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Ex situ remediation of polluted soils by absorptive polymers, and a comparison of slurry and two-phase partitioning bioreactors for ultimate contaminant degradation

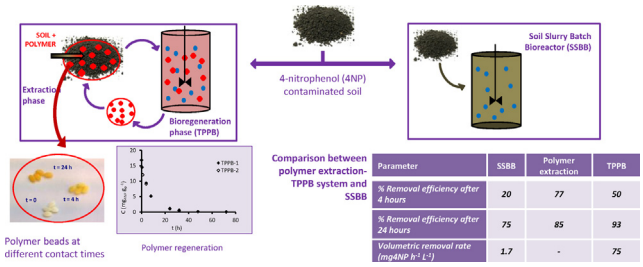
M. Concetta Tomei[a,*], Domenica Mosca Angelucci[a], M. Cristina Annesini[b], Andrew J. Daugulis[c]

[a] *Water Research Institute, C.N.R., Via Salaria km 29.300, Monterotondo Scalo, 00015 Rome, Italy*
[b] *Department of Chemical Engineering Materials and Environment, Sapienza University of Rome, Via Eudossiana 18, 00184 Rome, Italy*
[c] *Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6*

HIGHLIGHTS

- We investigate absorptive polymers for *ex-situ* soil bioremediation.
- We compare the performance of the novel technology with a slurry bioreactor.
- The polymer is very effective in decontaminating the soil (77% removal in 4 h).
- The polymer is readily regenerated in a two phase partitioning bioreactor.

GRAPHICAL ABSTRACT



Parameter	SSBB	Polymer extraction	TPPB
% Removal efficiency after 4 hours	20	77	50
% Removal efficiency after 24 hours	75	85	93
Volumetric removal rate ($mg4NP\ h^{-1}\ L^{-1}$)	1.7	-	75

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ABSTRACT

The present study has provided a comparison between a conventional *ex situ* method for the treatment of contaminated soil, a soil slurry bioreactor, with a novel technology in which a contaminant is rapidly and effectively removed from the soil by means of absorptive polymer beads, which are then added to a two-phase partitioning bioreactor (TPPB) for biodegradation of the target molecule. 4-nitrophenol (4NP) was selected as a model contaminant, being representative of a large class of xenobiotics, and the DuPont thermoplastic Hytrel™ 8206 was utilized for its extraction from soil over ranges of soil contamination level, soil moisture content, and polymer:soil ratios. Since the polymers were able to rapidly (up to 77% and 85% in 4 and 24 h respectively) and selectively remove the contaminant, the soil retained its nutrient and microflora content, which is in contrast to soil washing which can remove these valuable soil resources. After 4 h of reaction time, the TPPB system demonstrated removal efficiency four times higher (77% *vs* 20%) than the slurry system, with expected concomitant savings in time and energy. A volumetric removal rate of 75 $mg4NP\ h^{-1}\ L^{-1}$ was obtained in the TPPB, significantly greater than the value of 1.7 obtained in the slurry bioreactor. The polymers were readily regenerated for subsequent reuse, demonstrating the versatility of the polymer-based soil treatment technology.

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1. Introduction

The treatment of contaminated soil is a global concern that has arisen from expanded industrialization, non-uniform and inconsistently enforced environmental regulations, as well as tragic pollution legacies from earlier periods when the harmful effects of contaminant dumping were either unknown or were

* Corresponding author. Tel.: +39 06 90675800; fax: +39 06 90672787.
E-mail addresses: tomei@irsa.cnr.it, tomeimc@live.it (M.C. Tomei).

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of minimal societal concern. In the search for effective, and economically competitive, soil remediation strategies, particularly for organic contaminants rather than heavy metals, several options have been proposed including solvent extraction, chemical treatment with strong oxidizing agents such as ozone and Fenton's reagent, photocatalytic degradation, electrokinetic remediation, thermal processes (*i.e.* incineration, thermal desorption, thermally enhanced soil vapour extraction) and bioremediation (*i.e.* the biological removal of the contaminants) [1]. Bioremediation is in principle preferable to physico-chemical processes because the contaminants are degraded through the natural biological activity of microorganisms without addition of chemicals. This makes the process more sustainable and, in the most favourable case, is able to attain complete mineralization of the pollutants. Moreover, bioremediation techniques are typically cheaper than thermal and physico-chemical remediation methods. In classifying bioremediation technologies it is possible to distinguish between two broad categories, *in situ* and *ex situ* methods, which are applied depending on specific site factors such as soil contamination level, time required for decontamination, health and environmental risk [1].

In situ methods, that can include phytoremediation, biostimulation and bioaugmentation, are among the most widely employed, owing to their relatively low cost, but suffer from long remediation timescales, poor control of operating conditions, and the potential for contaminant spreading during the treatment process. *Ex situ* methods, in which the soil is removed from the contaminated site, contained and treated, and then returned to the original location can generally overcome the above shortcomings, however they are generally more complex and expensive.

Within the *ex situ* methods, two approaches have dominated: soil washing to extract the contaminant(s) followed by treatment [2] or disposal (*e.g.* incineration) of the liquid phase, and slurry bioreactors in which the entire mass of contaminated soil is contacted in a treatment vessel [3–5]. Although able to decontaminate the soil, the first approach can also result in decreased quality of the treated soil by the removal of the microflora and soil nutrients, and could potentially result in residual extractant remaining with the soil, which could either represent a new contaminant, or merely an economic loss. Slurry bioreactors can also result in depletion of the biological and nutrient content of the soil, and are also prone to reactor abrasion as well as the need to subsequently dispose of the relatively large volumes of water (3–10 times the volume of the soil) originally used to slurry the soil.

The use of inexpensive, inert, commercial polymers to absorb organic contaminants and to concentrate them into much smaller volumes/masses has recently been shown to be feasible [6,7]. The subsequent addition of pre-loaded polymer beads to a pre-inoculated two phase partitioning bioreactor (TPPB) for contaminant release and biodegradation, followed by multiple reuse of the polymers is a potentially attractive alternative to the above *ex situ* methods, and overcomes many/all of the stated drawbacks. It is important to stress that the mechanism of solute sorption by soft, amorphous polymers utilized in TPPBs is *via* absorption [8], and is the basis of controlled drug release, an area that has been studied and demonstrated for more than 30 years, and is in contrast to the uptake mechanism of solutes using hard, crystalline polymeric resins, which is by surface adsorption [9,10].

In this work, we have provided for the first time a quantitative comparison between a conventional slurry bioreactor system and the innovative approach of polymer extraction–bioregeneration for the treatment of contaminated soil. Tests were performed with the Hytrel^{TM} 8206 a commercial amorphous thermoplastic polymer which has already been successfully utilized in TPPBs [11] and 4-nitrophenol (4NP) which was selected as a model compound representative of a large class of xenobiotics generated as a contaminant in many production processes in the chemical industry.

2. Experimental

2.1. Chemicals, polymer and soil

4NP (purity >99%), and methanol (purity >99.7%) were obtained from Fluka (Italy) and Sigma–Aldrich (Italy), respectively. All other chemicals were commercial grade and were purchased from Carlo Erba (Italy). The partitioning phase, Hytrel^{TM} 8206, (DuPont, Canada), is a commercial grade polyether-ester copolymer, in the form of oval shaped beads (5 mm length, 1.5 mm diameter) with density 1.17 g cm^{-3} and melting point 189 °C. The structure of Hytrel^{TM} 8206 has been previously reported in Prpich and Daugulis [12]. All experiments were performed with artificial soil comprised of 10% organics (peat), 20% clay and 70% industrial sand at pH 6 as reported in the OECD method 207 [13], and purchased from ECOTOX LDS (Italy).

2.2. Biomass

The mixed culture utilized in the experiments was originally acclimatized to phenolic compounds in previous experiments [14]. In this work the cells were grown on 4NP at concentrations gradually increased to 500 mg L^{-1}. Nutrients and microelements, were added with a mineral medium dosed to obtain a C:N:P ratio of 100:5:1.

2.3. Analysis in liquid and solid phases

4NP concentrations in liquid samples (water or methanol) were analyzed spectrophotometrically at 320 nm (Varian, model Cary 1) after centrifugation (6 min; 10,000 rpm; 25 °C) to eliminate interference by suspended matter.

4NP concentrations in soil and polymer beads were determined by a multistep extraction procedure of the soil/polymer with methanol, repeated until negligible residual 4NP values were detected. Each extraction was performed by contacting a known mass of dried soil (~0.5 g) or polymer (0.1–0.5 g) with 10 ml of methanol in a 20 mL sealed glass flask mixed with a magnetic stirrer for 2 h.

4NP concentrations in soil slurry samples were determined by a similar procedure: 5 ml of soil slurry was centrifuged (10 min; 4000 rpm; 25 °C) and the precipitated soil layer was air-dried for 24 h at room temperature to remove moisture content as suggested by Venkata Mohan et al. [15]. The 4NP was then extracted from the soil with methanol as described above.

All of the analytical determinations of soil, considering the complexity of the matrix and procedure, were made at least in duplicate.

Volatile Suspended Solid (VSS) concentrations were determined according to standard methods [16] as an estimate of the biomass concentration.

2.4. Soil contamination

Soil was contaminated in flasks by spiking with a 4NP-methanol solution at a known concentration. The soil was mixed for 30 h at 20 °C to ensure uniform distribution of 4NP in the sample, then was placed in an open aluminium tray for a time sufficient (~24 h) to allow solvent evaporation. Contaminated soil was then stored in sealed glass flasks in the dark and at room temperature for 5 weeks before use, and 4NP concentrations in the soil were determined on three replicate samples. The intended soil contamination levels, based on the procedure described above, were confirmed experimentally by assaying the 4NP levels in the soil, which were found to be 0.08 ± 0.03, 0.92 ± 0.07, 7.9 ± 0.76 g kg_{ds}^{-1} for the three investigated cases.

Table 1
Summary of the operating conditions for the extraction test plan. Target, target value; exp., experimental value; ds, dry soil.

Test	Polymer/soil ratio target % (w/w)	Polymer/soil ratio exp. % (w/w)	Moisture content % (w/w)	Contamination level target (g kg_{ds}^{-1})	Contamination level exp. (g kg_{ds}^{-1})
E1	**10**	10.08 ± 0.11	50	1	0.92 ± 0.07
E2	***5***	5.19 ± 0.14	*50*	*1*	0.92 ± 0.07
E3	**2.00**	2.42 ± 0.06	50	1	0.92 ± 0.07
E4	5	5.24 ± 0.11	**35**	1	0.92 ± 0.07
E2	*5*	5.19 ± 0.14	***50***	*1*	0.92 ± 0.07
E5	5	5.27 ± 0.05	**100**	1	0.92 ± 0.07
E6	5	5.19 ± 0.14	50	**0.1**	0.08 ± 0.03
E2	*5*	5.19 ± 0.14	*50*	***1***	0.92 ± 0.07
E7	5	5.19 ± 0.08	50	**10**	7.90 ± 0.76

2.5. Polymer extraction tests

Extraction of 4NP from soil was evaluated in three series of tests performed by varying the polymer to soil ratio (E1, E2, E3), the moisture content (E4, E2, E5) and the contamination level (E6, E2, E7), as reported in Table 1. The experiments were designed with the aim of covering the range of variability of interest for application reported in the specialized literature for the soil contamination level and the moisture content while the percent of polymer was selected on the base of the results of previous applications of TPPBs for industrial wastewater treatment. In the table, to better highlight the different operating conditions, the parameter varied in each series of tests is reported in bold while test E2 is highlighted in Italics to point out that is the same test whose operating parameters are of relevance for the three series. Target values and measured experimental values with related standard deviations calculated from replicates are also shown.

For each test 5 g of contaminated soil were added to each of 6 flasks (25 mL volume) at the established polymer/soil ratio and moisture content. The flasks were maintained at 25 °C and mixed with magnetic stirrers for 24 h. At 4 and 24 h, triplicate samples were analyzed to determine the amount of 4NP absorbed into the polymer, and, through mass balance, the residual amount in the soil. It was also verified that no appreciable variation of the removal efficiency was observed by extending the contact time beyond 24 h.

2.6. Biodegradation in soil slurry batch bioreactor

A soil slurry batch bioreactor (SSBB) (working volume 1 L) was utilized for biodegradation experiments. The bioreactor was operated at 25 ± 0.5 °C, with mixing and aeration. The slurry phase consisted of 0.2 kg of contaminated soil and tap water at a soil–water ratio of 20% (w/v) supplemented with biomass inoculum (0.66 gVSS).

During biodegradation tests, 4NP was analyzed until almost complete soil decontamination was observed. Concentrations were determined in duplicate in the aqueous and soil phases to evaluate the distribution of 4NP within both phases [17]. An abiotic parallel test was also performed by contacting the contaminated soil and tap water at the same water/soil ratio without biomass addition to evaluate the possibility of any "soil washing" effect: rapid desorption of 4NP was observed with 87% being removed from the soil in 24 h (data not shown).

2.7. Biodegradation of absorbed 4NP in TPPBs

The polymers loaded with 4NP in the extraction phase were used as the partitioning phase in a TPPB. Tests were performed at 25 ± 0.5 °C in an aerated and well-mixed batch reactor of 0.1 working volume with 7% v/v of added polymer and the same amount of biomass inoculum (0.66 gVSS) utilized in the SSBB. In order to compare the proposed technology with the SSBB on an equal basis, the amount of polymer beads (10 g), required for the treatment of 0.2 kg of contaminated soil at a 5% polymer/soil ratio, was loaded with 4NP by contacting the beads with a solution at a desired concentration of 4NP, calculated on the basis of partitioning coefficient and mass balance according to the procedure described in Rehmann and Daugulis [18]. All tests were undertaken in duplicate.

3. Results and discussion

3.1. Decontamination of soil by polymer beads

The use of polymers to remove 4NP from soil was examined over a wide range of experimental conditions (Table 1) with the objective of verifying the effect of the operating parameters on soil decontamination performance. The contamination values, 0.1–10 g kg_{ds}^{-1}, were chosen to reflect the wide range of literature data spanning low, medium and high contamination levels of real soils. The polymer/soil ratios (2–10%) tested were based on previous studies on the removal of the same target compound from aqueous matrices [11], while the moisture content was varied taking into account the need for adequate mixing and, at the same time, minimization added water.

Fig. 1 provides a dramatic, qualitative indication of the absorptive uptake of 4NP by the polymer beads from 0 to 24 h. The yellow colour representative of the target compound clearly shows the effective sorption by the polymer beads, which was evident even at a very short contact time of 4 h.

Table 2 provides an overview of the 4NP removal efficiencies for all the tests and the amount sorbed by the polymer as calculated by mass balance. To make it easier to compare the effects of the investigated operating parameters on extraction performance the results of run E2 have been listed repeatedly for each series of tests.

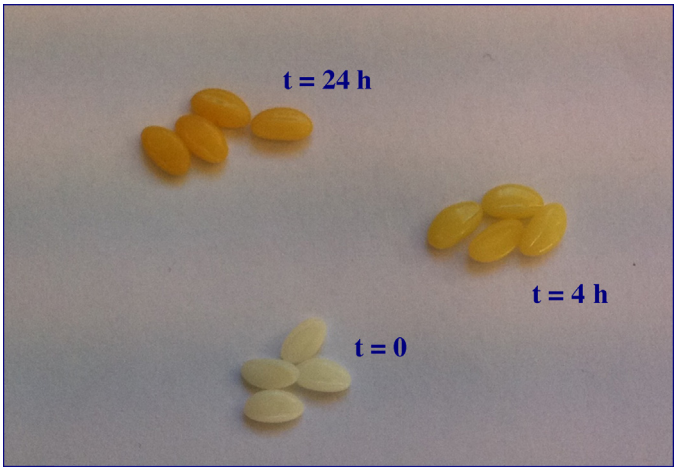

Fig. 1. Polymer beads utilized in test E2 at different contact times.

Table 2
Overview of the removal efficiencies and related amount retained in the polymer obtained in the different soil decontamination tests. Reported values are calculated from the experimental values as the average of triplicate tests ± standard deviation.

Test	Fraction of original 4NP sorbed by the polymer (%)		Mass of 4NP sorbed by the polymer (mg4NP g_p^{-1})
	4 h	24 h	24 h
E1	66.28 ± 2.37	68.88 ± 1.37	6.3 ± 0.1
E2	*59.60 ± 1.93*	*68.82 ± 2.99*	*12.3 ± 0.9*
E3	54.62 ± 0.90	67.17 ± 3.09	25.8 ± 0.5
E4	56.84 ± 9.10	69.48 ± 9.61	12.2 ± 1.5
E2	*59.60 ± 1.93*	*68.82 ± 2.99*	*12.3 ± 0.9*
E5	76.80 ± 3.65	84.88 ± 2.45	14.8 ± 0.3
E6	45.19 ± 1.93	75.90 ± 2.42	1.2 ± 0.1
E2	*59.60 ± 6.64*	*68.82 ± 2.99*	*12.3 ± 0.9*
E7	31.04 ± 0.38	74.32 ± 4.10	112.0 ± 7.2

All tests have a low standard deviation (at least one order of magnitude lower than the mean value) indicative of minimal scatter of the data, which is a positive finding, as it confirms the reliability of the applied experimental procedure. In the majority of the investigated cases, with the exception of test E7 (the most contaminated soil), the extraction process occurs rapidly, with 60–96% of the final removal efficiency occurring in the first 4 h. As seen in Table 2 the polymers are able to absorb a high percentage of the original amount of the contaminant present in the soil, with polymer uptake varying in a narrow range of 67–85%, thereby confirming efficient extraction performance by the polymers, even for highly contaminated soils. It is also worth noting the high sorption potential of the polymers, expressed as mass of 4NP sorbed per gram of polymer, seen in the right hand column for tests E6, E2, E7 carried out at the same polymer fraction (5%), which show a polymer retention capacity spanning two orders of magnitude for the different levels of contamination in the soils. This last finding demonstrates that low polymer fractions may be under-loaded for low and medium levels of contamination in soils and that the polymer can be efficiently re-utilized for treating soils at increased contamination levels. The high affinity of 4NP by Hytrel™ 8206 resulted in effective contaminant transfer from the soil, as well as high desorption efficiencies achieved with tap water, without the use of a mobilizing agent.

A summary of the decontamination of soil by polymer beads over all operating conditions is provided in Fig. 2, which shows that even a very low polymer/soil ratio can be employed with satisfactory results, although care may need to be taken with even lower polymer amounts to ensure complete and homogeneous contact with the soil. With respect to moisture content, the results suggest that the contaminant is conveyed through the water from the soil to the polymer as an increase in moisture content results in improved remediation, particularly as seen in test E5 which gave the best performance. The operating conditions of test E5 were therefore chosen as the reference for comparison between the two systems, extraction-TPPB and SSBB.

A quantitative, albeit first approximation, analysis can be carried out to characterize the 4NP partitioning between the wet soil and the polymer phase. The 4NP mass balance per unit of dry solid at equilibrium conditions is given by:

$$\frac{M_0}{S} = \frac{M_s}{S} + \frac{P}{S} \cdot w_p \quad (1)$$

where M_0 is the amount of contaminant loaded in the soil, M_s is the amount of contaminant in the wet soil (M_s/S is expressed as mg4NP/g_{ds}), P and S are the amounts of polymer and dry soil respectively, and w_p is the contaminant content sorbed into the polymer.

From Eq. (1) w_p is obtained as:

$$w_p = \frac{M_0/S}{(1/P_{p/ws}) + (P/S)} \quad (2)$$

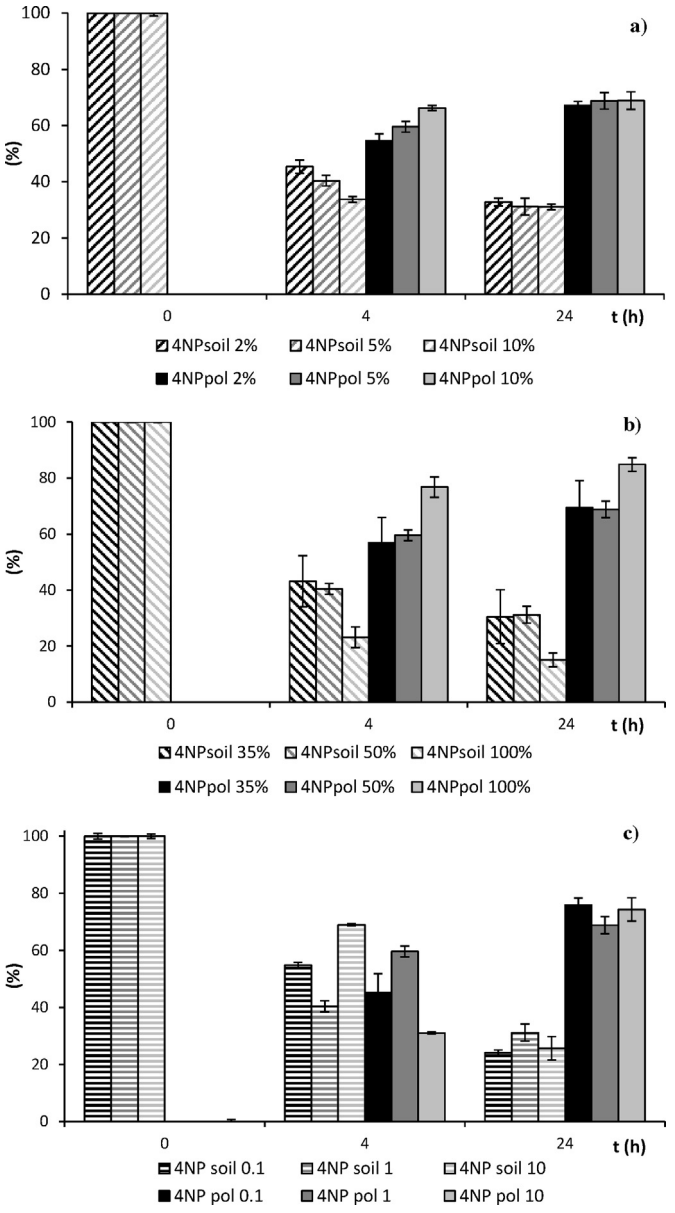

Fig. 2. Distribution of 4NP between soil (striped bars) and Hytrel™ 8206 (closed bars). The values are the means of three replicates and the error bars the standard deviations. (a) Tests at different polymer/soil ratio (E1, E2 and E3) in the range of 2–10%. (b) Tests at different moisture content (E4, E2 and E5) in the range of 35–100%. (c) Tests at different contamination level (E6, E2 and E7) in the range of 0.1–10 g4NP kg_{ds}^{-1}.

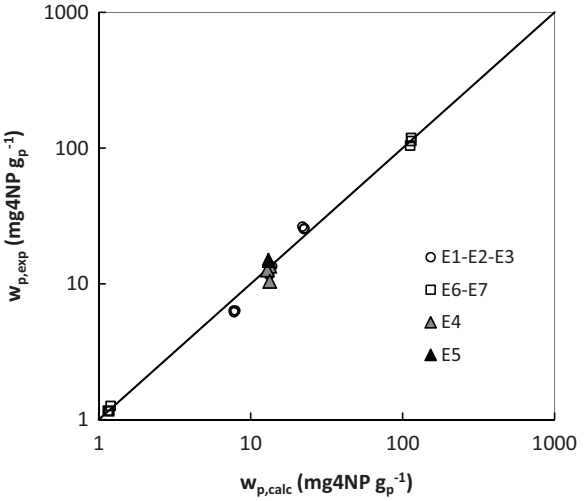

Fig. 3. Comparison of the experimental data and model correlation (Eq. (1)) with $P_{p/ws} = 57.6\,(mg4NP\,g_p^{-1})\,(mg4NP\,g_{ds}^{-1})^{-1}$.

where $P_{p/ws}$ is the effective 4NP partition coefficient between the polymer and the wet soil phase defined as:

$$P_{p/ws} = \frac{w_p}{M_s/S} \tag{3}$$

Due to the complexity of the system $P_{p/ws}$ cannot be considered to be a rigorous thermodynamic partition coefficient, but rather an effective partition coefficient, useful to evaluate the removal efficiency, or affinity, of the polymer and will depend on the operating conditions. In particular, $P_{p/ws}$ defined as in Eq. (3) is dependent on the moisture content of the soil.

The value of the effective partition coefficient can be obtained from the data obtained after 24 h, since no appreciable variation of the removal efficiency was observed by further extending the contact time beyond this time. A nonlinear least-squares fitting of data obtained by minimizing the sum of the squared differences between the experimental and calculated values of w_p in runs E1–E3 and runs E6 and E7 (with a constant moisture content of 50%) provides a value of the effective partition coefficient $P_{p/ws} = 57.6 \pm 3.4\,(mg4NP\,g_p^{-1})\,(mg4NP\,g_{ds}^{-1})^{-1}$. A comparison of the experimental and calculated values of the 4NP content in the polymer reported in Fig. 3 (since the data span three orders of magnitude, a log-log scale is used in the figure) shows that the simple proposed model is able to describe the removal efficiency, or affinity, of the polymer over the whole range of investigated operating conditions (*i.e.* contaminant loading, polymer-to-soil ratio and moisture content). Interactions between Hytrel™ 8206 and 4NP in tap water (*i.e.* partition coefficient and sorption data) have been extensively investigated and reported in Tomei et al. [19]. The 4NP partition coefficient between polymer and wet soil is comparable to the value (61) obtained for Hytrel™ 8206 in tap water [19], suggesting that preferential sorption of 4NP by Hytrel™ 8206 can be obtained regardless of where the contaminant is located. In the same figure the results of tests E4 and E5, corresponding to a lower and a higher moisture content respectively, have also been reported, and the results suggest that an increase in the moisture content may result in a higher extraction efficiency of the polymer.

3.2. Biodegradation tests in SSBB

The results of two replicate tests in the SSBB system are shown in Fig. 4. Concentration profiles of 4NP measured in the soil and water

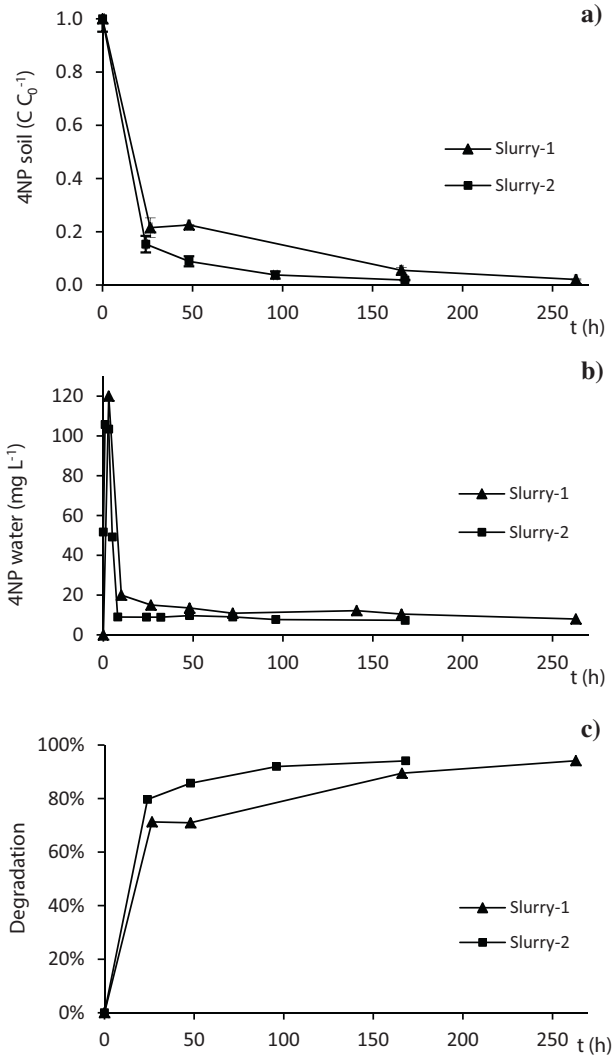

Fig. 4. Two replicates of biodegradation test in the SSBB: 4NP concentration pattern in soil (a) and aqueous phase (b) and corresponding percent biodegraded fraction (c). C_0 is the initial 4NP concentration in soil.

phases are reported in Fig. 4a and b while the percent biodegraded is shown in Fig. 4c and demonstrate satisfactory reproducibility of the tests. A distinct "soil washing" effect can be seen in the first 10 h of the test characterized by a rapid increase followed by a decrease of 4NP concentration in the aqueous phase over 24 h. The soil washing effect along with the use of acclimatized biomass resulted in excellent SSBB performance, which reached a 4NP removal efficiency of 80% after 24 h, a relatively short time for these systems. This rapid biodegradation in the SSBB may be attributed to the relatively low hydrophobicity of 4NP, and therefore its relatively low affinity for the organic fraction in the soil, as well as to the fact that the soil was not aged, as ageing is known to decrease the bioavailability of contaminants [20–22]. This behaviour can be explained by both the hydrophilic nature of the compound and the short period of contamination which could have facilitated the 4NP "washing" from the soil. It is worth noting that from 24 to 100–150 h biodegradation proceeds with a gradual decrease in the 4NP concentration in the soil while the 4NP in the aqueous phase remains constant. This behaviour is likely due to a balance between the 4NP being released from the soil and 4NP removal by the biomass.

Table 3
Summary of the operating conditions for the different process units.

Operating parameter	Units	SSBB	Polymer extraction	TPPB
Mass of treated dry soil	g	200	200	–
Initial 4NP concentration in soil	g 4NP kg_{ds}^{-1}	1	1	–
4NP load	mg g_p^{-1}	–	–	16.8
Bioreactor volume	L	1	0.4	0.1
Polymer mass	g	–	10	10

Table 4
Efficiencies and removal rates for polymer extraction, SSBB, and TPPB (average values for the replicates). Removal rates are calculated with respect to the time required to achieve 85% removal efficiency.

Parameter	Units	SSBB	Polymer extraction	TPPB
Removal efficiency after 4 h	%	20	77	50
Removal efficiency after 24 h	%	75	85	93
Removal rate with respect to treated dry soil	mg4NP h^{-1} kg_{ds}^{-1}	8.7	32.5	–
Volumetric removal rate	mg4NP h^{-1} L^{-1}	1.7	–	75

3.3. Biodegradation tests of 4NP removed from soil by polymer beads

Biodegradation tests of 4NP were performed in a batch TPPB bioreactor, and Fig. 5 shows the 4NP concentration profiles in the polymers for two replicates. In this case excellent reproducibility of the data is also seen, as well as efficient performance, with practically complete 4NP depletion from the polymer after 45 h. These results confirm previous results [11] obtained with the same contaminant/polymer pair in the treatment of contaminated water, and allow direct comparison of the performance of the SSBB with respect to the TPPB system.

Moreover, the possibility of multiple absorption regeneration cycles for Hytrel™ 8206 polymer utilized for 4-nitrophenol removal without losing absorption performance was previously demonstrated and reported in Tomei et al. [19].

3.4. Comparison between the extraction-TPPB system and the SSBB

A comparison between the SSBB and the extraction-TPPB operating conditions based on the same amount of contaminated soil treated is provided in Table 3.

A notable aspect seen in Table 3 is the very low reactor volume required (0.1 L) for the TPPB for the biodegradation of 4NP, which was removed from the soil by the polymer beads. This is a consequence of the contaminant concentrating effect performed by the polymers. Table 4 shows a performance comparison between the two investigated systems.

Superior performance by the polymer extraction-TPPB system in comparison to the SSBB is evidenced several ways. First, it can be seen that a very short time, 4 h, is required by the polymers to reach 77% removal efficency, with only 20% removal being achieved by the SSBB in the same time period. More significantly, the removal rate, expressed with respect to 85% removal efficency, was four times higher, with expected concomitant savings in time and energy. Ultimate 4NP removal in the TPPB reactor requires a volume that is one order of magnitude lower than the SSBB as evidenced by the high volumetric removal rate of 75 mg4NP h^{-1} L^{-1}.

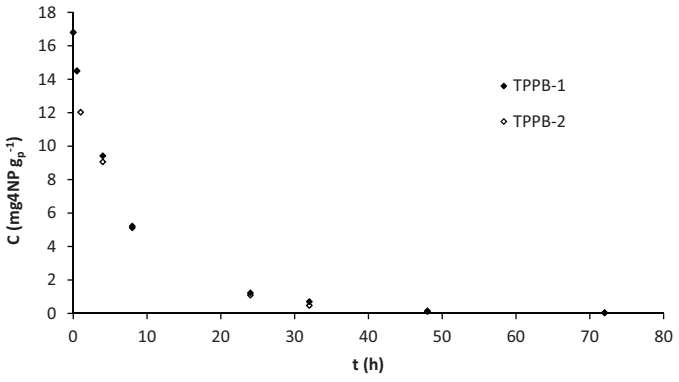

Fig. 5. Two replicates of TPPB biodegradation test: 4NP residual in the polymer.

In addition to the improved overall performance in soil decontamination (extraction plus biodegradation), the polymer extraction-TPPB system, in comparison to the SSBB, is characterized by ease of operation as it handles only a relatively small mass of clean polymer beads, whereas the SSBB must deal with larger amounts of actual soil, with all of its heterogeneous complexity, including rocks, stones, insects and other life forms. When added to the SSBB such components could also cause abrasion and other mechanical problems within the SSBB bioreactor. Finally, in contrast to polymer extraction-TPPB operation, the direct biological treatment of soils by the SSBB could remove nutrients and indigenous microbes from the soil, which could decrease the soil value upon its return to the original environment.

An important feature of polymers is their easy regeneration and reutilization. For example, it was previously demonstrated that separation of used polymers from the treated soils can be easily performed by utilizing magnetized polymer beads [23]. In this way the polymer can be easily recovered and reused for more cycles in treating soils at increasing contamination levels. Once saturated they can be regenerated biologically (as was demonstrated in this study).

4. Conclusions

Among *ex situ* methods for treating contaminated soil, soil slurry batch bioreactors have been one of the most common technological approaches, notwithstanding the fact that they require significant soil pre-handling (sieving), large volumes of co-treated water require disposal, and the fact that the soil may become depleted of nutrients and microflora as a result of SSBB treatment. In this work, we have shown that small amounts of absorptive commercial polymer beads can readily (up to 85%) and rapidly (within 4 h) remove contaminants from soil, concentrating them within the polymer matrix, while leaving the soil otherwise intact. Once these loaded beads are added to a bioreactor the contaminants are readily released to a cell-containing aqueous phase in response to the cells' metabolic demand. Virtually complete contaminant degradation is achieved, allowing reuse of the polymers for the decontamination

of more soil. Relative to conventional SSBB operation, the TPPB platform has shown significantly reduced reactor volume requirements (due to the polymer concentration effect) and 4NP removal efficiencies that were 4 times higher. Our ongoing research involves determining the impact of soil composition (*e.g.* clay, organic fractions) on polymer removal efficiency, as well as the presence of multiple target contaminants, perhaps leading to the use of additional polymers targeted for each specific contaminant type.

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