as well as minimizing the disadvantages of each treatment method when used alone [21].

Consequently, the main goal of this work was to investigate at a laboratory and pilot-scale the influence of various operating parameters on the combined slurry and solid-phase bioremediation technique for a diesel fuel contaminated soil. It should be noted that laboratory and pilot-scale experiments play an essential role in the feasibility studies required before the actual clean up of a contaminated site. These studies cannot be avoided since bioremediation is a scientifically intensive procedure that must be tailored to the site-specific conditions.

2. Materials and methods

Three different slurry-phase bioreactors were used. They were mainly characterized by their size ranging from a typical laboratory-scale value of 1 l volume up to a pilot-scale reactor with a capacity of 200 l. All the reactors were closed tanks equipped with a variable-speed stirrer. To reduce biomass damage the stirring rate utilized was the lowest value able to completely suspend the soil. Aeration was provided by compressed air injected through a diffuser on the bottom of the reactor. Before entering the reactor, the air was saturated by bubbling in water to reduce evaporation losses from the reactor. Air flowrates were adjusted to maintain an oxygen concentration in the reactor close to the saturation value, that is, approximately 6.5 mg/l. The dissolved oxygen concentration was measured by an Amel 366 oxymeter. The pH was monitored electrochemically (with a Metrhom 691 pH-meter) and adjusted daily to a value close to 8 by adding a 10% NaOH solution. Reactor vents of the smallest reactors were vented through an activated carbon bed to quantify VOC loss due to air stripping.

The solid-phase bioreactors were charged with dewatered slurry drawn from the 200 l reactor. Piles with dimension of 0.60 m × 0.60 m × 0.18 m were prepared outdoors and

covered with black plastic. Water and air distributions were provided through 16 mm diameter geotextile tubes. While air was provided continuously, irrigation was only utilized to maintain the moisture in the piles at a value between 15 and 20 wt.%. In addition, humidity, pH, nutrient concentration and temperature were also monitored for each pile.

Contaminated soil was prepared by mixing a sieved clean soil (with aggregate dimension lower than 3 mm) with either *n*-dodecane (chosen as a diesel fuel surrogate) or commercial car diesel fuel. A typical contaminated soil contains approximately 25 g of total hydrocarbons per kg of dry soil (this concentration corresponds to a COD of about 90 g/kg of soil). Contaminated soil has been aged for at least 2 months and fortified with $(NH_4)_2HPO_4$ to obtain a COD:N:P ratio greater than 100:5:1. The aging was carried out by leaving the contaminated soil in sealed plastic containers at ambient conditions. This aging did not remove any significant amount of contaminant, as confirmed by analyses on both the fresh and the aged soil.

Samples were removed from both the reactors and analyzed for total petroleum hydrocarbons (TPH) by carbon disulfide (CS_2) extraction followed by gas chromatography (GC HP 5890 Series II). The CS_2/GC procedure for slurry and soil samples was as follows: 1 ml of slurry (sampled from a 50 ml sample taken from the reactor and vigorously stirred in a beaker to reduce sample heterogeneity) or 0.5 g of soil (taken from six different 10 g samples from different sites in the pile and mixed together for volume-average measurements, or from a single 10 g sample for point measurements) was placed in a tarred vial. For each sample, 2 ml of CS_2 (purity greater than 99.5%) was added to the vial together with 2 μl of *n*-octane as an internal standard. The vial was vigorously stirred and then placed for 60 min in a Danetzki T32C centrifuge at its maximum speed to separate the water phase, CS_2 phase and soil.

Following this, 1 μl of extracted CS_2 was injected into the gas chromatograph equipped with FID detector operated at 300 °C. An HP 5 M.S. (crosslinked 5% Ph Metil silicone) column was used for the analysis. The column temperature was increased from 50 to 275 °C linearly at 10 °C/min and then hold isothermally for 10 min. Quantification of THP (expressed as *n*-octane equivalent) was made by external calibration using contaminated soil standards prepared at various THP concentrations.

No specific microbial population was used since biomass selection was forced from the endogenous population by alternating substrate availability conditions, as discussed in the following.

The chromatographic analyses carried out in this work showed that there was no preferential removal of any chemicals since almost all the chemical species involved in the diesel fuel were reduced approximately by the same amount.

3. Results

Various SPB utilized different reactor sizes ranging from 1 to 200 l. This procedure allowed us to investigate not only the effect of several operating parameters on the SPB performance but also the possibility of scaling up the results from small-scale laboratory reactors to pilot-scale ones.

3.1. Preliminary 1 l SPB experiments

Several operating parameters can influence SPB performance, e.g. the soil concentration in the slurry, the amount of slurry left in the reactor for seeding the following cycle and the hydraulic retention time (HRT, defined as the average reaction time experienced by the soil and computed as the ratio of the reactor volume to the volume of slurry withdrawn from the bioreactor in the drawn step times the reaction time).

The smallest bioreactor was used preliminarily to perform some tests with soil contaminated by *n*-dodecane as a diesel fuel surrogate. The use of a pure compound as a diesel surrogate allows for eliminating all the uncertainties related to commercial products thus enhancing the experimental reproducibility and allowing for a comparison of results using different experimental conditions. This allowed us to evaluate the effects of the aforementioned operating parameters as summarized in Table 1 (Runs 1–5).

Preliminarily, the influence of VOC stripping was assessed. This evaluation was accomplished both by analyzing the amount of organic collected by the activated carbon trap located on the vent line of the reactor as well as by comparing the results of a typical run with those of a similar run carried out with a pH value equal to 2, a value which inhibited any bacterial activity. Both the tests confirmed that volatilization does not play a relevant role and that TPH removal is essentially due to microbial degradation. The results of two runs performed at pH 2 and 8 are reported in Fig. 1. We can see that the TPH reduction after 7 days when the microbial activity was inhibited by the pH 2 solution is lower than 3%, while at the same time the bioreactor with pH 8 TPH abatement was approximately 95%.

A typical periodic behavior of the SPB is shown in Fig. 2. We can see that, after an acclimatization period (not shown in the figure), the system exhibits a steady state behavior. The TPH value is reduced from its initial value during the react step (of 2 days duration in this case) and then, after the instantaneous draw and fill steps, it suddenly increases to the initial value and the cycle is repeated. The figure shows two cycles, but the same behavior is repeated indefinitely.

Table 1
Summary of the SPB runs which involve various values of hydraulic retention time (HRT), slurry concentration, slurry recycled, and reactor volume, as well as two different soil contaminants

Run	HRT (day)	Soil concentration (wt.%)	Slurry recycled (%)	Reactor volume (l)	Contaminant
1	10	10	80	1	*n*-Dodecane
2	20	10	90	1	*n*-Dodecane
3	10	10	30	1	*n*-Dodecane
4	10	40	30	1	*n*-Dodecane
5	10	20	30	1	*n*-Dodecane
6	10	40	30	5	Diesel fuel
7	8.75	40	20	10	Diesel fuel
8	8.75	40	20	200	Diesel fuel
9	35	40	20	200	Diesel fuel

HRT: defined as the ratio of the reactor volume to the volume of slurry withdrawn from the bioreactor in the drawn step times the reaction time; slurry concentration: defined as the wt.% of dry soil in the slurry; slurry recycled: defined as the percentage of the slurry volume left in the reactor at the end of the draw step.

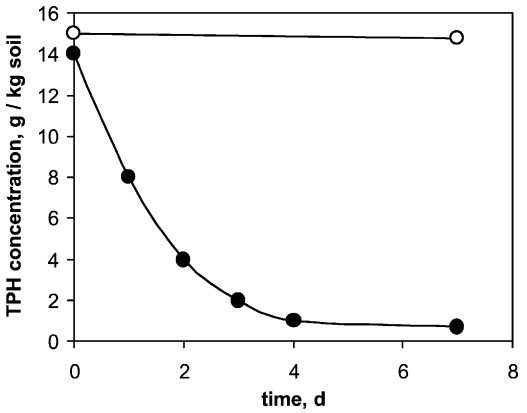


Fig. 1. Comparison between (●) a standard run with pH 8, and (○) a similar run with pH 2 where microbial activity was inhibited. Operating parameters as for Run 3 in Table 1.

The same figure also shows the influence of HRT by comparing the results of Runs 1 and 2 in Table 1. Note that different HRT values were obtained with the same react time (2 days for both the runs) by recycling a different amount of slurry at the end of the draw step. We can see that the influence of doubling HRT (from 10 to 20 days) on the reactor behavior is almost negligible in terms of final contaminant concentration, which is approximately 1 g/kg soil. At the beginning of each react step, the TPH increases to different value since, for Run 1, during the draw and fill steps 20% of the cleaned slurry is suddenly replaced with contaminated slurry, while for Run 2 only 10% of the slurry is replaced. Since for both runs the concentration values at the end of the react step are almost the same, replacing a larger amount of cleaned slurry with contaminated slurry leads to a larger initial concentration value. However, this result also means that a lower HRT (Run 1) induces a larger average

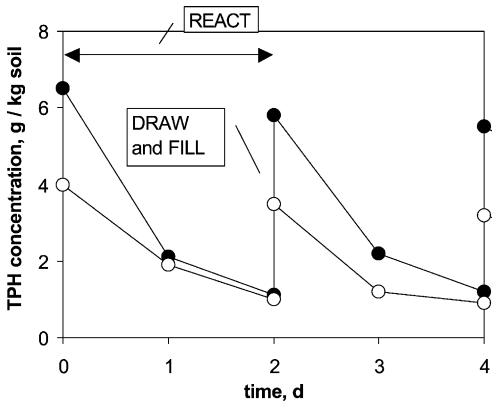


Fig. 2. Comparison between (●) a run with HRT = 10 days (Run 1 in Table 1), and (○) a run with HRT = 20 days (Run 2 in Table 1).

contaminant removal rate in the bioreactor since during the same time (2 days, in this case) a larger amount of contaminant is removed. This result is a consequence of the aforementioned reduction of the contaminant bioavailability as the contaminant concentration decreases; we can clearly recognize in each cycle shown in Fig. 2 the aforementioned first phase with a high contaminant removal rate followed by the second phase with a definitely lower rate of contaminant abatement rate. Therefore, at the end of the react cycle, the contaminant removal rate is limited by the contaminant mass transfer from the soil to the microbial cells and not by the biomass growth rate. In other words, the biomass experiences *famine* conditions. As the contaminant concentration increases at the beginning of each cycle, a larger amount of substrate becomes available for biomass growth: *feast* conditions are established. This alternating in substrate availability conditions (which is called *feast and famine regime* in SBR wastewater treatment plants), modifies the metabolic potential of the microorganisms, and as a consequence, improves their performance in contaminant removal. Moreover, the larger the substrate concentration at the beginning of the cycle, the larger the consequent biomass increase and contaminant removal rate. This condition is maintained until the low contaminant concentration reduces the bioavailability and establishes *famine* conditions again. The finding from these experiments is that, as far as *famine* conditions are attained at the end of the react cycle, a low HRT results in a better utilization of the reactor volume.

However, the same HRT can be obtained from different combinations of react time and amount of slurry drawn from the reactor. For instance, Runs 1 and 3 (Table 1) had the same HRT which was achieved by removing 20% of the slurry every 2 days (Run 1) or 70% of the slurry every 7 days (Run 3). From the previous analysis we expect no significant differences between these two conditions: Run 3 will attain a larger contaminant concentration at the beginning of the react step that will induce a larger removal rate and will lead to almost the same concentration at the end of each react step (that is, after 2 days for Run 1 and after 7 days for Run 3). These predictions are confirmed by the results of Runs 1 and 3 summarized in Fig. 3 where we can see that the contaminant concentrations at the end of each react step are almost the same. This means that is more cost-effective, reducing the amount of slurry

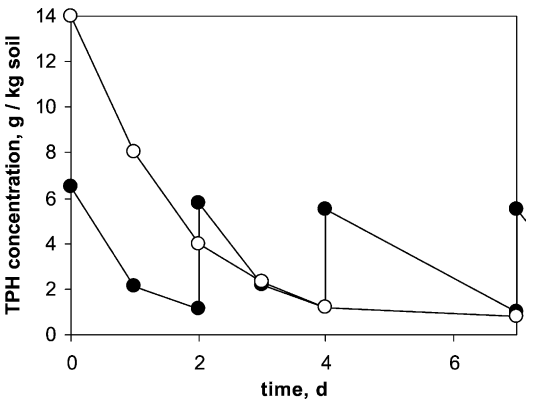


Fig. 3. Comparison between (●) a run with 20% of slurry drawn from the reactor at the end of the draw step (Run 1 in Table 1), and (○) with 70% of slurry drawn from the reactor at the end of the draw step (Run 3 in Table 1).

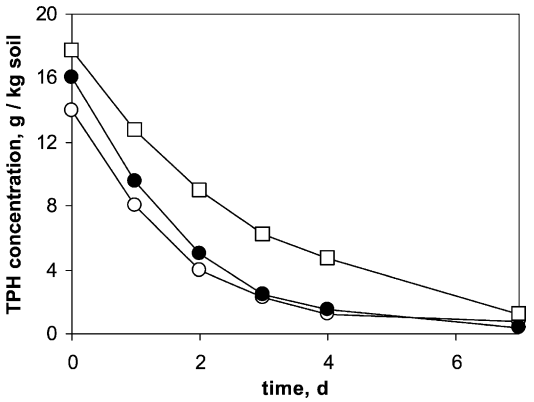


Fig. 4. Influence of the soil concentration in the slurry on the SPB performances: (○) 10 wt.% (Run 3 in Table 1); (●) 20 wt.% (Run 5 in Table 1); (□) 40 wt.% (Run 4 in Table 1).

recycled thus increasing the react time and reducing the cycle frequency. This procedure would lead to reduce the operating costs related to the fill and draw procedures.

The influence of the amount of soil in the slurry has been investigated by comparing the results of Runs 3–5 (Table 1, and Fig. 4). We can see that in this case, the differences between the various runs do not have an important impact on the final contaminant concentration. We also note that during the react step the transition from the first phase to the second one (where bioavailability limits the pollutant removal rate) is less pronounced for Run 4 (the run with the highest soil content). This result should be probably ascribed to the higher amount of substrate per unit volume available leading to an increase of the time required for the whole contaminant removal. However, since we are not interested in reaching the second phase of the SPB (since we wish to complete the treatment in the SoPB), a react time of 7 days should be adequate also for a soil load of 40%. This value (40 wt.%) can therefore be roughly considered as the highest soil concentration that can be processed under these conditions. Obviously, the larger the soil concentration, the higher the volume reactor utilization with a resultant lowering of the plant costs.

3.2. Laboratory-scale 5 and 10 l SPB experiments

The main goal of these experiments was to confirm the results obtained with the surrogate fuel as well as to investigate the effect of an initial scale-up of the SPB.

Based on the 1 l SPB experiments the operating conditions summarized in Table 1, Run 6, were chosen. A comparison between the results obtained using diesel fuel and the surrogate are shown in Fig. 5. Note that the results have been made dimensionless by using the contaminant concentration at the beginning of each react step (that is, at the beginning of each cycle). This procedure allowed us to disregard the affect of small changes in the initial contaminant load from cycle to cycle thus allowing for a fairer comparison of the different experimental results. We can see that there is a good agreement between the results obtained using diesel fuel and the surrogate contaminant. We can therefore conclude that

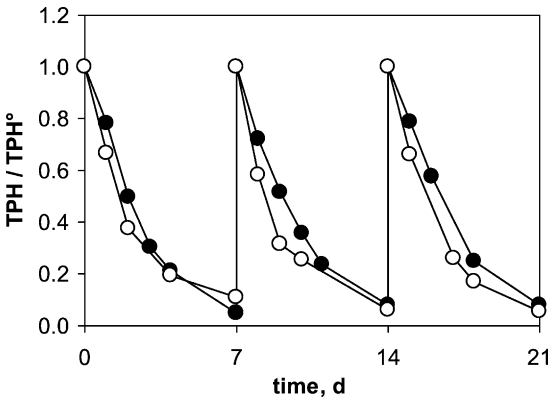


Fig. 5. Comparison between different SPB experiments: (●) 1 l with soil polluted by *n*-dodecane (Run 4 in Table 1); (○) 5 l with soil polluted by diesel fuel (Run 6 in Table 1). TPH/TPH^0 is the ratio of the contaminant concentration to the contaminant concentration at the beginning of each react step.

the operating parameters utilized using a small-scale reactor and a surrogate fuel can be used for larger scale reactors with diesel fuel.

This result is confirmed by the results of experiments carried out at an even larger scale, namely those of Run 7 in Table 1. In these experiments the HRT as well as the amount of slurry recycled in the next cycle have been reduced. These results are compared with those of a small-scale experiment involving the fuel surrogate (Fig. 6). One can see that, in spite of the results of the two experiments not exactly being the same, the main findings discussed in Section 3.1 are confirmed. In particular, the transition from the first phase to the second one of SPB arises after approximately 6 days, thus confirming the shift towards a higher treatment time evidenced in Section 3.1 for the higher soil load (see Fig. 4). Moreover,

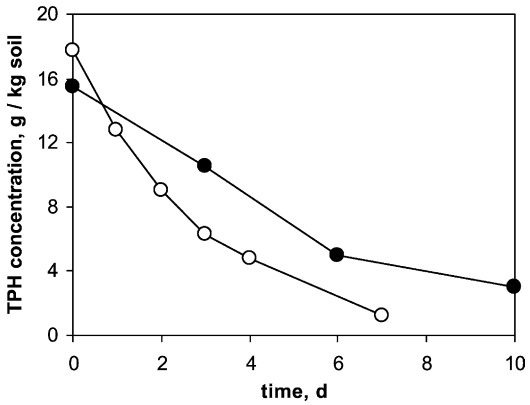


Fig. 6. Comparison between different SPB experiments: (○) 1 l with soil polluted by *n*-dodecane (Run 4 in Table 1); (●) 10 l with soil polluted by diesel fuel (Run 7 in Table 1).

reducing the HRT and the slurry recycle ratio leads to a slight reduction in the contaminant removal at the end of the react step. However, after 7 days the contaminant load is reduced to approximately 70%, which is reasonable as a first treatment step.

As easily deduced from the final slope of the curve shown in Fig. 6, achieving a complete elimination of the contaminant would require a very long time. As previously discussed, this residual contaminant can be more conveniently removed using a SoPB. Moreover, we can conclude that the operating parameters of these last runs are suitable for the pilot-scale SPB runs discussed in Section 3.3.

3.3. Pilot-scale 200 l SPB experiments

The purpose of these experiments was two-fold: first it was designed to confirm the reliability of the previous conclusion at a larger scale; second it was designed to prepare the partially cleaned soil for feeding the SoPB. The results are summarized in Fig. 7 where some typical data from the 200 l SPB are compared with the results of similar experiments carried out in the 10 l SPB. We can see that there are no significant differences between the two sets of experiments, thus confirming the reliability of laboratory-scale experiments for scale-up purposes. The contaminant removal at 7 days was less than the 60–70% found in the 10 l reactor being only 50–60%. This result should be probably ascribed to the increased difficulties in mixing efficiently a larger slurry volume, but it could be easily overcome at larger scales using more efficient industrial mixers.

3.4. SoPB runs

The slurry drawn from the 200 l SPB has been used, after partial dewatering, to construct various SoPBs (Table 2). These units allowed to investigate not only the effectiveness of coupling SPB with SoPB, but also to investigate the affect of some operating parameters on the SoPB performances.

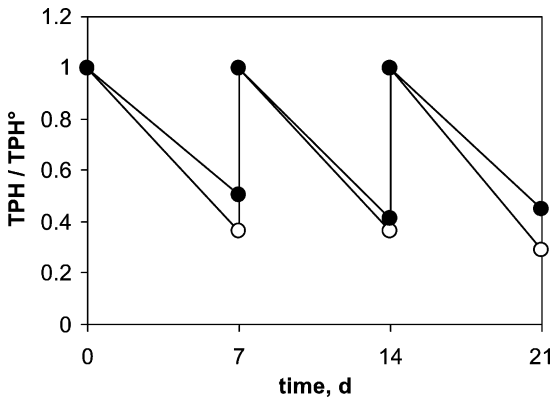
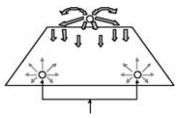
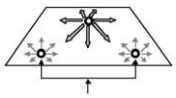
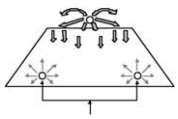
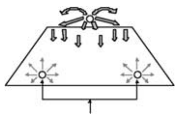


Fig. 7. Influence of different reactor size: (○) 10 l (Run 7 in Table 1); (●) 200 l (Run 8 in Table 1). TPH/TPH^0 is the ratio of the contaminant concentration to the contaminant concentration at the beginning of each react step.

Table 2
Summary of the SoPB runs which involve various pile configurations, such as the location of both irrigation and aeration, as well as the presence of additives (i.e. sand and surfactant)

Run	Initial contaminant concentration TPH^0 (g/kg soil)	Main experimental details	Sketch of the pile
1	9.3	External irrigation and internal aeration with pH 2	
2	7.3	Internal irrigation and aeration	
3	8.3	External irrigation and internal aeration with surfactant	
4	8.3	External irrigation and internal aeration with sand	
5	7.9	Neither irrigation nor aeration	

In the sketches, larger arrows indicate irrigation, while thinner arrows indicate aeration.

In all the runs, pH values were in the range 7–8 and the concentration of nutrients was always in excess with respect to the desired C:N:P ratio. No adjustments were made in the SoPB during the reaction period. The temperature values, both ambient and inside the pile, were also monitored. The temperature inside the pile was more constant than the ambient temperature being approximately 5 °C higher.

Two piles were used as controls (Runs 1 and 5) to verify that the contaminant removal has to be ascribed to the enhanced microbial activity. Run 1 involves an acidified SoPB, in which all the biological activities were inhibited, while Run 5 was carried out without providing any air and water to the reactor, thus representing the capability of the biomass present in the soil from SPB to decrease contaminants without any biological activity enhancement. A comparison between the results of these two runs is reported in Fig. 8 where no significant differences are evident. In both the cases, a contaminant reduction of approximately 5% was found, an amount which is of the same order of the experimental uncertainty. This result means not only that contaminant removal by air stripping and water leaching are both negligible in these conditions, but also that, in spite of the presence of a large microbial population grown in the SPB, biostimulation with air and water cannot be avoided.

Some more insights on this aspect of the treatment process can be obtained by noting that the values reported in Fig. 8 are, as all the other results of the SoPB runs, volume average concentrations since they were measured as the mean of six samples collected at different

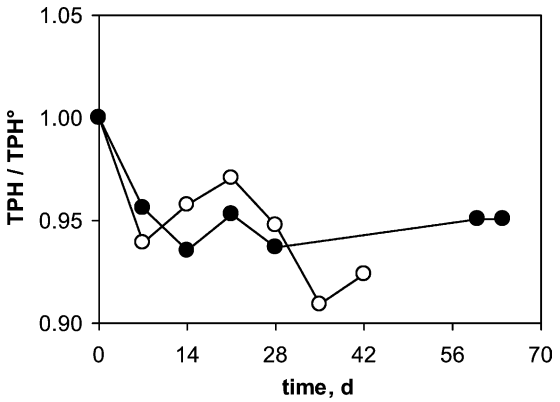


Fig. 8. Comparison between (○) acidified pile (Run 1 in Table 2), and (●) pile without biostimulation (Run 5 in Table 2). TPH/TPH^0 is the ratio of the contaminant concentration to the initial contaminant concentration.

locations and depths. Looking at point concentration values, as shown in Fig. 9, we can see that for Run 1 the reduction of the contaminant concentration is almost uniform along the pile depth and therefore it can be reasonably ascribed to air stripping and water leaching. However, the opposite is true for Run 5, where almost all the contaminant depletion is localized close to the pile top, i.e. close to the atmosphere where oxygen uptake occurs. This result clearly indicates that in this case contaminant removal has to be ascribed to

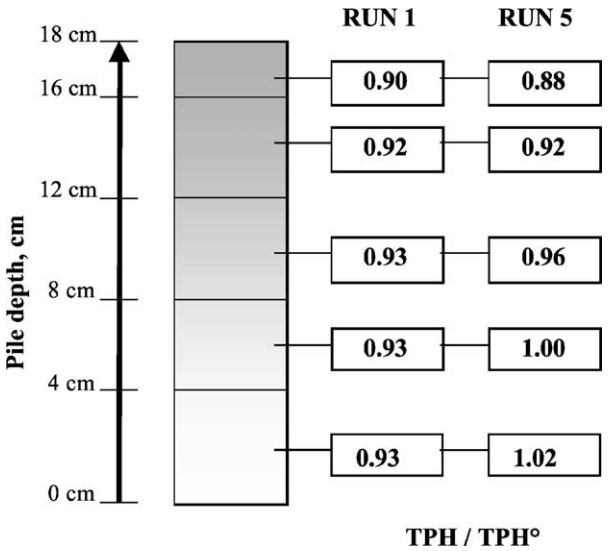


Fig. 9. Contaminant concentration values as a function of the pile depth for Runs 1 and 5 in Table 2. TPH/TPH^0 is the ratio the of the contaminant concentration to the initial contaminant concentration, while depth = 0 is the bottom of the pile.

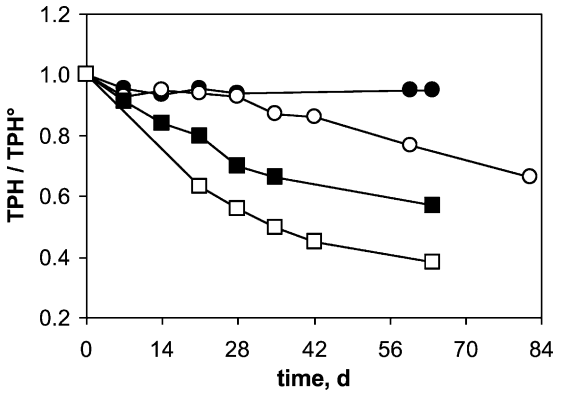


Fig. 10. Influence of various additives on SoPB performances: (●) without irrigation and aeration (Run 5 in Table 2); (○) without additives (Run 2 in Table 2); (■) with surfactant (Run 3 in Table 2); (□) with sand (Run 4 in Table 2). TPH/TPH^0 is the ratio of the contaminant concentration to the initial contaminant concentration.

microbial activity that is possible only close to the pile boundary where atmospheric oxygen is available for contaminant aerobic degradation.

Run 2 in Table 2 refers to a standard SoPB obtained partially dewatering the slurry drawn from the SPB. The results obtained in this case are shown in Fig. 10, where they are compared with those of a control run (Run 5). We can see that at the beginning the results of the two experiments are quite similar. However, while contaminant depletion in Run 5 stops after approximately 4 weeks the depletion of contaminant of Run 2 continues at a low, but almost constant, rate. The low removal rate results in only a 30% reduction of the initial contaminant after 12 weeks. This low removal rate can be ascribed both to a low porosity of the soil that limits oxygen diffusion, as well as to limited bioavailability of the contaminant. To investigate the limiting factor, two more bioreactors were prepared using soil additives, namely sand and surfactants. While the first additive improves pile porosity and consequently oxygen diffusion, the latter increases contaminant bioavailability. Both the additives can be conveniently added to the slurry just before the draw step allowing for a cheap and efficient mixing with the soil.

The results of Run 3, also shown in Fig. 10, involved the addition of anionic surfactants (sodium alchilbenzensulfonate and sodium alchiletossisulfate, with a concentration equal to 0.5 wt.%). These data clearly indicate that adding a surfactant significantly increases the initial contaminant removal rate. However, after approximately 4 weeks the degradation rate is reduced and becomes close to that of Run 2. This behavior was probably a result of the biodegradation of the surfactant. In the first period, the surfactant increases the contaminant solubility and consequently its bioavailability; however, microbial cells not only degrade the dissolved contaminant, but also the surfactant. Once almost all the surfactant is consumed no increase of the bioavailability is possible and the degradation proceeds at the same rate as the SoPB without surfactant. A possible solution to this problem would be to continuously add a small amount of surfactant to the irrigation water. In any case, the initial larger rate of degradation has led to a contaminant removal of about 40% of the initial contaminant load in 9 weeks.

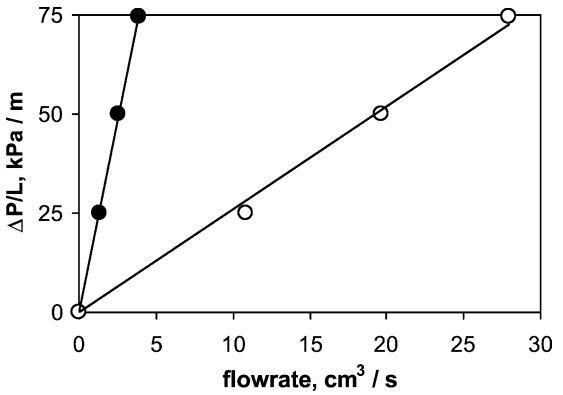


Fig. 11. Pressure drop (ΔP) per unit bed length (L) as a function of air flowrate for (●) soil and (○) soil with 10 wt.% sand.

In Run 4 we investigated the influence of changing the soil porosity. This investigation was done by adding some sand (10 wt.% with particle size less than 3 mm) to the soil before preparing the SoPB. The change in soil porosity was quantified by measuring the pressure drop as a function of the gas velocity for two 5 cm long beds of soil with and without sand (Fig. 11). One can see that pressure drop increases linearly with flowrate in agreement with the Darcy's law and that adding a 10 wt.% sand to the soil results in a ratio of pressure drop

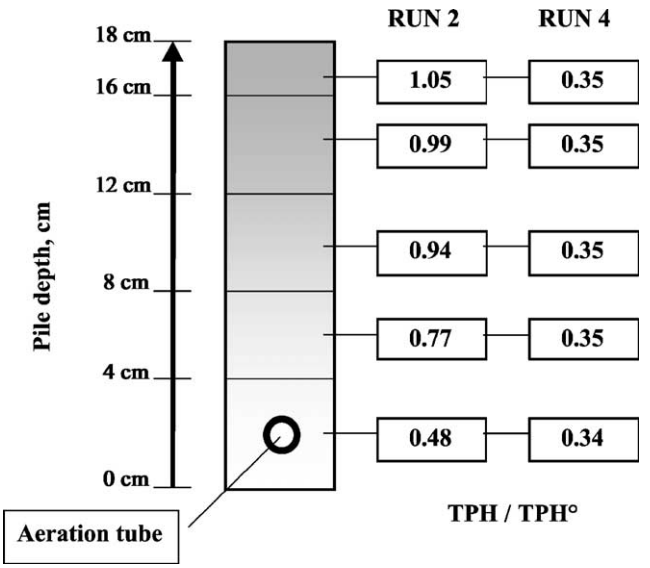


Fig. 12. Contaminant concentration values as a function of the pile depth for Runs 2 and 4 in Table 2. TPH/TPH^0 is ratio of the contaminant concentration to the initial contaminant concentration, while depth = 0 is the bottom of the pile.

to flowrate (that is, the slope of the lines in Fig. 11) that is approximately seven times lower than that of the soil without sand. This means that soil porosity is strongly increased by sand addition.

The improved porosity of the soil finally results in a strong enhancement of the contaminant removal rate, as shown in Fig. 10 where one can see that more than 60% of the initial contaminant load is removed in 9 weeks. The increase of the oxygen diffusion results also in a much more uniform contaminant depletion inside the pile, as shown in Fig. 12 where the contaminant concentration along the pile depth is reported for both Runs 2 and 4. One can see that while for Run 4 the contaminant concentration is almost uniform along the pile depth, the opposite is true for Run 2, where almost all the contaminant depletion is localized near the air distribution tube close to the bottom of the pile.

4. Conclusions

In this work we have investigated the possibility of coupling slurry-phase bioreactors with solid-phase bioreactors in order to combine the advantages and minimize the disadvantages of each treatment method when used alone for cleanup a diesel contaminated soil.

It has been found that for SPB, under certain constraints, a low hydraulic retention time and a low slurry recycle ratio allow for a better utilization of the reactor volume, thus leading to a fast reduction of a large part of the contaminant load. The optimal conditions can be determined through small-scale laboratory experiments and then scaled-up to a larger reactor. In the case investigated, a 7-day SPB treatment has been shown to provide enough contaminant removal allowing the soil drawn from the SPB to be fed effectively to the SoPB for completion of the soil cleanup. An important improvement of the SoPB performances was achieved using soil additives, namely sand and surfactants. While the sand improved pile porosity and consequently oxygen diffusion, the surfactant increased contaminant bioavailability. Both the additives can be conveniently added to the slurry just before the draw step, allowing for a cheap and efficient mixing with the soil.

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