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Research article

Polymer extraction and e*x situ* biodegradation of xenobiotic contaminated soil: Modelling of the process concept

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ABSTRACT

An integrated model of a two-step process for the *ex situ* bioremediation of xenobiotic contaminated soil has been formulated. The process is characterized by an initial extraction step of the organic contaminants from the polluted soil by contact with inexpensive and commercially-available polymer beads, followed by release and biodegradation of the xenobiotics, with parallel polymer bioregeneration, in a Two-Phase Partitioning Bioreactor (TPPB). The regenerated polymer is cyclically reused in the extraction step, so reflecting the robust and otherwise-inert properties of such polymers. The model was calibrated and validated for a soil contaminated with 4-nitrophenol (4NP) and treated with the DuPont polymer Hytrel 8206. In the model calibration, the partition coefficient polymer-soil, P_{ps}, and the mass transfer coefficient, K, were evaluated, as 105.3 and 0.24 h^{-1} respectively. A diffusion coefficient within the polymer of 6.3 10^{-8} $cm^2 s^{-1}$ was determined from the fitting of sorption/desorption data. The model was then tested for two alternative process configurations consisting of either one or two soil extraction units, followed by the biodegradation/bioregeneration step. The latter configuration resulted in more effective polymer utilization and is suitable if each extraction step requires a shorter time than the regeneration step. The model predicted that an extraction time of 12 h was sufficient to reach removal efficiencies ≥90% while the biodegradation/bioregeneration step required 24 h to reach efficiencies ≥93%, with a good agreement with experimental data ($R^2 > 0.98$ for both cases). The simulation of the process operated with two extraction units showed a better performance with a final concentration ~0.2 g_{4NP} kg_{ds}^{-1} vs. 1.69 g_{4NP} kg_{ds}^{-1} obtained with single extraction unit, for a soil contaminated with 10 g_{4NP} kg_{ds}^{-1}. Corresponding extraction efficiencies were 96 and 83%, respectively.

1. Introduction

An innovative bio-treatment system has recently been shown to be effective for the *ex situ* remediation of soils contaminated with refractory organic compounds: solid phase extraction performed with amorphous polymer beads followed by their biological regeneration, and contaminant biodegradation, in Two-Phase Partitioning Bioreactors (TPPB) as depicted in Fig. 1. This decontamination strategy involves two sequential process steps: contacting contaminated soil with polymers, during which the pollutants are sorbed from the soil into the polymeric absorbent phase (polymer-extraction step), followed by pollutant release and biodegradation under controlled conditions (bioregeneration step) in a pre-inoculated TPPB. The strategy behind the use of inert and commercially available polymers to extract contaminants from soil is based on the high affinity of the target organic contaminants for the polymeric phase and on the ease of regenerating the "contaminated polymer", thus generating "fresh" polymer for its subsequent reuse.

A variety of chemically distinct polymers, under a number of operating conditions (i.e. use of various mobilizing agents, polymer-to-soil ratio and contaminant soil concentration), have been tested to characterize the polymer-extraction step. Prpich et al. (2006) used Hytrel 8206 to remove phenol from a contaminated soil achieving removal of 95% in 24 h. Similar results were obtained with the same polymer in treating soil contaminated with 4-nitrophenol: 4 h were sufficient to reach 77% extraction efficiency by using only tap water (100% w/w) as a mobilizing agent (Tomei et al., 2013). Rehmann and Daugulis (2008) treated a soil contaminated by the polychlorinated biphenyl (PCB) Aroclor 1242 with Hytrel: after two days of contact time and using 15% w/w of isopropyl alcohol as mobilizing agent, the PCB concentration in

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Nomenclature

c	substrate concentration
$\mathcal{D}$	diffusion coefficient
E_R	regeneration efficiency
k	substrate maximum specific removal rate
K	mass transfer coefficient
K_O	overall mass transfer coefficient
$K_{i,j}$	mass transfer parameter from i to j phase
K_S	half-saturation constant
K_I	inhibition constant
M	solid (soil or polymer) mass
η	extraction removal efficiency
P_i	polymer stream at stage i
P	partition coefficient
r	radial position
R	bead radius
r_s	substrate consumption rate
S_i	soil stream at stage i
V	volume
X	biomass concentration

Superscripts

*	equilibrium conditions

Subscripts

0	initial value
∞	at infinite time
4NP	4-nitrophenol
ds	dry soil
p	in polymer phase
ps	between polymer and soil phase
pw	between polymer and aqueous phase
s	in soil phase
sw	between soil and aqueous phase
w	in aqueous phase of the bioregeneration step

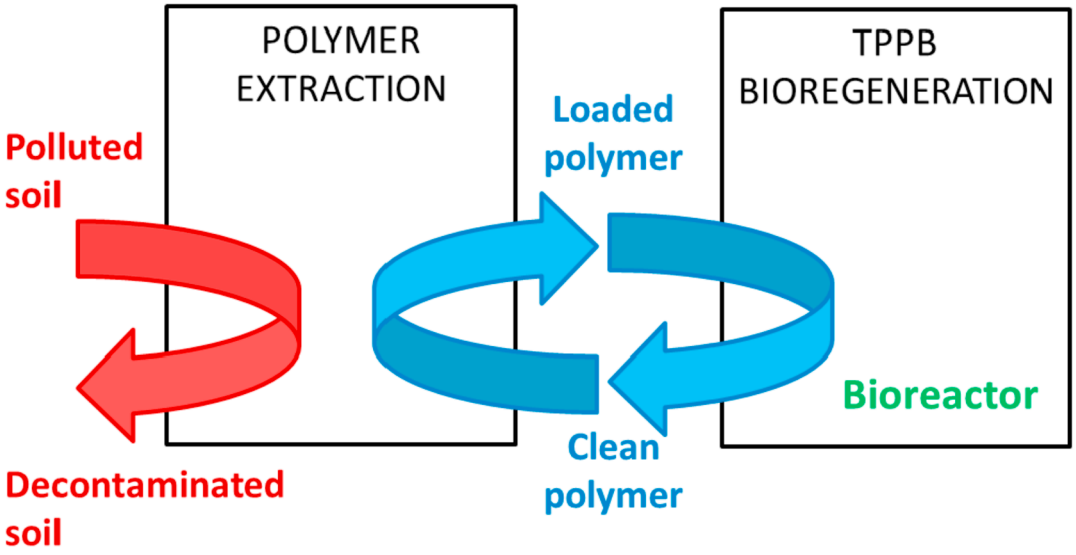

Fig. 1. Two-step extraction-bioregeneration process: schematic representation and operating principle.

the soil decreased by 48–68%. Peyda et al. (2013) investigated the combined use of polyurethane Desmopan beads and 2-propanol as a mobilizing agent to extract 80% of petroleum hydrocarbons from a clay soil in three days.

Several studies also demonstrated the feasibility of the second regenerative or organic biodegradation step: Prpich et al. (2006) regenerated the polymer by adding the loaded Hytrel beads to a cell-containing TPPB for contaminant desorption and biodegradation, after which the polymers were used again for the extraction of phenol from soil, with no loss in absorptive efficiency. Rehmann et al. (2008) also confirmed the biodegradation of three polycyclic aromatic hydrocarbons (PAHs), and polymer regeneration, in a solid-liquid TPPB fed with PAH-loaded polymer beads arising from soil decontamination: 78%, 62%, and 36% of phenanthrene, pyrene, and fluoranthene, respectively, were degraded within a 14-day period. Furthermore, in a recent study, Mosca Angelucci and Tomei (2015a) demonstrated the biological polymer regeneration strategy for contaminated polymers employed to treat a soil contaminated with the mixture of 4-chlorophenol and pentachlorophenol and found a consistent reduction of the operating costs of the bio-regeneration in comparison to solvent extraction used to regenerate the loaded polymer beads.

The potential advantages of the two-step process described above relative to conventional *ex situ* bioremediation systems (i.e. slurry and solid-phase bioreactors) are the dramatic reduction of the processing times and the possibility of achieving complete mineralization of the pollutants through polymer bioregeneration (Mosca Angelucci and Tomei, 2016). Practical application of this TPPB-based soil remediation process requires the easy separation of the beads from the contaminated soil after absorbing the pollutants. It was previously demonstrated that separation of used polymers from the treated soils can be easily performed by utilizing magnetized polymer beads (Yeom et al., 2010). In this way the polymer can be easily recovered and reused for more cycles in treating soils at increasing contamination levels and, once saturated it can be regenerated biologically.

Previous studies on modelling of the two-step process have been focused on the two separate processes of extraction, and biodegradation/bioregeneration. Tomei et al. (2015) have recently proposed a "lumped parameter" model of solid extraction, which was calibrated and validated with experimental data on soil contaminated with substituted phenols. With respect to the biological regeneration of the polymer, models have been developed for two-phase partitioning bioscrubber (Littlejohns et al., 2010), solid-liquid TPPBs applied to air pollution control (Dorado et al., 2015) and fed-batch TPPBs applied to the removal of xenobiotics from concentrated aqueous streams