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Remediation of PAH contaminated soils: Application of a solid–liquid two-phase partitioning bioreactor

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ABSTRACT

The feasibility of a two-step treatment process has been assessed at laboratory scale for the remediation of soil contaminated with a model mixture of polycyclic aromatic hydrocarbons (PAHs) (phenanthrene, pyrene, and fluoranthene). The initial step of the process involved contacting contaminated soil with thermoplastic, polymeric pellets (polyurethane). The ability of three different mobilizing agents (water, surfactant (Biosolve) and isopropyl alcohol) to enhance recovery of PAHs from soil was investigated and the results were compared to the recovery of PAHs from dry soil. The presence of isopropyl alcohol had the greatest impact on PAH recovery with approximately 80% of the original mass of PAHs in the soil being absorbed by the polymer pellets in 48 h. The second stage of the suggested treatment involved regeneration of the PAH loaded polymers via PAH biodegradation, which was carried out in a solid–liquid two-phase partitioning bioreactor. In addition to the PAH containing polymer pellets, the bioreactor contained a microbial consortium that was pre-selected for its ability to degrade the model PAHs and after a 14 d period approximately 78%, 62% and 36% of phenanthrene, pyrene, and fluoranthene, respectively, had been desorbed from the polymer and degraded. The rate of phenanthrene degradation was shown to be limited by mass transfer of phenanthrene from the polymer pellets. In case of pyrene and fluoranthene a combination of mass transfer and biodegradation rate might have been limiting.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds consisting of over 100 individual moieties composed of 2 or more fused aromatic rings. Some PAHs have been shown to possess carcinogenic characteristics and their release and subsequent accumulation in terrestrial environments is cause for concern (Cerniglia, 1992). The US Environmental Protection Agency has listed 16 PAHs as priority pollutants, and soils containing these substances require remediation (Shuttleworth and Cerniglia, 1995; Kanaly and Harayama, 2000). A variety of physical, chemical and biological remediation techniques have been proposed and have been demonstrated to have varying degrees of success (Wilson and Jones, 1993; Khodadoust et al., 2000; Rivas, 2006; Gong et al., 2007). Often a single remediation strategy, whether it is a physical, chemical or biological technique, will not provide sufficient removal. Combining two or more remediation techniques may provide superior results and there exist a number of examples involving treatment trains specific to PAH remediation (Srivastava et al., 1994; Liu et al., 1995; Nam et al., 2001; Saichek and Reddy, 2005; Niqui-Arroyo and Ortega-Calvo, 2007).

In this study, a simple two-step treatment process is described that combines the affinity of thermoplastic polymers for organic molecules with the degradative capability of a microbial consortium utilized within a solid–liquid two-phase partitioning bioreactor (TPPB). The proposed process is schematically shown in Fig. 1. Polymeric materials have been shown to absorb a variety of organic compounds from solution (Bowen, 1970; Rzeszutek and Chow, 1999) and in particular have been demonstrated to effectively recover phenol from soil (Prpich et al., 2006). When contacted with soil, the polymer acts as a "solid solvent", scavenging organic contaminants and concentrating them within the polymer matrix. Contained within a polymer matrix, PAHs may be conveniently removed from the terrestrial environment by simply separating soil and polymer, which may be accomplished via sieving.

The extremely hydrophobic nature of PAHs may hinder their recovery from soil as the contaminants will bind tightly to, or become entrapped within, the soil particles (Means et al., 1980). To assist in the recovery of these contaminants a mobilizing agent may be utilized to promote mass transfer. In this study three mobilizing agents are utilized including water, a commercially available surfactant (biosolve) and an organic solvent (isopropyl alcohol, IPA). A vast number of studies have been performed on the

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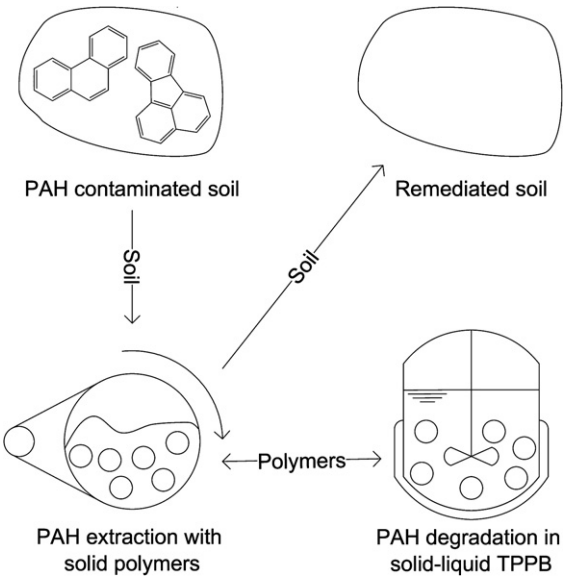

Fig. 1. Treatment process for the remediation of PAH contaminated soil. Treatment involves recovery of PAHs from soil followed by PAH degradation in a TPPB. PAHs are recovered from soil via a polymeric sorbent followed by PAH degradation in a solid–liquid TPPB (microbial consortium).

capacity of surfactants to enhance recovery and/or biodegradation of PAHs in soil systems (Mulligan et al., 2001). Organic solvents have been shown to be effective mobilizing agents during the washing of soils contaminated with PAHs (Khodadoust et al., 2000). The difficulties associated with organic solvents lie with their recovery and re-use. Solvents present in soil are often removed by flushing the soil with water followed by chemical/thermal treatment to isolate contaminants and separate liquid fractions (Khodadoust et al., 1999).

The second step in this proposed treatment system involves the biodegradation of PAHs taken up by the polymer absorbents. Biodegradation of PAH contaminated soils is considered a cheap and environmentally friendly means of clean-up, however, the highly insoluble nature of PAHs may lead to poor bioavailability of these contaminants that will have a negative impact on PAH degradation (Semple et al., 2003). *Ex-situ* PAH biodegradative treatments, such as the use of slurry bioreactors, are often favored as they permit control over operating conditions thus ensuring a favorable microbial environment leading to rapid PAH biodegradation (Woo and Park, 1999). Alternative bioreactors include liquid–liquid TPPBs that have been shown to effectively degrade PAHs (Guieysse et al., 2001; Vandermeer and Daugulis, 2007), but are limited to pure microbial strains or small well-defined consortia. Capable of treating aqueous solutions, the liquid–liquid TPPB may not be practical for treating soil environments, as solvents that can be used for soil extraction, such as IPA (US EPA, 1994), do not fulfill the requirements of a delivery phase in a liquid–liquid TPPB as outlined elsewhere (Bruce and Daugulis, 1991).

Concentration of the soil contaminants within polymeric matrices (assisted by a mobilizing agent) reduces the mass/volume of material to be treated, analogous to solvent extraction. Moreover, since the polymers are virtually inert (non-biodegradable) they allow transfer and delivery of the target molecules directly to efficient mixed populations of degrading organisms in solid–liquid TPPBs, where conditions for microbial biodegradation can be carefully controlled, while the soil can be returned to the environment after the polymer assisted contaminant extraction. It was the object of this study to demonstrate the feasibility of such a treatment train for PAH contaminated soils as outlined in Fig. 1 at laboratory scale.

2. Materials and methods

2.1. Chemicals and polymers

All chemicals used in the fermentation media and the solvents were obtained from either Sigma Aldrich (Oakville, ON, Canada) or Fisher Scientific (Ottawa, ON, Canada). All polymers are of commercial grade. Desmopan (polyurethane) was supplied by Bayer, (Leverkusen, Germany), Hytrel was supplied by DuPont, (Kingston, ON, Canada) and polyethylene was supplied by Scientific Polymer Products Inc., (Ontario, NY, USA). Biosolve, a commercial surfactant, was supplied by The Westford Chemical Corporation, (Westford, MA, USA).

2.2. Analysis of PAHs

PAH concentration within the soil was determined by contacting a known mass of soil (about 1 g) with 5 ml of methanol in a 20 ml glass vial. The vial was agitated for 24 h at 180 rpm and 20 °C. Three 5 ml extractions were carried out for each soil sample and the resulting cumulative methanol extract was analyzed via fluorescence spectrometry using a QuantaMaster QM-2000-6 fluorescence spectrometer (Photon Technology International, London, ON, Canada). Samples were diluted to be in the linear range of the machine (0–0.1 mg l^{-1}). The machine was operated in synchronous-scan mode, which allowed to obtain separate peaks for all three PAHs. The technique is described in detail elsewhere (Vandermeer and Daugulis, 2007).

PAH concentration within the polymer was determined by desorption of a small quantity of polymers (about 0.1 g) in 5 ml of methanol in a 20 ml glass vial. The vial was agitated for 24 h at 180 rpm and 20 °C; after this time the extract was removed and 5 ml of fresh methanol were added. The polymers were desorbed in three 5 ml volumes and the 15 ml volume of cumulative extract was analyzed via fluorescence spectrophotometry.

PAHs in aqueous medium could be analyzed directly or after appropriate dilutions (to <0.1 mg l^{-1}) via fluorescence spectrophotometry, also described by Vandermeer and Daugulis (2007).

2.3. Partition coefficients for PAHs between water and polymers

Partition coefficients were determined for phenanthrene, pyrene and fluoranthene in a polymer/water system. Partition experiments were carried out in 20 ml glass vials containing 10 ml of distilled water, 0.2 g of polymer and varying amounts of PAHs (between 0.06 mg and 1.4 mg each (dissolved in methanol at 6000 mg l^{-1} each), 6 different amounts for each polymer). Due to the hydrophobic nature of the PAHs, the added PAHs did not remain in solution. The vials were sealed and allowed to equilibrate at 20 °C and 180 rpm until no visible PAHs remained (approximately 7 d); after this time the concentration of PAHs remaining in water was measured as described previously (Vandermeer and Daugulis, 2007). Polymer pellets were desorbed in methanol and the PAH content was determined by fluorescence spectrometry as described above to close the mass balance.

2.4. Preparation of PAH-contaminated soil

All experiments were undertaken with artificial soil composed of 10% organics (peat), 20% clay and 70% industrial sand at pH 6 as outlined in OECD method 207 (OECD, 1984). Soil was contaminated in open aluminum trays through the addition of PAHs dissolved in IPA. The soil was mixed manually for 20 min to ensure equal distribution of the PAHs in the soil. The IPA was allowed to evaporate for 72 h and equal distribution of PAHs in the soil was

verified by analyzing soil samples from different positions in the tray (data not shown).

2.5. Recovery of PAHs from soil using polymers

Standardized soil was spiked with equal masses of the three model PAHs resulting in a total PAH concentration of 900 mg kg^{-1}. To 20 ml glass vials 10 g of contaminated soil was added at a 10% mass fraction of polymer to soil. Four experimental conditions were investigated including examination of PAH recovery from dry soil as well as recovery of PAHs in the presence of three mobilizing/moisturising agents (30% w/w water, 30% w/w water containing 3% Biosolve, or 30% IPA). The vials were maintained at 20 °C, and 180 rpm for up to 48 h and at 0, 4, 24, and 48 h triplicates were sacrificed and analyzed for the presence of PAHs in both the soil and polymer.

2.6. Release of PAHs into aqueous medium

Desmopan polymer pellets (1 g) were loaded with similar amounts of the three PAHs via equilibration in PAH containing IPA. The IPA was removed by washing of the pellets with water for 3 min. This step removed residual IPA from the pellet surface and did not significantly reduce the amount of PAHs present in the pellets (confirmed by re-equilibrating the washed pellets with IPA and measuring the PAH concentration in IPA, data not shown). The IPA-free pellets were added to 75 ml cell-free culture medium and agitated at 600 rpm. Aqueous phase samples were periodically analyzed for their PAH concentration.

2.7. Biodegradation of PAHs recovered from contaminated soil

A microbial consortium was developed to degrade the PAHs absorbed within the polymer pellets. The consortium was grown in a 5 l Bioflo III bioreactor (New Brunswick Scientific, Edison, NJ, USA) containing 3 l of minimal salts medium (Pprich and Daugulis, 2006) and equal masses of the three model PAHs as sole carbon sources which provided both selection pressure and a source of carbon and energy. Inoculum for the reactor originated from a sample of soil contaminated with PAHs, as well as a sample of biosolids taken from a wastewater treatment facility located at a plastics manufacturing plant. The bioreactor, so called the inoculum reactor, was maintained for a period of 3 wk over which time cell viability was monitored via light microscopy. PAHs were added on a weekly basis to ensure selection pressure. The inoculum reactor was used to inoculate the Bioflo I reactors used to study the biodegradation of PAHs absorbed within the polymer pellets. The microbial composition of the consortium was not further characterized as the main scope of this study was to show the general ability of the proposed treatment train towards hydrophobic soil contaminants, rather than a detailed characterization of the microbial PAH degradation step.

For the biodegradative study 100 g of polymer pellets were loaded with the three model PAHs by contacting the pellets with 1 kg of standardized soil contaminated with equal parts of the three model PAHs, totally 1200 mg kg^{-1}, in a 10 l glass roller jar. A mobilizing agent (30% w/w IPA) was added to the system and the jar was rotated at 20 rpm for 72 h and maintained at 20 °C. After 72 h the pellets were separated from the soil using a 7 mesh screen (2.81 mm) and placed within a bioreactor (Bioflo I, New Brunswick Scientific, Edison, NJ, USA). The pellets contained about 7300 mg kg^{-1} phenanthrene, and 7100 mg kg^{-1} pyrene and fluoranthene. The bioreactor contained 300 ml of minimal salt medium and 10% mass fraction of PAH loaded polymer pellets. The system was maintained at 200 rpm, 30 °C, and aerated at 0.3 l min^{-1}. The inoculum was prepared by removing 1 l of liquid culture from the inoculum bioreactor and filtering it through glass wool to remove any residual solid PAHs. The contents were centrifuged at 3500 rpm for 15 min and the supernatant was decanted, the cells were re-suspended in fresh medium and added to the Bioflo I bioreactor. The initial biomass concentration was determined to be 1.4 g l^{-1} (dry cell weight).

A control bioreactor, containing a heat-sterilized inoculum and a 10% mass fraction of PAH loaded polymer pellets was operated in parallel to the experiment to measure abiotic losses. Disappearance of PAHs was tracked by desorption of a small mass of polymer pellets at pre-determined intervals. No significant decrease of PAH concentration in the polymers could be observed in the control experiment, verifying that loss of PAHs in the reactor containing active biomass was due to biodegradation and not due to sequestration of PAHs onto the glass vessel or into the biomass (data not shown).

3. Results and discussion

3.1. Polymer selection

Polymers that are to be considered for a soil remediation process consisting of solid-phase contaminant extraction followed by PAH biodegradation in solid–liquid TPPBs have to fulfill the requirements of both aspects of the overall process shown in Fig. 1. The key property driving the initial extraction stage is the affinity of the polymers for the targeted PAHs. A shortlist of polymers that fulfilled the requirements for sorption of PAHs from soil was created according to a polymer selection strategy that is described in detail elsewhere (Rehmann et al., 2007). The two commercially available polymers Hytrel and Desmopan were previously used successfully for the recovery of polychlorinated biphenyls (PCBs) (Rehmann and Daugulis, 2007, 2008) and were therefore also considered in this study targeting PAHs, which share various key properties with PCBs such as aromatic structure and hydrophobicity. Polyethylene was considered due to its abundance and low costs.

To fulfill the biodegradative aspect of the process it was essential that the polymers were neither toxic nor bioavailable to the degrading organisms (Rehmann et al., 2007), which has previously been shown with a different consortium for the employed polymers (Pprich and Daugulis, 2006) and it was assumed that the consortium used in this study was equally unable to degrade significant amounts of polymer over the experimental time scale. Further benefits in utilizing thermoplastic materials arise from the fact that the materials are moldable and re-shapeable; thus all considered polymers may be transformed into extraction phases of any convenient shape and size as shown in a related study (Prpich and Daugulis, 2007).

The affinity of the selected polymers for the three model PAHs was quantified through determination of partition coefficients as shown in Table 1. Linear partitioning isotherms were found for all three PAHs in combination with all three polymers over the

Table 1
Polymer water partitioning coefficients (presented as the dimensionless log of the PAH concentration ratio [(mg kg^{-1}) (mg kg^{-1})$^{-1}$]) and their 95% confidence limit of various PAHs for three selected polymers

Polymer	Polymer/water partitioning coefficient log $K_{S/W}$		
	Phenanthrene	Fluoranthene	Pyrene
Desmopan	4.946 ± 0.003	5.375 ± 0.026	5.384 ± 0.023
Hytrel	4.379 ± 0.003	4.836 ± 0.004	4.859 ± 0.004
Polyethylene	4.035 ± 0.019	4.587 ± 0.022	4.485 ± 0.020

The partitioning coefficients were obtained via linear regression of seven data points each.

observed range of concentrations (low-density polyethylene < 1.7 g kg^{-1}, Hytrel < 5.5 g kg^{-1}, Desmopan < 6.4 g kg^{-1}). The partitioning of PAHs between the polymers and water is analogous to the partitioning of solutes between two immiscible liquid phases. Similar partitioning behavior has been founds for phenols, biphenyl and PCBs (Pprich and Daugulis, 2006; Rehmann and Daugulis, 2007, 2008).

It can be seen from the partitioning coefficients shown in Table 1 that Desmopan has the highest affinity for the selected PAHs of the three tested polymers, followed by Hytrel. The partitioning coefficient appears to correlate with PAH hydrophobicity where pyrene ($\log K_{O/W}$ = 5.18 (Means et al., 1980)) and fluoranthene ($\log K_{O/W}$ = 5.20 (Scheele, 1980)) have higher partitioning coefficients than phenanthrene ($\log K_{O/W}$ = 4.46 (Hansch and Toshio, 1964)). This behavior cannot clearly be resolved for pyrene and fluoranthene, whose polymer/water partitioning coefficients and $\log K_{O/W}$ values are in all cases very similar to each other. In addition, the partition coefficients for the three model PAHs between water and Desmopan are higher than their equivalents between octanol and water. Desmopan's high affinity for the PAHs, as well as its competitive sorption performance compared to organic solvent such as octanol, resulted in its selection and use as the extraction phase for soil remediation and subsequently as the delivery phase in the solid–liquid TPPB.

3.2. PAH extraction from soil

PAHs were extracted from soil using Desmopan polymers as the solid phase extractant under four different soil conditions. It was expected that the extent of mass transfer of PAHs from soil into the polymer would be low under dry soil conditions, as PAHs tend to sorb to the soil matrix (Means et al., 1980), thus making them non-available to the extraction phase. The extractability of PCBs could be enhanced by the addition of mobilizing agents (Berselli et al., 2006), and therefore the effect of three mobilization agents on the extent of PAH extraction from soil was also tested.

Fig. 2a shows the time course of PAH extraction from soil under dry soil conditions. It can be seen that the concentration of all three PAHs was substantially reduced over the 48 h extraction period (hollow bars), while the recovered amount of PAHs in the polymer increased over time (shaded bars). About 44% of the mass initially present in soil was recovered by the polymer pellets for fluoranthene and phenanthrene (Fig. 2a); about 40% recovery was obtained for pyrene. The employed polymer to soil ratio was 10% (w/w) and although the amount of PAHs remaining in soil after 48 h and the amount that could be recovered from the polymer were equal, the final concentration in the polymer was 10 times higher than in the soil, showing the high affinity of the polymer for the selected PAHs. An increase in the polymer to soil ratio or the use of multiple contact stages in sequence may be expected to decrease the amount of PAHs remaining in the soil further and is the subject of current research.

Water, a mix of water and the commercially available surfactant Biosolve, and the water miscible solvent IPA were added at 30% (w/w) to form wet soil. It can be seen in Fig. 2b and c that water and the surfactant mix had a negative impact on the extraction process. This was not expected, as it was assumed that the addition of these agents would result in improved contact between PAHs and polymer. The reason for the poor extraction performance of the polymer under wet condition was most likely due to a reduced contact between PAHs and polymer. At 30% moisture content (w/w) the soil formed agglomerates, disrupting direct contact between the soil inside the agglomerate and the polymer, thereby introducing a new mass transfer barrier. Further, a layer of soil covering the

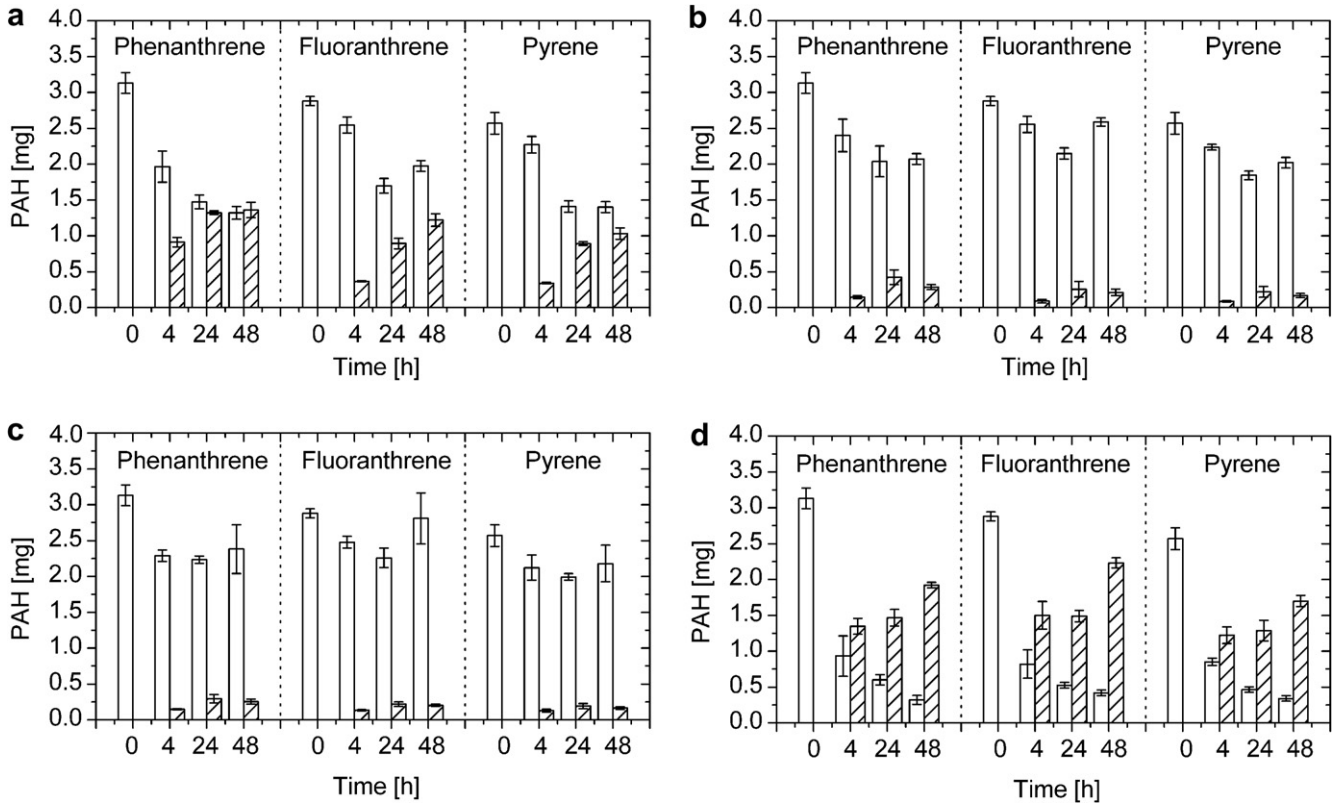

Fig. 2. Distribution of PAHs between soil (empty bars) and Desmopan (shaded bars) in microcosms containing 10 g soil and 1 g Desmopan as a function of time. The bars are the mean of three replicates and the error bars show the 95% confidence limit. The soil conditions were: (a) dry, (b) 30% water content, (c) 30% water plus Biosolve, (d) 30% IPA.

individual polymer pellets was found, which also inhibited mass transfer. The anticipated increased PAH mobility did not result in increased contact between PAHs and polymer as the contact area of the soil particles was reduced through the formation of the agglomerates mentioned above. These findings suggest that direct contact of PAHs with the polymer is required for their extraction and that intensive mixing of polymer and soil will therefore enhance extraction. PAH molecules that are not in direct contact with the polymer have to diffuse through soil agglomerates, which seems to limit the rate of uptake under the conditions presented in Fig. 2b and c. The diffusion coefficients of PAHs in water are very low (e.g. 7.74×10^{-10} m^2 s^{-1} for phenanthrene and 7.24×10^{-10} m^2 s^{-1} for pyrene) and an additional 10 orders of magnitude lower in sediments (Chai et al., 2006), and it can be assumed that diffusion in soil occurs at equally low rates. A more effective mobilizing agent might be able to increase PAH diffusivity in soil and therefore reduce the required mixing. The addition of a biosurfactant however did not increase the PAH uptake in comparison to water only (Fig. 2c).

The organic solvent IPA was used as an alternative mobilizing agent. The solubility of PAHs in IPA is higher than in water; the solubility of pyrene (as an example) in water is 1.32×10^{-8} mol mol^{-1} at 25 °C (Wauchope and Getzen, 1972) while it is 2.4×10^{-4} mol mol^{-1} in IPA (Iyoki et al., 1993). The solubility increase of over 4 orders of magnitude was expected to translate into an increase in mobility. The data shown in Fig. 2d confirm this as the concentration of all three PAHs was reduced to <15% of their initial concentration within 48 h, however a detailed thermodynamic description of the entire system is beyond the scope of this study.

The use of an organic mobilizing agent enhanced the extent and rate of PAH recovery from the soil when compared to extraction in the presence of dry soil. After 4 h more than 70% of all three of the initially present PAHs were removed from the soil in the presence of IPA, while the removal of PAHs under dry conditions was ~30% for phenanthrene and ~15% for fluoranthene and pyrene after 4 h. The addition of IPA to soil is a simple method used to promote the transfer of PAHs from soil to a polymeric extraction phase. In this case IPA did not function as an extractant, as it was not removed from the soil. Its only function was to assist in the transfer of PAHs from soil into the polymers, which were then removed from the soil. The extent of PAH recovery using polymers and IPA is similar to results obtained by Khodadoust et al. (2000) who used organic solvents in ratios of 1 g soil:4 ml extraction solution to recover a mixture of PAHs from soil. Solid phase extraction of PAHs offers operational benefits, compared to traditional solvent washing techniques, as solid polymers are easier to recover, generate a reduced (and more concentrated) mass of contaminated material, and require less chemical and energy inputs during material recycle (Means et al., 1980). Due to the ability of IPA to enhance PAH recovery, IPA was used subsequently to extract PAHs from a larger mass of soil, followed by regeneration of the PAH loaded polymers in a solid–liquid TPPB via biodegradation. Though the addition of IPA is beneficial in laboratory-scale studies, it might not be feasible in pilot-scale soil remediation schemes, which are currently under investigation. This limitation is mainly due to the anticipated costs of IPA. This can potentially be circumvented by reselecting the polymeric extraction phase with special emphasis on polymers that do not collect a soil layer in the presence of water as a mobilizing agent. This might also be overcome through optimization of the soil/polymer mixing conditions. An additional parameter that will require further investigation is the effect of soil aging. Sorption of PAHs to aged soil is known to inhibit PAH biodegradation (Weissenfels et al., 1992), and might also reduce the extractability of PAHs using the suggested methodology. Further studies will be required to investigate the extractability of aged PAHs; this is however beyond the scope of this study, which aims to show that the concept of solid-phase contaminant extraction, followed by contaminant degradation in a solid–liquid TPPB, is feasible at laboratory scale.

3.3. PAH release to aqueous medium

Removal of PAHs from soil is the first step in the overall process suggested in Fig. 1. The subsequent release into aqueous medium followed by microbial degradation is necessary in order to destroy the PAHs and to allow recycling of the polymer extraction phase. The release of hydrophobic compounds from polymer pellets similar to the ones employed in this study has recently been shown to follow first order kinetics according to

$$\frac{dS_{aq}}{dt} = \frac{K_t A}{V_{aq}}\left(S_{aq}^{eq} - S_{aq}\right) \quad (1)$$

where S_{aq}[g m^{-3}] is the PAH concentration in the aqueous phase, S_{aq}^{eq}[g m^{-3}] is the equilibrium PAH concentration based on the concentration in the polymer pellets, K_t [m h^{-1}] is the release constant, A [m^2] is the surface area of the polymer pellets and V_{aq} [m^3] is the volume of the aqueous phase (Rehmann and Daugulis, 2008). S_{aq}^{eq} can be assumed to remain constant (if no degradation occurs in the aqueous phase) during release experiments as the mass of PAH released from the polymers into the aqueous phase is very low compared to the total mass of PAH present in the polymer, due to the high partitioning coefficient of PAH between polymer and water and the low PAH solubility in water. This assumption allows integrating (Eq. (1)) to

$$S_{aq} = S_{eq}\left(1 - \exp\left(-\frac{K_t A}{V_{aq}}t\right)\right) \quad (2)$$

Fig. 3 shows the time course of aqueous phase PAH concentration released from 1 g Desmopan polymer into 75 ml aqueous medium. Non-linear regression analysis was applied to estimate the mass transfer coefficient K_t for the three PAHs, shown by the solid lines in Fig. 3. The mass transfer coefficients could be estimated to be $K_t = 0.067 \pm 0.003$ m h^{-1} for pyrene, $K_t = 0.060 \pm 0.007$ m h^{-1} for fluoranthene and $K_t = 0.063 \pm 0.008$ m h^{-1} for phenanthrene. The numbers are very similar to each other, suggesting similar release rates of all three PAHs. The mass transfer

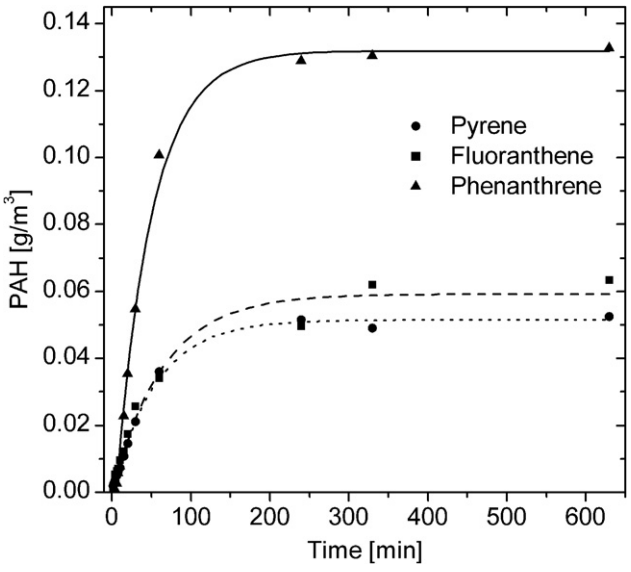

Fig. 3. Release of pyrene (squares), fluoranthene (circles) and phenanthrene (triangles) from Desmopan polymer pellet into aqueous medium. The solid lines show the non-linear regression of the data using (Eq. (2)).

coefficient for biphenyl from Hytrel polymer pellets has previously been estimated to be $K_t = 0.334 \pm 0.005$ m h^{-1} (Rehmann and Daugulis, 2007), approximately five times higher than the mass transfer coefficients of the PAHs used in this study. The difference is most likely due to the chemical structure and physical properties of the observed compounds. Biphenyl is a smaller and significantly more water-soluble (two orders of magnitude) molecule than the three PAHs. The chemical structure of Hytrel (butylene terephthalate–butylene ether glycol terephthalate co-polymer), containing an aromatic motive, is also different from the structure of Desmopan (polyurethane of poly(oxytetramethylene)glycol and methyldiisocyanate) as employed in this study. However, no reliable framework linking the chemical structure of polymers to the diffusivity of organic molecules in polymers currently exists.

The calculated mass transfer coefficients can be used to estimate the rate at which PAHs can be released from the Desmopan polymers into aqueous medium under bioreactor conditions. The release rate is dependent on the difference between the actual aqueous phase substrate (PAH) concentration and the concentration in equilibrium with the concentration in the polymer (Eq. (1)). The actual aqueous phase concentration in a bioreactor also depends on the microbial degradation rate. However, the maximum release rate can be estimated based on the assumption that the biodegradation rate is significantly higher than the physical release rate of PAHs. Doing so allows setting the aqueous phase concentration in (Eq. (1)) equal to zero and the equation can be written for the polymer as follows:

$$\frac{dS_{pol}}{dt} = -\frac{K_t A}{M_{pol}} \frac{S_{pol}}{K_{S/W}} 1000\text{l m}^{-3} \quad (3)$$

where S_{pol} [g kg^{-1}] is the PAH concentration in the polymer, M_{pol} [kg] the mass of the polymer, $K_{S/W}$ is the polymer/water partitioning coefficient. $S_{pol}/K_{S/W}$ is the aqueous phase PAH concentration in equilibrium with the PAH concentration S_{pol} in the polymer.

(Eq. (3)) can be solved with the estimated mass transfer coefficients and initial conditions as would be employed in a solid liquid TPPB (initial PAH concentration in the polymer of 20 g kg^{-1}). The solution of (Eq. (3)) for all three PAHs is shown in Fig. 4a. It can clearly be seen that the PAH release is not rapid and would most likely be the limiting step in the degradation of PAHs in a solid–liquid TPPB. It is estimated that the degradation of the initially present PAHs would take longer than 3 wk even under ideal microbial conditions, based on the estimated release rate, as shown in Fig. 4a.

3.4. Biodegradation of PAHs in a solid liquid TPPB

The three PAHs, loaded within the Desmopan polymer pellets, were degraded in a solid–liquid TPPB. Delivery and degradation of toxic molecules via polymeric materials has been demonstrated to be an effective means of not only the destruction of contaminant molecules but also as a means of polymer regeneration (Amsden et al., 2003; Pprich and Daugulis, 2006; Rehmann and Daugulis, 2008). A microbial consortium, developed for the specific degradation of the three PAHs, achieved 78%, 62% and 36% removal of phenanthrene, pyrene and fluoranthene respectively, over a 14 d period (Fig. 4b). The weak performance with respect to fluoranthene might be due to the increased recalcitrance of the compound due to the pyrol ring (Kelley and Cerniglia, 1991). Comparing Fig. 4a and b, shows that the PAH biodegradation occurs at almost similar rates as the previously estimated maximum release rate. This suggests that the mass transfer rate of PAHs from the polymers into the aqueous phase is the main limitation of the overall PAH degradation process. This is most dominant in the case of phenanthrene. Further process optimization should therefore target to increase the transfer rate from the polymeric delivery phase into aqueous medium, which might be achieved by increasing the available surface area of the polymer, or by employing a polymer with superior release rates. Mass transfer limitations have been shown to play a prominent role in suppressing microbial activity (Bosma et al., 1997) and under such conditions it is reasonable to suppose that starvation conditions may have led to the inability of the cells to substantially reduce PAH concentrations within the polymers after an approximately 14 d incubation period.

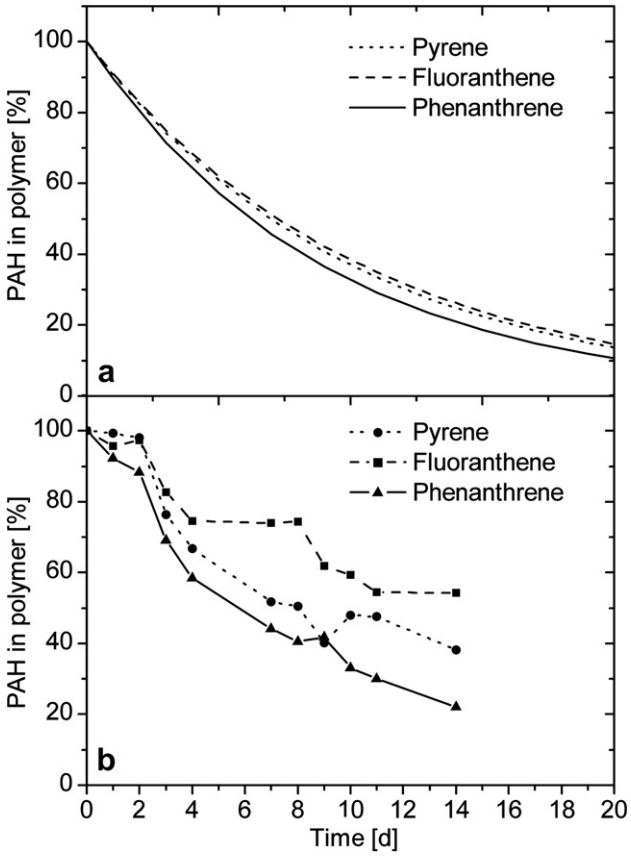

Fig. 4. Simulated release of PAHs from Desmopan polymer pellets. It is assumed that the biodegradation occurs instantaneously as soon as the PAHs enter the aqueous phase (a). Biodegradation of PAHs in solid liquid TPPB (b).

Biodegradation of PAHs from polymer pellets represents a means for polymer regeneration thus promoting re-use of the material in subsequent contaminated soil applications (Prpich et al., 2006). This method of regeneration is advantageous as it occurs under ambient conditions in a TPPB, not requiring chemical or thermal treatments, often associated with regeneration of liquid sorbents (Khodadoust et al., 1999).

4. Conclusions

A simple, two-step process in which inexpensive and inert polymer pellets are used to effectively extract a mixture of PAHs from soil has been demonstrated in laboratory scale. However, pilot-scale experiments are still required in order to verify technical and economical feasibility of this technology. PAH extraction can be enhanced with the mobilizing agent IPA, however, even dry soil extraction with low pellet loading has been shown to be effective (40–44% recovery). The extent of contaminant removal may be improved via additional contact, either by higher polymer-to-soil ratios, or multiple contact stages. The PAH contaminants, now concentrated in the polymers, can be easily separated from the soil,

and added to a solid–liquid partitioning bioreactor where a microbial consortium is able to degrade a large fraction of the PAHs, thereby also decontaminating the polymer pellets for subsequent re-use. Current research is investigating the application of this polymer remediation technology to a range of contaminants in soil and water environments, with subsequent contaminant degradation in TPPB systems.

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