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Research article

A novel continuous two-phase partitioning bioreactor operated with polymeric tubing: Performance validation for enhanced biological removal of toxic substrates

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ABSTRACT

A continuous two-phase partitioning bioreactor (C-TPPB), operated with coiled tubing made of the DuPont polymer Hytrel 8206, was tested for the bioremediation of 4-chlorophenol, as a model toxic compound. The tubing was immersed in the aqueous phase, with the contaminated water flowing tube-side, and an adapted microbial culture suspended in the bioreactor itself, with the metabolic demand of the cells creating a concentration gradient to cause the substrate to diffuse into the bioreactor for biodegradation. The system was operated over a range of loadings (tubing influent concentration 750 −1500 mg L^{-1}), with near-complete substrate removal in all cases. Distribution of the contaminant at the end of the tests (96 h) highlighted biological removal in the range of 87–95%, while the amount retained in the polymer ranged from ~1 to 8%. Mass transfer of the substrate across the tubing wall was not limiting, and the polymer demonstrated the capacity to buffer the substrate loadings and to adapt to microbial metabolism. The impact of C-TPPB operation on biomass activity was also investigated by a kinetic characterization of the microbial culture, which showed better resistance to substrate inhibition after C-TPPB operation, thereby confirming the beneficial effect of sub-inhibitory controlled conditions, characteristic of TPPB systems.

1. Introduction

The presence of cytotoxic substrates constitutes the main limitation in the application of biological processes in industrial wastewater treatment arising from a reduction in microbial activity. In recent decades, the increased attention devoted to environmental safety and sustainability has promoted a renewed interest in the use of biological processes, which, in contrast to the majority of chemical-physical processes, are able in principle to provide complete degradation of target contaminants (Daugulis, 2001). The capability of microorganisms to metabolize complex and biorefractory substrates has been demonstrated for a variety of contaminants, but microbial biocatalysts in practice require integration with carefully engineered processing configurations to be able to achieve biodegradation rates suitable for application (Field and Sierra-Alvarez, 2008). Two-phase partitioning bioreactors (TPPBs) have proven to be a robust and effective technological platform for reducing or eliminating the cytotoxicity of xenobiotic contaminants and the use of polymer beads as the partitioning phase has been successfully tested for the treatment of industrially-relevant contaminants (Muñoz et al., 2007; Quijano et al., 2009) and in soil bioremediation (Tomei and Daugulis, 2013).

A new TPPB configuration suitable for continuous biodegradation of inhibitory substrates has recently been proposed (Tomei et al., 2016). The principle of operation, similar to extractive membrane bioreactors (EMBs) (Freitas Dos Santos and Livingston, 1995; Livingston et al., 1998), is based on the physical separation of the toxic contaminated wastewater and the biomass: the pollutants are transported from the contaminated stream across a polymeric membrane, and are degraded in a cell-containing host bioreactor. In one such configuration, EMBs operated with silicone-rubber membranes, the mass transfer of toxic compounds occurs across a non porous-silicone membrane due to the presences of a concentration gradient, while the bioreactor acts as a sink. A modified configuration can be conceptualized by substituting the silicone membrane with a selected polymeric membrane consisting

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of extruded polymer tubing coiled inside the bioreactor. The contaminated stream flows inside the tubing and the target substrate, possessing a high affinity for the polymer, diffuses through the tubing walls into the bulk phase of the bioreactor containing the microbial culture catalyzing the biodegradation process. This system is a continuous TPPB in which the partitioning phase is the polymer tubing itself, which allows continuous feeding of the wastewater and, in contrast to TPPBs operated with polymer beads, ensures the separation of wastewater/microbial culture. This new configuration is suited to the treatment of industrial wastewaters characterized by high salinity, extremes of pH, and toxic inorganic components such as metals, along with the target organic contaminant(s), in that only the organics will diffuse through the polymer to the microbial phase (Yeo et al., 2015). The effective separation exerted by the polymer can enhance microbial growth by preventing exposure to the complete "hostile" wastewater environment and, at the same time, provides a gradual delivering of the organic substrate driven by the metabolic demand of the bacterial culture, which is exposed to sub-inhibitory concentration levels. Furthermore, according to Livingston et al. (1996) this configuration creates a selection pressure of the target pollutants to promote the adaptation of the microbial culture and enhancing the biodegradation rate.

Polymers used in the fabrication of such tubing can be specifically selected, based on the affinity for the target contaminant(s), and the characteristics of the wastewater. The silicone-rubber membranes were previously demonstrated to be effective for highly hydrophobic VOCs, while for the application to other biorefractory organic pollutants as chlorophenols, more complex approaches are required. For instance, Liu et al. (2001) for the treatment of an acidic effluent containing high concentration of chlorophenols and salts, proposed a hybrid multi-step process combining liquid-liquid extraction, stripping, and a membrane bioreactor.

With the aim of demonstrating the applicability of a C-TPPB operated with polymer tubing for the treatment of organic molecules other than VOCs, such as chlorophenols, in this study we applied a C-TPPB operated with a coiled tubing made of the commercial DuPont polymer Hytrel 8206, to the removal of 4-chlorophenol (4CP). In a previous study (Tomei et al., 2016), Hytrel tubing was characterized in terms of its mass transfer properties, and the feasibility of the proposed reactor tested with "simulated kinetics" in an abiotic system and with a single, preliminary biotic test. In this study, a complete demonstration of a biological C-TPPB with a mixed culture acclimatized to the compound was performed for the first time. Increasing loading conditions were applied and the effect of the different operation modes, i.e. single phase SBR (Sequencing Batch Reactor) and C-TPPB, on biomass activity were also investigated by a kinetic characterization of the microbial culture in the different periods of the experimental campaign.

2. Materials and methods

2.1. Chemicals

4-chlorophenol (4CP), (CAS number 106-48-9, molecular weight 128.56 g mol^{-1} and purity > 99%) was selected as the target compound and was purchased from Sigma-Aldrich (USA). All other chemicals (sodium acetate and mineral medium components) were of commercial grade and obtained from Carlo Erba (Italy).

2.2. Analysis

Measurement of 4CP concentrations in aqueous samples were performed after centrifugation (8 min at 13,000 rpm), through UV absorbance readings (Spectrophotometer PerkinElmer, Lambda 25) at 279 nm.

Volatile suspended solid (VSS) concentration was determined according to Standard Methods (APHA, 2012) to quantify the biomass concentration in the bioreactor.

pH was measured according to Standard Methods (APHA, 2012).

Chloride concentration in the liquid phase of the bioreactor was measured with an ionic chromatograph (DIONEX) according to the procedure reported in Standard Methods (APHA, 2012).

2.3. Biomass

An inoculum previously adapted to 2,4-dichlorophenol (Tomei et al., 2014) was progressively acclimated to 4CP in a lab-scale SBR. Sodium acetate (SA) was used as biogenic substrate, and was fed to the bioreactor in addition to the 4CP solution. After reaching stable performance, SA was progressively reduced (from 40 mg L^{-1} to 0) and the 4CP concentration was increased from 60 up to ~ 230 mg L^{-1}. A mineral salt medium (Williams and Unz, 1989) was added to the feed solution to ensure the required contribution of nutrients and microelements and dosed to get a C:N:P ratio of 100:5:1. In the acclimatization phase a rapid culture adaptation to the compound (data not shown) was observed with practically complete removal after 3 days for a feed 4CP concentration of 60 mg L^{-1}. The fed acetate was eliminated after 20 days of operation. Then, 4CP was fed as the sole carbon and energy source, and, after a few days of a slight increase in the effluent concentration, complete removal was restored. The developed 4CP-degrading biomass was utilized to inoculate the C-TPPB bioreactor.

2.4. SBR bioreactor

The lab-scale SBR was employed for the enrichment of the 4CP-degrading biomass and for the kinetic tests performed to characterize the microbial culture in the different periods of the experimental campaign. It consisted of a 2.5 L glass vessel (2 L working volume), interfaced with a dedicated control computer and Labview software to automatically manage the timing of the operational sequence of the work cycle and the Dissolved Oxygen (DO) control. The reactor exchange ratio (added volume/total volume) was 0.5 for the entire experimental period. The reactor was equipped with a magnetic stirrer, two peristaltic pumps (Cellai, Perinox SF3) for feeding and discharging, a thermostat (set point value of temperature was 27 ± 0.5 °C), a glass diffuser connected to a compressor for the oxygen supply and an oximeter (Oxi 538, WTW) for online DO monitoring and control via on/off strategy. DO concentration was controlled in the range of 3–4 mg L^{-1}.

Each SBR work cycle lasted 12 h, consisting of feed (15 min), aerobic reaction (630 min), settle (60 min) and effluent discharge (15 min) phases. During the feed phase, the bioreactor was mixed while during the reaction phase was operated under mixed and aerated conditions. DO data were recorded (time intervals of about 15 s) and employed for the Specific Oxygen Uptake Rate (SOUR) evaluation according to the procedure described in Tomei et al. (2004).

During the acclimatization, SBR performance was monitored by daily 4CP concentration measurement in the influent and effluent, while biomass concentration was analyzed on weekly basis. Additional information of the bioreactor and control system is reported elsewhere (Mosca Angelucci and Tomei, 2015).

2.5. Continuous TPPB bioreactor

Tubing made of Hytrel 8206 polymer was obtained from DuPont

(Canada) and was utilized in the C-TPPB. The bioreactor consisted of a glass vessel of 5 L (working volume ~ 3.3 L) equipped with a magnetic stirrer, a thermostat for temperature control (set point 27 ± 0.5 °C) and a tubing support. The Hytrel tubing (length of 3.5 m, external and internal diameters of 6 and 5 mm, respectively, external surface area of 6.6 dm^2, internal volume of 0.07 L) was spirally coiled on the support. The tubing/liquid volume ratio was ~3% (v/v). A peristaltic pump (Watson-Marlow, Cellai, Italy) provided the feeding of the 4CP solution to the tubing. The flowrate was adjusted to give established desired Hydraulic Retention Time (HRT) in the tubing, and the effluent was collected in a sealed glass flask. The liquid phase of the bioreactor consisted of an inoculum (approximately 1 L) coming from SBR, added tap water and the mineral salt medium, dosed on the basis of the fed 4CP amount. DO was monitored and controlled (within the range of 3–4 mg L^{-1}) with the same apparatus described for the SBR, and SOUR profiles were estimated also in this case. Furthermore, the pH was also monitored and controlled (set point value 7.5) by dosing NaOH solution (1 M) through a timed peristaltic pump. A schematic representation of the C-TPPB is reported in Fig. 1.

2.6. Continuous biodegradation tests: C-TPPB

4CP removal was investigated in the C-TPPB with continuous tests at increasing 4CP influent loads in the range of 9.6–21 mg h^{-1}. The biomass concentration was in the range of 1100–2100 mg_{VSS} L^{-1}. Three series of tests were performed at tubing influent 4CP concentrations of approximately 750 (I), 1000 (II), and 1500 (III) mg L^{-1}. The initial concentration of 4CP in the bioreactor was ~0. The HRT in the tubing was set at 6 h and each test lasted 96 h. Two replicates were performed for each test. Periodic samples from the reactor and the tubing effluent were analyzed for 4CP concentration at time intervals of 15–60 min in the first day, then at longer time intervals in the following days. Tubing effluent was collected and periodically analyzed (at 6, 24, 48, 72, 96 h) for 4CP and the data were utilized for the mass balance giving the 4CP distribution vs. time.

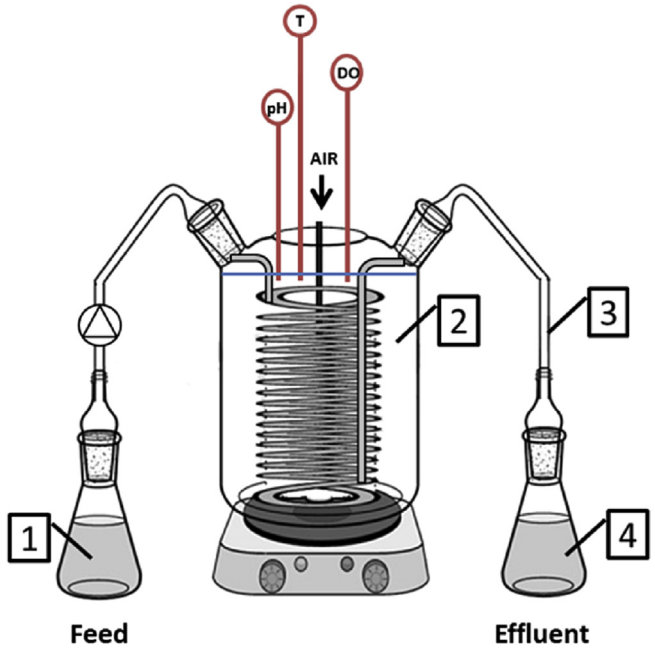

Fig. 1. Schematic representation of the experimental apparatus for the C-TPPB. The numerical labels indicate the sampling points: 1. Tubing influent; 2. Bioreactor; 3. Tubing effluent; 4. Tubing collected effluent.

Biomass was monitored daily and the chlorides derived from the 4CP biodegradation and accumulated in the liquid phase of the bioreactor were measured to evaluate the 4CP removal rates (Caldeira et al., 1999). The chloride concentration was measured at time intervals of 2 h in the first part of the test, than at longer time intervals (4–24 h).

The 4CP amount absorbed into the polymeric tubing has been evaluated with the mass balance (referred to the time interval 0-t):

$$M_0 + M_{fed} = M_{l,tub} + M_{e,tub} + M_{bio} + M_{rem} + M_{pol}$$

where the terms in the equation express the different 4CP amounts as:

- M_0: in the tubing at t = 0 (the test started with the filled tubing);
- M_{fed}: fed in the tubing in the related time interval;
- $M_{l,tub}$: in the liquid phase within the tubing at time t;
- $M_{e,tub}$: in the collected effluent from the tubing in the related time interval;
- M_{bio}: in the bioreactor at time t;
- M_{rem}: biologically removed (estimated by chloride accumulation in the related time interval);
- M_{pol}: absorbed into the polymer in the related time interval.

M_{pol} is the only unknown of the above equation, being the other 4CP amounts measured (M_0, M_{fed}, $M_{l,tub}$, $M_{e,tub}$, M_{bio}) or calculated (M_{rem}).

2.7. Kinetic tests: SBR

Biodegradation kinetic tests were conducted in the SBR bioreactor to kinetically characterize the biomass in the different experimental periods before and after C-TPPB operation. The influent 4CP concentration was ~100 mg L^{-1} and the biomass concentration was in the range of 1300–2600 mg_{VSS} L^{-1}. 4CP concentration was measured in the aqueous samples, taken from the reactor at intervals of 5–30 min during the feed and reaction phases. The biomass concentration was monitored at time intervals of hours due to its very low variation with respect to the typical concentrations utilized in the bioreactor.

4CP biodegradation was analyzed with the classical Haldane model, generally employed to describe the inhibitory effect of a substrate on biodegradation (Sahinkaya and Dilek, 2005; Lepik and Tenno, 2012):

$$r_s = k \cdot X \cdot \frac{S}{S + K_S + S^2/K_I}$$

where r_s is the substrate consumption rate, X and S are the biomass and substrate concentrations, respectively, k is the substrate maximum specific removal rate in absence of inhibition, and K_S and K_I the half-saturation and inhibition constants, respectively. The

Table 1
C-TPPB biodegradation tests: overview of the operating conditions and removal efficiency in tubing. X = biomass concentration; C_0 = Influent tubing concentration; IOL = Influent Organic Load; HRT = 6 h.

Test	C_0 mg L^{-1}	IOL mg h^{-1}	X g_{VSS} L^{-1}	Removal (%)
I-a	711.19	9.57	2.09 ± 0.28	99.8
I-b	751.70	10.14	1.53 ± 0.09	99.8
II-a	1025.71	13.32	1.63 ± 0.20	99.9
II-b	1010.68	13.49	1.38 ± 0.25	99.9
III-a	1479.83	16.69	1.25 ± 0.14	99.8
III-b	1535.09	20.79	1.12 ± 0.12	99.9

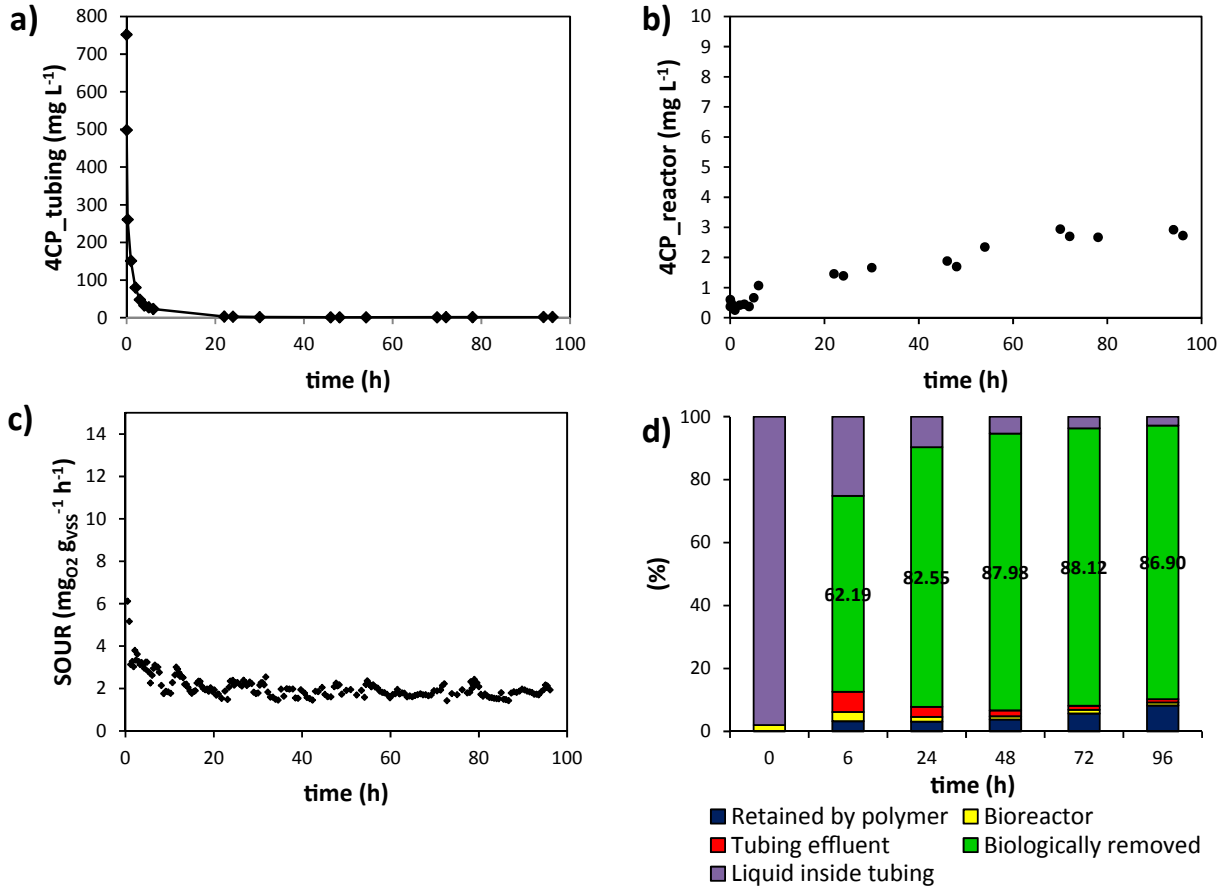

Fig. 2. Run I: 4CP concentration profiles in tubing (a) and in the bioreactor (b), SOUR (c) and 4CP distribution vs. time.

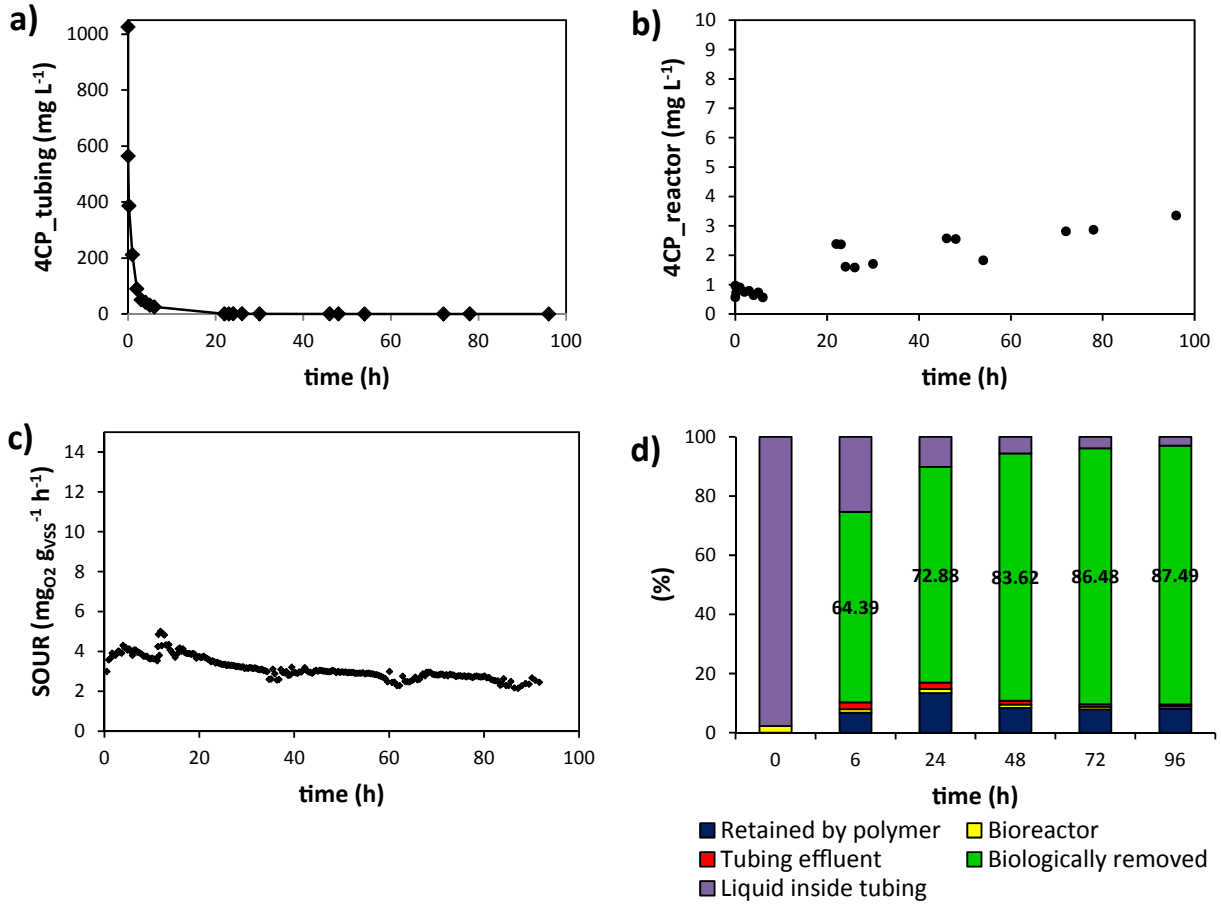

Fig. 3. Run II: 4CP concentration profiles in tubing (a) and in the bioreactor (b), SOUR (c) and 4CP distribution vs. time.

software package Scientist 3.0 for Windows (Micromath, USA) was applied to estimate the kinetic parameters (k, K_S, K_I). Based on the experimental evidence that the biomass variation due to growth is not appreciable with respect to the amount of the biomass utilized in the tests, the biomass concentration was assumed to be constant for a single work cycle.

Respirometric data collected during the reaction phase of biodegradation kinetic tests were employed to evaluate the biomass growth yield coefficient, Y, and the endogenous respiration rate, b, according to the procedure suggested by Tomei et al. (2004).

3. Results and discussion

3.1. Continuous biodegradation tests: C-TPPB

Table 1 shows a summary of the operating conditions for the three series of tests and the removal efficiency referring to the stream flowing inside the tubing. The first important observed result is the practically complete removal of 4CP under all the investigated loading conditions.

A more detailed presentation of the experimental results in these tests is shown in Figs. 2–4 for the 3 loading conditions. In each figure, in order to give a detailed characterization of the bioreactor performance, the concentration profiles vs. time in the tubing effluent before collection (a) and in the bioreactor (b), SOUR (c) and the distribution (as % of the fed amount) of the compound at the different times as resulting from the mass balance (d) are reported.

In all cases, a rapid decrease of the tubing effluent concentration is observed: in only 2.5 h it is reduced to one-tenth of the initial value while 48 h are sufficient for the system to reach steady state operating conditions, even at the highest 4CP load. Final concentrations in the tubing effluent were always <3 mg L^{-1}, while concentrations in the reactor ranged from 2 to 5 mg L^{-1} depending on the applied load. The rapid decrease of 4CP in the tubing effluent is a demonstration of the absorptive nature of the polymer tubing in that there is an effective mass transfer through the tubing walls and an effective biodegradation on the bioreactor side. According to the principle of operation of TPPBs, once the substrate is biodegraded, restoration of the thermodynamic equilibrium causes 4CP transfer from the tubing-side to the bioreactor-side thereby decreasing the concentration inside the tubing.

Quantification of the distribution of the target compound at the end of the test (after 96 h) is shown in Table 2. Biological removal is in the range of 87–95% while the percent retained in the polymer ranges from ~1 to 8%.

To demonstrate that the effective mineralization of the compound and not only sorption took place, biological removal was verified by measurement of an independent parameter, the percent increase of chloride concentration in the bioreactor assuming that 4CP degradation results in a stoichiometric release of Cl^- (Melin et al., 1993; Caldeira et al., 1999; Katsivela et al., 1999; Field and Sierra-Alvarez, 2008). This methodology allowed evaluation of the contribution of biological degradation to the observed substrate removal, and highlighted the absence of inhibitory effects as confirmed by the chloride evolution profiles reported in Fig. 5. A linear trend (correlation coefficients $R^2 > 0.99$) of the chloride concentration is observed in all cases with rates proportionally

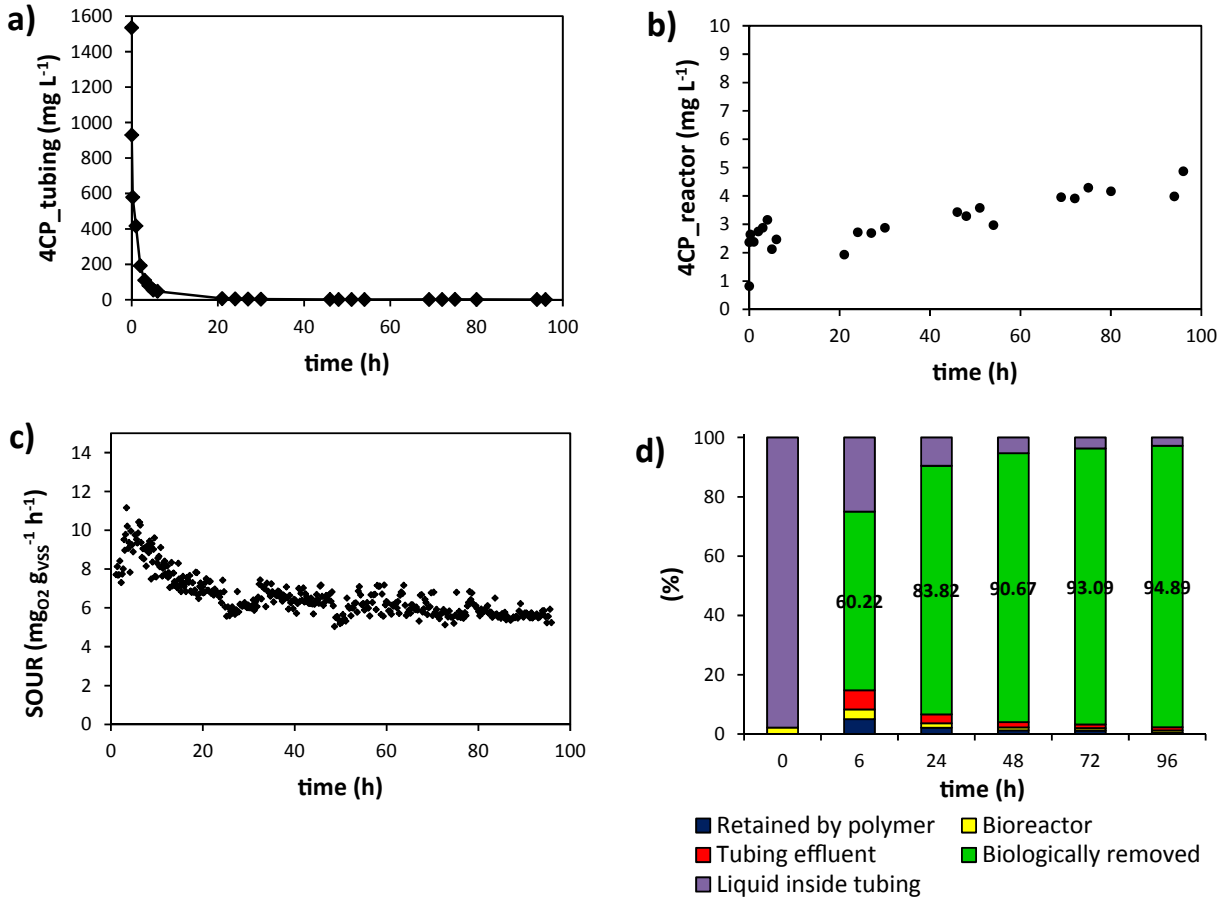

Fig. 4. Run III: 4CP concentration profiles in tubing (a) and in the bioreactor (b), SOUR (c) and 4CP distribution vs. time.

Table 2
4CP distribution at the end of the test: percent values of the fed amount (%). The biologically removed fraction is highlighted in bold.

Run	Absorbed into the polymer	In the liquid phase within the tubing	In the collected effluent leaving the tubing	In the aqueous phase within the reactor	Biologically removed
I-a	6.70	3.68	1.07	1.61	**86.94**
I-b	8.26	2.85	1.05	0.95	**86.90**
II-a	8.11	2.94	0.65	0.81	**87.49**
II-b	7.77	3.74	1.44	0.33	**86.72**
III-a	5.06	3.95	1.51	2.18	**87.29**
III-b	0.45	2.83	1.00	0.83	**94.89**

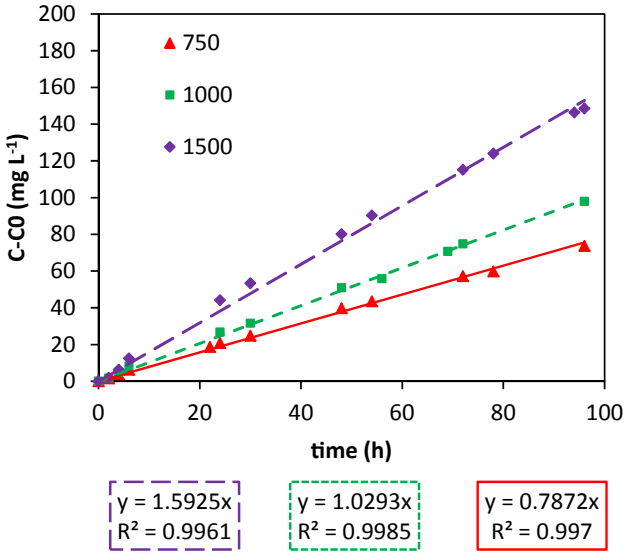

Fig. 5. Chloride evolution profiles for the three influent concentrations.

increasing from 0.8 to 1.6 mg L^{-1} h^{-1} with the tubing influent concentration.

The wide interval of values for the amount retained in the polymer demonstrates the capacity of the polymer of "adapting" to the microbial activity. Higher biological removal rates results in a higher release (i.e. lower retained fraction), while in the presence of lower biodegradation rates the polymer acts as a buffer retaining the absorbed substrate, thus avoiding a deterioration of the effluent characteristics.

No appreciable performance differences are observed for the highest Influent Organic Load (IOL), suggesting that in the first run the bioreactor likely operated at under-loaded conditions, and a progressive improvement of the microbial activity is detected with the IOLs. This is consistent with the SOUR profiles, which show steady state values ranging from 2 to 6 mg O_2 g_{VSS}^{-1} h^{-1} and increasing with the organic load.

In a previous study (Tomei et al., 2016), the proposed C-TPPB was characterized in terms of its mass transfer properties and a mass transfer coefficient $k_O = 2.341 \cdot 10^{-7}$ m s^{-1} was estimated for the same apparatus and operating conditions of the present experimentation. This value has been employed to calculate the predicted mass transfer rates, in the three series of tests of this study. The values are reported in Fig. 6 (dashed lines), and in all cases are higher than the observed biological removal rates, thus confirming that there is no limiting effect due to the mass transfer resistance through the tubing walls relative to biological process. A comparison of mass vs. biological rates is an important aspect in evaluating TPPB and other polymer-based biotreatment processes (Pittman et al., 2015).

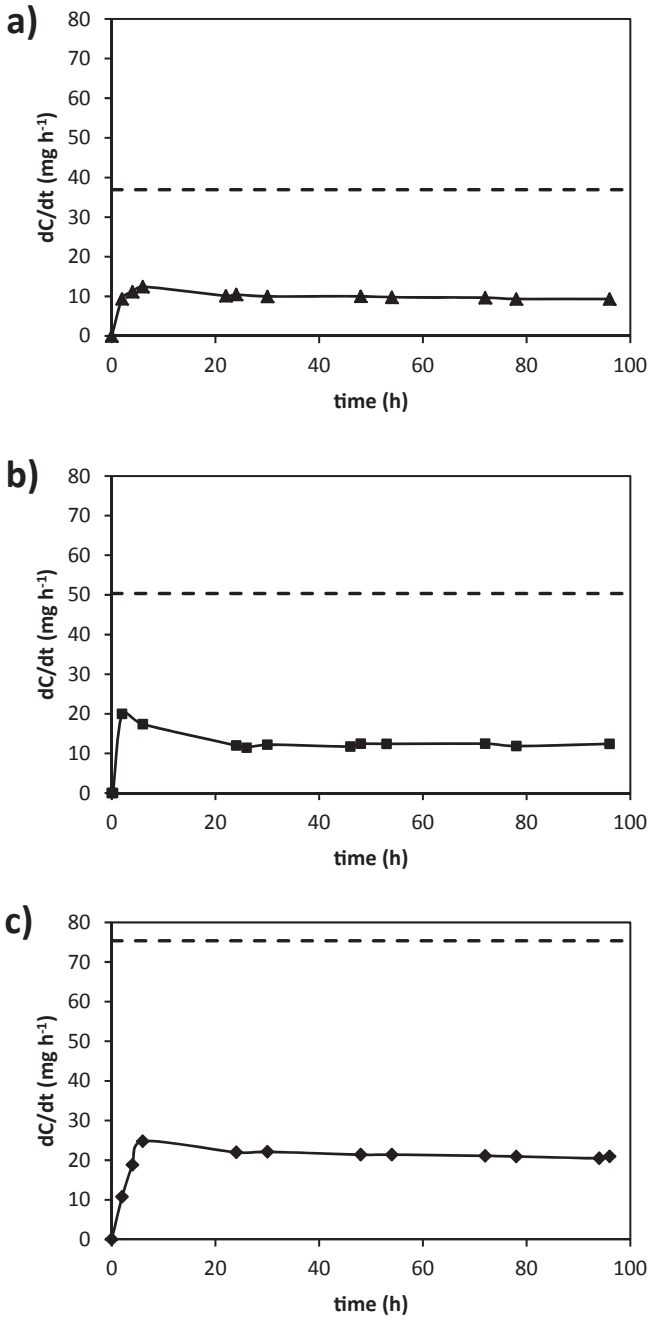

Fig. 6. Evolution of the biological removal rates in Run I (a), Run II (b) and Run III (c). Dashed lines are the predicted mass transfer rates.

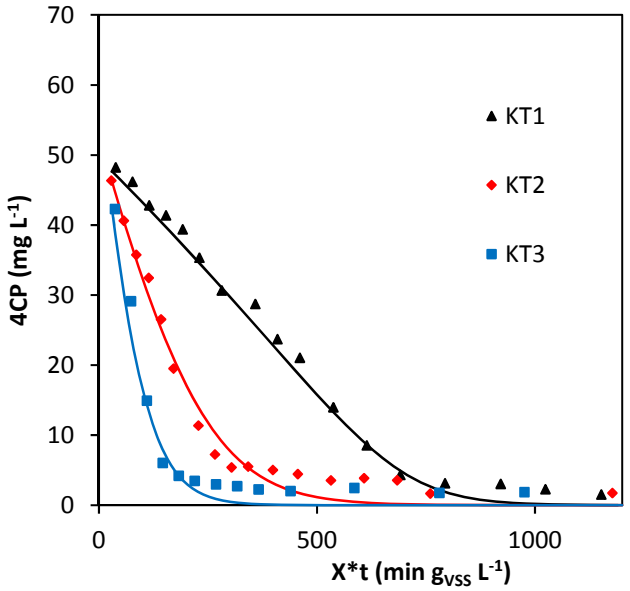

Fig. 7. Experimental (symbols) and calculated (lines) concentration profiles in the kinetic tests for biomass characterization.

equation is modified in the Monod equation generally applied to model non-inhibited kinetics.

Improved performance even if with reduced biomass concentration, and better resistance to self-inhibition demonstrated the beneficial effect of the operation under sub-inhibitory controlled conditions characterizing the C-TPPB. Tomei et al. (2010) observed similar results for a sequencing TPPB applied to removal of 4-nitrophenol.

The biomass characterization has been completed with the evaluation of the stoichiometric yield coefficient Y and the endogenous decay rate b determined from the SOUR profiles. Values of 0.47 ± 0.07 (on COD basis) for Y and 0.028 ± 0.006 d^{-1} for b are obtained, which are in the range of values reported in the specialized literature for the biomass operating in wastewater treatment plants (Sahinkaya and Dilek, 2007; Ezechi et al., 2015; Mosca Angelucci and Tomei, 2015).

4. Conclusions

This study has demonstrated the performance of a continuous two-phase partitioning bioreactor (C-TPPB), operated with a mixed culture for the biological removal of a representative chlorophenol compound, 4CP. Excellent performance was obtained with practically complete removal of 4CP in the tubing under all the investigated IOLs. Mass transfer through the tubing walls did not exert a limiting effect on the biodegradation kinetics. Only a small 4CP amount was retained in the polymer, which allows the system to maintain a buffering effect against increased or transient substrate loadings. Finally, C-TPPB operation mode exerted a positive effect on the biomass adaptation to an inhibitory substrate as demonstrated by the kinetic characterization tests.

Current research involves the testing of the C-TPPB on a model wastewater characterized by the presence of high concentrations of metals, i.e. chromium in leather factory wastewater, along with biodegradable organics.

Table 3
SBR kinetic tests: overview of the operating conditions (X = biomass concentration; C_0 = Influent tubing concentration; IOL = Influent Organic Load) and best fitting parameters obtained from kinetic analysis.

Test	X g_{VSS} L^{-1}	C_0 mg L^{-1}	IOL mg h^{-1}	K_S mg L^{-1}	K_I mg L^{-1}	k mg mg_{VSS}^{-1} d^{-1}	R^2
KT1	2.56	110.78	9.23	11.5	48.7	0.08	0.998
KT2	1.90	103.61	8.63	23.2	10^{21}	0.23	0.989
KT3	1.32	119.01	9.92	18.9	10^{23}	0.59	0.987

3.2. Kinetic characterization of the biomass

One of the claimed advantages of the EMBs is the possibility to enhance the performance of the microbial culture avoiding direct contact of the toxic substrates with the cells, thus maintaining a selection pressure of the target pollutants favoring the adaptation of the microbial culture.

This feature is also expected for the C-TPPB where the biomass is not in contact with the fed wastewater and substrate delivery across the tubing wall is driven by cellular metabolism.

With the aim of verifying this hypothesis, the biomass utilized in the experiments was kinetically characterized by tests performed in the SBR at the end of the acclimatization phase and on the biomass utilized in the C-TPPB tests.

Kinetic tests were conducted in the SBR, at the same influent concentration (nominal value 100 mg L^{-1}), on the microbial cultures just after the acclimatization (KT1), and after the Runs II (KT2) and III (KT3) of the C-TPPB. Fig. 7 shows the experimental and the predicted substrate concentration profiles, while Table 3 gives the operating conditions and the best fitting parameters determined with the Haldane model.

A first qualitative analysis of the concentration profiles shows an increase in the removal rate from KT1 to KT3 with a modification of the shape of the curve, which from the characteristic trend of inhibited kinetics (i.e. the double slope profile) changes to a profile typical of non-inhibited kinetics. This finding is confirmed by the best fitting parameters of the Haldane model: an increase (from 0.08 to 0.6 mg mg_{VSS}^{-1} d^{-1}) of k and a corresponding increase of K_I up to values of the order of 10^{23} are observed. These K_I values correspond to a negligible effect of the inhibition term and the Haldane

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