

Two-Step Bioreactor Process for Removal of Contaminants with Low Bioavailability

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**TWO-STEP BIOREACTOR PROCESS FOR REMOVAL OF CONTAMINANTS
WITH LOW BIOAVAILABILITY**

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Paper presented at ACHEMA 2000 – *International Meeting on Chemical Engineering, Environmental Protection and Biotechnology* / Frankfurt (Main) Germany 22 – 27 May

Abstract:

The paper reports on attempts to develop an economically feasible bioremediation technique for contaminants with low bioavailability. To this end different options for a combined physicochemical and biological treatment process were evaluated for soils contaminated with polycyclic aromatic hydrocarbons (PAH). Options evaluated for enhanced bioremediation included pre-extraction with surfactant solutions, a washing pretreatment, which consisted of attrition in the presence of different additives and fractionation by size as well as biodegradation in presence of different additives. Pre-extraction with surfactant solutions will not be feasible because of associated surfactant costs. Washing pretreatment resulted in a seriously enhanced bioavailability, even when performed without additives. Special designed surfactant combinations, which stimulate biodegradation without preferential degradation of surfactants, exhibited substantial enhancement of biodegradation rates if their composition and concentration is adapted to the actual contaminated soil. However, even under improved conditions biodegradation rates were too slow to obtain low enough residual values in reasonable times. Therefore, a new two-stage bioreactor system was developed, which enhances removal rates drastically (> 90 % in 3 days). Progress achieved was illustrated in relation to published results of other bioreactor approaches.

Keywords:

bioavailability, bioreactors, soil remediation, surfactant combinations, PAH, pyrene, biodegradation, soil washing, soil fines

Introduction

Bioremediation, often a very economical option for soil decontamination, has restricted applicability for soils contaminated with pollutants having low bioavailability and/or low biodegradability, such as polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs).

So far different attempts have been made to overcome these problems by developing bioreactor processes and/or by adding surfactants. However, removal rates obtained used to be very low. For example in an investigation of Haeseler et al. with soil samples of different PAH-contaminated sites it was found that an extent of degradation of only 50 % could be observed after 3 month, despite the presence of active PAH degrading microorganisms, even under efficiently stirred conditions (Haeseler et al. 1998). Furthermore, the removal rates became extremely low at the end of this period of biological treatment.

The paper gives a short analysis of factors limiting the availability of contaminants for clean-up processes and of different attempts in the authors laboratories to overcome these limitations. Finally, a novel bioreactor approach is reported which drastically enhances the removal of contaminants with low bioavailability.

Different additives and components of surfactant combinations mentioned in this paper are biodegradable and are available at the market at reasonable prices. For more details about the confidential information please contact the first author.

Physico-chemical factors limiting the availability of contaminants

The limited availability of pollutants is connected with their physical and chemical state in the soil/water-system. A schematic overview of the contaminant distribution in the soil/water-system is given in Fig. 1.

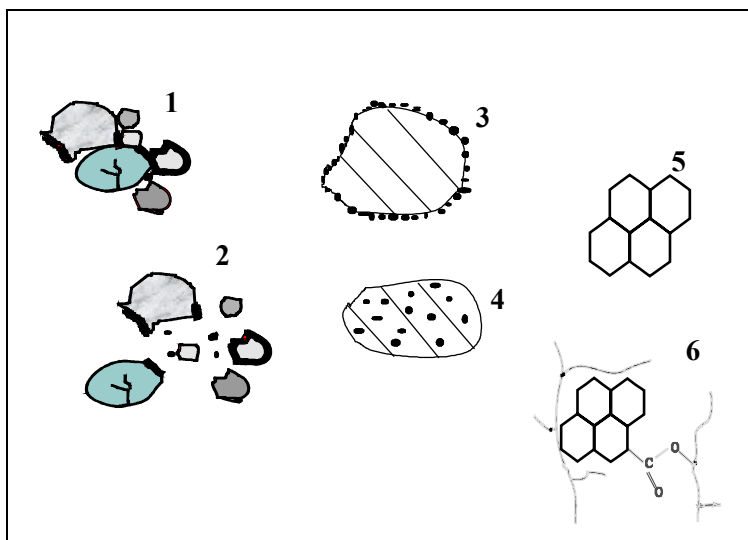


Fig. 1 Schematic representation of different physical and chemical states of pollutants in the soil/water-system (contaminant marked dark)

1: soil agglomerates, 2: suspended soil particles, 3: adsorbed state, 4: absorbed state, 5: contaminant in solution, 6: contaminant chemically bound to the soil matrix

The contaminant may be present in soil agglomerates (1) or on suspended soil particles (2), in an adsorbed (3) or an absorbed state (4), as separate phase (layers, dispersed particles or oil) or in solution (5), on the surface or in pores. With progressive aging the contaminants will be bound chemically to the soil matrix (6) to an increasing extent.

The availability of contaminants is proportional to their area of contact with water or air. The transfer to the degrading organisms will be especially hindered if contaminants are

present in micropores, absorbed in a dense matrix, if they are in a separate phase or if they are bound chemically. Biofilm formation onto the substrates will enhance biodegradation in a first phase but will finally contribute to transport limitations, i.e. acting as a kinetic barrier.

Options to enhance contaminant removal

In principle, transfer may be enhanced by dispersion, solubilization, emulsification and attrition of surfaces by mechanical forces with or without the help of selected additives.

To this end, the authors evaluated different options for enhanced biodegradation (Sobisch and Niebelschütz 1998b,c; Sobisch et al. 2000). These included pre-extraction with surfactant solutions, a washing pretreatment, which consisted of attrition in the presence of different additives and fractionation by size as well as biodegradation in the presence of different additives.

A feasibility study for extraction of contaminated soils revealed that surfactant costs will be high even when surfactant combinations with a pronounced extraction efficiency are applied. PAH exhibit a low solubility in organic solvents too. Bonkhoff et al. compiled the following data for the solubility of pyrene – in water 0.0001, in 10 % aqueous solution of the technical surfactant C12/C14EO7: 0.7, in n-hexane: 17.2, in rapeseed oil: 50.5 and in rapeseed methyl ester: 69.5 mg/l (Bonkhoff et al. 1995). Extracting a fraction of soil fines from a soil washing plant with a pyrene load of 530 mg/kg (EPA PAH 3000 mg/kg) the same authors transferred 67.5 mg/l pyrene (94%) to a microemulsion containing 22 % of a nonionic surfactant and 39 % of rapeseed methyl ester (43°C, 2 h extraction, soil/microemulsion ratio 1/6). Evaluating the extraction efficiency of different surfactant

combinations on the same contaminated soil fraction a 2 % surfactant solution could solubilize 30 mg/l pyrene (30 %) at best (room temperature, 1 h extraction, soil/water ratio 1/4) (Sobisch 1999). In both cases associated surfactant costs will prevent the implementation of a process with pre-extraction of contaminated material.

The investigations described in the following were carried out mainly on a sandy soil of a former gas work site with an initial PAH load of 1100 mg/kg (in the following the term PAH concentration refers to the sum of 16 specific EPA PAHs). All soil samples, except fractions of soil fines from a soil washing plant, were homogenized to avoid ill reproducibility of the initial composition by passing through a 4 mm screen and by mixing. Often, the concentration of pyrene was chosen to measure changes in the contaminant load because it can be easily and selectively measured by UV-derivative spectrometry (for details see Sobisch et al. 2000, Sobisch 1999). Applicability of pyrene content as indicator is based on the following. Pyrene is a major constituent of the overall PAH contamination. In case of the sandy gas work soil the initial pyrene concentration was 420 mg/kg, i.e. 38 % of the PAH concentration measured. Further, it is well known that most of the lower condensed PAH exhibit higher and most of the higher condensed PAH show lower availability for degradation and removal.

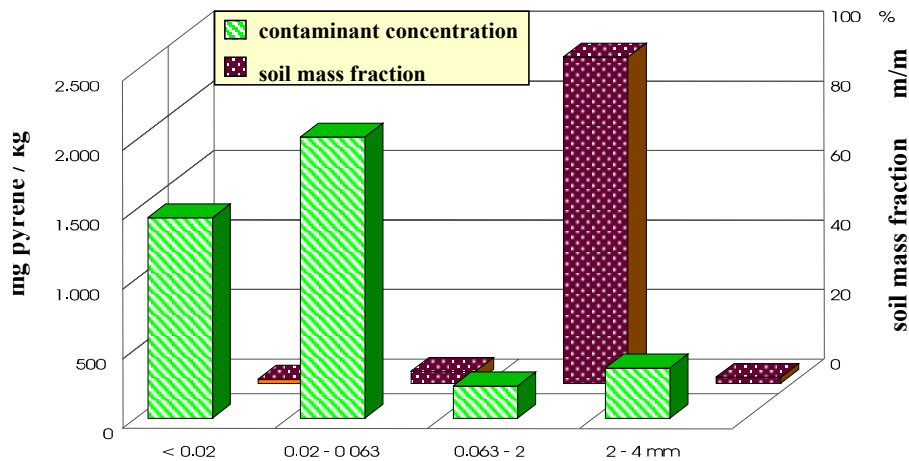


Fig. 2 Distribution of size fractions and pyrene contamination in a sandy soil of a gas work site obtained after mechanical disintegration and wet sieving

Fig. 2 shows the mass and contaminant distribution between different size fractions obtained after mechanical disintegration in a laboratory attrition cell (30 g soil, 30 g water, 10 min at 80 rpm) and wet-sieving into size fractions 4 – 2 mm, 2 mm – 63 μm and 63 – 20 μm . The dispersion of soil particles < 20 μm was centrifuged at 3600 rpm for 5 min.

The results suggested that although the fraction of soil fines was small and had a substantially higher PAH concentration, treatment by simple soil washing alone was not promising because a PAH load of 470 mg/kg was measured for the "cleaned" sand fraction.

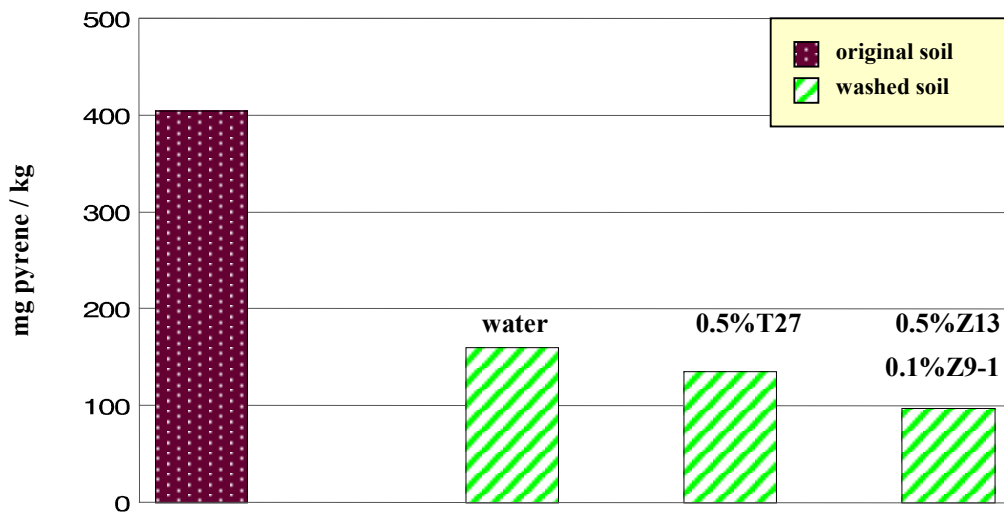


Fig. 3 Results of a washing pretreatment of the gas work soil

pyrene concentration remaining in soil after attrition and removal of soil fines

Tests of a washing pretreatment were conducted with first washing in the presence of different additives in a laboratory attrition cell (10 min, 30 g soil, soil/water ratio 1/1). Then the soil dispersion was transferred into a graduated cylinder. Soil fines and light particles were removed by alternating steps (three times) of dispersion with water (soil/water ratio 1/4), sedimentation and removal of the supernatant along with unsettled particles. Sedimentation time and distance had been chosen to remove mineral particles smaller than $< 50 \mu\text{m}$. Removed soil fines were approximately 8 % of the whole soil mass. After decanting and air drying the residual pyrene concentration was determined by UV-derivative spectrometry (10 g of air dried soil samples were extracted with 50 ml methanol over 1 h at 40 °C in an ultrasonic bath). The tests resulted in the following. By washing without additives a reduction in the pyrene load of more than 50 % was achieved. Addition of a surfactant combination (T27, 0.5 % m/m per soil) with high extraction efficiency (Sobisch 1999) to the soil resulted in a further contaminant reduction of 15 %. The best

result was obtained by adding 0.5 % of a hydrophobic cosolvent and 0.1 % of a dispersant simultaneously.

When shaken with a dilute nutrient solution over a period of several weeks the kinetics of pyrene removal from soil are characterized by a leveling-off after two weeks (Fig. 4).

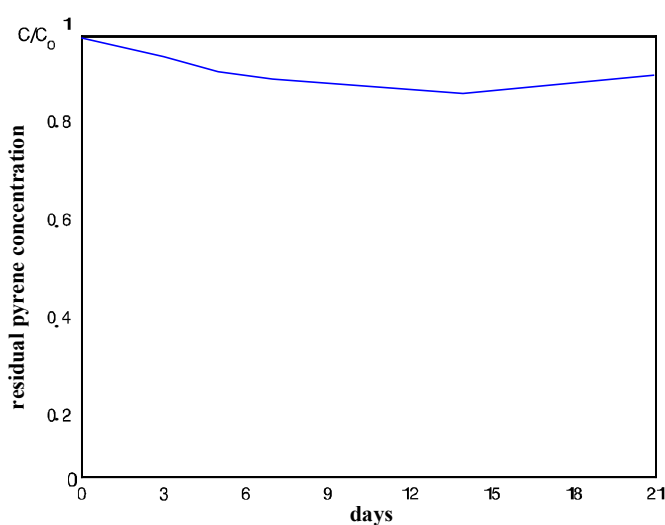


Fig. 4 Kinetics of pyrene removal from a gas work soil

shaker table test – ratio soil/mineral salt solution 1:2, 5 g soil

The pyrene concentration used as a measure of the more recalcitrant compounds reduced by less than 20 %.

The influence of washing pretreatment on biodegradation is shown in Fig. 5. The initial and residual values for PAH concentration in soil are compared for samples differently treated before the biodegradation slurry test, which was run for 10 days with 20 g soil and 180 ml mineral salt solution.

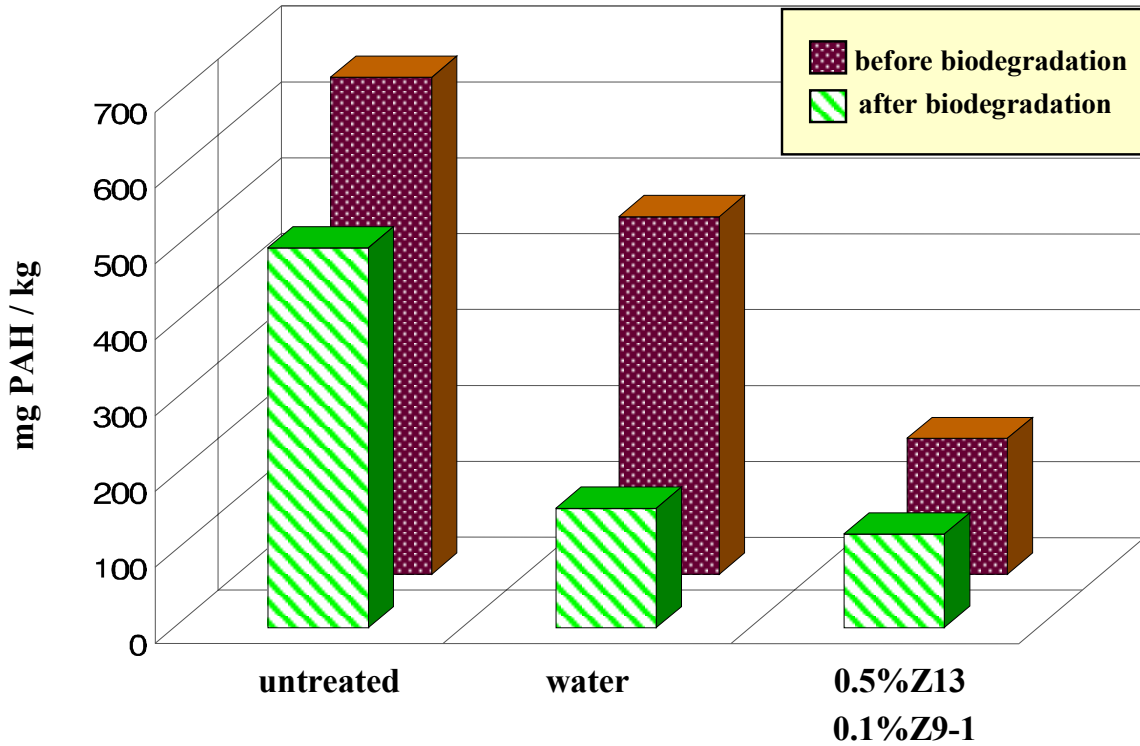


Fig. 5 Influence of washing pretreatment on biodegradation

The washing pretreatment resulted in a seriously enhanced bioavailability, even when performed without additives. Whereas for the original soil sample the PAH load reduced to 500 mg/kg, the residual concentration for the sample washed previously with water alone was 150 mg/kg. The sample washed with additives showed only a minor further improvement, therefore the associated costs are not justified.

Addition of surfactants to improve bioavailability has been conversely discussed in literature. Diverse experimental observations were compiled by Liu et al. (Liu et al. 1995). In previous investigations we identified special surfactant combinations which enhanced the biological activity in tar-oil-water systems without preferential degradation of

surfactants. The surfactant combinations are mixtures of a hydrophilic and a hydrophobic non-ionic compound. The evaluation of their applicability for soil remediation revealed some interesting features (Sobisch et al. 2000).

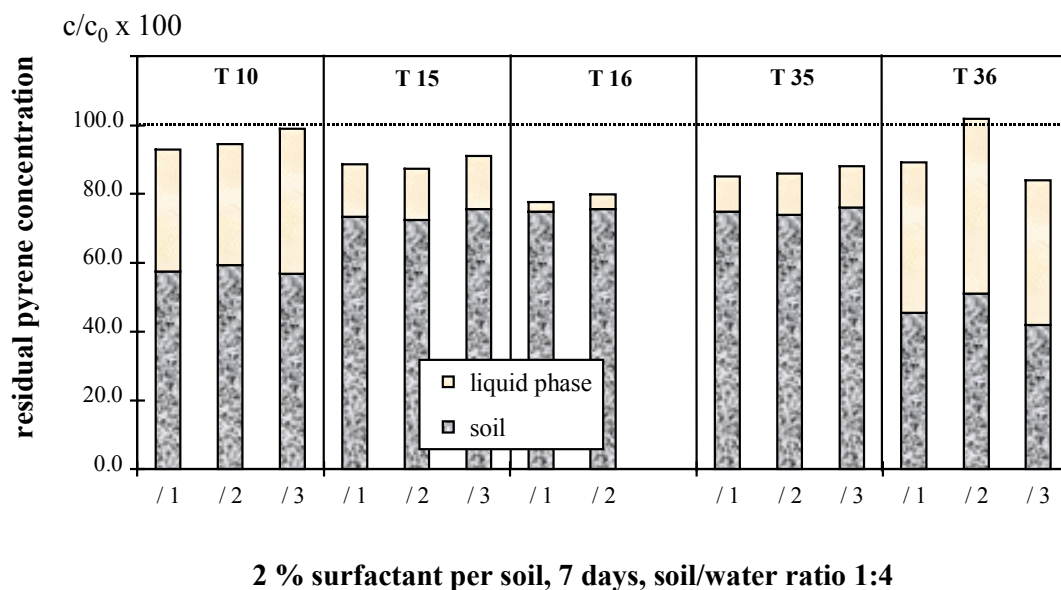


Fig. 6 Influence of surfactant composition on solubilization and removal of pyrene from a gas work soil

Comparison of the effect of different surfactant combinations, each composed of different pairs of a hydrophobic and a hydrophilic nonionic compound, /1, /2, /3 mark different mixing ratios (37, 50, 70 % hydrophobic compound)

Fig. 6 shows the influence of these surfactant combinations on solubilization and degradation of PAH in the case of the sandy gas work soil. The residual pyrene concentration in soil and in water phase was analyzed after one week of shaking of the soil suspension (5 g / 20 ml) amended with nutrients and 2 % surfactant per soil mass. UV-derivative spectrometry of pyrene remaining in soil was conducted after extraction as

described above. Pyrene in the aqueous phase was determined directly after separation by centrifugation.

The lower part represents the fraction of pyrene remaining in soil, the upper part the fraction solubilized, the difference to 100 the fraction degraded. Surfactant combinations T10 to T36 consist of different pairs of hydrophobic/hydrophilic components. In the order from /1 to /3 the content of the hydrophobic component increases from 37, over 50, to 70 %.

The solubilizing action of the surfactant combinations used is not solubilization in terms of 'preparation of thermodynamically stable isotropic solutions of substances otherwise only slightly soluble' (Elworthy et al. 1968), i.e. micellar solubilization. Because of these surfactant combinations are only dispersed (not solved) in the water phase, the PAH will partition between the soil, water and the dispersed surfactant phase. Therefore, the critical volume necessary for solubilization of PAH of high molecular weight (Klevens 1950) seems to be not a limiting factor (Sobisch et al. 2000).

Surprisingly, the ratio of the two components has no distinct influence on residual and solubilized amounts of pyrene. However, combinations with different pairs of compounds differ markedly in solubilization power. Interestingly, the combinations most efficient in solubilization - T10 and T36 - show the lowest degree of degradation and vice versa. From this it is concluded that high concentrations of PAH in the liquid phase may exert a toxic or inhibiting effect on the soil microflora.

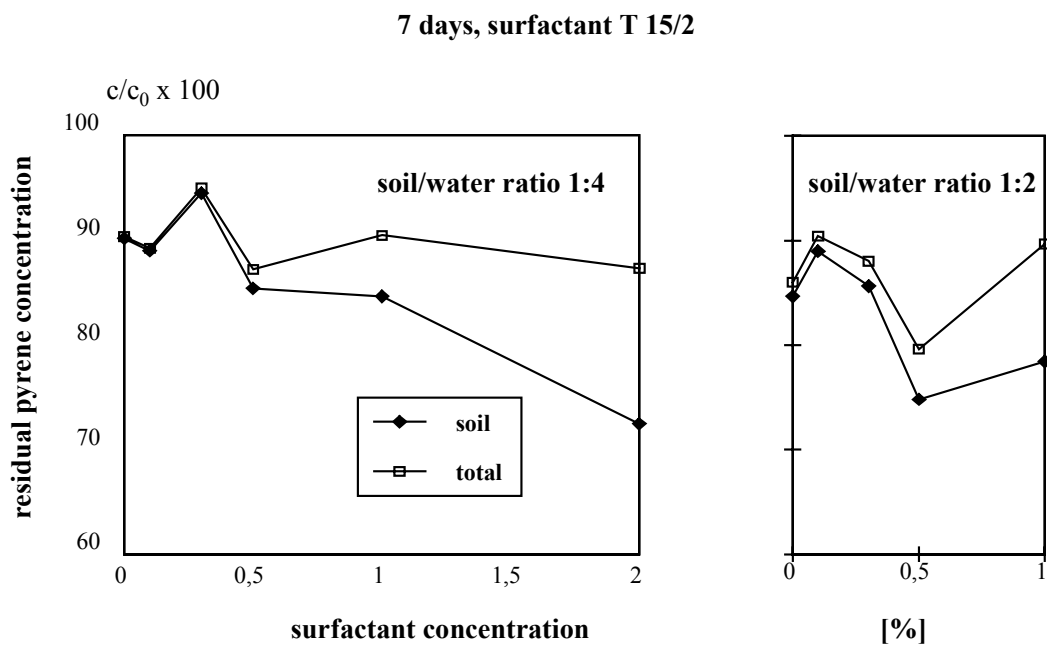
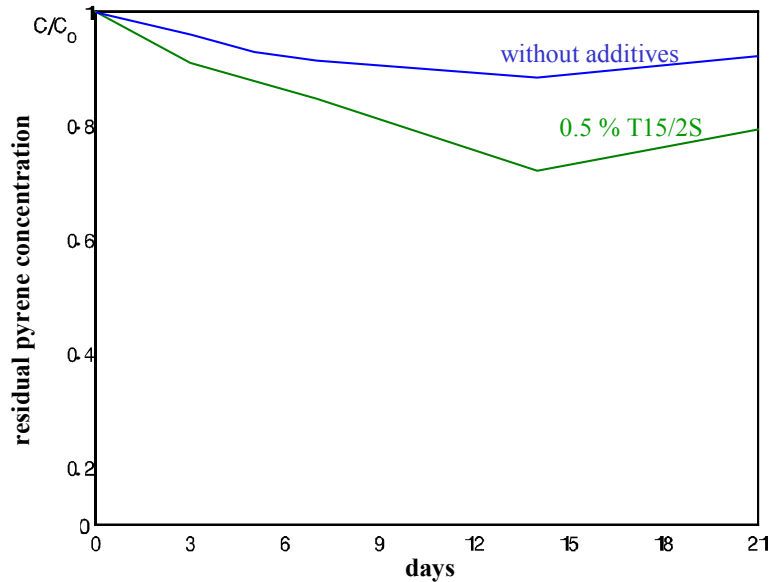


Fig. 7 Effect of surfactant concentration on solubilization and removal of pyrene from a sandy gas work soil, 5 g soil

The degree of solubilization and the remaining fraction of pyrene in soil after one week was measured as a function of concentration of surfactant combination T15 (Fig. 7). Two different soil/water ratios were applied (5 g soil samples). As expected, by increasing surfactant concentration, the degree of solubilization was increased. However, the total residual contaminant concentration in soil and water was lowest at 0.5 % surfactant in each case.

The behavior shown on the last two figures suggest that biodegradation could be stimulated significantly if the composition and concentration of the surfactant combination

is selected properly. Bioavailability should be enhanced to the optimum, whereat no adverse effects on the soil microflora occur.



**Fig. 8 Kinetics of pyrene removal from a sandy soil of a gas work site
Comparison between shaker table tests with and without surfactant
ratio soil/mineral salt solution 1:2, 5 g soil**

Figure 8 compares the kinetics of pyrene removal from the sandy gas work soil without surfactants (Fig. 4) with the kinetics in the presence of 0.5 % T15/2S. The removal rate could be doubled by adding 0.5 % T15/2S, however, most of the pyrene remained on the soil.

In summary, the investigation of different alternatives for an enhanced biological treatment process led to the conclusion that in all cases biodegradation rates were too low to obtain acceptable residual values (i.e. Dutch guideline values for PAH B: 20 mg/kg, C: 200 mg/kg) in reasonable times, even under improved conditions. At this stage an attempt was

made to design a new system that combines intensive attrition of soil grains, removal of pollutants from solution by a sorbent and biodegradation, and which could be optimized further by selected additives.

Concept of a new two-stage bioreactor process

The new bioreactor system consists of a reactor for simultaneous biological and wet processing and a filled column reactor (Fig. 9).

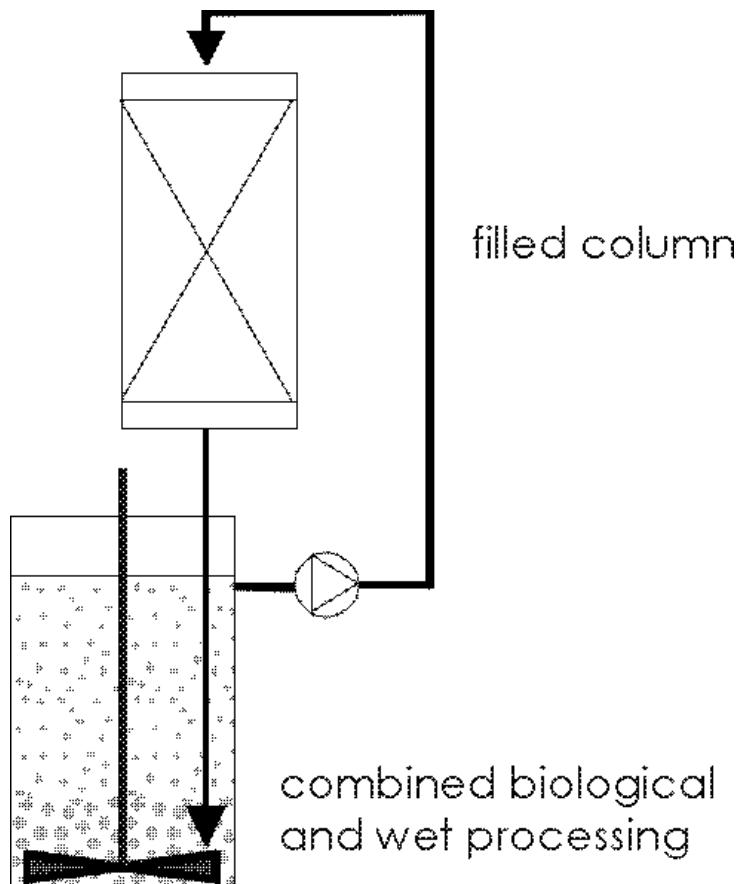


Fig. 9 Two-stage bioreactor scheme

In the stirred tank reactor contaminant material is under continuous agitation, thus adhering particles, contaminant layers and biolayers are continuously removed and suspended. Stirring is adjusted so that soil fines (fraction of approx. $< 50 \mu\text{m}$) are suspended fully but sand grains remain concentrated at the bottom underlying mutual attrition. The reactor may also be aerated. The slurry of suspended soil fines and particles of low density is continuously transferred to a trickling filter, a column filled with a material of high sorption capacity, i.e. activated carbon, etc., which filters off fine particles and binds contaminants. After passing the column, the suspension is recirculated.

The treatment is designed as batch process. After removal of the contaminants the soil is separated and the liquid phase is reused in the next step. The system does not require replacement of the column filling as cycles of back-washing maintain permeability and continuous biological regeneration takes place.

Advantages of the system described are

- Simultaneous mechanical and biological stressing of contaminant layers
- The material of high sorption capacity acts as a buffer. Contaminants can be degraded after soil processing. Adapted microorganisms are provided with a large surface for biofilm formation and a continuous supply of oxygen, nutrients and with contaminants.
- By recirculating the suspension additional active biomass is delivered into the first stage of the reactor.
- In the case of sandy soils, the fines and light material are separated during passing the trickling filter. This way, soil cleaning by separation and biodegradation can be carried out simultaneously.

Applications

The new system proved to be very effective. The first experiments were conducted using a miniaturized version of the reactor system (samples of 10 g soil, soil/water ratio 1/4, height/diameter ratio of the stirred reactor 6/1, of the column 9/1, 10 g activated carbon of cylindrical shape 1 mm in diameter). The laboratory system was scaled up to treat 1 liter soil slurries (samples of 200 g soil, same soil/water ratio, height/diameter ratio of the stirred reactor 5/1, of the column 5/1, 200 g of the same activated carbon).

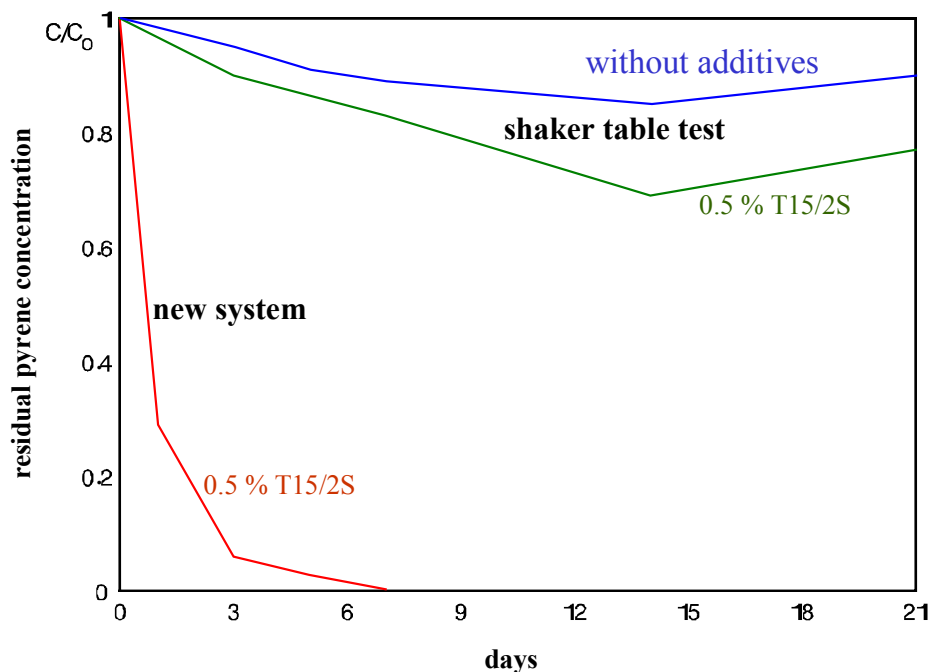


Fig. 10 Kinetics of pyrene removal from a sandy soil of a former gas work site

Comparison between shaker table tests and two-step bioreactor process

ratio soil/mineral salt solution - shaker table test 1:2 (5 g soil), - bioreactor 1:4 (10 g soil)

Fig. 10 depicts the improvement in relation to the results of shaker table tests shown previously (Fig. 8). (10 g of soil treated in both cases, for the reactor system stirring speed and recycle rate were adapted, so that sand fraction remains in the lower third of reactor

volume, residual pyrene concentration measured in the soil fraction without 5 to 15 % of fines and light material removed). The improvement is obvious. During three days more than 90 % of pyrene could be removed from soil applying the new concept.

In addition to this encouraging result, further optimization could be achieved (Fig.11).

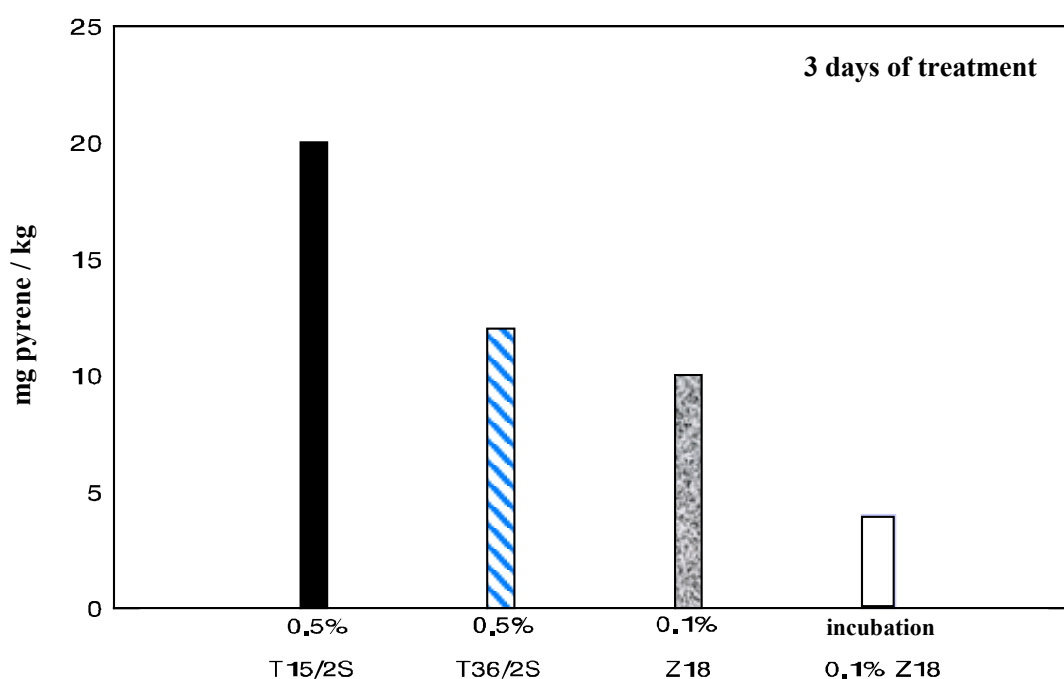


Fig. 11 Optimization of contaminant removal in the two-stage bioreactor for a sandy soil of a gas work site, ratio soil/mineral salt solution 1:4 (10 g soil)

The results after 3 days of treatment using the same reactor and conditions are displayed. The residual pyrene content could be reduced from 20 mg/kg for T15/2S to 12 mg/kg by choosing a surfactant combination with higher solubilization power (T36/2S). In contrast to the biodegradation tests in suspension discussed previously, high solubilization rates show no adverse effects. That means the buffer function of the trickling filter works. If no

surfactant was added but a polymeric additive that supports biofilm formation (Z18), a concentration of 0.1% was sufficient to obtain a residual pyrene load of 10 mg/kg. With preceding incubation of the soil (adding the nutrient solution 1 week before bioreactor treatment), the latter value could be reduced further to 4 mg/kg. The contaminant load of the treated soil reduced further if maintained in wet condition. For the soil processed 3 days with 0.1 % Z18 and stored 1 week the pyrene content reduced from 10 mg/kg to 6 mg/kg.

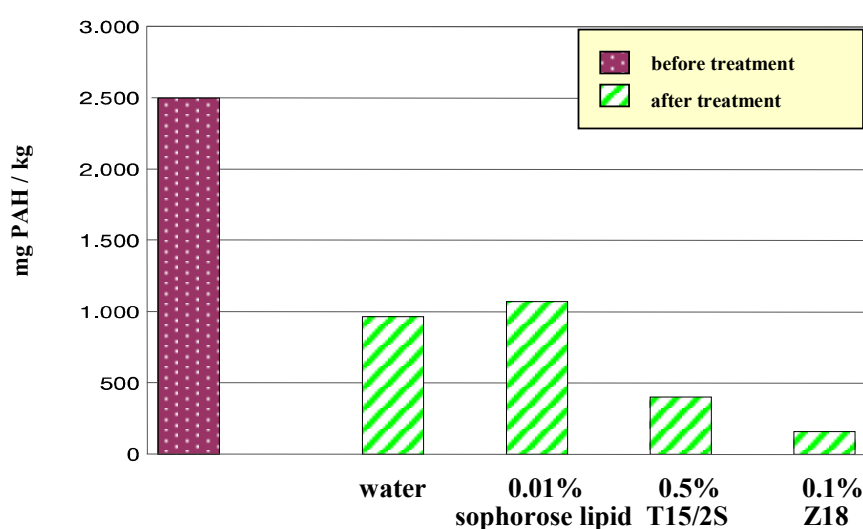


Fig. 12 PAH-removal in the two-stage bioreactor - influence of different additives ratio soil/mineral salt solution 1:9 (100 g soil)

Fig. 12 shows another set of results obtained with a soil of a higher contamination of 2500 mg PAH/kg. (100 g of soil treated, treated slurry volume 1 liter, 20 g of activated carbon described above – used only once and analyzed after treatment of one batch, residual PAH concentration measured in the soil fraction without 5 % of fines and light material removed).

With water alone a reduction of more than 60 % was achieved in three days, addition of a small amount of biosurfactant (0.01 % sophorose lipid) had no positive effect. Adding 0.5 % T15/2S the residual PAH load reduced to 400 mg/kg. If 0.1 % Z18 was added, the concentration in soil reduced to 160 mg/kg. For the treatment without additives and the treatment with Z18, a mass balance was determined for the PAH, which could be analyzed in soil, water, separated soil fines, and on the activated carbon used as filling material. This balance suggested that 60 % of the PAH were biologically converted without additives and 90 % when Z18 was added. In both cases the aqueous PAH concentration was below 0.01 mg/l. After treatment without further additives the activated carbon contained 8 mg/kg PAH, the separated fine fraction 1500 mg/kg PAH. After treatment with 0.1 % Z18 the PAH content in the activated carbon was 11 mg/kg, in the separated fine fraction 2100 mg/kg.

The treatment procedure could be adapted to different soils and to fractions of soil fines from soil washing plants.

In the latter case, the procedure can be used for reduction of the contaminant load of the fine fraction to reduce the contamination of the entire soil to target levels. In these investigations contaminant load of soil fines treated ranged between 2000 to 4000 mg/kg PAH and 300 to 700 mg/kg pyrene. Soil fines also contained heavy metals, i.e. arsenic (50 mg/kg), lead (550 mg/kg), copper (150 mg/kg), mercury (3 mg/kg) and zinc (650 mg/kg). Activated carbon (as described above), shredded tar contaminated wood or bark mulch were used as column fillings. Batches of 10 to 200 g were treated (soil/water ratio 1/4) for three days. Increasing the batch size additional aeration was necessary to maintain removal

rates. Soil fines were pretreated one or three days (soil/water ratio 1/1, addition of 0.5 % H₂O₂ per soil mass as chemical oxidant) followed by addition of 0.5 % surfactant T36/2 and 0.3 % of an additional dispersant to produce fully disaggregated slurries. Pre-oxidation only caused small variations in extractable contaminant concentration. However, pre-oxidation resulted in higher bioavailability and higher removal rates. The reactor treatment with pre-oxidation removed 30 to 60 % of the initial pyrene load. Shredded tar contaminated wood and bark mulch as column fillings normally resulted in higher removal rates than activated carbon. Soil fines removed from the column fillings for determination of the contaminant load exhibited no enhanced pyrene concentration. Analysis of shredded tar contaminated wood after treatment of 20 batches revealed no accumulation of pyrene. Actually, the pyrene content was reduced from an initial value of 650 to 140 mg/kg.

In contrast to soil treatment by conventional biological techniques, by soil washing, or incineration, the treated soil fines exhibit a substantial potential for further biodegradation. An example is given in Fig. 13. It can be seen that an aged sample of the soil fines showed no more significant pyrene degradation during incubation with nutrients, whereas the pyrene content of the same sample reduced further when incubated after the pre-oxidation and treatment in the two stage reactor.

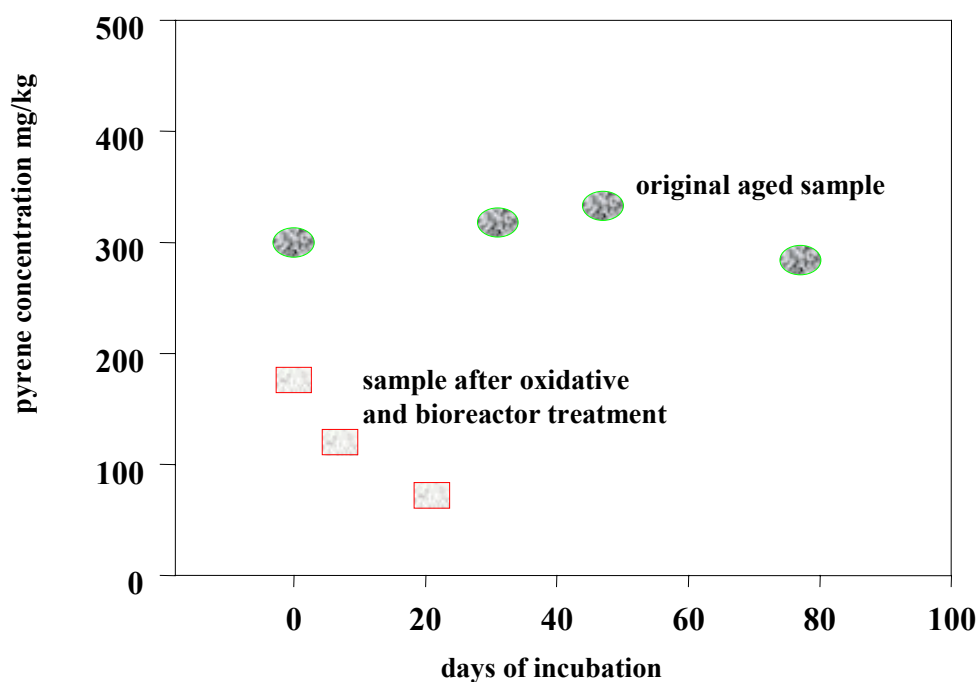


Fig. 13 Comparison of biodegradation activity of an aged fraction of soil fines from a soil washing plant before and after bioreactor treatment

Comparison of the two-stage bioreactor performance with other approaches

Unfortunately, direct comparison with other approaches described in literature is impossible because of the lack of identical contaminated soil samples. However, a short roundup of results published so far should illustrate the progress that has been made.

Joshi et al. (Joshi et al. 1995) proposed a combination of soil washing with micellar solutions of nonionic surfactants with subsequent biotreatment of the leachate. A minimum of a 2 % solution of Igepal CA-720 was required for a 50 % contaminant removal in case of a contaminated soil fraction < 425 μm (3200 mg/kg PAH, contact time 3 to 5 min, soil/water ratio 1/10 – 1/20, which means 2 – 4 g surfactant were used per 10 g of soil!).

The following leachate treatment (3 – 5 weeks with acclimated *Acinetobacter* sp. at 30 °C) showed a removal efficiency of 80 % or more. As pointed out earlier pre-extraction with surfactant solutions will be very costly. Results obtained for packed-bed biofilm reactors in continuous treatment of PAH contaminated waters (Guerin 2002, Guieysse et al. 2000) demonstrate that this reactor type with hydraulic retention times as low as 3 hours and removal rates typically > 90 % is far more efficient than treatment in an aerated tank. The packed bed biofilm unit as part of the two-stage bioreactor system proved to be able to effectively remove contaminants from the aqueous phase and degrade PAH sorbed on the column.

Alternatively to the more common slurry reactors Woo et al. evaluated a drum bioreactor (Woo et al. 1999) for simultaneous treatment of soils in suspension phase (silt and clay) and sediment phase (sand). With an optimal water content of 30 to 40 %, variable according to the soil texture, this reactor type has clear advantages in relation to high soil through-put. Over 95 % of PAHs with three or four rings (fluorene, phenanthrene, anthracene, pyrene, artificial contamination) were degraded at 270 mg/kg soil within 20 days.

Jankowski et al. presented results of a two-step procedure – first extracting a spiked soil containing naphthalene, phenanthrene, acenaphthene and anthracene with a dodecane-ethanol solvent mixture, then treating the solvent in a two-phase partitioning bioreactor (Janikowski et al. 2002). This approach would require an additional soil washing step to clean the soil from the water-immiscible solvent. This problem can be circumvented by using a two-liquid-phase slurry bioreactor (Villemur et al. 2000). They report on treatment of slurry systems containing 30 % (w/v) sterilized soil artificially contaminated with

pyrene, chrysene and benzo[a]pyrene with volumes of silicone oil up to 30 % (v/v). In the slurry reactor containing 30 % silicone oil degradation rates of pyrene, chrysene and benzo[a]pyrene were, respectively, 19, 3.5 and 0.94 mg per liter and day, no pyrene was detected after 4 days. For comparison, during treatment of the sandy gas work soil described above approx. 80 mg pyrene were removed per liter slurry during 3 days.

Some paper relate to optimization of slurry reactors by addition of surfactants. Palepu et al. carried out experiments with spiked soils (PAHs with 2 – 4 rings) in presence of a nonionic surfactant (Palepu et al. 1995). Two- and three-ring compounds were degraded about 96 – 99 percent in 15 days compared to 30 days required without surfactant. Namkoong et al. investigated the effect of the nonionic surfactant Triton X-100 above the critical micelle concentration (10 and 100 times the cmc) on the removal of model compounds naphthalene, phenanthrene and pyrene from spiked loam (30 % w/v solids) in bench-scale slurry bioreactor (Namkoong et al.). Addition of surfactant significantly reduced half-life of pyrene from 33 to 10 days (approx. 400 mg/kg pyrene initial concentration) but not for the two- and three-ring compounds.

Except the first, all cited evaluations of soil clean-up were conducted with artificially contaminated samples. However, weathered contaminated soils usually exhibit considerably lower biodegradability.

A bench-scale fluidized bed reactor (BIODYN process) processing at a 50 % (w/w) soil concentration removed more than 97 % of PAH of a soil with lower contamination (760 mg/kg with mainly two- and three-ring PAH) after 10 days. However, in case of a highly contaminated sample (3900 mg/kg PAH) 3 weeks were necessary for removal of 89 % of contamination, with only minor changes in concentration of PAH with four and more rings

(Mann et al. 1995). On two other contaminated materials this reactor approach was tested in comparison to soil pot experiments (Landesumweltamt Nordrhein-Westfalen 1997). After four weeks 0 and 81 % of PAH could be removed, respectively, compared to 21 and 90 % during 74 weeks in the soil pot experiments.

Gustavsen et al. demonstrated the effectiveness of a slurry reactor to remediate coal tar contaminated material (Gustavsen et al. 2000). The treatment of a mixed fill material contaminated with coal tar (initial concentration 2300 – 5500 mg/kg PAH) downsized to < 3 or < 8 mm was investigated with batch sizes ranging between 1 and 45.000 liter. The slurry reactors were operated with complete mixing and automated control of temperature, pH and dissolved oxygen. Reduction from 4000 mg/kg to 1000 mg/kg could be achieved during 12 days of operation.

An USEPA report on a slurry phase bioremediation demonstration at a former wood preserving site revealed that treatment goals of total PAHs (950 mg/kg) and B(a)P-equivalent PAHs (180 mg/kg) were achieved (USEPA 1995). Soil directly applied to a land treatment unit could not meet the targeted treatment standards in the timeframe set. The slurry phase bioremediation system consisted of a power screen, a soil washing unit with removal of the sand fraction, slurry conditioning (addition of nutrients, a dispersant and defoaming agent) and stirred/aerated slurry reactors for treatment of soil fines. Average total PAH concentration was reduced from 8500 to 630 mg/kg within approx. 19 days.

The examples show that bioreactor treatment can effectively remediate PAH contaminated soils. However, not too stringent treatment standards, i.e. the Dutch guideline value B: 20 mg/kg PAH, are a prerequisite for applicability of common bioreactor or bioremediation

approaches (Landesumweltamt Nordrhein-Westfalen 1997). Results obtained with the new two-step bioreactor process suggest that substantial improvements in relation to treatment time reduction as well as in relation to low residual values are possible to achieve.

Conclusions

The limited availability of pollutants is connected with their physical and chemical state in the soil/water-system. In principle, transfer may be enhanced by dispersion, solubilization, emulsification and attrition of surfaces by mechanical forces and/or with the help of selected additives. Surfactant costs for a pre-extraction of contaminated materials before biological treatment will be high, even with surfactant combinations with high extraction efficiency, and therefore will not be feasible economically. Washing pretreatment resulted in a seriously enhanced bioavailability, even when performed without additives. Specially designed surfactant combinations that stimulate biodegradation without preferential degradation of surfactants exhibited substantial enhancement of biodegradation rates when their composition and concentration was adapted to the actual contaminated soil. However, even under improved conditions biodegradation rates were too slow to obtain acceptable residual values in reasonable times. Therefore, a new two-stage bioreactor system was developed that enhances removal rates drastically (> 90 % in 3 days). The performance of the system could be optimized further by selected additives and/or pretreatment. In conclusion it can be stated that a step forward has been made in broadening the application range of biological processes for the clean-up of soils.

Acknowledgements

We gratefully acknowledge the support of the Bundesministerium für Bildung, Forschung und Technologie under grant number FKV 0211001J6 and FKV 0150402J6.

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