

A Sustainable Approach For TCE Contaminated Groundwater Remediation: Polyhydroxyalkanoates (PHA) from waste as Electron Donor for biological reductive dechlorination

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Purpose of study. Previous studies showed the potentialities of bio-based materials for bioremediation purposes, including polyhydroxybutyrate (PHB), a biodegradable microbial polyester tested as a fermentable source of slow-release electron donor for sustaining the biological reductive dichlorination (BRD) (Marta M Rossi et al. 2022). On the other hand, a low-cost biobased material, biochar (BC), also used as sorbent, has recently been proposed to accelerate the BRD reactions. Here we proposed a Coupled Adsorption and Biodegradation (CAB) process for trichloroethylene (TCE) removal in a mini-pilot-scale reactor filled with a raw PHA produced from mixed microbial cultures (MMC) and fermented organic waste (as feedstock) and pinewood BC. This work aimed to evaluate the performance of the CAB process with particular regard to the effectiveness of the BC in sustaining the dechlorinating biofilm (mostly enriched by *Dehalococcoides mccartyi* (Dhc)) growth, and the effects of a raw PHA as source of electron donor.

Methodology. The Reactor was carried out in a column of 150x10 cm, in which the dechlorinating biofilm was supported by pinewood biochar (4% wt), which has been completely characterized in a previous study (M.M. Rossi et al. 2021), mixed with sand for the entire length of the reactor. Moreover, in the first half of the column, from the bottom, called the "fermentation zone", a dry raw PHA-rich biomass (35 %wt of PHA) in powder form was added. This biomass was produced at pilot scale from a three-stage process by MMC and fermented organic fraction of municipal solid waste (OFMSW) as feedstock (Valentino et al. 2018). The reactor was equipped with 13 gates for lateral sampling. The start-up was carried out with an active TCE-to-Ethylene consortium. After the tracer test, the flow rate was maintained at 2.9 ± 0.6 L/d on average, with 94 hours as Hydraulic Retention Time (HRT). The feed solution consisted of contaminated tap water, resulting in a final TCE concentration of 100 μ M. A summary of operative conditions and some monitored parameters are reported in table 1. The monitoring of volatile fatty acids (VFA) and Chlorinated compounds was carried out through regular sampling of the side doors of the column. Samples were stored for microbiological analysis.

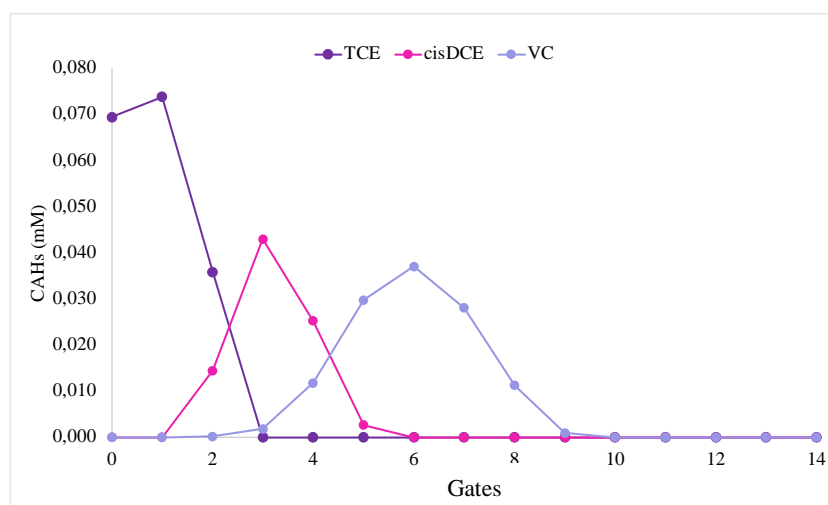
Results. During the first two months of operation, the reactor has treated 180 Liters of contaminated water (10.5 ± 1.7 mg L⁻¹ was the average of TCE_{IN}) removing 2.6 g of TCE. The PHA compartment yielded a very high concentration of total VFA at the beginning of the experiment (1.3 g/L of VFA during the first week, at the outlet), decreasing progressively until a constant concentration of 6 mg/L from day 118 to 206. After 214 days of operation (Figure 1), a complete conversion of TCE to cis-dichloroethylene (cisDCE) and the following daughter product vinyl chloride (VC) was observed in the fermentative zone, while the final product, ethylene, was detected only in outlet. A slow and constant release of Acetate from the PHA compartment and the high flow rate used are interesting conditions for field applications. This configuration also allowed the treatment of high contaminant load at high solution feed rate (30.6 mg TCE day⁻¹; 1.5 m day⁻¹).

Conclusion. Recent field application studies in Italy have shown the effectiveness of combining the immobilization of chlorinated solvents and the biostimulation, allowing the quick reduction of dissolved contaminant levels and promoting the BRD kinetics. In compliance with sustainability and circular economy principles, the current research interest is focused on alternative materials such as long-lasting electron donors and possible growth support for biofilm as adsorbents. This study is particularly relevant for possible field application, indeed the tubular reactor configuration could be applied on a larger scale for an ex situ treatment of a contaminated groundwater. On the other hand, the same technology could be involved in a PRB configuration. The promising results open doors to the circular economy concept where a by-product of biomass thermal treatment and a biopolymer obtained from organic waste could support specific dechlorinating biofilm for bioremediation application.

Table 1. Operative conditions and reactor parameters.

Operative days	214
Flow rate (L/d)	2.9 ± 0.6
HRT (h)	94.4 ± 0.2
Retention time (h)	35.0 ± 8.2
Linear velocity (m/d)	1.0 ± 0.2
TCE _{in} (mg/d)	35 ± 3
Treated water volume (L)	560

Figure 1. TCE, cisDCE and VC profiles along the reactor at day 206.



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