SBR Reactors for Xenobiotic Removal: Dynamic Simulation and Operability Criteria

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Sequencing Batch Reactors (SBR) appear to be an effective technological solution in order to obtain a versatile microorganism culture able to develop metabolic pathways required for degradation of bioresistant substances. Nevertheless, the performance of these devices is limited by the inhibitory kinetics of xenobiotic biodegradation that results in a significant reduction of the removal rate if the biomass experiences high substrate concentrations. In this work a dynamic model is formulated to describe the behavior of an SBR reactor for xenobiotic removal and to investigate the influence of the kinetic parameters and the operating on the biodegradation efficiency. In particular, the model shows that for inhibitory kinetics an abrupt change from low to high substrate concentrations in the outlet stream (i.e from a high to a low process efficiency) can occur, depending on the kinetic and operating parameter values.

1. Introduction

The environment continues to be challenged by the increasing amount and variability of toxic contaminants that are emitted by industrial activities worldwide. Such contaminants are becoming more widespread as industrial activity accelerates, especially in developing countries, and also as a consequence of the transport of the emissions of industrial activity across national boundaries.
Among the most serious contaminants (both in terms of their impact and their resistance to treatment) are toxic organic compounds, including aromatic, polyaromatic and halogenated compounds and the subset of these known as xenobiotics. Xenobiotic compounds are molecules that are man-made and are "foreign to nature" in the sense that they have been present in the ecosphere for relatively short periods of time and therefore efficient biodegradation pathways have not had adequate time to evolve. As a

result, the biological treatment of these materials is extremely challenging due to the inhibition and/or toxicity of these compounds when they serve as microbial substrates.

An effective approach to the biological treatment of xenobiotic compounds is via the use of Sequencing Batch Reactors (SBRs), which provide a dynamic environment for cells to adapt to recalcitrant compounds and develop efficient degradative pathways. Such SBR systems have been experimentally demonstrated to be effective in the treatment of a variety of xenobiotic compounds, including substituted phenols (Tomei and Annesini, 2005, Tomei et al. 2009).

In this work we describe the modeling of SBR systems degrading toxic substrates with the aim of identifying the operability of such systems, including stable and unstable operating regions.

2. Kinetics of Xenobiotic Removal

The kinetics of biological removal of xenobiotic compounds usually shows a substrate inhibition effect. As suggested by Andrews (1968), the classical Haldane equation is often used for data correlation:

$$r_S = v \frac{C}{C + K_S + \dfrac{C^2}{K_I}} = k^* X \frac{C}{C + K_S + \dfrac{C^2}{K_I}} \tag{1}$$

where X and C are the biomass and substrate concentration, respectively. In order to develop a general description of the reactor behavior, the above equation may be rewritten in a dimensionless for as:

$$\frac{r_S}{k^* X} = \frac{S}{1 + S + \lambda S^2} \tag{2}$$

where $S = C/K_s$ and $\gamma = K_s/K_i$. As shown in Fig. 1, γ parameter accounts for the extent of the inhibitory effects: equation (2) reduces to Monod kinetics for $\gamma = 0$, while the larger the value of γ the larger the removal rate reduction at high substrate concentration; a maximum removal rate is observed for $S = 1/\sqrt{\gamma}$.

If the reaction is carried out in a batch mode, the substrate concentration is given by the substrate and biomass mass balance equations:

$$\frac{ds}{d\vartheta} = -\frac{X}{X_0} \frac{S}{1 + S + \lambda S^2} \tag{3}$$

$$\frac{d(X/X_0)}{d\vartheta} = Y \frac{S}{1 + S + \lambda S^2} - \frac{k_e X}{k X_0} \tag{4}$$

where Y is the biomass yield, k_e the endogenous kinetic constant and θ the dimensionless reaction time defined as t/t_c and $t_c = K_s/(k^* X_o)$. If a constant biomass

concentration can be assumed, the reactor model simplifies to equation (3), that can be easily solved analytically. In this case, the final substrate concentration (S) is given as a function of the initial substrate concentration and the reaction time by:

$$S + \frac{Y}{2}S^2 + \log S = S_0 + \frac{Y}{2}S_0^2 + \log S_0 - \vartheta \tag{5}$$

While for $\gamma=0$ the curve $S=f(S_0)$ for a given θ value is concave upward with two limiting asymptotes $S=S_0 exp(\theta)$ $(S_0<<K_s)$ and $S=S_0-\theta$ $(S>>1/\gamma)$, with an inhibitory kinetics the curve $S=f(S_0)$ (i.e. for a fixed reaction time) has an S-shape, with very low outlet substrate concentration obtained for low S_0 values, but with a sharp increase of the final substrate concentration as S_0 exceeds a critical value (depending on γ);
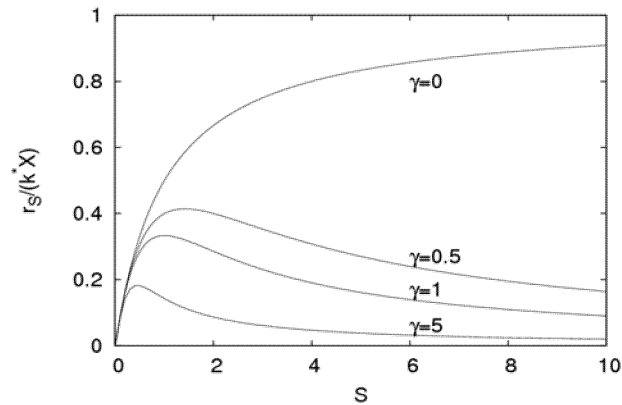

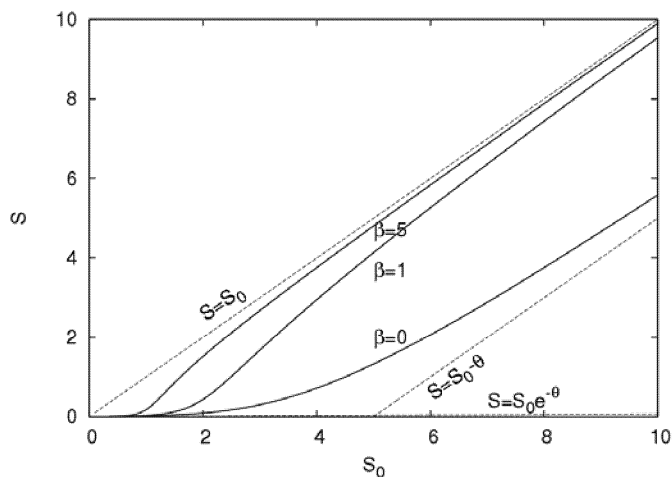
Figure 1. Kinetics of xenobiotic removal

Figure 2. Substrate concentration obtained for $\theta=5$ for different inhibition levels

for high S_0 the process is almost ineffective and the final concentration is only slightly lower than the inlet value. In other words, there is an S_0 value (depending on γ) which allows removal of the maximum amount of substrate with the assigned θ value, but the removal capacity of the reactor decreases if the substrate inlet concentration exceeds this critical value (it can be proved that the critical value of the inlet substrate concentration corresponds to $dS/dS_0=0$).

3. Xenobiotic Removal in a Sequencing Batch Reactor

In a sequencing batch reactor, the feed containing the xenobiotic at concentration S_F to be removed is added to reactor and mixed with a residual volume of the previous cycle, that is still present in the reactor after the settling and draw phases and contains biomass. Indeed, the substrate concentration at the beginning of a work cycle depends on the substrate concentration obtained at the end of previous one, according to the mass balance equation:

$$RS_F + (1 - R)S = S_0 \qquad (6)$$

where R is the exchange ratio defined as the ratio between the added influent volume, V_F and the work volume V.

Therefore, the SBR reactor working with a reaction time θ follows a periodic behaviour that can be determined by solving equations (5) and (6). Equations (5) and (6) are plotted in fig. 3a as a function of the substrate concentration at the beginning of the reaction phase. Equation (5) is represented by an S-shaped curve described in the previous paragraph; for a fixed S_F value, equation (6) represents a family of straight lines pivoting around the point (S_F, S_F) with slope $1/(1-R)$, while for a fixed R value, the equation represents a family of parallel lines, depending on the S_F values. In any case, the substrate concentration at the beginning and at the end of the reaction phase, S_0 and S, is obtained as the intersection of the S-shaped curve of the mass balance in the reaction phase with the straight line of the mass balance in the feed phase. The internal feedback between subsequent cycle and the inhibition kinetics results in complex reactor behaviour. In the following, we consider a feed at a substrate concentration S_F and we discuss the effect of the exchange ratio. For a low R value, the working point corresponds to a very low outlet substrate concentration (point A in figure 3a) and the reactor works with a substrate concentration ranging from an initial value $S_0 \sim S_F$ and a final concentration $S \sim 0$. On the other hand, for high R values, the intersection point occurs in the upper part of the S-shaped curve (point B) and the reactor operates at a substrate concentration ranging from $S_0 \sim S_F$ and $S \sim S_F$. Operating points such as B are not of practical interest since the substrate removal efficiency is too low. For intermediate R values three intersections are observed (points C, D and E); therefore three periodic behaviours are possible. It is easy to prove that D represents an unstable state and depending on the conditions at the start-up of the reactor the working point moves toward point C or E, resulting in a high or low removal efficiency.

Therefore, as shown in fig. 3b there is a limiting exchange ratio R^* corresponding to a shift between a high removal efficiency to a low removal efficiency working point. If the exchange ratio increases up to R^* the final substrate concentration slowly increases as indicated by the lower branch of the S-curve, but as R slightly exceeds R^* the reactor conditions jump to the upper part of the curve and the substrate removal efficiency steeply decreases.
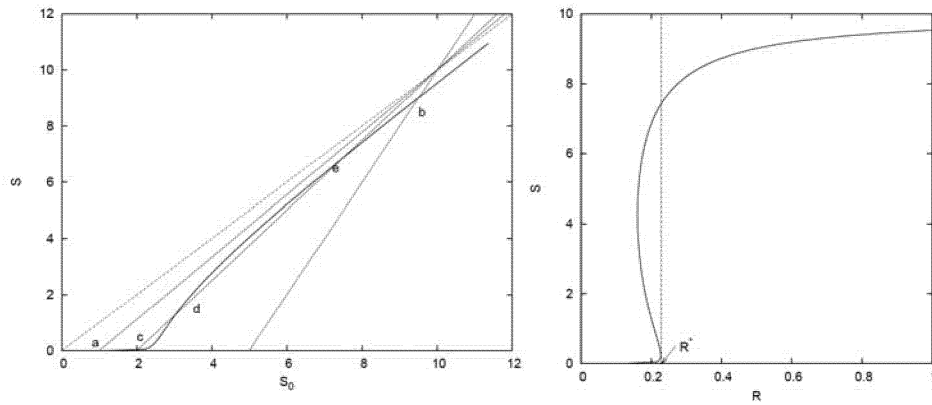

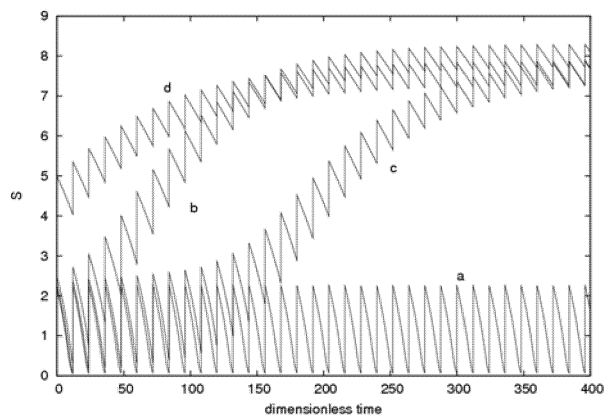Figure 3.final substrate concentration as function of the initial concentration and the exchange ratio in SBR (β=2.5, θ=12, Sf=10).

Figure 4.Substrate concentration vs. dimensionless time during reactor operative cycles. a: R=0.22, S0=2.2; b:R=0.25, S0=2.5; c: R=0.23, S0=2.3, d:R=0.22, S0=5.

Such behaviour can be explained by considering how the SBR reactor arrives at this periodic behaviour, starting from an initial condition with the polluted wastewater fed to a reactor filled with pure water. As shown in Fig.4, for low and high exchange ratios the reactor attains a periodic working condition in a few cycles, corresponding to a high and a low removal efficiency respectively. On the other hand, for R slightly higher than R^* the reactor seems to arrive at a periodic working condition with high efficiency, but subsequently the removal efficiency deteriorates toward a no removal condition

4. Remarks for Reactor Design

The above considerations can be very useful for reactor design. First, a low exchange ratio is not desirable since it corresponds to a low wastewater volume being treated per unit time. It is therefore desirable to work with a higher R value that provides a practically complete substrate removal (R^*) . Since, for a given feed concentration S_F, R^* depends on the reaction time (θ), the optimal design, that corresponds to the maximum amount of substrate removal per unit time, should be obtained by minimizing the ratio θ/R^*

Moreover, it should be kept in mind that an exchange ratio near R^* would lead to an extremely sensitive reactor, which would easily jump to a working point corresponding to ineffective reactor performance that does not provide a significant substrate removal.

References

Andrews, J. F., 1968, A mathematical model for the continuous culture of microorganisms utilizing inhibitory substrates, Biotechnol. Bioeng., 10, 707-723.

Ellis, T. G., Smets B. F., Magbanua, B. S., Jr., & Grady, C. P. L., Jr., 1996, Changes in measured biodegradation kinetics during the long-term operation of completely mixed activated sludge (CMAS) bioreactors. Water Science and Technology, 34, 35–42.

Tomei, M. C. and Annesini, M. C., 2005, 4-nitrophenol biodegradation in a sequencing batch reactor operating with aerobic-anoxic cycles. Environmental Science and Technology, 39, 5059–5065.

Tomei, M.C., Annesini, M.C. Prpich, G.P, Daugulis, A. J., 2009, Biodegradation of 4-Nitrophenol in a Two-Phase System Operating with Polymers as the Partitioning Phase Environ. Sci. Technol, 43, 7105–7110.