Chemical Engineering Journal 296 (2016) 428–436

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Xenobiotic removal from wastewater in a two-phase partitioning bioreactor: Process modelling and identification of operational strategies

M. Cristina Annesini [a,*], M. Concetta Tomei [b], Vincenzo Piemonte [c], Andrew J. Daugulis [d]

[a] Department of Chemical Engineering Materials Environment, University of Rome "La Sapienza", Via Eudossiana 18, 00184 Roma, Italy
[b] Water Research Institute, C.N.R., Via Salaria km 29.300, 00015 Monterotondo Stazione, Rome, Italy
[c] Unit of Chemical-physics Fundamentals in Chemical Engineering, Department of Engineering, University Campus Bio-Medico of Roma, Via Álvaro del Portillo 21, 00128 Rome, Italy
[d] Department of Chemical Engineering, Queen's University, Kingston, Ontario K7L3N6, Canada

HIGHLIGHTS

- A dynamic model of a solid–liquid TPPB operated with polymers is proposed.
- The model is applied to the biological removal of xenobiotics from wastewater.
- Sensitivity analysis highlights a critical reaction period determining low/high performance.
- A case study on 4-nitrophenol removal in a TPPB operated with Hytrel is reported.
- The model provides a powerful tool to identify operating strategies.

ARTICLE INFO

Article history:
Received 9 February 2016
Received in revised form 24 March 2016
Accepted 25 March 2016
Available online 29 March 2016

Keywords:
TPPB dynamic modelling
Solid–liquid TPPB
Xenobiotic removal
Sensitivity analysis
Operational strategies

ABSTRACT

This paper proposes a dynamic model simulating the performance of a fed batch system operated as solid–liquid two-phase partitioning bioreactor, with polymer beads as the sequestering phase, applied to the removal of xenobiotic compounds from concentrated aqueous streams, in which substrate inhibition is significant. The model takes into account substrate mass transfer into, and within, the solid particles. Outputs of the models are xenobiotic concentrations in the liquid and solid phases and the concentration profile within the solid polymer beads. Sensitivity analyses have been performed on the influent concentration and on the main operating parameters, which can be modified to control the process performance (i.e. polymer/feed ratio, reaction and loading times). With an inhibitory substrate, the selected duration of the reaction period exhibits a critical value which determines the transition from high to low efficiency of the bioreactor. Application examples are provided for a target compound, 4-nitrophenol, previously investigated in TPPBs with an immiscible organic solvent, while Hytrel 8206 has been considered as the polymer partitioning phase. The proposed model has been shown to be a powerful tool to predict suitable operating conditions for TPPB systems treating inhibitory substrates.

1. Introduction

Two phase partitioning bioreactors (TPPBs) represent a technology platform that has been shown to be effective in overcoming the toxicity associated with the biodegradation of xenobiotic compounds [1–3]. The introduction of a second immiscible phase, into a cell-containing aqueous phase, is intended to generate spontaneous partitioning of the toxic substrate into the sequestering phase based on its high affinity for the target molecule [4–6]. Not only does this spontaneous partitioning reduce the aqueous-phase concentration of the substrate to below cytotoxic levels, but it also results in sequestered substrate that can, when the aqueous phase concentration has been reduced through biological activity, return to the aqueous phase for subsequent degradation. TPPBs therefore operate on the spontaneous processes of thermodynamic equilibrium and cellular metabolism, and thus can operate with minimal external intervention to maintain high biodegradation performance. Depending on the application, an immiscible organic solvent or a solid polymer can be utilised as the partitioning phase: the first approach, due to possible parallel solvent biodegradation caused by biomass acclimatisation, is preferable when the process is undertaken with pure microbial cultures, while the second is particularly suitable

* Corresponding author.
E-mail address: mariacristina.annesini@uniroma1.it (M.C. Annesini).

http://dx.doi.org/10.1016/j.cej.2016.03.123
1385-8947/

List of symbols

C	substrate concentration (mg/L)
C^*	substrate concentration giving the maximum removal rate (parameter in Haldane equation) (mg/L)
C_{in}	inlet substrate concentration (mg/L)
C_p	substrate concentration in the polymer phase (mg/g)
$C_{p,n-1}^{RP}$	substrate concentration in the polymer phase at the end of the $(n-1)$ cycle (mg/L)
C_w	substrate concentration in the aqueous phase (mg/L)
$C_{w,n-1}^{RP}$	substrate concentration in the liquid phase at the end of the $(n-1)$ cycle (mg/L)
C_w^{FP}	substrate concentration in the liquid phase at the end of the loading period (mg/L)
D	substrate diffusivity in the polymer phase (cm^2/s)
F_{in}	inlet flow rate (L/h)
F_{out}	outlet flow rate (L/h)
f	exchange ratio
k_e	endogenous respiration coefficient (1/d)
K_I	inhibition constant in the Haldane equation (mg/L)
k_{max}	maximum removal rate at $C = C^*$ (parameter in Haldane equation) (1/h)
K_S	saturation constant in the Haldane equation (mg/L)
P	partition coefficient (L/g)
r	radial coordinate for the polymer beads (mg/L)
R	polymer bead radius (dm)
r_S	substrate degradation rate (mg/(L h))
t	time
t_D	characteristic diffusion time (h)
t_{LP}	duration of the loading period (h)
t_{RP}	duration of the reaction period (h)
t_{RPC}	critical reaction time (h)
V_p	polymer volume (L)
V_w	volume (L)
V_{max}	reactor volume in the reaction period (L)
V_{w0}	residual volume (L)
X	biomass concentration (mg/L)
X_0	initial value of the biomass concentration (mg/L)
X_{sp}	set point value of the biomass concentration (mg/L)
Y	growth yield coefficient (mg biomass/mg substrate)
α	partition capacity ratio
β	inhibition parameter in Haldane equation
γ	removal capacity ratio ($F_{in}C_{in}/(k_{max}X_{sp})$)
τ_D	characteristic diffusion time (h)
τ_R	characteristic biodegradation time (h)

when mixed culture are employed [7,8]. In the case of xenobiotic biodegradation from wastewater utilising mixed cultures, the solid–liquid TPPB is the preferred configuration. Indeed, large MW polymers have been shown to be completely biocompatible with the biomass, non-biodegradable, and can be easily separated from the microbial culture for reuse. Polymers can be formulated in an almost infinite number of molecular structures (e.g. as homo-and-copolymers) and molecular weights, and are significantly less expensive than organic solvents. Such partition/equilibrium-based operation with polymers is in contrast to the use of adsorptive materials, such as granular activated carbon or ion exchange resins, for the sequestration of target solutes. That is, the mechanism of uptake/release by amorphous polymers is by ***absorption*** (similar to organic acid extraction) and is governed by thermodynamic partition coefficient considerations, as has recently been demonstrated [9], unlike activated carbon uptake which is a physical ***adsorptive*** process governed by adsorption isotherms. Moreover, activated carbon adsorption is often non-selective to many organic molecule species, unlike the use of absorptive polymers, which can be selected or tailored to discriminate between similar or disparate chemical structures [9,10].

TPPBs have been demonstrated effective for the removal of many groups of xenobiotic compounds including volatile organic compounds (VOCs), benzene, toluene, ethylbenzene, and xylenes (BTEX), substituted phenols, polycyclic aromatic hydrocarbons (PAHs) from air, water, soil [1]. They have been extensively investigated at laboratory scale but to move towards full-scale application, operating conditions need to be further scrutinised to ensure robust operation. Models have been proposed for liquid–liquid TPPBs for both continuous-flow [11–13] and fed-batch systems [14–16]. For solid–liquid TPPB systems, Littlejohns et al. [17] proposed a model for the continuous treatment of gaseous waste streams, Choi and Yeom [18] performed a simulation study on a polymer loaded TPPB applied to biobutanol production, and Fakhru'l-Razi et al. [19] modelled a TPPB operated in batch mode applied to crude oil biodegradation. At present, to the best of our knowledge, a complete model of a fed batch solid–liquid TPPB applied to the remediation of liquid streams (i.e. industrial wastewater) is not available. In this case the complexity of modelling the overall system is increased by the significant effect that the mass transfer resistance within the solid phase can exert on the overall process kinetics [14] as also seen in [20].

In a previous study [21] we provided a dynamic model of a single aqueous phase Sequencing Batch Reactor (SBR) whose sensitivity in biodegradation performance showed a steep shift from high to low substrate removal efficiency depending on the feed substrate concentration and the selected SBR exchange ratio. The purpose of this paper is to formulate a dynamic model of a fed batch system operated as solid–liquid TPPB applied to the removal of xenobiotic compounds from concentrated aqueous streams. The model takes into account the substrate mass transfer phenomena into, and within, the solid particles, and was applied to analyse the reactor performance for different sets of operating parameters.

2. Model description

The proposed model describes a sequencing batch TPPB reactor in which a substrate is degraded by aerobic microorganisms. The work cycle in this system includes four periods: feed, reaction, settling, and effluent discharge; if necessary, depending on the influent characteristics, an additional "idle" phase between cycles can be considered. A schematic representation of the fed batch TPPB is reported in Fig. 1.

Specifically, in the feed period, a volume of the solution containing a high xenobiotic substrate concentration is fed to the reactor and mixed with the residual volume of the previous work cycle, that is still present in the reactor and contains biomass, polymer and unconverted substrate. If the duration of this period is not too short, significant biodegradation and sorption of substrate into the polymer beads occurs. In the reaction period, the reactor is no longer fed; in this period, biodegradation proceeds in the aqueous phase and the reduction of the substrate concentration in the aqueous phase drives the substrate desorption from the polymer beads, based on the system maintaining a thermodynamic equilibrium of substrate between the 2 phases. With a suitable duration of the reaction period, substrate removal from the aqueous phase and polymer regeneration is obtained. The operating cycle is completed with a settling period, without aeration and stirring of the reactor, and the discharge of the supernatant from the reactor.

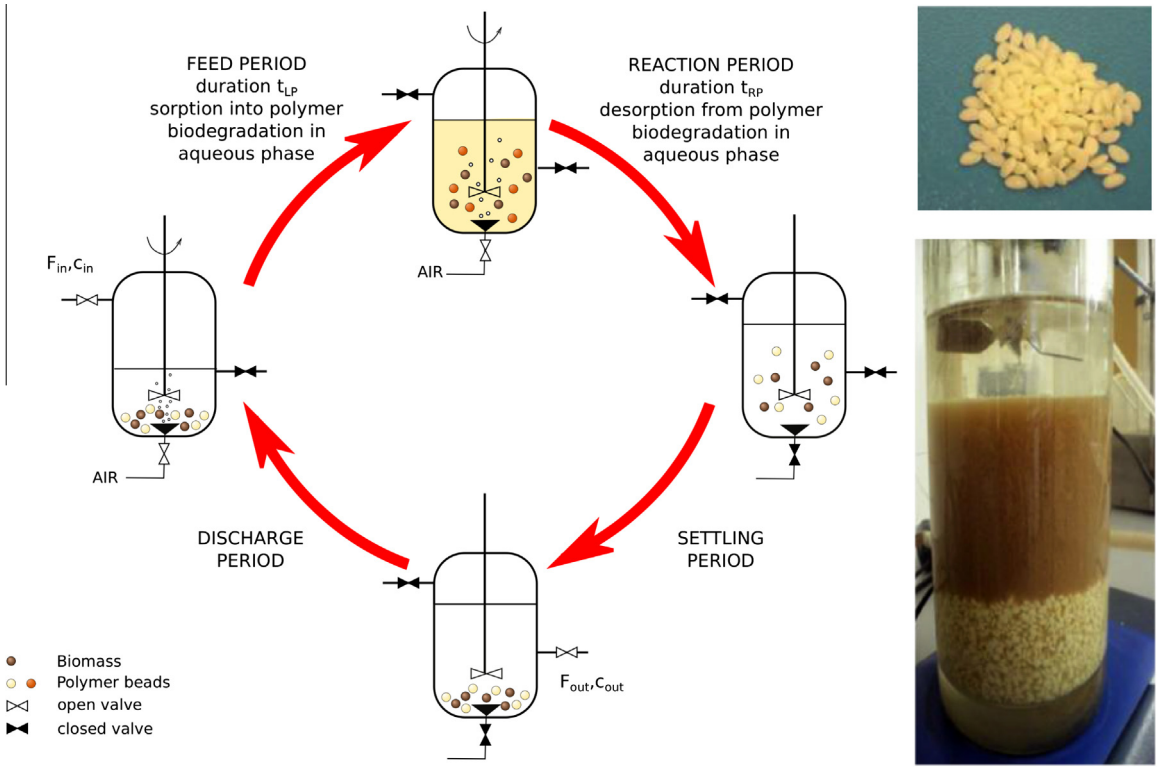

Fig. 1. Schematic representation of a fed batch TPPB. On the right, above, a photo of the polymer before use for 4NP removal and, below, a photo of the reactor during the settling period, with the polymer completely regenerated. The brown material above the regenerated polymer is the biomass. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The model focuses on the feed and reaction periods during which the biodegradation process takes place. Biodegradation and mass transport between polymer beads and liquid phase in the settling and discharge periods are not considered. It is assumed that a perfect separation of polymer beads and biomass can be obtained in the settling period and only a liquid phase is withdrawn during the discharge period. Perfect mixing is assumed in the liquid phase, while a radial substrate distribution is considered within the polymer bead, which is assumed perfectly spherical. Mass transfer resistance is considered to be negligible in the liquid film near the polymer bead surface (as demonstrated in [20]), while Fickian diffusion is considered within the polymer. As for substrate biodegradation and biomass growth rate, a dependence on the substrate concentration is assumed, while oxygen is considered not to be a limiting factor for biomass growth. The mass balance equations are reported in the following for the feed and reaction phases.

Hydraulic mass balance is given by:

$$\frac{dV_w}{dt} = F_{in} \tag{1}$$

where F_{in} is the inlet flow rate, which, in the feed period, is given by the ratio between the exchange volume (fV_{max}) and the loading time ($F_{in} = fV_{max}/t_{LP}$); in all the other periods $F_{in} = 0$.

As for the substrate, the mass balance in the liquid phase is written as:

$$\frac{d(C_w V_w)}{dt} = F_{in}C_{in} - r_s V_w - \frac{3DV_p}{R}\frac{\partial C_p}{\partial r}\bigg|_{r=R} \tag{2}$$

while, in the solid phase, we have

$$\frac{\partial C_p}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial}\left(r^2\frac{\partial C_p}{\partial r}\right) \tag{3}$$

Finally, the biomass mass balance in the liquid phase is given by

$$\frac{d(XV_w)}{dt} = Yr_s V_w - k_e X V_w \tag{4}$$

As previously reported, a substrate profile inside the polymer beads is considered with substrate concentration in the polymer depending on the radial position, r, and the time, t; a time dependent average substrate concentration in the polymer phase is then obtained as:

$$C_p = \frac{1}{R^3}\int_0^R C_p r^2 dr \tag{5}$$

Equations from (1) to (4) can be integrated with the following boundary and initial conditions

$$r = 0 \quad \frac{\partial C_p}{\partial r} = 0 \quad r = R \quad C_p = PC_w$$

$$t = 0 \; V_w = (1-f)V_{max}; \; C_w = C_{w0}; \; C_p = 0; \; X = X_0$$

for the first cycle, while for the following cycles a residual volume is still present in the reactor after the settle and draw phases with the substrate concentration obtained at the end of the previous cycle. Furthermore, a target biomass concentration X_{sp} is defined as a set point value, and, if necessary, biomass withdrawal is considered in order to control the biomass concentration (if $X > X_{sp}$ at the end of a reaction phase, the biomass concentration is reset to X_{sp}, assuming that the excess biomass is discharged). Therefore, for the following cycles the following initial conditions are assumed:

$$t = 0 \; V_w = (1-f)V_{max}; \; C_w = C^{RP}_{w,n-1}; \; C_p = C^{RP}_{p,n-1}$$
$$X = X_{n-1}/f \text{ if } X_{n-1} < X_{sp} \text{ or } X = X_{sp}/f \text{ if } X_{n-1} > X_{sp}$$

where subscript $n-1$ refers to the value at the end of the reaction period (RP) of the previous cycle.

The substrate degradation rate was modelled by the Haldane equation, which is commonly utilised for substrate inhibited

Table 1
Summary of the input data.

Parameter	Definition	Value	Units
Substrate removal and kinetic coefficients			
C^*_w	Concentration value giving the maximum biodegradation rate	34.7	mg4NP/L
k_{max}	Maximum removal rate	0.093	mg4NP/(mgVSS h)
β	Inhibition parameter	0.6	
k_e	Endogenous decay rate	0.08	1/d
Y	Biomass yield coefficient	0.478	
Polymer characteristics			
D	Diffusion coefficient	$6.5{\cdot}10^{-6}$	cm^2/s
P	Partition coefficient	60	–
R	Bead radius	2	mm
Operating conditions			
V_{max}	Influent volume to be treated on daily basis	4	m^3
f	Exchange ratio	0.5	
X_0	Initial biomass concentration	1000	mgVSS/L
X_{sp}	Biomass concentration work value (set point value)	500	mgVSS/L
C_{in}	Influent substrate concentration	250–500[a]	mg/L
V_p/V_{max}	Polymer fraction	0–10	%
t_{LP}	Duration of the loading period	τ_D	h
t_{RP}	Duration of the reaction period	1–3[a]	h
α	PV_p/V_{max}	0–6[a]	

[a] Range of values utilised in the sensitivity analysis.

kinetics. The equation was rearranged in a normalised form as suggested by [22]:

$$r_S = k_{max} \cdot X(2+\beta)\frac{C/C^*}{1+\beta(C/C^*)+(C/C^*)^2} \quad (6)$$

In Eq. (6) $C^* = \sqrt{K_s \cdot K_I}$ is the substrate concentration at which the maximum removal rate occurs, k_{max} is the maximum removal rate observed at $C = C^*$ and $\beta = \sqrt{K_I/K_s}$ is a parameter that accounts for the extent of the inhibitory effect.

Mass balance equations can be rewritten in a dimensionless form assuming:

$$\overline{C_w} = C_w/C^*_w;\ \overline{C}_p = C_p/PC^*_w;\ \overline{V_w} = V_w/V_{max};\ \overline{X} = X/X_{sp}$$

The dimensionless equations are reported in the following again for the feed and reaction periods.

Hydraulic mass balance

$$\frac{d\overline{V}_w}{dt} = \frac{F_{in}}{V_{max}} \quad (7)$$

Substrate in liquid phase

$$\frac{d(\overline{C}_w\overline{V}_w)}{dt} = \frac{F_{in}C_{in}}{k_{max}X_{sp}\tau_R} - \overline{V}_w\frac{\overline{X}}{\tau_R}(2+\beta)\frac{\overline{C}_w}{1+\beta\overline{C}_w+\overline{C}_w^2} - \frac{3\alpha}{\tau_D}\frac{\partial\overline{C}_p}{\partial\overline{r}}|_{\overline{r}=1} \quad (8)$$

Substrate in solid phase

$$\frac{\partial\overline{C}_p}{\partial t} = \frac{1}{\tau_D}\frac{1}{\overline{r}^2}\frac{\partial}{\partial\overline{r}}\left(\overline{r}^2\frac{\partial\overline{C}_p}{\partial\overline{r}}\right) \quad (9)$$

Biomass

$$\frac{d(\overline{X}\overline{V}_w)}{dt} = k_{max}Y\overline{V}_w\overline{X}(2+\beta)\frac{\overline{C}_w}{1+\beta\overline{C}_w+\overline{C}_w^2} - k_e\overline{X}\overline{V}_w \quad (10)$$

Initial and boundary conditions:

$$\overline{r}=0\ \frac{\partial\overline{C}_p}{\partial\overline{r}}=0 \quad \overline{r}=1\ \overline{C}_p=\overline{C}_w$$

$$t=0\ \overline{C}_w=0;\ \overline{C}_p=0;\ \overline{X}=X_0/X_{sp};\ \overline{V}_w=V_{w0}/V_{max} \quad \text{for the first cycle}$$

$$t=0\ \overline{V}_w=V_{w0}/V_{max}\ \overline{C}_w=\overline{C}_{w,n-1};\ \overline{C}_p=\overline{C}_{p,n-1};\ \overline{X}=\overline{X}_{n-1}/f \text{ or } \overline{X}=1/f \quad \text{for the following cycles}$$

In the model equations two characteristic times are introduced, the biodegradation time, $\tau_R = C^*_W/k_{max}X_{sp}$ that depends on the biodegradation kinetics and on the biomass concentration, and the diffusion time within the polymer beads, $\tau_D = R^2/D$, which mainly depends on the polymer properties of bead size (radius) and substrate diffusivity within the polymer bead. Simulation of the process can now be carried out by choosing different operating conditions: in particular different values of the partition capacity ratio, $\alpha = PV_p/V_{max}$, the duration of the loading time period t_{LP}, and of the reaction time t_{RP}.

3. Results and discussion

3.1. Simulation results of the start up and periodic operation

In order to investigate the behaviour of a sequencing TPPB reactor and to identify suitable operating conditions, simulations have been carried out using the values of the model parameters reported in Table 1. The simulated bioreactor is a solid–liquid TPPB operated with Hytrel 8206 (Du Pont, Canada) polymer beads as the partitioning phase. Kinetic and stoichiometric parameters (k_{max}, β, C^*, Y, k_e) have been determined in previous papers [23,24], and refer to the biological removal of 4-nitrophenol in a sequencing batch reactor operated with a mixed culture acclimatised to the compound. Partition and diffusion coefficients of the commercial polymer were assumed from previous studies, as this polymer has been successfully employed in TPPBs as the partitioning phase for the removal of substituted phenols [25,26], and a number of other xenobiotic substrates [3,20,27]. It should be noted however, that a vast array if absorptive polymers, including waste rubber tires [28,29], have been successfully used in solid–liquid TPPB applications [30,31]. In the following, simulations have been carried out choosing to work with a duration of the loading period equal to the diffusion time; in this condition, the loading time is long enough to allow the polymer to sorb a significant fraction of the substrate.

Fig. 2a and b show the results of the simulation for the first two cycles, for $\alpha = 6$, $t_{RP} = 1.52$ h, $t_{LP} = \tau_D = 1.71$ h. The influent concentration is 350 mg/L, and the simulation begins with the assumed initial condition that the reactor is filled with pure water. Concentration profiles in the aqueous phase (continuous line) and mean concentrations in the polymer (dotted line) are reported in Fig. 2a while Fig. 2b shows the radial concentration profiles from the surface (dimensionless radial position 1) towards the centre (dimensionless radial position 0) of the polymer beads at different times during the feed and reaction periods. The substrate concentration in the aqueous and polymer phases (Fig. 2a) shows the typical "sawtooth" trend, with a rising substrate concentration in the feed period, followed by a decrease of the substrate concentration in the reaction period; the labels a–f indicate the different feed and reaction times corresponding to the radial concentration profiles reported in Fig. 2b. Concentration profiles inside the polymer show the gradual increase of the substrate concentration in the polymer beads during the feed period (times *a*, *b*, *c* in the ascending segment), starting from the outer part of the bead; this is due to the increase of the substrate concentration in the liquid phase and to the substrate diffusion inside the particles.

At the end of the feed period, which has a duration equal to the diffusion characteristic time, the polymer is almost saturated with

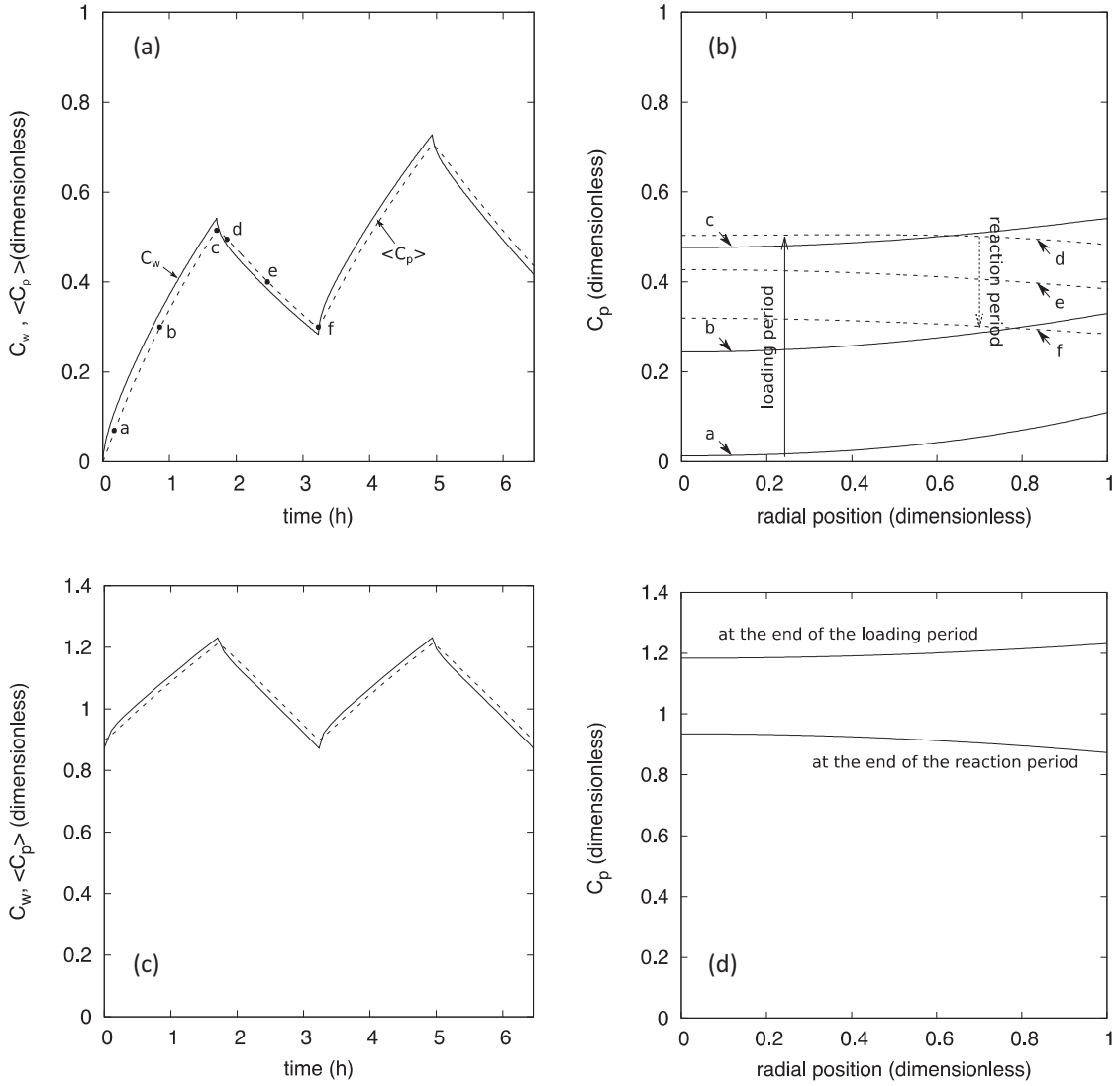

Fig. 2. Concentration profiles in the aqueous phase (continuous line) and mean concentration in the polymer (dotted line) at the start up (a) and during periodic operation (c). Radial concentration profiles in a single polymer bead at different times during the feed and reaction periods at the start up (b) and during periodic operation (d). The labels a–f in figures (a) indicate the different feed and reaction times corresponding to the radial concentration profiles reported in (b). Operating parameters: $\alpha = 6$, $t_{RP} = 1.52$ h, $t_{LP} = \tau_D = 1.71$ h. Influent concentration = 350 mg/L.

the substrate present in the liquid phase. The decreasing radial concentration profiles in the reaction period (*d*, *e*, *f* in the descending segment) highlight the partial polymer regeneration during the reaction phase due to substrate biodegradation in the aqueous phase and the subsequent substrate release from the polymer.

In sequential systems, the initial concentrations in the liquid and in the polymer phases depend on the residual concentrations at the end of the previous cycle and an internal feedback is determined. During the start-up the residual concentrations increases after each cycle until reaching a stable value characteristic of periodic operation. In this condition, the sawtooth concentration trend, both in aqueous and polymer phases, are reported in Fig. 2c, while Fig. 2d shows the concentration profiles inside the polymer beads at the end of the reaction period (or at the beginning of the loading period) and at the end of the loading period.

For the assumed operating conditions, the substrate concentration in the aqueous phase (expressed in dimensionless terms) during periodic operation decreases from 1.23 (corresponding to 42.7 mg/L), at the end of the feed period, to 0.87, at the end of the reaction period. This value corresponds to an effluent concentration of about 30.3 mg/L. Specifically, in the loading period about 37% of the substrate fed to the system is sorbed into the polymer, while about 47% is biodegraded by the biomass. In the reaction period, the substrate previously sorbed into the polymer returns to the aqueous phase where about 44% of the substrate fed to system is biodegraded. The system is operating, in this case, with high removal efficiency.

It is worth noting in Fig. 2a and c that the mean substrate concentration in the polymer beads is always almost equal to the equilibrium concentration with the liquid phase, while in Fig. 2b and d no sharp concentration gradients occur within the polymers. These results clearly indicate that in these conditions there is no significant mass transfer resistance and the process is controlled by the biodegradation kinetics. On the other hand, simultaneous polymer sorption and biodegradation avoid a high increase in substrate concentration in the loading period and the reactor always operates close to the substrate concentration (C^*) at which the maximum removal rate occurs ($\overline{C}_w$ in the range 0.87–1.23) with associated high biodegradation kinetics.

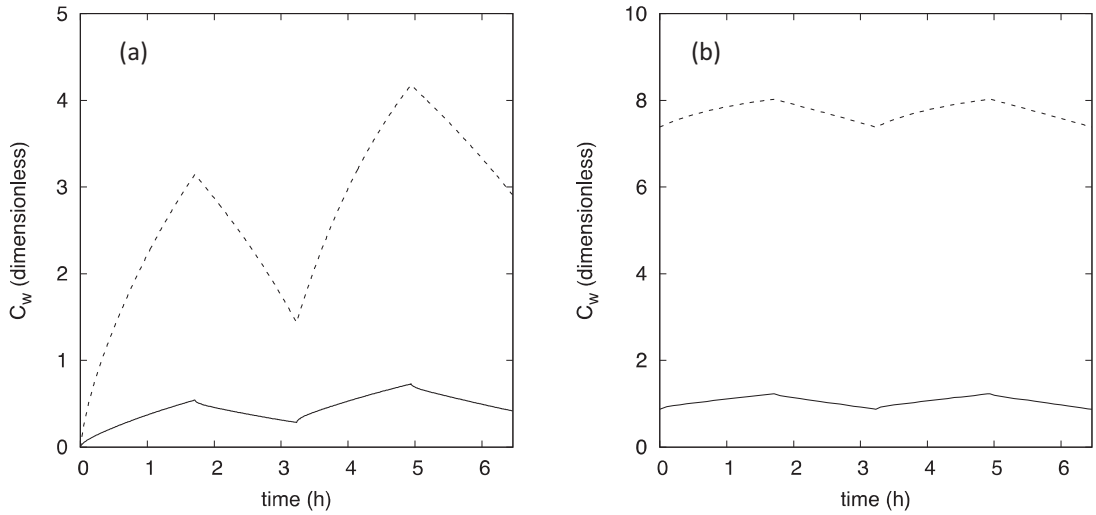

Fig. 3. Concentration profiles in the aqueous phase at the start up (a) and during periodic operation (c) in a TPPR with $\alpha = 6$ (continuous line) and in a single phase reactor (dotted line). Operating parameters: $t_{RP} = 1.52$ h, $t_{LP} = \tau_D = 1.71$ h. Influent concentration = 350 mg/L.

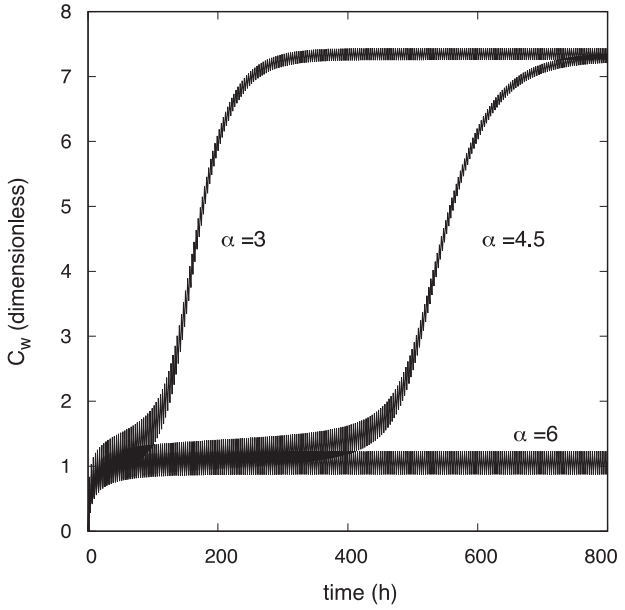

Fig. 4. Concentration profiles vs. time for different capacity ratios. Operating conditions: $t_{RP} = 1.52$ h, $t_{LP} = 1.71$ h. Influent substrate concentration = 350 mg/L.

Finally, it is worth comparing the simulation results obtained in a TPPB with those obtained in a single phase reactor (without polymer) with the same duration of the loading and reaction periods. As reported in Fig. 3a, while in both cases the substrate concentration has a "sawtooth" trend, in the single phase reactor the substrate concentration increase in the loading period is considerably larger, mainly due to the absence of the sorbent polymer; consequently, the higher substrate concentration results in inhibition of the biological kinetics and in a poor substrate removal during the reaction period. Due to this internal feedback, the substrate concentration increases after each cycle, reaching the periodic operating condition reported in Fig. 3b. In this case, the substrate concentration (dimensionless) varies from about 8 (corresponding to about 275 mg/L) to 7.4 (corresponding to an effluent concentration of about 265 mg/L). Ultimately, the removal efficiency is quite low, with only about 25% of the substrate fed to the system being removed by the biomass.

3.2. Sensitivity analyses

The model was employed to undertake a sensitivity analysis on the operating parameters to evaluate their effect on process performance. The first series of simulations was performed by varying the partition capacity ratio α in the range of 3–6. The variation of this parameter is determined by the polymer amount V_P and/or by the partition coefficient P; these depend on the selected amount of polymer employed, and its partition coefficient for the target solute.

As seen in Fig. 4 an increase in α from 3 to 6 (i.e. higher polymer addition or the use of a polymer with a higher partition coefficient) results in a substantial modification of the reactor performance, from a low to a high removal efficiency condition. With $\alpha = 3$ polymer saturation is reached in a very short period of time and the residual substrate concentration (at the end of the reaction period) increases rapidly. Considering that, in this simulation, the initial dimensionless substrate concentration is about 10, it is evident that this operating condition is not of practical interest since the substrate removal efficiency is unacceptably low, with an effluent concentration of about 250 mg/L. On the other hand, $\alpha = 6$ corresponds to an operating condition with low residual substrate concentration and high substrate removal efficiency, with an effluent concentration of about 30 mg/L; actually in this condition, the polymer is also "bioregenerated" by the biomass during the reaction period and substrate accumulation in the polymer is avoided. Intermediate conditions (e.g. $\alpha = 4.5$) can be used for several working cycles, but it is necessary to provide periodic polymer substitutions or regenerations to guarantee adequate substrate removal efficiency.

The duration of the reaction period also strongly affects the process performance: obviously, a higher duration of the reaction period results in a lower substrate concentration in the liquid phase and more polymer regeneration, therefore higher process efficiency is obtained. Results of the sensitivity analysis with respect to the reaction time are reported in Fig. 5; Fig. 5a shows the substrate concentration in the liquid phase vs. time for different reaction times in the range of 1–2 h, while Fig. 5b shows the concentration of the effluent (i.e. at the end of the reaction period) vs. the reaction time. The low removal observed for $t_{RP} = 0$ is explained by the fact that removal is occurring during the feed period, which in this case has a duration comparable to the reaction period. The effluent concentration (for fixed t_{LP}) is dependent on the reaction time and decreases as t_{RP} increases.

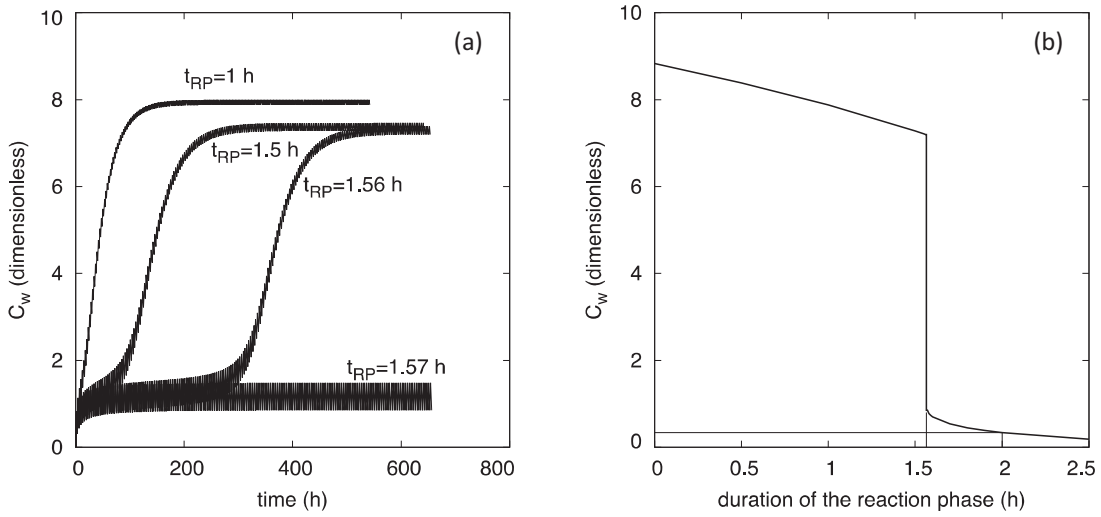

Fig. 5. Concentration profiles vs. time for the liquid phase (a) and effluent concentration vs. t_{RP}. (b) Operating conditions: $\alpha = 3$, $t_{LP} = 1.71$ h. Influent substrate concentration = 350 mg/L.

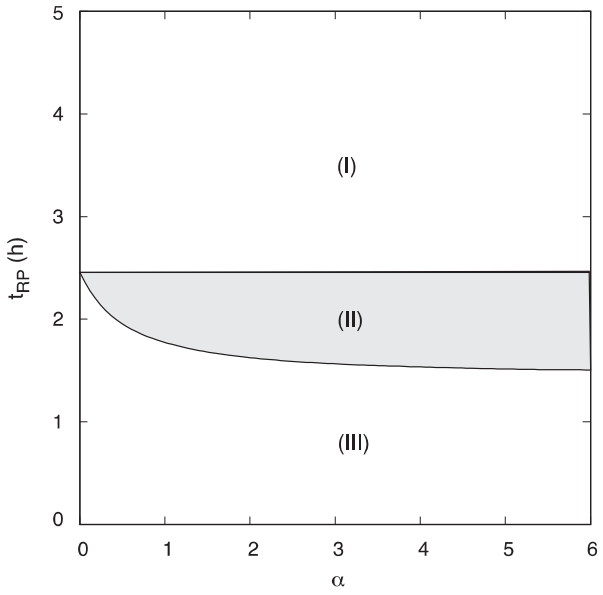

Fig. 6. Critical reaction time vs. partition capacity ratio. (I): high removal efficiency operation can be obtained also with a single-phase system, (II): high removal efficiency operation is feasible only with appropriate polymer addition, and (III): only low removal efficiency operation can be achieved.

It is worth noting that the decrease is not gradual, and that there is a critical value of the reaction time t_{RPC} resulting in an abrupt change of the bioreactor performance, and in a subsequent variation of the effluent substrate concentration. In our specific case study, the dimensionless liquid concentration decreases from 7.2 to 0.75 (corresponding to 250 and 26 mg/L, respectively) at $t_{RP} = 1.565$ h. The critical value t_{RPC} is the operating parameter determining the transition from high to low efficiency of the bioreactor, but, for more stringent limit values of the effluent concentration, higher reaction times have to be applied.

The presence of a critical reaction time value, was also seen in a single phase SBR and discussed in a previous study [21] and it is determined by the internal feedback of residual substrate between subsequent cycles, which is a characteristic of the sequential operation mode, and by the substrate inhibition effect on the biodegradation kinetics.

The critical reaction time is an operating parameter strongly affecting the operation of the bioreactor, thus it is important to evaluate its correlation with other operating parameters in order to determine reactor performance. A sensitivity analysis to evaluate the dependence of t_{RPC} on α was performed with the data reported in Fig. 6. The curve shows the values of $t_{RPC,}$ i.e. required to achieve high removal efficiencies, vs. α. For $\alpha = 0$ we have a single phase reactors and substrate is removed only due to the biodegradation reaction that occurs in the loading and reaction period; in this case, the critical value of the duration of the reaction period is ~2.5 h. On the other hand, for increasing α values (i.e. TPPBs operated with increased polymer fractions) a progressively reduced t_{RP} is sufficient to achieve high removal efficiency. Consequently, for $t_{RP} > 2.5$ (i.e. zone I) the system is always able to achieve a high removal efficiency even if operated without polymer. The opposite behaviour is observed in zone III (i.e. with t_{RP} values lower than the limit values); in this case, even the TPPB system is not able to reach high removal efficiencies. Finally, zone

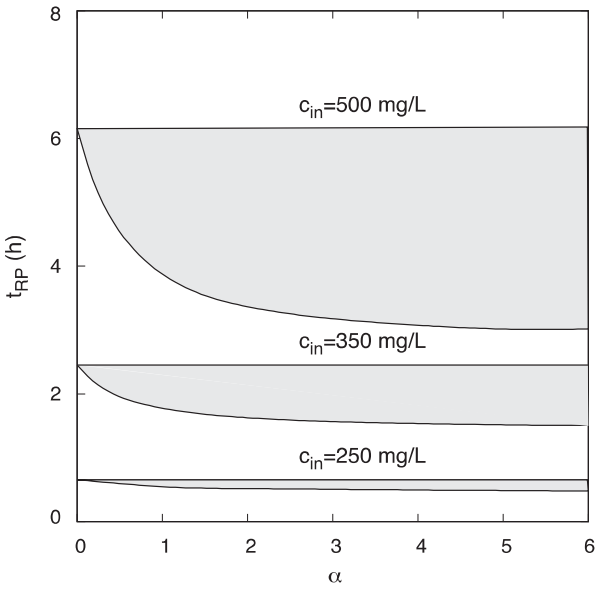

Fig. 7. Critical reaction time vs. partition capacity ratio for three different substrate feed concentrations.

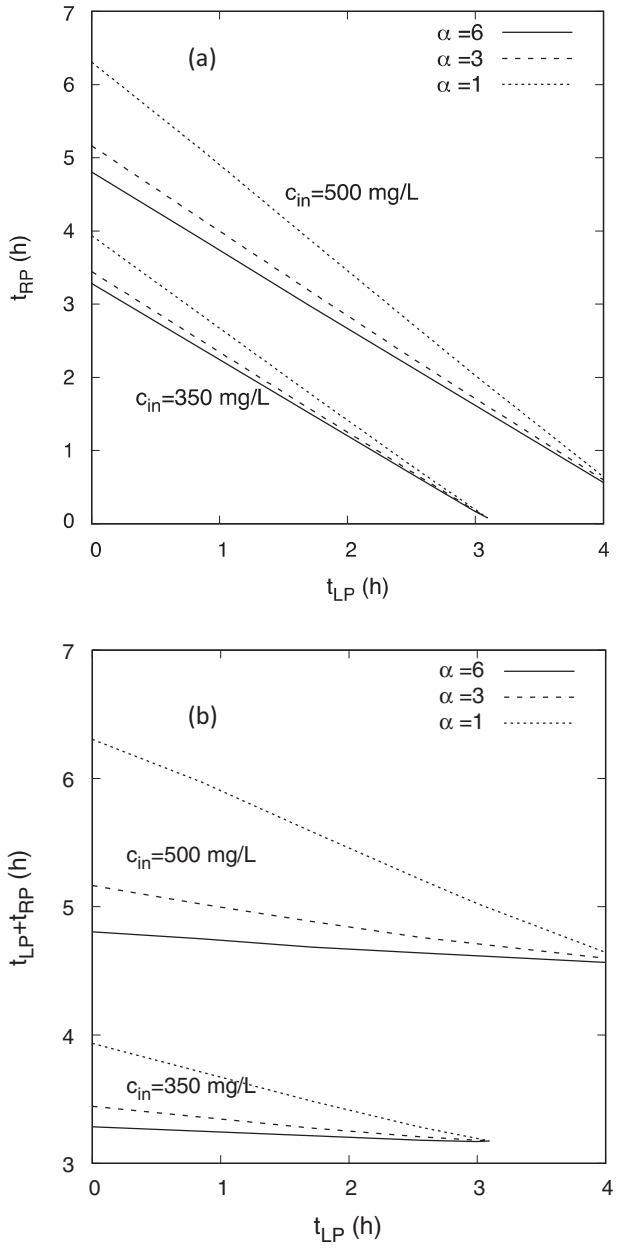

Fig. 8. Minimum duration of reaction period (a) and of the whole work cycle (b) vs. loading time.

II identifies a range of t_{RP} values (for each α), where it is possible to have high removal efficiencies only by operating with a TPPB bioreactor. In other words the crosshatch area represents the "gain" in terms of the duration required for the reaction period, which we can obtain with a two-phase system.

It can also be observed that this "gain" increases with increasing α; nevertheless, after a certain α value (in this example $\alpha = 3$) the reduction of the t_{RPC} is no longer significant. This behaviour has also been found in experimental tests carried out with different polymer amounts and could be explained by considering that the higher polymer amounts give a concomitant reduction of the solid–liquid concentration gradient and therefore of the mass transfer rate between the two phases which become the controlling phenomenon on the overall process rate.

In Fig. 7, the same operation diagram is shown for three different feed concentrations of 250, 350 and 500 mg/L. With increasing feed concentration the advantage of operating as a TPPB with respect to a single-phase reactor becomes more evident: for example in the TPPB case for the highest concentration, it is possible to operate with half of the time required in the conventional system for $\alpha \geqslant 3$.

In the following Fig. 8a and b the sensitivity analysis was performed with respect to the t_{LP} as a key operating parameter in sequential bioreactors to deal with influent substrate toxicity. The minimum duration of the reaction period (Fig. 8a) and of the whole work cycle (Fig. 8b) required to achieve high removal efficiency are reported vs. t_{LP} for the two influent concentrations of 350 and 500 mg/L and α varying in the range of 1–6. These findings are in agreement with the results reported in [25] relating the effects of substrate feed concentrations and polymer amounts. The advantage of polymer addition is more evident for short feed times when the biomass activity is strongly affected by the substrate concentration peaks, while for longer feed times the gradual influent addition mitigates the toxicity effect. The feed time necessary to have effective performance increases with the influent concentration, and the beneficial effect of polymer addition is more evident for higher influent concentrations. It is also important to note (Fig. 7b) that higher polymer amounts (i.e. $\alpha = 6$) allow operation in precautionary conditions even at low t_{LP}, because the polymer acts to effectively reduce the substrate toxicity. For lower polymer amounts (i.e. $\alpha = 1$) the toxicity reduction exerted by the polymer is not enough and the additional effect of gradual feed is beneficial.

4. Conclusions

The proposed model is an effective tool for predicting the behaviour of a solid liquid TPBB operated in sequencing batch mode. The model can aid operators in defining appropriate operating parameters for an influent of defined characteristics and/or facing the presence of periodic substrate surges. The main parameter influencing process performance is the duration of the reaction period, which, for inhibitory compounds, exhibits a critical value determining the transition from high to low efficiency of the bioreactor. In TPPB systems, the value of this critical time also depends on the polymer fraction and polymer partition coefficient, thus providing an additional degree of freedom in comparison to conventional single-phase systems.

As already demonstrated, the polymer can consistently reduce the substrate toxicity effect on biomass activity, and for sequential bioreactors, a synergic effect can be exerted by the loading time. Higher loading times as well as higher polymer/water ratios can reduce the inhibitory toxic effect and their best combination can be evaluated with the proposed model.

References

[1] A.J. Daugulis, Two-phase portioning bioreactors: a new technology platform for destroying xenobiotics, TRENDS Biotechnol. 19 (2001) 457–462.
[2] T.A. Hameda, E. Bayraktar, U. Mehmetoglu, T. Mehmetoglu, The biodegradation of benzene, toluene and phenol in a two-phase system, Biochem. Eng. J. 19 (2004) 137–146.
[3] G.P. Prpich, A.J. Daugulis, Biodegradation of a phenolic mixture in a solid-liquid two phase partitioning bioreactor, Appl. Microbiol. Biotechnol. 72 (2006) 607–615.
[4] C.T. MacLeod, A.J. Daugulis, Biodegradation of polycyclic aromatic hydrocarbons in a two-phase partitioning bioreactor in the presence of a bioavailable solvent, Appl. Microbiol. Biotechnol. 62 (2003) 291–296.
[5] B. Mahanty, K. Pakshirajan, V. Venkata, Biodegradation of pyrene by *Mycobacterium frederiksbergense* in a two-phase partitioning bioreactor system, Bioresour. Technol. 99 (2008) 2694–2698.
[6] J. Marcoux, E. Deziel, R. Villemur, F. Lepine, J.G. Bisaillon, R. Beaudet, Optimization of high-molecular-weight polycyclic aromatic hydrocarbons' degradation in a two-liquid-phase bioreactor, J. Appl. Microbiol. 88 (2000) 655–662.

[7] R. Muñoz, M. Chambaud, S. Bordel, S. Villaverde, A systematic selection of the non-aqueous phase in a bacterial two liquid phase bioreactor treating pinene, Appl. Microbiol. Biotechnol. 79 (2008) 33–41.
[8] G.P. Prpich, A.J. Daugulis, Enhanced biodegradation of phenol by a microbial consortium in a solid-liquid two phase partitioning bioreactor, Biodegradation 16 (2005) 329–339.
[9] T. Craig, A.J. Daugulis, Polymer characterization and optimization of conditions for the enhanced bioproduction of benzaldehyde by Pichia pastoris in a two-phase partitioning bioreactor, Biotechnol. Bioeng. 110 (2013) 1098–1105.
[10] J.T. Dafoe, J.T. Parent, A.J. Daugulis, Block copolymers as sequestering phases in two-phase biotransformations: effect of constituent homopolymer properties on solute affinity, J. Chem. Technol. Biotechnol. 89 (2014) 1304–1310.
[11] S.M. Cruickshank, A.J. Daugulis, P.J. McLellan, Modelling of a continuous two-phase partitioning bioreactor for the degradation of xenobiotics, Process Biochem. 35 (2000) 1027–1035.
[12] M. Hernández, G. Quijano, R. Muñoz, S. Bordel, Modeling of VOC mass transfer in two-liquid phase stirred tank, bio-trickling filter and airlift reactors, Chem. Eng. J. 172 (2011) 961–969.
[13] R. Muñoz, A.J. Daugulis, M. Hernández, G. Quijano, Recent advances in two-phase partitioning bioreactors for the treatment of volatile organic compounds, Biotechnol. Adv. 30 (2012) 1707–1720.
[14] M.C. Tomei, M.C. Annesini, V. Piemonte, G.P. Prpich, A.J. Daugulis, Two phase reactors applied to the removal of substituted phenols: comparison between liquid-liquid and liquid-solid systems, Water Sci. Technol. 62 (2010) 776–782.
[15] M.C. Tomei, M.C. Annesini, S. Rita, A.J. Daugulis, Biodegradation of 4-nitrophenol in a two-phase sequencing batch reactor: concept demonstration, kinetics and modelling, Appl. Microbiol. Biotech. 80 (2008) 1105–1112.
[16] M.C. Tomei, M.C. Annesini, Removal of xenobiotics in a two phase sequencing batch reactor: kinetics and modelling, Water Sci. Technol. 58 (2008) 385–390.
[17] J.V. Littlejohns, K.B. McAuley, A.J. Daugulis, Model for a solid-liquid stirred tank two-phase partitioning bioscrubber for the treatment of BTEX, J. Hazard. Mater. 175 (2010) 872–882.
[18] J.M. Choi, S.H. Yeom, Simulation study of biobutanol production in a polymer-loaded two-phase partitioning bioreactor (PL-TPPB): model development, Korean J. Chem. Eng. 28 (2011) 2170–2177.
[19] A. Fakhru'l-Razi, M. Peyda, W.A.K.G. Wan Azlina, Z.Z. Abidin, M.P. Zakaria, H. Moeini, Modeling of crude oil biodegradation using two phase partitioning bioreactor, Biotechnol. Prog. 30 (2014) 797–805.
[20] H. Fam, A.J. Daugulis, Substrate mass transport in two-phase partitioning bioreactors employing liquid and solid non-aqueous phases, Bioprocess Biosyst. Eng. 35 (2012) 1367–1374.
[21] M.C. Annesini, V. Piemonte, M.C. Tomei, A.J. Daugulis, Stability and operability regions for sequencing batch reactors treating xenobiotic substrates, Chem. Eng. J. 235 (2014) 167–175.
[22] M.C. Tomei, M.C. Annesini, Biodegradation of phenolic mixtures in a sequencing batch reactor a kinetic study, Environ. Sci. Pollut. Res. Int. 15 (2008) 188–195.
[23] M.C. Tomei, M.C. Annesini, S. Bussoletti, 4-Nitrophenol biodegradation in a sequencing batch reactor: kinetic study and effect of filling time, Water Res. 38 (2004) 375–384.
[24] M.C. Tomei, M.C. Annesini, 4-Nitrophenol biodegradation in a sequencing batch reactor operating with aerobic-anoxic cycles, Environ. Sci. Technol. 39 (2005) 5059–5065.
[25] M.C. Tomei, M.C. Annesini, G.P. Prpich, A.J. Daugulis, Biodegradation of 4-nitrophenol in a two phase system operating with polymers as the partitioning phase, Environ. Sci. Technol. 43 (2009) 7105–7110.
[26] M.C. Tomei, S. Rita, D. Mosca Angelucci, M.C. Annesini, A.J. Daugulis, Treatment of substituted phenol mixtures in single phase and two-phase solid-liquid partitioning bioreactors, J. Hazard. Mater. 191 (2011) 190–195.
[27] K.F.L. Hagesteijn, A.J. Daugulis, Passive/aggressive detoxification of continuous flow biotreatment systems using absorptive polymers: partitioning bioreactors treating transient phenol loadings, Biotechnol. Lett. 34 (2012) 1817–1824.
[28] M.C. Tomei, M.C. Annesini, A.J. Daugulis, Solid-liquid two-phase partitioning bioreactors (TPPBs) operated with waste polymers. Case study: 2,4-dichlorophenol biodegradation with used automobile tires as the partitioning phase, Biotechnol. Lett. 34 (2012) 2037–2042.
[29] M.C. Tomei, A.J. Daugulis, Feasibility of operating a solid-liquid bioreactor with used automobile tires as the sequestering phase for the biodegradation of inhibitory compounds, J. Environ. Manage. 125 (2013) 7–11.
[30] E.E. Poleo, A.J. Daugulis, A comparison of three first principles' methods for predicting solute-polymer affinity, and the simultaneous biodegradation of phenol and butyl acetate in a two-phase partitioning bioreactor, J. Chem. Technol. Biotechnol. 89 (2014) 88–96.
[31] E.E. Poleo, A.J. Daugulis, Simultaneous biodegradation of volatile and toxic contaminant mixtures by solid-liquid two-phase partitioning bioreactors, J. Hazard. Mater. 254–255 (2013) 206–213.