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Substrate inhibition kinetics in a fluidized bioparticle

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Abstract

An analysis of substrate inhibition kinetics in a fluidized bioparticle is presented. A model which considers the interactions between intrabiofilm mass transfer and bacterial rate processes is developed based on Haldane inhibition kinetics. The model predicts that, under given circumstances, a bioparticle effectiveness factor of greater than unity is attainable for a range of biofilm thicknesses, indicating that a bioparticle is effective as an inhibitory substrate. The bioparticle effectiveness factor can be used in conjunction with fluidization correlations to predict the overall efficiency of a biological fluidized bed reactor in the presence of substrate inhibition. © 1997 Elsevier Science S.A.

Keywords: Bioparticle; Effectiveness factor; Mass transfer; Substrate inhibition; Thiele modulus

1. Introduction

Biological treatment processes have been employed for the treatment of a wide variety of hazardous and inhibitory wastes [1–10]. Many process configurations and treatment schemes are available, among which a biological fluidized bed (BFB) reactor, with its unique biological and geometric features, provides a number of advantages over the suspended growth processes [2,3,6–9,11]. The formation of biofilms on fluidized media particles allows us to attain a high reactor biomass hold-up and a long mean cell residence time, so sustaining high substrate utilization in a BFB reactor [8]. A 'bioparticle' (biofilm-coated media particle) is capable of maintaining its metabolic functions under low substrate concentration conditions, whereas a suspended growth process may be susceptible to excessive washout of bacterial cells under similar conditions [6,12]. Furthermore, the transport of an inhibitory substrate through a biofilm may be retarded, so reducing the impact of substrate inhibition on bacterial cells [12–14].

The interactions between mass transfer and bacterial rate processes in bioparticles are of critical importance for the efficiency of a BFB reactor [15–19]. While most biofilm research has been focused on uninhibitory substrates, recent studies reported elsewhere have used inhibitory substrates [1,12–14,21]. In addition, many studies have confirmed that the Haldane equation is applicable for various inhibitory substrates, such as for amines, ammonia, chlorophenol, naphthalene, phenanthrene, phenol, toluene, trichloroethylene and xylene [1–6,11,20].

This paper analyzes the kinetics of substrate inhibition in a fluidized bioparticle. In addition to presenting the development and solution of a bioparticle model that incorporates intrabiofilm mass transfer resistances and Haldane inhibition kinetics, the bioparticle effectiveness factor is developed for assessing bioparticle efficiencies under circumstances characterized by the inhibitory substrate and bacterial population present.

2. Model development

A fluidized bioparticle is used as the basis for model development, with the following assumptions (Fig. 1):

a spherical media particle with a uniform size;
a homogeneous biofilm with a uniform thickness;
negligible mass transfer resistances at the biofilm–liquid interface;
intrabiofilm mass transfer described by Fick's first law;
a single soluble inhibitory substrate that exhibits Haldane inhibition kinetics;
constant biological and mass transfer parameters;
steady state conditions.

A mass balance on the substrate in a biofilm shell yields the mass balance equations

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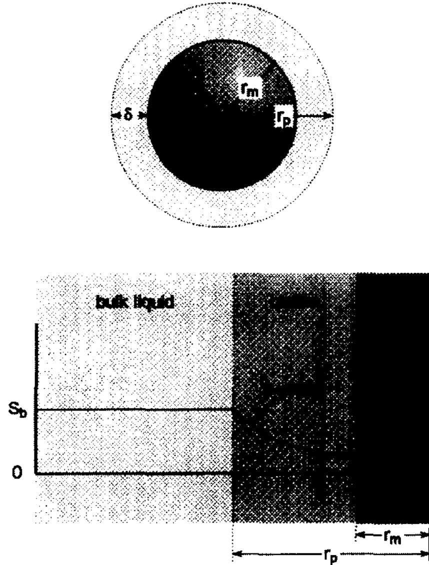

Fig. 1. (a) Schematic diagram of a bioparticle, and (b) the substrate concentration profile for a biofilm grown on a fluidized bioparticle.

$$\frac{D_e}{r^2}\frac{d[r^2(dS/dr)]}{dr}=\rho R \quad (1)$$

$$R=\frac{kS}{K_s+S+(S^2/K_i)} \quad (1a)$$

$$S=S_b \text{ at } r=r_p \quad (1b)$$

$$\frac{dS}{dr}=0 \text{ at } r=r_m \quad (1c)$$

The above equations can be made dimensionless, such that we have

$$\frac{d^2S^*}{dr^{*2}}+\frac{2\delta^*}{1+\delta^*(r^*-1)}\frac{dS^*}{dr^*}=\frac{\phi^2S^*}{1+\alpha S^*+\beta S^{*2}} \quad (2)$$

$$S^*=1 \text{ at } r^*=1 \quad (2a)$$

$$\frac{dS^*}{dr^*}=0 \text{ at } r^*=0 \quad (2b)$$

The dimensionless parameters are as follows. The dimensionless substrate concentration in the film is

$$S^*=S/S_b$$

The dimensionless radial distance measured from the bioparticle center is

$$r^*=(r-r_m)/\delta$$

The dimensionless biofilm thickness is

$$\delta^*=\delta/r_p$$

The Thiele modulus is

$$\phi=(\rho k/D_eK_s)^{0.5}\delta$$

and

$$\alpha=S_b/K_s$$

$$\beta=S_b^2/K_sK_i$$

Here, D_e is the substrate effective diffusivity in the biofilm (L^2/T); r is the radial distance measured from the bioparticle center (L); S is the substrate concentration in the biofilm (M/L^3); ρ is the biofilm dry density (M/L^3); R is the Haldane inhibition expression ($M/M-T$); k is the maximum substrate utilization rate ($M/M-T$); K_s is the half-velocity constant (M/L^3); K_i is the inhibition constant (M/L^3); S_b is the bulk-liquid substrate concentration (M/L^3); r_p is the bioparticle radius (L); r_m is media particle radius (L); and δ is the biofilm thickness (L).

The bioparticle effectiveness factor η is defined as the ratio of the observed bioparticle reaction rate to the bioparticle reaction rate under bulk-liquid conditions, i.e.

$$\eta=\frac{(1+\alpha+\beta)\phi^{-2}}{1-\delta^*+(\delta^{*2}/3)}\left[\left(\frac{dS^*}{dr^*}\right)\bigg|_{r^*=1}\right] \quad (3)$$

3. Model solution

The Runge–Kutta–Nyström method is used to obtain the numerical solutions of Eq. (1) [22]. First, Eq. (1) is rearranged as

$$f(r^*,S^*,S^{*\prime})=\frac{d^2S^*}{dr^{*2}}$$

$$=\frac{\phi^2S^*}{1+\alpha S^*+\beta S^{*2}}-\frac{2\delta^*}{1+\delta^*(r^*-1)}S^{*\prime} \quad (4)$$

where $S^{*\prime}=dS^*/dr^*$.

At given α, β and ϕ values, a substrate concentration value at the biofilm–media interface is assumed and a given step length h (i.e. 10^{-3}) is used to initiate the iterative process. The substrate concentrations and substrate concentration gradients at different locations in the biofilm (i.e. at $r_1^*=1/n$, $r_2^*=2/n$, ...) are respectively calculated as

$$S_{n+1}^*=S_n^*+h(S_n^*+k_n) \quad (5)$$

$$S_{n+1}^{*\prime}=S_n^{*\prime}+k_n^* \quad (6)$$

where $k_n=(a_n+b_n+c_n)/3$ and $k_n^*=(a_n+2b_n+2c_n+d_n)/3$, and n ranges from 0 to 999.

The four auxiliary terms a_n, b_n, c_n and d_n are [22]

$$a_n=0.5hf(r_n^*,S_n^*,S_n^{*\prime}) \quad (7a)$$

$$b_n=0.5hf(r_n^*+0.5h,S_n^*+\gamma_n,S_n^{*\prime}+a_n) \quad (7b)$$

$$c_n=0.5hf(r_n^*+0.5h,S_n^*+\gamma_n,S_n^{*\prime}+b_n) \quad (7c)$$

$$d_n=0.5hf(r_n^*+h,S_n^*+\zeta_n,S_n^{*\prime}+2c_n) \quad (7d)$$

where $\gamma_n=0.5h(S_n^{*\prime}+0.5a_n)$ and $\zeta_n=h(S_n^{*\prime}+c_n)$.

The substrate concentration calculated at the biofilm–liquid interface, i.e. S_{n+1}^*, is checked against Eq. (2) using the following convergence criterion:

$$|S^*_{n+1} - 1| < 10^{-4} \quad (8)$$

If the convergence criterion is not satisfied, then the iterative process will be repeated using a new substrate concentration value at the biofilm–media interface. Once the desired substrate concentrations in the biofilm are obtained, the effectiveness factor is calculated from Eq. (3), by recognizing that

$$S^*_{n+1} = \left(\frac{\mathrm{d}S^*}{\mathrm{d}r^*}\right)\bigg|_{r^*} = 1$$

4. Results and discussion

The solutions of Eqs. (2) and (3) were obtained numerically for $0 \le \alpha \le 25$, $0 \le \beta \le 500$ and $0 \le \phi \le 24$. α characterizes the kinetics of substrate utilization within the uninhibitory region, whereas β measures the magnitude of the substrate inhibition. The Haldane equation states that the maximum utilization of substrate occurs when the dimensionless substrate concentration is at $\beta^{-0.5}$. Consequently, both α and β are constant when the inhibitory substrate and bacterial population are specified. However, while the Thiele modulus ϕ measures the intrabiofilm mass transfer resistances relative to the intrinsic reaction rate, it is an operating parameter, because the biofilm thickness δ—which is a controllable—is included in the definition of ϕ. In practice, the biofilm thickness can be controlled by allowing the expanded media bed height to vary over a narrow range. This can be accomplished by wasting the overgrown bioparticles accumulated near the top of the expanded media bed[25].

Fig. 2 presents the effects of α and β on η. According to the definition of the bioparticle effectiveness factor, $\eta > 1$ would indicate that a fluidized bioparticle is effective in the presence of substrate inhibition, because its overall substrate utilization rate would be greater than that in the bulk liquid.

Curve (A) in Fig. 2, which was prepared using $\alpha = 5$ and $\beta = 25$, shows that a thin biofilm grown on a fluidized bioparticle is more effective than a thick biofilm for a slightly

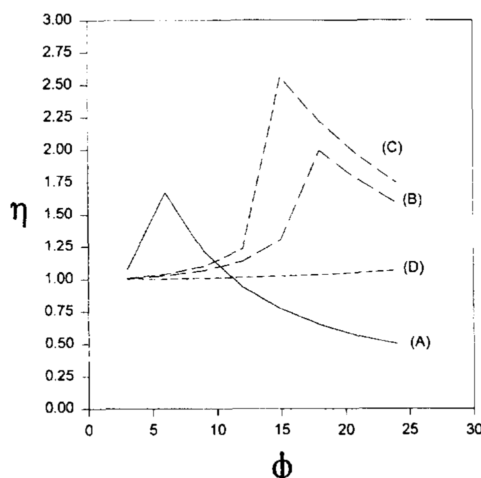

Fig. 2. The bioparticle effectiveness factor η plotted as a function of the Thiele modulus ϕ. See text for details.

inhibitory substrate (i.e. a small β value) whose utilization is of the first order at low concentrations (i.e. small α values). Because penetration of the substrate into a thick biofilm will be retarded, the substrate concentration in the biofilm—except for near the biofilm–liquid interface (Fig. 1)—will probably be reduced to levels that limit the substrate utilization. As a result, the overall bioparticle efficiency can be approximated using the first-order effectiveness factor expression [23,24], which states that η is less than unity and will decrease continuously with increasing ϕ, as shown in Fig. 2.

However, the substrate concentration in a thin biofilm may be reduced slightly to levels that are less inhibitive compared with the bulk liquid, so yielding $\eta > 1$. η will increase continuously with decreasing ϕ (or δ) until the substrate concentration in the bulk of the biofilm is within the inhibitory range. Then, η will decrease from a maximum value and asymptotically approach unity, because the substrate concentration in the biofilm will approach S_b.

Curve (B) in Fig. 2, which was prepared using $\alpha = 5$ and $\beta = 250$, shows that a thick biofilm grown on a fluidized bioparticle is more effective than a thin biofilm for an inhibitory substrate whose utilization is of the first order at low concentrations. Because the substrate concentration in a thick biofilm will be reduced to levels at which the substrate inhibition is less severe than that in the bulk liquid, the bioparticle efficiency will increase with increasing ϕ (or δ) until a threshold ϕ is reached. Beyond that, intrabiofilm mass transfer resistances will reduce the substrate concentration to first-order levels that limit the bioparticle efficiencies. However, over the range of ϕ values simulated, η is consistently greater than unity.

Curve (C) in Fig. 2, which was prepared using $\alpha = 25$ and $\beta = 250$, also shows that a thick biofilm grown on a fluidized bioparticle is preferable for an inhibitory substrate whose utilization is of zero-order utilization at low concentrations. Because the substrate concentration in a thick biofilm is now more likely to be reduced to zero-order levels than is that in a thin biofilm, the bioparticle efficiency is directly proportional to the percentage of the biofilm that is within the zero-order range and, therefore, is proportional to the biofilm thickness [12,20]. However, as the biofilm thickness exceeds a threshold value, the portion of the biofilm that is deprived of substrate (so is inactive) will increase, as a result of intrabiofilm mass transfer resistance. Consequently, η will decrease as shown in Fig. 2.

Curve (D) in Fig. 2 represents the cases in which the substrates are highly inhibitive (i.e. $\beta = 500$). No discernible enhancement in the bioparticle efficiencies can be anticipated because of the magnitude of substrate inhibition involved. For the ranges of β and ϕ values simulated, η falls within the range 1.001–1.065.

5. Model application

The bioparticle effectiveness factor η cannot be used alone to estimate the overall efficiency of a BFB reactor, despite its

usefulness for the assessment of the efficiency of a bioparticle. The growth of a biofilm changes the overall density of the bioparticles, so changing the expansion of the fluidized bed. Consequently, the number of bioparticles per unit of fluidized bed volume is another critical piece of information that is needed in addition to η for estimating the overall efficiency of a BFB reactor. For instance, the overall substrate utilization rate in a completely mixed BFB reactor is given by [25]

$$R_s = \frac{\rho \eta N k S_b}{K_s + S_b + (S_b^2/K_i)} \quad (9)$$

where R_s is the overall substrate utilization rate in a BFB reactor $(M/L^3 - T)$ and N is the number of bioparticles in the BFB reactor.

According to Eq. (9), R_s can be maximized under given circumstances, by maximizing ηN. This can be accomplished using a BFB design algorithm described elsewhere [25]. In this design algorithm, N is calculated independently, using the correlations developed on the basis of the fluidization mechanics that prevail in a BFB reactor [25].

6. Conclusions

The kinetics of substrate inhibition in a fluidized bioparticle are analyzed through the definition of a bioparticle effectiveness factor. The Runge–Kutta–Nyström method with a stringent convergence criterion is used to obtain numerical solutions over wide ranges of biological and mass transfer parameter values. The model predictions are summarized as follows.

- A bioparticle effectiveness factor greater than unity can be attained for a range of biofilm thicknesses, indicating that a bioparticle is effective in the attenuation of substrate inhibition.
- A thin biofilm grown on a bioparticle is more effective than a thick biofilm for a slightly inhibitory substrate whose utilization is of the first order at low concentrations. A thick biofilm may retard the transport of a substrate and limit its utilization, so yielding a first-order effectiveness factor that is less than unity.
- A thick biofilm grown on a bioparticle is better than a thin biofilm for an inhibitory substrate. A bioparticle is marginally better than its suspended growth counterpart when the substrate is highly inhibitory.
- The bioparticle effectiveness factor is a convenient parameter that can be used in conjunction with the fluidization correlations to estimate the overall efficiency of a biological fluidized bed reactor.

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Appendix A. Nomenclature

D_e	substrate effective diffusivity in the biofilm (L^2/T)
k	maximum substrate utilization rate $(M/M - T)$
K_i	inhibition constant (M/L^3)
K_s	half-velocity constant (M/L^3)
N	number of bioparticles in the BFB reactor
r	radial distance measured from the bioparticle center (L)
r_m	media particle radius (L)
r_p	bioparticle radius (L)
R	Haldane rate expression $(M/M - T)$
R_s	overall substrate utilization rate in a BFB reactor $(M/L^3 - T)$
S	substrate concentration in the biofilm (M/L^3)
S_b	bulk-liquid substrate concentration (M/L^3)
S^*	dimensionless substrate concentration in the biofilm $(= S/S_b)$
r^*	dimensionless radial distance measured from the bioparticle center $(= (r - r_m)/\delta)$

Greek letters

α	S_b/K_s
β	S_b^2/K_sK_i
δ	biofilm thickness (L)
δ^*	dimensionless biofilm thickness $(= \delta/r_p)$
ϕ	Thiele modulus $(= (\rho k/D_eK_s)^{0.5}\delta)$
η	bioparticle effectiveness factor
ρ	biofilm dry density (M/L^3)
ϕ	biofilm thickness (L)

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