$$\text{Da} = \frac{\text{maximum rate of bioconversion}}{\text{maximum rate of diffusion}} = \frac{r_{\max}}{(D_e/\delta)S_0} \tag{9.48}$$

where $r_{\max}$ is the maximum rate of bioconversion (mg S/l h), D_e is the effective diffusivity of the rate-limiting substrate, δ is the thickness of diffusion path (or liquid film), and S_0 is the bulk substrate concentration in liquid phase. When the film-theory model applies, D_e/δ is the mass transfer coefficient (i.e., $k_L = D_e/\delta$).

If Da >> 1, the rate of bioconversion is diffusion limited; for Da << 1, the rate is limited by the rate of bioconversion; and for Da ≈ 1, the diffusion and bioreaction rates are comparable. It is desirable to keep Da < 1 to eliminate diffusion limitations when the productivity of a cell population does not improve upon immobilization due to cell–cell contact and nutrient gradients.

Diffusional limitations may be external (that is, between fluid and support surface in adsorption and covalent binding), intraparticle (i.e., inside particles in entrapment, encapsulation, or immobilization in porous particles), or both. If the external mass transfer is limiting, an increase in liquid-phase turbulence should result in an increase in the reaction rate. In case of intraparticle mass-transfer limitations, a reduction in particle size or an increase in the porous void fraction of the support material should result in an increase in the rate of the bioreaction.

In Chapter 3 we discussed in reasonable detail a mathematical model of the interaction of diffusion and reaction for surface immobilized or entrapped biocatalysts. These models apply directly to immobilized cells when the kinetics of bioconversion are described by a Michaelis–Menten type of kinetic expression. Thus, the reader may wish to consult Chapter 3 again.

Another interesting case is to consider biofilms where we allow cell growth. Models for immobilized enzymes have no terms for biocatalyst replication, so this case presents a new problem.

The thickness of a biofilm or the size of microbial floc increases with time during the growth phase. A *microbial floc* is an aggregation of many cells, and in some processes these aggregates can be more than 1 mm in diameter. However, since the rate of increase in biofilm thickness is much slower than the rate of substrate uptake, the system can be assumed to be at quasi-steady state for relatively short periods. The simplest case is to assume that the system is at quasi-steady state and all the cells inside the biofilm are in the same physiological state. In this situation we write a steady-state substrate balance within the biofilm by using average kinetic constants for the biotic phase (living cells).

A differential material balance for the rate-limiting substrate within the biofilm (see Fig. 9.11) yields at steady state

$$D_e \frac{d^2S}{dy^2} = \frac{1}{Y_{X/S}} \frac{\mu_m S}{K_s + S} X \tag{9.49}$$

where D_e is the effective diffusivity (cm^2/S) and $Y_{X/S}$ is the growth yield coefficient (g cells/g substrate).