Analysis of the performance and criteria for rational design of a sequencing batch reactor for xenobiotic removal

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HIGHLIGHTS

• The influence of substrate inhibition on biodegradation performance of SBRs has been analysed.
• Two original cases studies of "real" xenobiotic substrate degradation have been reported.
• Substrate removal efficiency can be either very high or very low, depending on the chosen operating conditions.

ABSTRACT

Substrate toxicity can impose operability challenges in the biological treatment of xenobiotic compounds. These can arise from transients in the feed to conventional continuous processes, as well as in more challenging systems, sequencing batch reactors (SBRs), whose operation is always inherently dynamic. Via the use of the classic Haldane model for microbial toxicity, and unsteady-state material balance equations for SBR operation, we have analysed the behaviour of an SBR reactor operating over multiple cycles and have shown that both high performance and low performance can be obtained depending on the feed substrate concentration and the selected SBR exchange ratio. That is, both the intrinsic microbial kinetics as well as the selection of process operating conditions can lead either to high performance (high removal efficiency) or low performance (low removal efficiency) operation. Using this approach, we have also discussed the performance for the SBR treatment of 2 "real" substrates possessing widely different kinetic parameters, showing the impact of these parameters, as well as process operating conditions, on the operability of SBR biotreatment systems handling xenobiotic compounds. This could be of significant value to practitioners wishing to select high performance operating regimes for the treatment of a specific xenobiotic compound. To our knowledge, this is the first systematic study of the impact of substrate toxicity on SBR operability, and is also a first step in modeling the impact of substrate detoxification, via the use of discontinuous Two-Phase Partitioning Bioreactors, on the dynamic performance of xenobiotic biotreatment processes.

1. Introduction

Steady state operation of well-mixed bioreactors (CSTRs) with Monod kinetics is characterized by consistent and predictable operation at all dilution rates less than the washout dilution rate. Such systems also exhibit operational stability, reflected in the term "chemostat"; this term arises from the fact that the effluent substrate concentration is independent of feed concentration and, when experiencing perturbations in feed concentration, the cell population responds by increasing/decreasing its size to return the system to the original steady state (static) substrate value. Undesirable operation of continuous bioreactors in the form of washout, multiple steady states oscillations, limit cycles, etc. arise when microbial kinetics are modified to accommodate substrate and/or product inhibition [1–3], or through uncommon control strategies [4–6]. In bioremediation processes, substrate inhibition is a common feature, and in such cases the dynamic behaviour of CSTRs has been analyzed via dynamic simulations [7], via bifurcation analysis [8], and via analysis of forced waveform feeding [9]. The impact of substrate inhibition on some conventional wastewater treatment processes such as organic substrate removal [10] and nitrification processes [11] has also been explored. In some cases...
“operability”, which refers to the identification of regions providing stable CSTR operation, have also been documented, which provides practitioners with valuable guidance on operating conditions that result in stable process performance.

In contrast to CSTRs, Sequencing Batch Reactors (SBRs) are characterized by discontinuous, dynamic operation, involving periods of Fill, React, Waste, Settle, and Draw. Such systems have the advantage of possessing a large range of operating conditions (easily obtainable by varying the times of the elements comprising the operating cycle) and high operational flexibility. They have not, however, been examined to this point in terms of the impact of substrate inhibition on process performance. For these bioreactors operating under dynamic conditions the term “steady state” may not be entirely appropriate, even if it is widely utilized in the literature. Multiple steady state conditions (intended to refer to stable operation conditions in terms of bioreactor performance) can occur in such systems, and are strongly dependent on the operating conditions as will be clearly evidenced in this study. A previous report [12] provided a preliminary description of the behaviour of an SBR treating xenobioc substrates, and identified possible design criteria. The present work represents an in-depth and systematic evaluation of the influence of substrate inhibition on biodegradation performance in SBRs, resulting in a powerful guide for identifying SBR process operability and stability aimed at obtaining high reactor performance. Additionally, the work also examined two cases studies of “real” xenobioc substrate degradation, which were used to illustrate the impact of degradation kinetic parameters on SBR process operation.

2. Xenobioc removal in batch reactors

2.1. Kinetics of xenobioc removal

The kinetics for the biological removal of xenobioc compounds usually demonstrate a substrate inhibition effect that can be due to multiple biochemical mechanisms. From a macroscopic point of view, this behaviour is commonly described as suggested by Andrews [13], with the kinetic equation known as the Haldane equation or Andrews equation. In dimensionless form [14,15] this equation is written as:

\[
\frac{r}{k'X} = \frac{S}{1 + S + \gamma S^2} \tag{1}
\]

where \(r\) is the substrate consumption rate, \(X\) is the biomass concentration, \(k'\) is a kinetic parameter related to the maximal removal rate, \(S\) is the dimensionless substrate concentration \(S = [S]/K_s\) with \(K_s\) the saturation constant and \(\gamma\) is an inhibition parameter \(\gamma = K_i/K_s\) with \(K_i\) the inhibition constant. A maximum reaction rate \(r_{\text{max}} = k'X/(2 + \gamma)\) occurs at \(S = 1/\sqrt{\gamma}\) (or \(S = \sqrt{K_s/K_i}\)). The higher the \(\gamma\) value, the higher the inhibition effect, and both \(S_{\text{max}}\) and \(r_{\text{max}}\) decrease. The kinetics reduce to Monod kinetics if \(\gamma = 0\) and to first order kinetics if \(S \ll 1\).

Given the importance of the above kinetic parameters to biodegradation performance, Table 1 displays values of characteristic parameters for two important groups of xenobioc, BTEX compounds (benzene, toluene, ethylbenzene and xylene) and substituted phenolics, and it can be seen that the range of values is strongly dependent on the microbial culture utilized, and on the operating conditions considered. This makes it difficult to extrapolate such values to other situations, but in industrial wastewater treatment the data in Table 1 for mixed cultures may be considered late such values to other situations, but in industrial wastewater treatment plants dealing with xenobioc compounds, the influent substrate concentrations are generally one order magnitude higher than \(S_{\text{max}}\), and therefore the removal rate can be very low due to the strong inhibitory effect of the xenobioc substrate. For example, phenol concentrations in chemical industry wastewater are reported to vary from 12 to 400 mg/L [17]; typical concentrations of phenolic compounds

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td><strong>Panel A</strong></td>
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<tr>
<td><strong>Compounds</strong></td>
</tr>
<tr>
<td>Benzene</td>
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<tr>
<td>m-Xylene</td>
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<td>p-Xylene</td>
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| **Panel B** |
| **Compounds** | **Biomass** | \(K_s\) (mg/L) | \(K_i\) (mg/L) | \(\gamma\) | **Reference** |
| Phenol | *Candida tropicalis* | 7.1 | 185.0 | 0.04 | 36 | [26] |
| | *P. putida* | 2.5–7.1 | 172.0–221.0 | 0.02–0.03 | 21–40 | [27] |
| | Activated sludge | 29.5 | 72.4 | 0.41 | 46 | [28] |
| | *Alcaligen* | 10 | 152.0–550.0 | 0.07–0.02 | 39–74 | [29] |
| 4-Nitrophenol | Mixed culture | 55.0 | 15.0 | 3.67 | 29 | [19] |
| 3,4 Di-methyphenol | Mixed culture | 427.59 | 549.8 | 0.77 | 485 | [30] |
| 2-Chlorophenol | Mixed culture | 12.1–26.6 | 11.1–1.7 | 11.00–15.65 | 4–7 | [31] |
| 4-Chlorophenol | Mixed culture | 35 | 79.7 | 0.43 | 53 | [32] |
| *Candida tropicalis* | 1113 | 4.3 | 258.84 | 69 | [33] |
| o-Cresol | Mixed culture | 13.8 | 44.5 | 0.31 | 25 | [34] |
| | Mixed culture-aerobic granules | 46.2 | 824.0 | 0.06 | 195 | [35] |
| | Arthrobacter | 48 | 800.0 | 0.06 | 196 | [35] |
| m-Cresol | Mixed culture-aerobic granules | 34.3 | 952.0 | 0.04 | 181 | [34] |
| | Mixed culture-aerobic granules | 29.1 | 617.0 | 0.05 | 134 | [34] |
| p-Cresol | Arthrobacter | 84 | 1050.0 | 0.08 | 297 | [35] |
reported in the literature for refinery effluents vary from 50 mg/l for distillation units to values greater than >500 mg/l in the case of spent caustic solutions [18].

Furthermore, when the biodegradation is carried out in batch mode, the biomass concentration in the reactor is of the order of 1000–3000 mgVSS/L (equivalent about 1500–4500 mg COD/L) and the feed substrate concentration is one order of magnitude lower; the small amount of biomass growth, with respect to substrate consumption, is at least partially balanced by the endogenous phenomena. It has been experimentally verified [14,19] that working at biomass concentrations of 2–3 g VSS/L, the biomass increase is not appreciable with respect to the amount of the biomass present in the system (in other words the increased amount is of the same order as the experimental VSS measurement error (10%)). Therefore a constant biomass concentration can be assumed in a batch reaction.

2.2. Performance of batch reactor

In this case, the substrate concentration as a function of the reaction time is easily obtained as:

$$\frac{dS}{dt} = -\frac{S}{1 + S + \gamma S^2} \quad \theta = t/t_c; \quad t_c = \frac{kS}{k'X_0}$$

(2)

with the initial condition $\theta = 0 = S_0$

In Eq. (2) the dimensionless time is defined as $t/t_c$ with $t_c$ being the characteristic time evaluated for first order (with respect to the substrate) kinetics.

The effluent substrate concentration as a function of the initial substrate concentration and the reaction time can then be obtained directly from the integration of Eq. (2):

$$\theta = \ln \frac{S_0}{S} + (S_0 - S) + \frac{\gamma}{2} (S_0^2 - S^2)$$

(3)

Eq. (3) shows that the time required to remove the xenobiotic substrate from its initial concentration $S_0$ to a fixed final value $S$ is the sum of three terms ($\theta = \theta_1 + \theta_2 + \theta_3$) corresponding to the times required if:

1. the substrate is removed according to first order kinetics $k'X_0S$; in this case $\theta_1 = \ln(S_0/S)$;
2. the substrate is removed with the maximal rate $k'X_0$; in this case $\theta_2 = S_0 - S$;
3. the substrate is removed with a reaction rate $k'X_0 K_I/S$ as for $S \gg S_{max}$; in this case $\theta_3 = \frac{(S_0^2 - S^2)^{2/3}}{S}$.

![Fig. 1](image1.png)

Fig. 1. Final substrate concentration as a function of the initial substrate concentration in a batch process with $\theta = 5$. Different curves refer to different $\gamma$ values: the curve for $\gamma = 0$ corresponds to Monod kinetics. For $\gamma = 3$ the limiting substrate concentration $S_0$ is reported.

Obviously, ($\theta_2 = 0$) for Monod kinetics and $\theta = \theta_1$ for very low $S_0$ values (first order kinetics). In many cases, in the treatment of xenobiotic compounds with inhibition kinetics, the initial substrate concentration is high enough that $\theta \approx \theta_2 + \theta_1$ and the time scale (characteristic time $t_c$) for substrate removal is $(\theta_2 + \theta_1) \cdot t_c$.

Alternatively, with a fixed $\theta$ value (i.e. for a fixed reaction time), the final substrate concentration, $S$, can be obtained as a function of the initial substrate concentration $S_0$. As shown in Fig. 1, while for Monod kinetics ($\gamma = 0$), the curve $S = f(S_0)$ is always concave upward, in the presence of an inhibition kinetics ($\gamma \neq 0$), the curve has an S-shape, with very low outlet substrate concentration for low $S_0$ values, but with a sharp increase in the final substrate concentration as $S_0$ exceeds a critical value depending on $\gamma$. From a mathematical point of view, the $S$ vs $S_0$ curve shows an inflection point corresponding to the maximum value of $dS/dS_0$ (i.e. corresponding to $d^2S/dS_0^2 = 0$). The tangent line to the $S$ vs $S_0$ curve in the inflection point defines a characteristic value of the initial
substrate concentration, as described in Fig. 1 for $\gamma = 5$ and $\varphi = 5$. With fixed reaction time $\varphi$, if the inlet substrate concentration is lower than $S_0$, the biodegradation process is very efficient and a very low final substrate concentration is obtained; on the other hand, if the initial substrate concentration exceeds $S_0$, the effectiveness of the biodegradation process drops rapidly and the final substrate concentration becomes slightly lower than the inlet one.

3. Xenobiotic removal in sequencing batch reactors

In a sequencing batch reactor, a volume $V_F$ of the solution containing the xenobiotic at a concentration $S_F$ is fed to the reactor (total volume $V$) and mixed with a residual volume of the previous work cycle, that is still present in the reactor after the settle and draw phases and contains biomass and unconverted substrate. After each work cycle, the increased biomass is wasted from the system so the new cycle starts at the same biomass concentration assumed for the previous one; therefore, as for a reactor operating in a simple batch mode, a constant biomass concentration can be considered.

The substrate concentration at the beginning of a reaction period ($S_0$) depends on the substrate concentration ($S$) remaining at the end of previous cycle. Assuming operation with a short feed time (negligible in terms of substrate removal in comparison with the reaction time) the mass balance equation, for the feed phase, is given by:

$$V_F S_F + (V - V_F)S = VS_0$$

or, in terms of the exchange ratio $R = V_F/V$

$$S = \frac{1}{1 - R} S_0 - \frac{R}{1 - R} S_F$$

(5)

which expresses the dependence of $S$ on $S_0$, $S_F$, $R$.

By solving Eq. (5) for $S_0$ and substituting the expression into Eq. (3), the implicit equation for $S$ is obtained

$$G(S, R) = \varphi - \ln \left(\frac{1 - R}{S} + R S_F - R(S_F - S) \right)$$

$$- \frac{\gamma R}{2} (S_F - S) \left[ (2 - R) S + R S_F \right] = 0$$

(6)

3.1. Response for Monod kinetics

In order to discuss how the behavior of a sequencing batch reactor depends on the operating parameters, it is interesting to analyze the solution of the Eqs. set (3) and (5) from a graphical point of view: on a plot of $S$ vs $S_0$ the relation between $S$ and $S_0$ given by the kinetic Eq. (3) is given by a curve as reported in Fig. 2a for Monod kinetics ($\gamma = 0$). In the same plot, Eq. (5) represents a working line passing through the points $(R S_F, 0)$ and $(S_F, S_F)$ and with a slope of $1/(1 - R)$. In other words, if we consider a feed stream at a concentration $S_F$, Eq. (5) gives a family of straight lines pivoting on the point $(S_F, S_F)$ and with a slope ranging from 1 (if $R = 0$ – no feed) to infinity (if $R = 1$ – no residual volume in the reactor). Therefore, the substrate concentrations at the beginning and at the end of the reaction phase, $S_0$ and $S$, for a given $R$ and $S_F$,
are obtained at the intersection points \((P)\) of the mass balance curves in the reaction phase (Eq. (3), represented by the curve in Fig. 2a) with the straight line of the mass balance in the feed phase (Eq. (5) represented by the working lines). Since the exchange ratio \(R\) is an operating parameter that can be modified by the operator to control the performance of the system, it is useful to evaluate the response curve, i.e. the residual substrate concentration, \(S\), as a function of \(R\), reported in Fig. 2b. The plot shows that an increase in the exchange ratio (without changing the other operating parameters) results in a gradual increase of the final substrate concentration. This result is theoretically supported by implicitly differentiating the \(G(S,R)\) function defined by Eq. (6) and proving that \(dS/dR\) is strictly positive in the region \(0 < R < 1\) and \(S < S_f\). Therefore, for a non-inhibitory substrate \((\gamma = 0)\) no critical value of the exchange ratio occurs.

3.2. Response for inhibition kinetics

Similar curves are reported in Fig. 3 in the case of inhibition kinetics \((\gamma > 0)\). In this case the internal feedback from the previous cycle results in complex reactor response. That is, in this case, we have a \(S\)-shaped kinetic curve (solid line, and as seen in Fig. 1), which results in unusual behavior of the system with an abrupt change from a low final substrate concentration to a high final substrate concentration depending on the value of \(R\) selected (broken lines). As an example, in Fig. 3 the case of Haldane kinetics with \(\gamma = 5\) is reported; the solid kinetic curve \(S = S_0\) refers to a reaction time of \(\theta = 5\) and, as in the previous example, the straight lines represent the working lines obtained if the reactor is fed with a solution with \(S_p = 5\) at different exchange ratios. In order to more clearly demonstrate the impact of this, the working conditions for different exchange ratio values have been reported in separate plots (Fig. 3a–c) while in Fig. 3d the final concentration \(S\) vs \(R\) is reported.

For low exchange ratios (e.g. \(R = 0.05\) in Fig. 3a), a solution with a very low residual substrate concentration is obtained (point A), corresponding to high removal efficiency. This, in the cyclic behavior characteristic of SBR operation, corresponds to an operating condition with the reactor handling a substrate concentration ranging from an initial concentration of \(S_0 = R S_F\) to a final substrate concentration of \(S = 0\). On the other hand, a high \(R\) value (e.g. \(R = 0.5\) in Fig. 3a) results in a solution in the upper part of the \(S(S_0)\) curve (point B), corresponding to an operating condition with high residual substrate concentration and low substrate removal efficiency. The reactor operates from a high initial substrate concentration \(S_0\) to a high final substrate concentration \(S = S_0\). Operating points such as B are not of practical interest since the substrate removal efficiency is unacceptably low. Interestingly, there are some intermediate exchange ratio values (e.g. \(R = 0.16\) in Fig. 3b) giving three possible intermediate solutions with low, medium and high effluent substrate concentrations (points C, D, and E, respectively). Point D represents a “tipping point”; depending on the condition at the start-up of a new cycle (i.e. depending on the residual substrate concentration from the previous cycle), the reactor working point moves either towards point C or point E, obtaining high or low substrate removal efficiency, respectively.

Fig. 4. Substrate concentration vs. dimensionless time during reactor operative cycle for \(S_p = 5\), \(\gamma = 5\) and \(\theta = 5\) \((R_1 = 0.13\) and \(R_2 = 0.172\)). Different exchange ratios and initial conditions are represented: (a) \(R < R_1\): a low substrate concentration is attained, independently on the initial substrate concentration; (b) \(R > R_2\): a high final substrate concentration is attained, independently on the initial substrate concentration; (c) \(R_1 < R < R_2\): a low or a high final substrate concentration is attained, depending on the initial conditions; (d) for \(R \sim R_2\) a quite good performance is attained, in the initial phase, which rapidly deteriorates towards very low removal periodic operating conditions.
In fact, there are two limiting working lines corresponding to two exchange ratios $R'_1$ (upper tangent to the curve from the point $S_R$, $S_T$) and $R'_2$ (lower tangent from the same point) delineating the $R$ interval that gives multiple (high or low treatment efficiency) solutions as is shown in Fig. 3c ($R'_1 = 0.13$ and $R'_2 = 0.172$ in the figure). This is better clarified in the response diagram reported in Fig. 3d, in which the final substrate concentration as a function of the exchange ratio is reported. The response diagram emphasizes the importance of the defining $R$ interval. If the exchange ratio is lower than $R'_1$, there is only one high efficiency working point; within the interval of values from $R'_1$ to $R'_2$ it is possible, depending on the initial substrate concentration, to have low or high efficiency working points, and if $R$ exceeds $R'_2$ the reactor conditions jump to the upper part of the curve giving a working point corresponding to low substrate removal efficiency. In the context of non-linear dynamical system, $R_1$ and $R_2$ correspond to bifurcation points, as the number of solutions of $G(S,R) = 0$ is not constant as $R$ varies in an arbitrary small neighborhood; analytical conditions for bifurcation points

\[
\frac{\partial R}{\partial S} \frac{\partial G}{\partial R} = 0
\]

\[
\frac{\partial^2 G}{\partial S^2} \neq 0
\]

can be useful to find the $R'_1$ and $R'_2$ values in different conditions and to investigate how they vary as other parameters are changed [20–22].

To further explore this behavior it is useful to predict how the SBR reactor can attain periodic operation over multiple operating cycles. This is shown in Fig. 4 which plots the behavior of a reactor fed with contaminated wastewater ($S_T = 5$) and working with a reaction time $\phi = 5$ as a function of the exchange ratio and the start up procedure. In particular two different start up procedures are considered: in the first one it is assumed that the reactor is initially loaded with a volume $(1 - R)V$ of substrate-free liquid ($S_0 = 0$) and then filled with a volume $R V$ of the contaminated wastewater; in the second one it is assumed that the reactor is initially loaded with a volume $(1 - R)V$ of a liquid with a substrate concentration $S_0 = S_R / 2$ and then filled with a volume $R V$ of the contaminated wastewater. As for the exchange ratio, several different cases are considered:

- low exchange ratios in a stable zone ($R < R'_1$) that allow the reactor to attain periodic operating conditions with high removal efficiency in a few cycles, independent of the start-up procedure (Fig. 4a); the same qualitative behavior is observed if, at the start up, the reactor is simply filled with the contaminated water, even if more cycles are required to reach high removal efficiency;
- analogously, high exchange ratios $R > R'_2$ causing the reactor to reach periodic operation independent of the initial substrate concentration but with low removal efficiency (Fig. 4b);
- intermediate $R$ values within the delineating range of $R'_1 - R'_2$, resulting in a final periodic operating condition that depends on the initial substrate concentration as shown in Fig. 4c. In this case, low or high removal efficiency can occur depending on the residual substrate concentration at the start up;
- exchange ratios equal or close to $R'_2$ are very critical for reactor operation because even a very small change in the $R$ value in a narrow interval can dramatically change the reactor operation from good to poor performance (see Fig. 4d for $R$ increasing from 0.17 to 0.175). It is worth noting that for $R = 0.175$ (a value slightly greater than $R'_2$) the reactor initially shows quite good performance but after a number of cycles the removal efficiency rapidly deteriorates towards very low removal periodic operating conditions.

As already pointed out, the final substrate concentration achievable in the SBR depends on intrinsic parameters (kinetic and stoichiometric), on the substrate concentration in the feed $S_R$ and on two controllable operating parameters, the duration of the reaction phase, $\phi$ and the exchange ratio, $R$. From a practical point of view it is useful to consider the relationship between $R$ and $\phi$ required to obtain a fixed removal efficiency to have an indication of the optimal choice of these two parameters, which can be independently selected by an operator. For this purpose, response curves for different $\phi$ values can be constructed, as reported in Fig. 5a. As previously discussed, for some $\phi$ values, two bifurcation point $R'_1$ and $R'_2$ exist (as shown in the plot for $\phi = 10$). On the other hand, there is a critical $\phi$ value ($\phi' \approx 40.291$ for $S_T = 5$ and $\gamma = 5$) corresponding to the condition $\partial^2 G / \partial S^2 = 0$ being violated; at $\phi = \phi'$ the two bifurcation points collapse into an inflection point with vertical tangent and above this $\phi$ value the bifurcation points vanish and the response curve is an always increasing function of $R$ with an inflection point (as shown in the plot for $\phi = 50$). For $\phi \geq \phi'$, the tangent to the response curve at the inflection point allows defining a limiting value of the exchange ratio, $R^*$, as graphically described in Fig. 5a for $\phi = 60$, such that a high substrate removal efficiency is obtained for $R < R^*$ while the process effectiveness is largely reduced for $R > R^*$. Therefore (Fig. 5b), the three zones are determined corresponding to different SBR performance. In region I, corresponding to $R < R'_1$ (for $\phi < \phi'$) or $R < R^*$ (for $\phi > \phi'$), a very low residual substrate concentration is obtained; this is a working region with high efficiency performance. Region II, corresponding

![Fig. 5. Response curves and limiting exchange ratio for efficient performance: (a) response curves for different $\phi$ values ($S_T = 5$, $\gamma = 5$); bifurcation points ($R'_1$ and $R'_2$) occur at $\phi < \phi' = 40.291$. (b) Working regions for different $R$ and $\phi$ values: Region I: working region with efficient performance. Region II: working region with poor performance. The shadow region (for $\phi < \phi'$) is a switching working zone.](image-url)
to \( R > R^*_2 \) (for \( \vartheta < \vartheta^* \)) or \( R > R^* \) (for \( \vartheta > \vartheta^* \)), is characterized by poor performance in which only high residual substrate concentrations are achieved. For \( \vartheta < \vartheta^* \) there is a switching region (the shadow region in the plot), corresponding to \( R^*_1 < R < R^*_2 \), where although it is possible to achieve a low final substrate concentration, poor removal can arise depending on the initial conditions selected.

The above analysis has demonstrated a number of important features of SBR systems used to treat xenobiotic substrates. Depending on selected operating conditions, reactor behaviour either resolves to high performance operation, or deteriorate into conditions of low treatment efficiency.

### 4. Examples of application: removal of 4-nitrophenol and 2-chlorophenol

The above dynamic analysis can be applied to determine operating strategies of SBR systems used to biodegrade actual xenobiotic compounds. The two proposed examples are for the treatment of 4-nitrophenol (NP) and 2-chlorophenol (ClP), which are characterized by substantially different toxicity levels as shown in Table 1. The kinetic and operating parameters considered in these case studies are reported in Table 2. The differences in NP and ClP biodegradability are evident on the basis of different \( \vartheta \) values, equal to 3.6 and 11, respectively. Actually, on the basis of the reported kinetic parameters, the removal rate at very low substrate concentrations is higher for ClP than for NP, due to the higher \( \vartheta \) value for ClP than for NP. Nevertheless as the substrate concentration increases a higher inhibition is observed for ClP than for NP, and a maximal removal rate of 1.25 mg/mg-d occurs at \( S_{\max} \) of about 29 mg/L (corresponding to a dimensionless substrate concentration \( S_{\max} = 0.53 \)) for NP, while for ClP a maximal removal rate of 0.33 mg/mg-d occurs at \( S_{\max} = 3.5 \) mg/L (\( S_{\max} = 0.3 \)), a difference in specific removal rate of almost 4-fold.

In the following analysis the SBR reactor was intended to treat a wastewater containing 500 mg/L of the toxic substrate (corresponding to \( S_0 = 9.1 \) for NP and 41.3 for ClP); this substrate concentration, which may be representative of an industrial effluent, is about 20 times higher than the one corresponding to the maximal removal rate for NP, while it is more than 130 times higher than \( S_{\max} \) for ClP.

A comparison of the performance of the SBR reactors for NP and ClP removal is presented in terms of an \( R - \vartheta \) plot in Fig. 6. Here, for each component, the two reported curves divide the high efficiency region (below the lower curve) from the poor performance region, with high residual substrate concentration (above the upper curve), while between the two curves (shadow regions) either a low or high residual substrate concentration can be achieved depending on the initial conditions. As for NP, a critical \( \vartheta \) value close to 115 occurs; above this value the two bifurcation point \( R_1^* \) and \( R_2^* \) vanish and the switching region disappears; as for ClP the critical \( \vartheta \) value is out of the region of practical interest. The operability spaces for the 2 distinct substrates can be seen to occupy substantially different regions of the \( R - \vartheta \) plot with the NP region allowing much higher operation in \( R \), at a range of much lower \( \vartheta \) values. Specifically, in the case of NP, it is possible to operate with an exchange ratio equal to 0.5, a typical value for industrial application, with a \( \vartheta \) of 56 (point A in Fig. 6) i.e. with a duration of the reaction phase of \( \sim 4 \) h. In contrast, for the treatment of 500 mg/L ClP, it is impossible to work with an exchange ratio of this magnitude (0.5); if it is desired to work with a reaction phase duration of about 8 h (i.e. with a \( \vartheta \) value of about 300) the system is restricted to a maximum exchange ratio of 0.055 (point B in Fig. 6) to get a high removal efficiency. This value may be unsuitable for practical application, since a too large reactor volume would be required (or a too low productivity, as defined below, would be obtained). For ClP it is also possible to work with an exchange ratio up to 0.17 (point C), however in the exchange ratio range between 0.055 and 0.17 the system is within the switching region.

An important feature of Fig. 6 is that it shows that different combinations of operating conditions, different exchange ratios and durations of the reaction phase, can be selected to achieve high substrate removal efficiency. As an example, for NP removal, it is possible to work with an exchange ratio 0.7 (point \( A' \) in Fig. 6).

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>4-Nitrophenol</th>
<th>2-Chlorophenol</th>
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<tr>
<td>( k^* ) (mg substrate/mg biomass d)</td>
<td>7</td>
<td>4.3</td>
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<tr>
<td>( K_s ) (mg/L)</td>
<td>55</td>
<td>12.1</td>
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<td>( X_{VSS} ) (mg biomass as VSS/mg substrate)</td>
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<td>0.67</td>
</tr>
<tr>
<td>( k_c ) (1/d)</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>( t_c ) (h)</td>
<td>3.6</td>
<td>11</td>
</tr>
<tr>
<td>( s_0 ) (mg/L)</td>
<td>0.075</td>
<td>0.027</td>
</tr>
<tr>
<td>( S_{\max} ) (mg/L)</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>( S_c ) (mg/L)</td>
<td>9.1</td>
<td>41.3</td>
</tr>
<tr>
<td>( X ) (mgVSS/L)</td>
<td>2500</td>
<td>2500</td>
</tr>
</tbody>
</table>

* Kinetic and stoichiometric data for 4-nitrophenol are from [17].

* Kinetic and stoichiometric data for 2-chlorophenol are from [29].

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![Fig. 6. Operability zones for 4-nitrophenol (NP) and 2-chlorophenol (ClP) removal in a SBR reactor.](image-url)
and a $\vartheta$ value of about 70 (i.e. with a reaction phase duration of 5.5 h) to obtain high removal efficiency. In fact, for each component to be removed, the lower boundary of the dashed region or the curve for $\vartheta \geq \vartheta'$ in Fig. 6 represents the highest exchange ratio that achieves high efficiency operation with a fixed duration of the reaction phase. With a $\vartheta$ value of about 160 (i.e. with a duration of the reaction phase of about 12 h) it is possible to get high efficiency also working with $R = 1$, i.e. in simple batch mode. This therefore provides a guide, depending on the nature of the xenobiotic, to determine effective (high treatment efficiency) operating conditions for each new substrate and feed concentration.

A complementary method for choosing the best operating conditions, can also be determined by considering process volumetric productivity, which is defined as the amount of substrate removed per unit reactor volume and unit time

$$E = \frac{Rk(T_{\text{d}} - S)}{t_0 \vartheta + t_0}$$  \hspace{1cm} (7)

where $t_0$ is the time required for the feed, settling and withdraw phases. Obviously, for a fixed $R$ value, the highest productivity is obtained working with the minimum $\vartheta$ value that allows operation at high performance. Therefore, the “best” operating condition is obtained by evaluating the maximum achievable productivity for each $R$ value and choosing the $R$ value corresponding to the highest $E$ value. In the case of NP, Fig. 7 shows the maximum productivity achievable as a function of the chosen $R$ value, evaluated assuming $t_0 = 45$ min; in the same figure, the $\vartheta$ value that allows achieving the maximum productivity for each $R$ value is also reported. To ensure that operation is within a no switching and high efficiency operating region, the best productivity is obtained with an exchange ratio of 0.4 and a $\vartheta$ value of about 40; in this case a productivity of about 50 mg/L h is obtained. Such a productivity is significantly higher than the productivity obtained in a simple batch mode ($E = 40$ mg/L h with a $\vartheta$ value of 100).

5. Conclusions: remarks for SBR reactor design and operation

This work has provided an analysis of the behaviour of an SBR for xenobiotic removal, showing, for the first time, an operational behaviour that included high and low treatment efficiency, as well as regions leading to a switching process performance. Process treatment efficiency was investigated as a function of the exchange ratio, $R$, which was shown to be the critical operating variable (i.e. one that can be operator controlled) influencing process behaviour. This insight would be potentially useful in actual SBR wastewater treatment applications. Moreover, this work also examined the impact of two substantially different xenobiotic substrates on operability during SBR operation, which demonstrated a high degree of sensitivity to the intrinsic microbial kinetic parameters of the 2 substrates. Such process sensitivity to substrate inhibition may be mitigated by the introduction of a second immiscible phase, which would serve to sequester the xenobiotic substrate and release it to the microbial population based on metabolic demand, as seen in Two-Phase Partitioning Bioreactors, and we are currently extending our above modeling to such systems.

References
