

DIFFUSION INTO MICROBIAL AGGREGATES

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Abstract—Theoretical work in the biological waste treatment field has been directed at modeling substrate removal processes in fluidized and fixed film microbial systems in terms of the basic rate processes. Much of the research has been directed at delineating the rate limiting steps to simplify the problem. Various researchers have shown that the rate limiting step can be mass transfer through the microbial aggregate to the active sites at the cells. Therefore, any mechanistic model that incorporates mass transfer must be sensitive to variations in the reactant diffusion coefficient through floc material. A direct measure of mass flux has been developed to determine the variations in the diffusion coefficients of glucose and oxygen through microbial aggregates grown under various experimental conditions. A factorial analysis indicated significant changes in the molecular diffusion coefficient with variations in sludge age and carbon–nitrogen ratio in the growth media. Oxygen diffusivity varied from 20 to 100% of its value in water, glucose from 30 to 50%. A simple zero order diffusion–reaction kinetic model for spherical floc was constructed. It indicated that oxygen diffusion limitations are possible in the high rate activated sludge processes with large floc particles.

NOMENCLATURE

C_s	species (substrate) concentration	mg l^{-1}
C_f	bulk liquid (at the floc surface) species concentration	mg l^{-1}
D_s	overall substrate diffusion coefficient across MTA	$\text{cm}^2 \text{s}^{-1}$
$D_{s,f}$	substrate diffusion coefficient in floc	$\text{cm}^2 \text{s}^{-1}$
k	zero order rate constant	$\frac{\text{mg s l}^{-1}}{\text{mg MLSS l}^{-1} \text{s}^{-1}}$
r	radial distance from floc center	cm
r_f	radius of spherical floc particle	cm
R	substrate reaction rate	mg S s^{-1}
t	time	s
v	reservoir volume	cm^3
x	length	cm
ρ_f	dry density of floc	mg l^{-1}
θ	sludge age	days.

INTRODUCTION

The reactions occurring in a biological reactor are of considerable complexity. Swilley (1964) noted that reactor kinetics can be an expression of the interplay among the various rate processes. Reaction rates under a variety of circumstances could be controlled by the transport of reactants to the microorganisms. Pasveer (1954) and Wuhmann (1963) speculated that the most significant rate process was the diffusion of reactants through the floc or films surrounding the organisms in the waste treatment reactors.

To test this hypothesis, a number of researchers attempted to measure the diffusion coefficients of various reactants through biological materials. Tomlinson (1966) measured the diffusivity of oxygen through slime grown on the inner surface of an inclined rotating tube partially submerged in water. The technique involved measurement of nitrite production in the anaerobic inner layer as an indicator of the

degree of oxygen penetration into the film. One oxygen diffusion coefficient was calculated to be approximately two-thirds the value for water.

Mueller (1966) measured the oxygen diffusion coefficient in a pure strain of *Zooglea ramigera*—a floc forming bacterium. The method involved the measurement of the oxygen uptake by the floc particles under a variety of dissolved oxygen concentrations. The technique was based on the assumption that floc particles exhibited maximum uptake when saturated with oxygen, but decreased as the external dissolved oxygen levels were lowered and anaerobic floc cores were developed. The curvilinear portion of the oxygen uptake curve was evaluated for a given floc size and geometric shape. The results indicated that the oxygen diffusivity was as low as 8% of that in water.

However, the accuracy of the measurement was largely dependent on a representative floc sizing technique, which was difficult due to irregular nature of the floc particles. Baillod (1970) used methods similar to Mueller to determine the glucose diffusion coefficient through *Zooglea ramigera*. Its effective diffusivity was calculated at 8% of that in water.

Pipes (1973) used an experimental apparatus identical to the one delineated in this paper to measure the diffusion coefficient of glucose through a mixed culture maintained in a fluidized reactor. He varied the carbon–nitrogen ratio of the growth media and cultured the organisms with two different substrates—glucose and methanol. Significant differences in the diffusivities were shown on the order of 6–60% of that in water, by varying the growth conditions.

Williamson (1973) measured the diffusivities of ammonia, nitrate, and oxygen through a film formed by filtration and compression of a fluidized culture

Table 1. Experimental reactant diffusion coefficient measurements from the literature

Author	Reactant	Diffusivity $10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$D_{\text{floc}}/D_{\text{H}_2\text{O}}$ $\times 100\%$	Biomass type	Growth system	Procedure
Tomlinson (1966)	Oxygen	1.5	70	Bacterial slime	Rotating tube	Reaction products analysis
Mueller (1966)	Oxygen	0.21	8	Fungal slime <i>Zooglea</i>	Fluidized reactor	Nonlinear curve fit
Baillo (1969)	Glucose	0.048	8	<i>Zooglea</i> <i>ramigera</i>	Fluidized reactor	Nonlinear curve fit
Pipes* (1974)	Glucose	0.06–0.6	10–100	Mixed culture	Fluidized reactor	Two chamber
Williamson (1974)	Oxygen	2.2	90	Nitrifier culture	Fluidized reactor	Two chamber
Matson* (1974)	Ammonia	1.3	80	Mixed culture	Fluidized reactor	Two chamber
	Nitrate	1.4	90			
	Oxygen	0.4–2.0	20–100			
	Glucose	0.06–0.21	10–30			

* Tests conducted under a variety of experimental conditions.

of nitrifying organisms. Two completely mixed chambers were separated by biological film. The various reactants were allowed to diffuse through the film from the high concentration chamber to the low one. The calculated diffusion coefficients ranged from 80 to 90% of that in water. Table 1 lists all reactant diffusion coefficient determinations previously described.

EXPERIMENTAL

A factorial design was used to test the significance of sludge age and the growth media conditions on reactant diffusivity and reaction rate in fluidized biological aggregates. The two variables were studied at three levels, with two different reactants—oxygen and glucose.

The biological material was extracted from nine fluidized aerobic reactors operating under three sludge ages (1, 5 and 20 days) and three growth media conditions (carbon-nitrogen (C/N) ratios of 5, 20 and 50). The growth media consisted of glucose and ammonium chloride with the other essential inorganic nutrients in excess.

The mass fluxes of the reactants through biological material were measured in an apparatus consisting of two well-mixed chambers separated by a membrane-template assembly (MTA). A diagram of the apparatus is shown in Fig. 1. It was a modified Millipore filtration apparatus. The MTA consisted of a perforated brass template of uniform thickness containing the biological material and a membrane on each side to insure immobilization of the biomass. The membranes were Silastic silicone, medical grade, 75 μm thick for the oxygen diffusivity experiments. These membranes had a low resistance to oxygen diffusion and a high resistance to the other reactants. For the glucose experiments, Millipore membrane filters, type HA, 0.45 μm pore size, were used.

The biological material was prepared by concentration in a centrifuge at low speed, then deactivation by either mercuric chloride or ultraviolet radiation. A series of experiments using nonmetabolizable salts and live organisms as well as deactivated ones were made to test the effects of the deactivating agents on substrate diffusivity. No differences were found indicating that the deactivation process had no effect on the diffusion process (Matson, 1975).

The most critical step in the procedure involved placement of the concentrated floc into the MTA. One prewetted membrane was placed under the template. The floc

was then carefully scraped with a metal spatula into the holes in the template. The spreading process was critical in that each hole had to be filled precisely. The packed template was checked visually for consistent translucency through all holes. The second membrane was placed on top of the template surface and the membrane-template assembly was ready to insert in the diffusion apparatus. Thus, the total volume and thickness of the biological material was fixed and known.

For the oxygen diffusivity measurement, the Millipore apparatus was modified by the insertion of a dissolved oxygen probe in the lower chamber. The lower chamber was filled with deionized water containing dissolved oxygen (DO) in the range of 8–9 mg l^{-1} . The upper chamber was filled with water with DO in the range of 30–40 mg l^{-1} . A diffuser was mounted inside the upper chamber, and connected to a pure oxygen source. During the course of a run, pure oxygen was diffused into the upper chamber at a rate of 100 ml min^{-1} to maintain the high DO concentration and to provide mixing. Oxygen diffused from the upper chamber through the membrane-template assembly into the lower chamber where the DO level was monitored by an oxygen probe. Results were checked by Winkler DO tests before and after each run. All experiments were run in duplicate at 20°C in a constant temperature room.

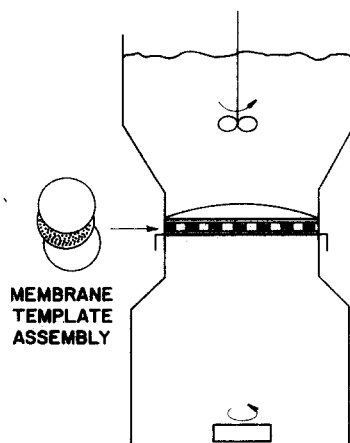


Fig. 1. Diffusion coefficient measurement apparatus (cut away view).

For the glucose measurements, high concentrations (100–1000 mg l⁻¹) were contained in the lower chamber of the apparatus. Small (2 ml) samples were taken periodically over 12 h from the upper chamber and stored for later analysis. Glucose concentrations were measured by the Glucostat test (Worthington Chemicals).

For the activity of the biological material, glucose uptake rates were measured in each slurry reactor prior to testing. Approximately 100 mg l⁻¹ of glucose was added to the reactor. Samples were periodically collected, filtered, and analyzed for glucose concentration by the Glucostat method. Solids concentrations were evaluated by total solids measurements. Activity was thus defined as the glucose uptake rate per unit solids in the reactor.

THEORY

The experimental apparatus consists of two well mixed reservoirs separated by the template sandwich through which substrate diffuses. The membranes on each side of the template prevent convective molecular transport. The floc in the template sandwich is deactivated, thus no reaction is occurring.

A mass balance over either reservoir follows.

Diffusional flux \times surface area = change in reservoir concentration

$$D_s \left(\frac{dc}{dx} \right)_s \cdot A = V \frac{dc}{dt} \quad (1)$$

where A = effective area of transfer in the template sandwich, D_s = overall diffusion coefficient of diffusing species through the template-membrane assembly, $[(dc/dx)]_s$ = overall concentration drop across the assembly, V = reservoir volume, c = species concentration, c_0 = initial species, t = time.

If the diffusional length across the sandwich is constant, and if the species concentration in the concentrated reservoir is considered constant at c_0

$$\left(\frac{dc}{dx} \right)_s = \frac{c_0 - c}{L}$$

where L is the template sandwich thickness.

The expression for the reservoir mass balance is

$$V \frac{dc}{dt} = \frac{D_s A}{L} (c_0 - c). \quad (2)$$

Solving for the diffusion coefficient yields

$$D_s = \frac{LV (dc/dt)}{A(c_0 - c)}. \quad (3)$$

The diffusional resistance through the sandwich is

$$\left(\frac{L}{AD_s} \right)_{\text{Total}} = \frac{(c_0 - c)}{V} \times \frac{1}{(dc/dt)}. \quad (4)$$

The total diffusional resistance consists of two membranes and the template. Therefore,

$$\left(\frac{L}{AD_s} \right)_{\text{Total}} = 2 \left(\frac{L}{AD_M} \right)_{\text{Membrane}} + \left(\frac{L}{AD_T} \right)_{\text{Template}}. \quad (5)$$

Each membrane has an effective surface area of 13.85 cm², and the surface area of the template (holes)

is 4.5 cm². The resistance and diffusivity of interest is that through the holes in the template.

$$D = \frac{(L/A)}{\left(\frac{L}{AD_s} \right) - 2 \left(\frac{L}{AD_M} \right)}. \quad (6)$$

In solving equation (6), $(L/AD_s)_{\text{Total}}$ can be determined experimentally by using equation (4). The concentration difference is measured, as (dc/dt) , by periodic sampling. The volume in the reservoir is known. The membrane resistance (L/AD_M) , specifically the species diffusivity, must be calculated from experimental data in which the membrane is placed in the apparatus and tested.

RESULTS

The analysis of variance technique involved a comparison of the error in replicate experiments expressed as variance with the differences between experiments differing by a change in variable or factor also expressed as variance. The ratio of variances between replicate experiments and among the factorial experiments was denoted as the $F_{\text{test}} = \sigma_{\text{between}}/\sigma_{\text{among}}$. Significance to some level of confidence was shown by the ratio, the higher the ratio, the greater the level of confidence that a given factor was significant.

The analysis of variance indicated that sludge age and C/N ratio had significant effect (95% level) on the diffusion coefficients of oxygen in the biological material. Sludge age and C/N ratio in the growth media also significantly affected the glucose unit reaction rate. A summary of the factorial analysis is shown in Table 2.

Table 2. Results of the factorial analysis to determine the effects of sludge age (θ) and carbon-nitrogen (C/N) ratio in growth media on diffusion coefficients in microbial aggregates

Effect	Sum of squares	Degrees of freedom	Mean sum of squares	Variance ratio
(A) Oxygen				
C/N	1.86	2	0.929	53.6
θ	2.19	2	1.097	63.5
C/N \times θ	0.80	4	0.200	11.7
Residual	0.156	9	0.0173	—
(B) Glucose				
C/N	0.00105	2	0.00053	4.8
θ	0.01958	2	0.00979	89
C/N \times θ	0.1576	4	0.0394	35.7
Residual	0.00104	9	0.00011	—
(C) Glucose reaction Rate				
C/N	41.14	2	20.57	6.02
θ	28.64	2	14.32	4.20
Residual	13.65	4	3.41	—

$F_{0.05} (2, 9) = 4.26$.

$F_{0.05} (4, 9) = 3.63$.

Variance ratios greater than stated $F_{0.05}$ values indicate significant effects at the 95% level. Numbers in parentheses refer to degrees of freedom for effects and residuals.

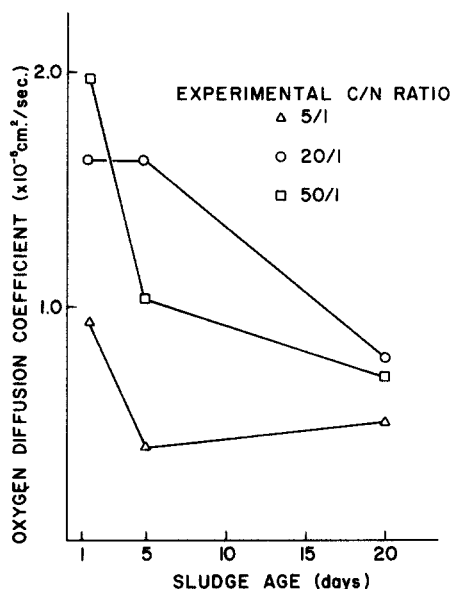


Fig. 2. Oxygen diffusion coefficient as a function of sludge age and carbon-nitrogen ratio.

The oxygen diffusion coefficient decreased with longer sludge age and lower C/N ratio growth media (Fig. 2). The trend for glucose was not consistent. The glucose diffusivity in biological material averaged 30% of that in water (Fig. 3). The glucose unit reaction rate decreased with longer sludge age and higher C/N ratios (Fig. 4).

Biological material was also obtained from three waste treatment plants in the Houston area. The results of the diffusion experiments are listed in Table 3. The values for the oxygen and glucose diffusion coefficients obtained were not markedly different from those found in the laboratory experiments.

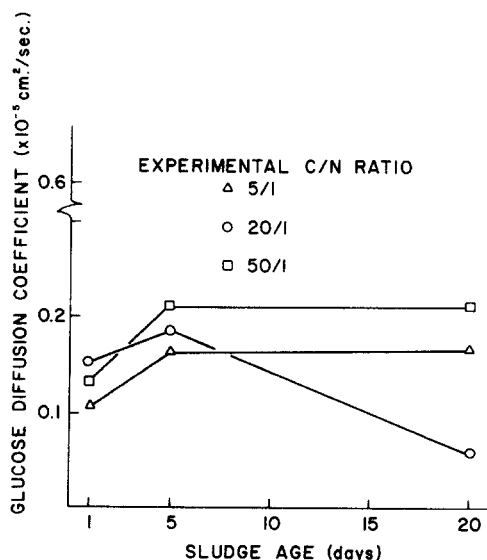


Fig. 3. Glucose diffusion coefficient as a function of sludge age and carbon-nitrogen ratio.

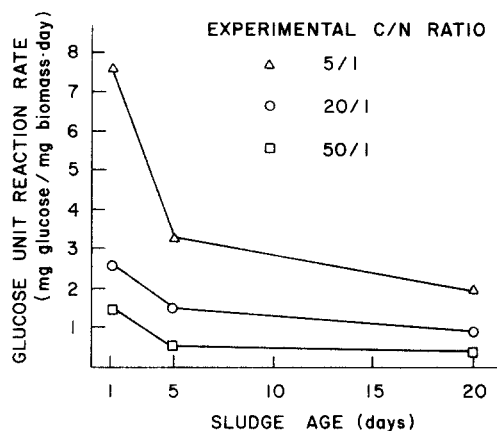


Fig. 4. Glucose unit reaction rate as a function of sludge age and carbon-nitrogen ratio.

DISCUSSION

The ability of ions and molecules to diffuse through biological materials depends on a number of factors. The sizes and distribution of holes or pores as well as the tortuosity of the various pathways will be significant. Intermolecular bonding may also play a role. A mixed culture of microorganism is a very complex material to analyze. The extracellular material that binds the matrix may vary from long chains of stringy polysaccharide to gumlike capsular compounds.

In these experiments, C/N ratio in the growth media was increased from 5 to 50 per l. to stimulate the production of microbial polymers. No tests to determine polymer concentrations in the biomass were made. However, Dydek (1971) found significant increases in carbohydrate content of mixed cultures going from C/N's of 15-50 per l. Sludge age or mean cell residence time was varied from one to twenty days. Sludge age defines microbial growth rate, giving an indication of the physiological state of the biomass. Typically, low sludge ages are characterized by high microbial growth rates, with primarily new cell formation and minimal production of extracellular material. Long sludge ages result in mature cultures with significant amounts of extracellular material. The

Table 3. Diffusion coefficients of oxygen and glucose in floc from various biological waste water treatment plants

Source of floc Type of plant	Diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)		Sludge Age (days)
	Oxygen $\times 10^{-5}$	Glucose $\times 10^{-5}$	
Municipal (domestic)	$1.37 \pm 2\%$	$0.25 \pm 20\%$	8-10
Municipal (combined domestic- industrial)	$1.17 \pm 21\%$	$0.35 \pm 10\%$	5
Industrial (petrochemicals)	$0.85 \pm 25\%$	$0.18 \pm 14\%$	20+
Pure water	$2.2 \pm 25\%$	$0.67 \pm 10\%$	

glucose reaction rate was high at low sludge ages and low C/N ratio growth media, indicating high activity. These conditions resulted in the highest resistance to oxygen diffusion. No definite trend was noted for glucose diffusion. The glucose diffusivity was fairly insensitive to all the factors. This is at variance with the findings of Pipes (1974), who found greater resistances to glucose diffusion at higher C/N ratios in the growth media.

Microbial populations in each of the nine experimental reactors displayed different macroscopic characteristics (color, settleability) which may have reflected a particular microbial species predominance. Consequently, the most important factor in determining the diffusional characteristics of biological material could have been the particular microbial species in residence. Microbial species differences, also, may have accounted for the wide range in reported diffusion coefficients in the literature. However, no effort was made to identify predominating microbial species in this study.

SIGNIFICANCE OF RESULTS

The reactant diffusion coefficient has significance if mass transport through the biological aggregate is potentially rate limiting. A number of researchers have incorporated this mass transfer step into mathematical models of biological reactors. Characklis (1967), Atkinson (1967), Jank (1971), Grieves (1972), Mehta (1972), and Williamson (1973) developed such models to explain experimental results obtained with fixed film reactors, while Swilley (1964), Mueller (1966), Baillod (1970), and Matson (1973) modeled fluidized reactors. The models indicated that overall reaction rates could be sensitive to reactant diffusivity. This was particularly true of fixed films where thick microbial aggregates were likely.

The ability of a given reactant to penetrate into a microbial film is also a function of film thickness, microbial activity, reactant bulk liquid concentration, and reaction stoichiometry. Mass transfer limitations are possible when: the liquid or biological film is so thick that the reactant cannot penetrate through it; the microbial activity is so high that the reactant is consumed in the outer layer; or reactant concentration in the bulk liquid is so low that insufficient driving gradient is available.

Reaction stoichiometry links together the electron donor (substrate) and electron acceptor (e.g. oxygen) which will establish various reaction zones in a mass transfer controlled film, Matson (1972). For example, if a given substrate will penetrate further into a biological film than oxygen, two reactions will be occurring simultaneously: an aerobic reaction near the surface and an anaerobic reaction where oxygen does not penetrate. If oxygen penetrates deeper into the film than the substrate, the reaction will be aerobic (Fig. 5). The unused zone where the reactant is not penetrating is pictured as the endogenous zone. The

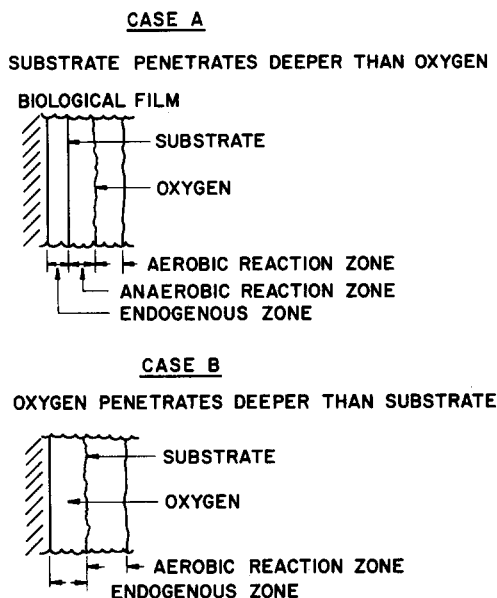


Fig. 5. Reaction zones in a fixed film.

term available reaction potential (ARP) has been used to describe a reservoir of microbial activity that can be utilized if the bulk liquid reactant concentration should rise, McLellan (1969).

KINETIC MODEL

Steady state diffusion and reaction of a given substrate through a spherical floc matrix containing a homogenous concentration of microorganisms can be described by the following equation:

$$\text{Steady state} \quad \frac{\partial C_s^0}{\partial t} + V \nabla C_s \quad \text{No convection}$$

diffusion-reaction

$$0 = D_{sf} \nabla^2 C_s - R$$

In spherical coordinates:

$$D_{sf} \left[\frac{\partial^2 C_s}{\partial r^2} + \frac{2\partial C_s}{r \partial r} \right] = R$$

in which D_{sf} is the diffusivity of a given substrate through the floc matrix, C_s is the concentration of substrate, r is the radial distance measured from the floc center, and R is the rate of substrate reaction.

Analytical solutions can be obtained if the reaction order is considered either zero or first between the substrate and the micro-organisms. The zero reaction order case is considered herein. The first order solution is shown in Appendix A. The actual reaction order inside the floc matrix is a function of the substrate, organism species, their physiological state, etc.

For the zero reaction order case, the reaction rate can be expressed as:

$$R = \rho_f k$$

in which ρ_f is the floc density and k is the reaction rate constant.

The boundary conditions are:

- (1) C_s finite for all r
- (2) $C_s = C_f$ at $r = r_f$.

The integration yields:

$$C_f - C_s = \frac{\rho_f k}{6 D_{sf}} (r_f^2 - r^2).$$

Of prime interest is the depth in the floc at which substrate disappears. Solving the above equation for r at the point $C_s = 0$, yields

$$r = \left[r_f^2 - \frac{6 C_f D_{sf}}{\rho_f k} \right]^{1/2}.$$

The distance substrate penetrates into the floc particle is $(r_f - r)$. Thus, the penetration of oxygen or any substrate into a floc particle can be calculated given the reaction rate constant, the diffusivity (D_{sf}) and the size and density of the floc particle. The equation can be rearranged and simplified to calculate the oxygen concentration at which diffusional limitations occur at a given floc radius. The radius (r) defining the distances from the center of the spherical floc oxygen penetrates is set to equal zero. The equation yields:

$$C_s = \frac{\rho_f k}{6 D_{sf}} \times r_f^2.$$

To illustrate the utility of this equation and the significance of diffusional limitations in floc, a so-called typical domestic activated sludge process was defined in Appendix B. A zero order reaction rate constant was calculated given the assumptions notes. Three cases were then described. Case I showed the parameters D_{sf} , ρ_f , and k that may have represented those found in the "average" aeration basin. Case II represented an estimate of the high rate processes. Case III represented the most conservative estimates of the process parameters. The range in the densities was selected from Mueller (1966), Williamson (1973), Hoehn (1973), and Kornegay (1968), the latter two representing biofilms. Floc particles appeared to have densities in the same range as biofilms. The range in floc oxygen diffusivities was taken from Williamson (1973) and Matson (1975) (Table 4).

For Case II, "high rate," the rate constant was double that of the other two cases; the density was

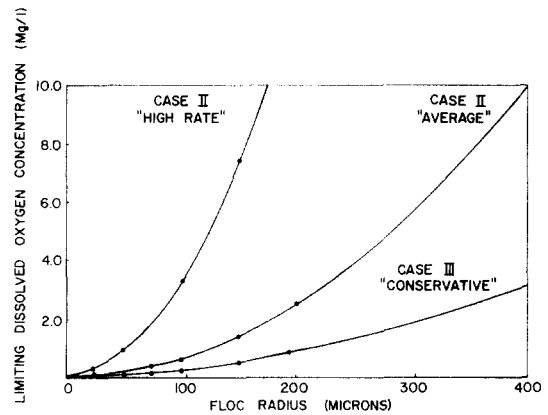


Fig. 6. Oxygen diffusion limitations as a function of floc size.

highest and diffusivity, the lowest. This case illustrates the most severe oxygen diffusion limitations, as shown in Fig. 6. Even at low floc sizes (r less than $100 \mu\text{m}$) the minimum dissolved oxygen concentration required to keep the floc aerobic is greater than 3.0 mg l^{-1} .

Floc size is largely a function of the shear forces in the aeration basin. Large floc particles (e.g. $r \geq 200 \mu\text{m}$) are generally found in basins with gentle agitation such as diffused air. Smaller floc sizes have been noted in basins that were mechanically agitated. Of course, floc particles are not spherical, and thus it is extremely difficult to size an irregular particle. Mueller (1966) relates these difficulties.

For Case I, the hypothetical "average" situation, the oxygen diffusivity was taken as an average of the actual field measurements (Table 3). As shown in Fig. 6, dissolved oxygen may become limiting at larger floc sizes in convention air activated sludge systems, which are usually designed to maintain a minimum of 2.0 mg l^{-1} dissolved oxygen in the basin.

In Case III, the most conservative estimates of parameters were made. Oxygen diffusion limitations would probably not result in this situation irregardless of floc size.

Many assumptions were made to arrive at these conclusions which may, or may not be valid, and will affect the results. It was assumed that the electron donor substrate was not diffusion limited in the floc particle. In completely stirred tank reactors, the substrate concentration throughout the basin is low, and

Table 4. Parameter estimates for three sewage treatment plant cases

Parameters	Case I (average)	Case II (high rate)	Case III (conservative)
Floc density (ρ_f) $\text{mg l}^{-1} \times 10^4$	7.5	10.0	5.0
Oxygen diffusivity (D_{sf}) $\text{cm}^2 \text{ s}^{-1} \times 10^{-5}$	1.0	0.5	2.0
Rate constant (k) $\text{mg O}_2 \text{ l}^{-1}$			
$\text{mg MLSS l}^{-1} \cdot \text{h}^{-1} \times 10^{-3}$	1.8	3.6	1.8

may, indeed, only diffuse into the outer shell of the floc. In this case the substrate will be diffusion limited. The stoichiometry of the reaction as well as the respective oxygen and substrate concentrations will influence the true diffusional regime in the floc particles. See Matson (1972, 1973, 1975) for a discussion of these ramifications. The active sites (organisms) may not be evenly dispersed throughout the floc. Most likely, the highest organism concentration will be at or near the surface. The non-spherical nature of the floc particles is probably the most serious limitation to the model. Any shape irregularity will increase the surface area to volume ratio and thereby lower the potential for diffusion limitations. Lastly, the zero order reaction assumption creates a sharp division between an aerobic zone and anaerobic zone in a floc particle. On the other hand, a first order rate assumption forces an exponential decrease in oxygen concentration approaching but not reaching zero at the floc center. Both zero order and first order reaction zones probably exist in a floc particle. A Monod type hyperbolic relationship may be most appropriate.

CONCLUSIONS

1. Oxygen and glucose diffusion coefficients in biological floc have been measured and found to be lower than their values in pure water in most cases. This indicates the potential for oxygen and substrate limitations in biofilms.

2. A simple zero order diffusion-reaction model was constructed. The results indicated the potential for oxygen diffusion limitations in high rate treatment processes and "average" processes containing large floc particles.

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APPENDIX A

Consider steady state diffusion with no convection into a spherical floc particle. For a first order reaction

$$D \left(\frac{d^2c}{dr^2} + \frac{2}{r} \frac{dc}{dr} \right) = Kc$$

or

$$\frac{d^2c}{dr^2} + \frac{2}{r} \frac{dc}{dr} - \frac{K}{D} c = 0$$

if

$$c = \frac{X}{r}$$

then

$$\begin{aligned} \frac{dc}{dr} &= \frac{d}{dr} \left(\frac{X}{r} \right) = \frac{1}{r} \frac{dX}{dr} - \frac{1}{r^2} X; \frac{d^2c}{dr^2} \\ &= \frac{1}{r} \frac{d^2X}{dr^2} - \frac{2}{r^2} \frac{dX}{dr} + \frac{2}{r^3} X \end{aligned}$$

so

$$\begin{aligned} \frac{d^2c}{dr^2} + \frac{2}{r} \frac{dc}{dr} - \frac{1}{r} \frac{d^2X}{dr^2} - \frac{2}{r^2} \frac{dX}{dr} + \frac{2}{r^3} X \\ + \frac{2}{r} \left(\frac{1}{r} \frac{dX}{dr} - \frac{1}{r^2} X \right) = \frac{1}{r} \frac{d^2X}{dr^2} \end{aligned}$$

And the differential equation for X is

$$\frac{d^2X}{dr^2} - \frac{K}{D} X = 0$$

with solution

$$X = A \cos \sqrt{\frac{K}{D}} r + B \sin \sqrt{\frac{K}{D}} r.$$

and \therefore

$$c = \frac{X}{r}$$

$$c = A \frac{1}{r} \cos \sqrt{\frac{K}{D}} r = B \frac{1}{r} \sin \sqrt{\frac{K}{D}} r$$

From this solution

$$\frac{dc}{dr} = A \left[-\frac{1}{r} \sqrt{\frac{K}{D}} \sin \sqrt{\frac{K}{D}} r - \frac{1}{r^2} \cos \sqrt{\frac{K}{D}} r \right] + B \left[\frac{1}{r} \sqrt{\frac{K}{D}} \cos \sqrt{\frac{K}{D}} r - \frac{1}{r^2} \sin \sqrt{\frac{K}{D}} r \right]$$

We may rewrite c and $\frac{dc}{dr}$ as

$$C = A \sqrt{\frac{K}{D}} \left[\frac{\cos \sqrt{\frac{K}{D}} r}{\sqrt{\frac{K}{D}} r} \right] + B \sqrt{\frac{K}{D}} \left[\frac{\sin \sqrt{\frac{K}{D}} r}{\sqrt{\frac{K}{D}} r} \right]$$

and

$$\frac{dc}{dr} = A \left(\frac{K}{D} \right) \left[-\frac{\cos \sqrt{\frac{K}{D}} r}{\left(\sqrt{\frac{K}{D}} r \right)^2} - \frac{\sin \sqrt{\frac{K}{D}} r}{\sqrt{\frac{K}{D}} r} \right] + B \left(\frac{K}{D} \right) \left[-\frac{\sin \sqrt{\frac{K}{D}} r}{\left(\sqrt{\frac{K}{D}} r \right)^2} + \frac{\cos \sqrt{\frac{K}{D}} r}{\sqrt{\frac{K}{D}} r} \right]$$

which are more useful for considering the limits of these functions produced by the boundary conditions

$$(1) \quad c = c_0 \quad \text{at} \quad r = r_f$$

$$(2) \quad \frac{dc}{dr} = 0 \quad \text{at} \quad r = 0$$

it also seems reasonable to require that c remain finite at $r = 0$.

Consider

$$\left. \frac{dc}{dr} \right|_{r=0} = 0 \text{ first.}$$

Let

$$R = \sqrt{\frac{K}{D}} r,$$

then

$$\frac{dc}{dR} = A \sqrt{\frac{K}{D}} \left[-\frac{\cos R}{R^2} - \frac{\sin R}{R} \right] + B \sqrt{\frac{K}{D}} \left[-\frac{\sin R}{R^2} + \frac{\cos R}{R} \right]$$

Now

$$\lim_{R \rightarrow 0} \left[-\frac{\sin R + R \cos R}{R} \right] \text{ is of form } \frac{0}{0}$$

hence

$$\lim_{R \rightarrow 0} \left[-\frac{\sin R + R \cos R}{R^2} \right] = \lim_{R \rightarrow 0} \left[-\frac{\cos R + \cos R - R \sin R}{2R} \right] = \frac{1}{2} \lim_{R \rightarrow 0} \sin R = 0.$$

But

$$\lim_{R \rightarrow 0} \left[-\frac{\cos R - R \sin R}{R^2} \right]$$

is of form

$$\frac{\text{const}}{0}$$

and hence undefined.

\therefore require

$$A \sqrt{\frac{K}{D}} = 0.$$

Since

$$\sqrt{\frac{K}{D}} \neq 0$$

must have $A = 0$. Since

$$\lim_{R \rightarrow 0} \frac{\sin R}{R} = \lim_{R \rightarrow 0} \cos R = 1$$

and

$$\lim_{R \rightarrow 0} \frac{\cos R}{R} \text{ is of form } \frac{\text{const}}{0}$$

so that $A = 0$ is also condition that c remain finite at $r = 0$.

Thus

$$C = B \frac{1}{r} \sin \sqrt{\frac{K}{D}} r.$$

The boundary condition $c = c_0$ at $r = r_f$ gives

$$c_0 = B \frac{1}{r_f} \sin \sqrt{\frac{K}{D}} r_f.$$

If

$$\sqrt{\frac{K}{D}} r_f \neq n\pi, n \text{ an integer, then}$$

$$B = \frac{C_0 r_f}{\sin \frac{K}{D} r_f}$$

And \therefore

$$C = C_0 \frac{r_f}{r} \frac{\sin \sqrt{\frac{K}{D}} r}{\sin \frac{K}{D} r_f}$$

APPENDIX B

Calculation of the zero order reaction rate constant for a typical domestic sewage treatment plant.

Assume: Aeration time = 6 h

$$\text{BOD}_5 \text{ in} = 240 \text{ mg l}^{-1}$$

$$\text{BOD}_5 \text{ out} = 24 \text{ mg l}^{-1}$$

Rate BOD_5 degradation = rate of oxygen consumption

$$1 \text{ g BOD}_5 \text{ degraded} = 1 \text{ g oxygen consumed}$$

$$\text{MLSS conc} = 2000 \text{ mg l}^{-1}$$

$$k = \frac{\text{BOD in} - \text{BOD out}}{\text{MLSS} \times \text{aeration time}} = \frac{(240 - 24 \text{ mg l}^{-1}) \text{ l mg l}^{-1} \text{ O}_2 \text{ mg}^{-1} \text{ l}^{-1} \text{ BOD}}{2000 \text{ mg l}^{-1} \times 6 \text{ h}}$$

$$k = 1.80 \times 10^{-3} \frac{\text{mg O}_2 \text{ l}^{-1}}{\text{mg l}^{-1} \text{ MLSS} \cdot \text{h}}$$

APPENDIX C

Sample calculation of oxygen diffusion into a spherical floc particle.

Given:

$$D_{sf} = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

$$r_f = 0.020 \text{ cm}$$

$$\rho_f = 5.0 \times 10^4 \text{ mg l}^{-1}$$

$$k = \frac{36 \text{ mg O}_2 \text{ l}^{-1}}{10^3 \text{ mg MLSS l}^{-1} \text{ h}^{-1}} \times \frac{\text{h}}{3600 \text{ s}}$$

$$= 1.0 \times 10^{-5} \frac{\text{mg O}_2 \text{ l}^{-1}}{\text{mg MLSS l}^{-1} \text{ s}}$$

$$c_f = 6 \text{ mg O}_2 \text{ l}^{-1}.$$

Calculate: the distance oxygen penetrates into the floc particles

$$r = \left[r_f^2 - \frac{6 c_f D_{sf}}{\rho_f K} \right]^{1/2}$$

$$= \left[(2.0 \times 10^{-2} \text{ cm})^2 - \frac{6 \times 6 \text{ mg O}_2 \text{ l}^{-1} \times 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}}{5.0 \times 10^4 \text{ mg MLSS l}^{-1} \times 1.0 \times 10^{-5} \frac{\text{mg O}_2 \text{ l}^{-1}}{\text{mg MLSS} \cdot \text{s}}} \right]^{1/2}$$

$$= 0.045 \text{ cm}$$

$$= 45 \mu\text{m}$$

$$r_f - r = 200 - 45 = 155 \mu\text{m}.$$