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THEORETICAL CONSIDERATION ON THE TREATMENT CHARACTERISTICS OF VOLATILE FATTY ACIDS IN COMPLETELY MIXED ANAEROBIC BIOFILM REACTORS

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A mathematical biofilm model was developed considering substrate decomposition and diffusion rates in a regime of consecutive reactions. By using the model, removal rates of propionate, butyrate and an acid mixture within anaerobic biofilms, as well as the rates of intermediate acetate, were analized to obtain biofilm parameters which specified treatment characteristics.

Variations of the biofilm parameters, i. e. dimensionless biofilm property (M_A, M_P, M_B) and operation parameter (Pe_A, Pe_P, Pe_B), were represented as a function of the attached biomass. By using these parameters, treatment characteristics of anaerobic biofilm reactors in the methane production phase were simply and accurately evaluated.

Keywords: *biofilm model, biofilm reactor, consecutive reaction, methanogenesis, volatile fatty acid*

1. INTRODUCTION

In recent years, performances of anaerobic biofilm reactors have been studied for the purpose of developing a low energy consumptive system in wastewater treatments[3]. Anaerobic decomposition processes of complex organics are usually divided in two stages which are the acid production phase and the methane production phase[7]. According to these processes, the performances are considered to depend on the bio-reaction rates in each phase. On the other hand, substrate (organics) removal rates are known to be affected by diffusion rates with an increment of attached biomass[1]. Therefore, analyses of substrate diffusion and decomposition rates are important to evaluate the performances rationally. From this point of view, the authors[2] analized the acetate removal rates within anaerobic biofilms as a fundamental study on the methane production phase. However, decomposition processes in this phase are multi-reactions in which propionate and butyrate, besides acetate, are main substrates, further, these processes include consecutive reactions such as acetate productions followed by acetate decompositions[7].

In this study, removal rates of propionate, butyrate and an acid mixture within anaerobic biofilms, as well as the rates of the intermediate acetate, were analized by using a biofilm model, and normalized biofilm parameters which specified the treatment characteristics were studied theoretically.

2. BIOFILM MODEL

Consider a biofilm reactor in which attached microorganisms utilize substrates from the completely mixed liquid phase, and also that consecutive reactions, shown in the following equation, are taking place

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within the biofilm. The biofilm reactor is illustrated in Fig. 1.

$$Si \rightarrow Y_{A/Si} \cdot A \rightarrow Y_{G/Si} \cdot G \quad \cdots\cdots (1)$$

In which, Si represents the i-th component of the first degradable or primary substrate, S, and A and G represent the intermediate and the final product, respectively. Further, $Y_{A/Si}$ and $Y_{G/Si}$ represent the conversion coefficients of A and G from Si, respectively.

According to the previous study[2),4)], the steady-state concentration profiles of A and Si, C_A and C_{Si}, within the biofilm are given by

$$D_A \frac{d^2C_A}{dy^2} + \Sigma Y_{A/Si} \cdot D_{Si} \frac{d^2C_{Si}}{dy^2} = \frac{\hat{\nu}_A \cdot \rho \cdot \alpha_A \cdot C_A}{K_A + C_A} \quad \cdots\cdots (2)$$

$$D_{Si} \frac{d^2C_{Si}}{dy^2} = \frac{\hat{\nu}_{Si} \cdot \rho \cdot \alpha_{Si} \cdot C_{Si}}{K_{Si} + C_{Si}} \quad \cdots\cdots (3)$$

in which D_A and D_{Si}=effective diffusion coefficients of A and Si within biofilm, $\hat{\nu}_A$ and $\hat{\nu}_{Si}$=maximum specific decomposition rates of A and Si, α_A and α_{Si}=mass fractions of A- and Si-decomposer, and ρ= biofilm density.

Boundary conditions of Eqs. (2), (3) are given at the support surface ($y=0$) and at the biofilm surface ($y=L$) as follows,

$$D_A \frac{dC_A}{dy}\bigg|_{y=0} = 0, \quad D_A \frac{dC_A}{dy}\bigg|_{y=L} = \frac{C_{Af} - C_A^*}{a \cdot \bar{\theta}} \quad \cdots\cdots (4)$$

$$D_{Si} \frac{dC_{Si}}{dy}\bigg|_{y=0} = 0, \quad D_{Si} \frac{dC_{Si}}{dy}\bigg|_{y=L} = \frac{C_{Sif} - C_{Si}^*}{a \cdot \bar{\theta}} \quad \cdots\cdots (5)$$

in which a=specific area of biofilm, $\bar{\theta}$=hydraulic retention time, C_{Af} and C_A^*=influent and effluent concentrations of A, and C_{Sif} and C_{Si}^*=influent and effluent concentrations of Si.

By using dimensionless parameters that correspond to biofilm properties and operation parameters, Eqs. (2)-(5) are normalized as follows,

$$\frac{d^2\omega_A}{dY^2} + \Sigma Y_{A/Si} \cdot \frac{D_{Si}}{D_A} \cdot \frac{d^2\omega_{Si}}{dY^2} = \frac{M_A^2 \cdot \omega_A}{1 + B_{Af} \cdot \omega_A} \quad \cdots\cdots (6)$$

$$\frac{d^2\omega_{Si}}{dY^2} = \frac{M_{Si}^2 \cdot \omega_{Si}}{1 + B_{Sif} \cdot \omega_{Si}} \quad \cdots\cdots (7)$$

$$\frac{d\omega_A}{dY}\bigg|_{Y=0} = 0, \quad \frac{d\omega_A}{dY}\bigg|_{Y=1} = Pe_A \cdot (\omega_{Af} - \omega_A^*) \quad \cdots\cdots (8)$$

$$\frac{d\omega_{Si}}{dY}\bigg|_{Y=0} = 0, \quad \frac{d\omega_{Si}}{dY}\bigg|_{Y=1} = Pe_{Si} \cdot (\omega_{Sif} - \omega_{Si}^*) \quad \cdots\cdots (9)$$

in which $Y = y/L$, and

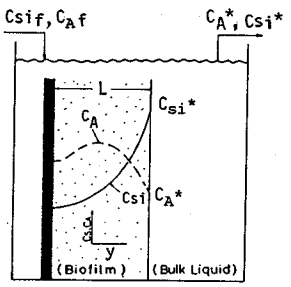

Fig. 1 Schematic diagram of biofilm reactor.

$$\left.\begin{aligned} \omega_A &= \frac{C_A}{C_{Tf}}, \quad \omega_{Af} = \frac{C_{Af}}{C_{Tf}}, \quad \omega_A^* = \frac{C_A^*}{C_{Tf}} \\ \omega_{Si} &= \frac{C_{Si}}{C_{Tf}}, \quad \omega_{Sif} = \frac{C_{Sif}}{C_{Tf}}, \quad \omega_{Si}^* = \frac{C_{Si}^*}{C_{Tf}} \end{aligned}\right\} \quad \cdots\cdots (10)$$

$$M_A = L\sqrt{\frac{\hat{\nu}_A \cdot \rho \cdot \alpha_A}{K_A \cdot D_A}}, \quad M_{Si} = L\sqrt{\frac{\hat{\nu}_{Si} \cdot \rho \cdot \alpha_{Si}}{K_{Si} \cdot D_{Si}}} \quad \cdots\cdots (11)$$

$$B_{Af} = \frac{C_{Tf}}{K_A}, \quad B_{Sif} = \frac{C_{Tf}}{K_{Si}} \quad \cdots\cdots (12)$$

$$Pe_A = \frac{L}{a \cdot \bar{\theta} \cdot D_A}, \quad Pe_{Si} = \frac{L}{a \cdot \bar{\theta} \cdot D_{Si}} \quad \cdots\cdots (13)$$

Where C_{Tf} is the influent concentration of total substrates, M_A and M_{Si} represent the normalized biofilm properties and also B_{Af}, B_{Sif}, Pe_A and Pe_{Si} are defined as the dimensionless operation parameters.

Removal efficiencies of total substrates, Et, are given by

$$Et=1-\omega_A^*-\Sigma\omega_{Si}^* \quad (14)$$

Removal fluxes or removal rates of A and Si, $N_{Af\mathrm{lux}}$ and $N_{Sif\mathrm{lux}}$ respectively, are given by

$$N_{Af\mathrm{lux}}=\left(\Sigma Y_{A/Si}\cdot\frac{D_{Si}}{D_A}\cdot\frac{d\omega_{Si}}{dY}\Big|_{Y=1}+\frac{d\omega_A}{dY}\Big|_{Y=1}\right)\cdot\frac{B_{Af}}{M_A^2}\cdot(N_A)_{\max} \quad (15)$$

$$N_{Sif\mathrm{lux}}=\frac{d\omega_{Si}}{dY}\Big|_{Y=1}\cdot\frac{B_{Sif}}{M_{Si}^2}\cdot(N_{Si})_{\max} \quad (16)$$

in which $(N_A)_{\max}$ and $(N_{Si})_{\max}$, maximum removal rates of A and Si respectively, are given by

$$\left.\begin{aligned}(N_A)_{\max}&=\hat{v}_A\cdot\rho\cdot\alpha_A\cdot L\\(N_{Si})_{\max}&=\hat{v}_{Si}\cdot\rho\cdot\alpha_{Si}\cdot L\end{aligned}\right\} \quad (17)$$

By using a normalized effluent concentration, B_{Si} $(=C_{Si}^*/K_{Si})$, and a half-velocity coefficient, K_{Si}^*, which changes with M_{Si}, $N_{Sif\mathrm{lux}}$ in Eq. (16) is approximated to Eq. (18)[2),4)]. $N_{Af\mathrm{lux}}$ in Eq. (15) is also approximated to Eq. (19) when C_{Sif} is negligibly smaller than C_{Af}.

$$N_{Sif\mathrm{lux}}=\frac{(N_{Si})_{\max}\cdot B_{Si}}{\lambda_{KSi}+B_{Si}}=\frac{(N_{Si})_{\max}\cdot C_{Si}^*}{K_{Si}^*+C_{Si}^*} \quad (18)$$

$$N_{Af\mathrm{lux}}=\frac{(N_A)_{\max}\cdot B_A}{\lambda_{KA}+B_A}=\frac{(N_A)_{\max}\cdot C_A^*}{K_A^*+C_A^*} \quad (19)$$

in which $\lambda_{KSi}=K_{Si}^*/K_{Si}$, $\lambda_{KA}=K_A^*/K_A$ and $B_A=C_A^*/K_A$.

3. MODEL APPLICATION AND ANALYSES

(1) Measurements of acid removal rates

Three identical, completely mixed, anaerobic biofilm reactors, which were the same as in the previous study[2)], were used in the experiments. By using the reactors, mesophilic (37°C) treatments of synthetic wastewaters, which were propionate, butyrate and an acid mixture as carbon sources, were carried out for 3 years continuously. The composition of the acid mixture was acetate : propionate : butyrate=0.56 : 0.32 : 0.12 on carbon basis. Biofilms were first build up for 3 months with a synthetic medium consisting of glucose, peptone and beef-extracts. Thereafter, these biofilms were acclimated independently to each of the synthetic wastewaters.

Removal rates of propionate, butyrate and the intermediate acetate in steady states were measured under a range of organic loadings in which influent concentrations varied from 100 to 1 500 mg-C/l, and HRT varying from 0.12 to 2 days. Then, acetate removal rates were measured by exchanging each of the used wastewater for an acetate-dominant wastewater. Steady states were assumed when the time course changes of gas production rates were very small (deviations were less than 3 %) and also when the values of dC_{Si}^*/dt were less than approximately 2 % of $(C_{Sif}-C_{Si}^*)/\bar{\theta}$. Detailed experimental conditions and experimental procedures are presented in the literature[2)].

Those experimental results showed that the removal rates of the individual acid were well correlated by Eq. (18) or (19). The observed kinetic parameters, i.e. the maximum removal rates and half-velocity coefficients, at various attached biomasses are listed in Table 1. Then, after 3 years of operation, the biofilms were exfoliated and suspended, and half-velocity coefficients were measured from substrate dissimilation curves in batch experiments. The observed results are also listed in the table.

(2) Analyses of the biofilm parameters

In the previous study[2)], the authors obtained the normalized biofilm properties by analizing half-velocity coefficients in methanogen attached biofilms, and showed that treatment characteristics were simply and accurately evaluated by using these parameters. In this study, the same analyses were done for each of the reaction steps of propionate, butyrate, the acid mixture and intermediate acetate.

In Fig. 2, a theoretical relation between λ_{KSi} and M_{Si} in Eq. (18) was represented as a solid line[2)]. For the propionate and butyrate decomposition steps, the values of λ_{KP} $(=K_P^*/K_P)$ and λ_{KB} $(=K_B^*/K_B)$ were calculated, and biofilm properties, M_P and M_B, were obtained according to this theoretical relation. In the

same manner, biofilm properties, M_A, for the intermediate acetate were also obtained from λ_{K_A} $(=K_A^*/K_A)$ values, which were measured in the acetate fed experiments. In these analyses, it was assumed, in accordance with the previous study[2], that each value of K_A, K_P and K_B was nearly equal to the value measured by the suspension. Thus, K_A=16 mg-C/l, K_P=12 mg-C/l and K_B=4 mg-C/l were given. The analized biofilm properties for each biofilm are listed in Table 1, and are also represented in Fig. 2 separately for each decomposition step. Then, as the biofilm properties less than 1 are not immediately obtainable from the theoretical relation, these properties were tentatively evaluated, according to Eq.

Table 1 Observed kinetic parameter of biofilm.

Biofilm [Acclimation substrate]	Acetate removal		Propionate removal		Butyrate removal	
	†) (N_A)max	††) K_A^*, (M_A)	†) (N_P)max	††) K_P^*, (M_P)	†) (N_B)max	††) K_B^*, (M_B)
[propionate]				†††) 12		
X_P=1.11 mg-C/cm²	0.50	16 (0.65)	1.18	19 (1.7)	—	—
X_P=2.89 mg-C/cm²	2.76	40 (2.7)	3.30	44 (3.7)	—	—
X_P=6.37 mg-C/cm²	5.50	80 (4.8)	6.13	88 (6.7)	—	—
[butyrate]						†††) 4.0
X_B=1.42 mg-C/cm²	1.21	19 (1.0)	—	—	1.81	8.3(2.3)
X_B=2.71 mg-C/cm²	2.40	40 (2.7)	—	—	4.95	36 (8.1)
X_B=4.50 mg-C/cm²	3.12	56 (3.5)	—	—	6.05	53 (12)
[acid mixture] ▽)						
X_H=0.43 mg-C/cm²	0.59	17 (0.7)	0.36	15 (0.6)	0.19	6.7(0.8)
X_H=1.39 mg-C/cm²	2.78	40 (2.7)	1.22	21 (1.8)	0.71	10 (2.7)
X_H=2.94 mg-C/cm²	5.12	82 (4.9)	2.11	47 (3.8)	0.85	20 (4.8)

†): (mg-C/cm²d) , ††) : (mg-C/l) , †††) : observed result in suspension
▽) acid composition ; acetate : propionate : butyrate = 0.56 : 0.32 : 0.12 (g-C/g-C)

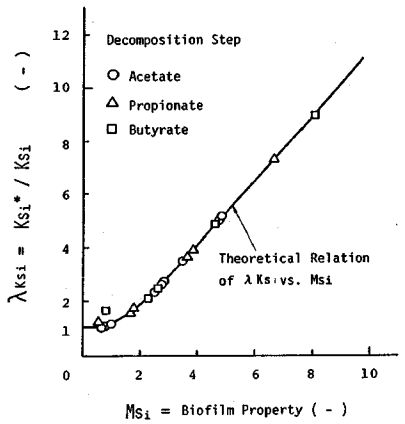

Fig. 2 Relation of the increment of half-velocity coefficient with biofilm property.

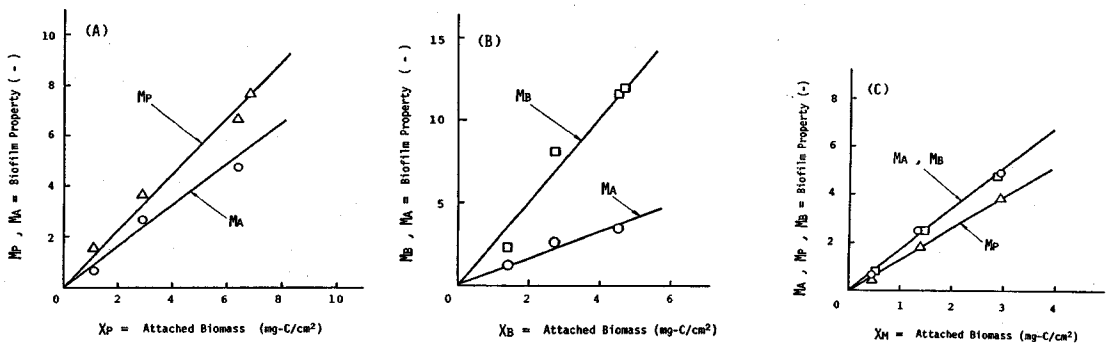

Fig. 3 Relations between biofilm property and attached biomass, (A) ; propionate acclimated biofilm, (B) ; butyrate acclimated biofilm, (C) ; acid mixture acclimated biofilm.

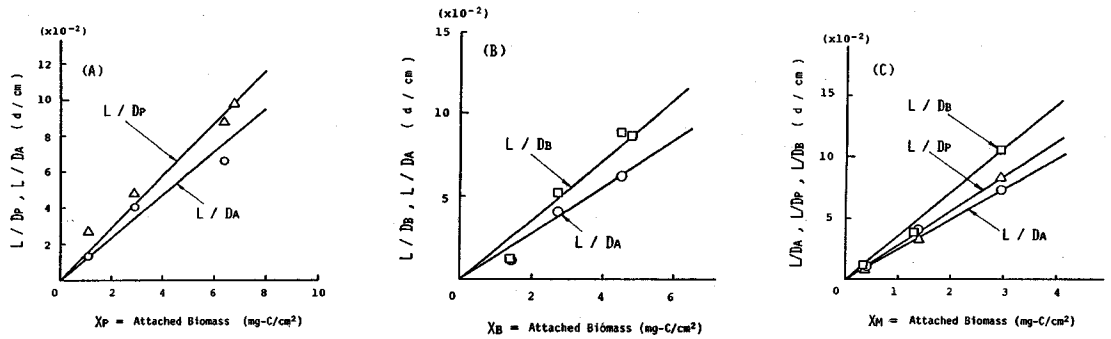

Fig. 4 Relations among L/D_A, L/D_P, L/D_B and attached biomass, (A) ; propionate acclimated biofilm, (B) ; butyrate acclimated biofilm, (C) ; acid mixture acclimated biofilm.

Table 2 Proportionality coefficients of biofilm property and operation parameter to attached biomass.

Biofilm	$\beta_{Si} = M_{Si} / X_{Si}$ (cm^2/mg-C)	$\gamma_{Si} = Pe_{Si} \cdot a \cdot \bar{\theta} / X_{Si}$, (cm · d/mg-C) [decomposition step]	
Propionate acclimated	$\beta_P = 1.1$ $\beta_A = 0.82$	$\gamma_P = 1.4 \cdot 10^{-2}$ $\gamma_A = 1.2 \cdot 10^{-2}$	[propionate] [acetate]
Butyrate acclimated	$\beta_B = 2.6$ $\beta_A = 0.83$	$\gamma_B = 1.8 \cdot 10^{-2}$ $\gamma_A = 1.4 \cdot 10^{-2}$	[butyrate] [acetate]
Acid mixture acclimated	$\beta_A = 1.7$ $\beta_P = 1.3$ $\beta_B = 1.7$	$\gamma_A = 2.5 \cdot 10^{-2}$ $\gamma_P = 2.8 \cdot 10^{-2}$ $\gamma_B = 3.6 \cdot 10^{-2}$	[acetate] [propionate] [butyrate]

(11), from the values obtained at the other conditions by using the maximum removal rate and the attached biomass.

As shown in Table 1, the biofilm properties for each acid decomposition step increased with the increments of attached biomass. Figs. 3(A)-(C) show the relations between the biofilm properties and attached biomasses for the propionate, butyrate and acid mixture acclimated biofilms, respectively. According to the previous study[2], these relations were approximated to the following linear equation.

$$M_{Si}=\beta \cdot X_{Si} \quad \cdots\cdots (20)$$

The proportionality coefficient, β, were read from the solid lines in these figures, and are listed in Table 2.

Transforming Eq. (11) to a following equation, the operation parameters of Pe_A in the acetate decomposition step, Pe_P in the propionate decomposition step and Pe_B in the butyrate decomposition step are obtainable[2].

$$L/D_{Si}=M_{Si}^2 \cdot K_{Si}/(N_{Si})_{max} \quad \cdots\cdots (21)$$

Figs. 4(A)-(C) show the relations of L/D_A, L/D_P and/or L/D_B with attached biomass for each of the biofilms. According to the previous study, these relations were approximated to the following linear equation.

$$Pe_{Si}=\gamma \cdot X_{Si} \cdot (a \cdot \bar{\theta})^{-1} \quad \cdots\cdots (22)$$

The proportionality coefficients, γ, were obtained from the solid lines in the figures, and are listed in Table 2. The ratios of the operation parameters were $Pe_P/Pe_A=1.2$ (propionate acclimated biofilm reactor), $Pe_B/Pe_A=1.3$ (butyrate acclimated biofilm reactor) and $Pe_A : Pe_P : Pe_B=1.0 : 1.1 : 1.4$ (acid mixture acclimated biofilm reactor). Further, these ratios were similar to the inversed diffusion coefficients estimated by a Wilke's relation[5] as $D_A/D_P=1.18$, $D_A/D_B=1.35$ and $1/D_A : 1/D_P : 1/D_B = 1.0 : 1.18 : 1.35$.

4. SIMULATIONS OF TREATMENT CHARACTERISTICS

The effluent acid concentrations and removal efficiencies can be calculated theoretically as functions of the operation parameters according to Eqs. (6)-(9), (14). Fig. 5 shows the treatment characteristics with the propionate acclimated biofilms, in which calculated results of effluent acid concentrations (ω_A^*, ω_P^*) and removal efficiencies (Et) under various biomasses (X_P) are represented as solid lines in comparison with the observed results. In the calculation, the ratios of effective diffusion coefficients (D_P/D_A, D_B/D_A) were obtained by a Wilke's relation[5], and $K_A=16$ mg-C/l and $K_P=12$ mg-C/l were given. Biofilm properties for each X_P were obtained by using Eq. (20) and the coefficient (β) listed in Table 2. Further, the influent concentrations, $B_{P,f}$, were obtained as the average values of the observed results. Operating conditions of the observed results were transformed to Pe_P or Pe_A by using Eq. (22) and the coefficients (γ) listed in Table 2. As shown in Fig. 5, the calculated results of ω_P^*, ω_A^* and Et for each X_P were in good agreement with observed values, except the results of ω_A^* and Et at $X_P=1.11$ mg-C/cm^2. The broken lines show the calculated results using $M_A=0.65$ listed in Table 1. These

lines fitted well with the observed results. Since, as shown in Table 1, the maximum specific removal rate of acetate was considerably small at X_P=1.11 mg-C/cm², it is shown that the value of M_A was overestimated by Eq. (20) so that the calculated results (solid line) for ω_A^* were smaller than the observed values, as well as the larger results for Et.

Fig. 6 shows the comparison of calculated and observed results in the propionate acclimated biofilm

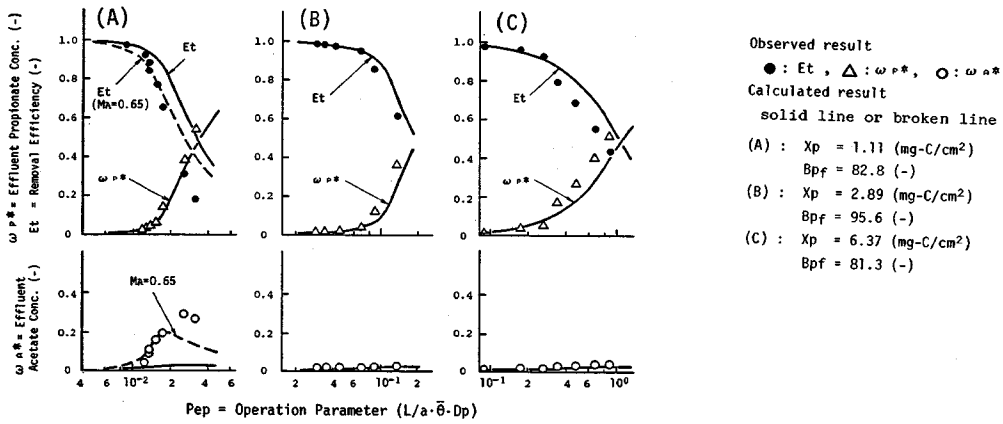

Fig. 5 Comparison of calculated and observed results of treatment characteristics for various attached biomasses in propionate acclimated biofilm reactor.

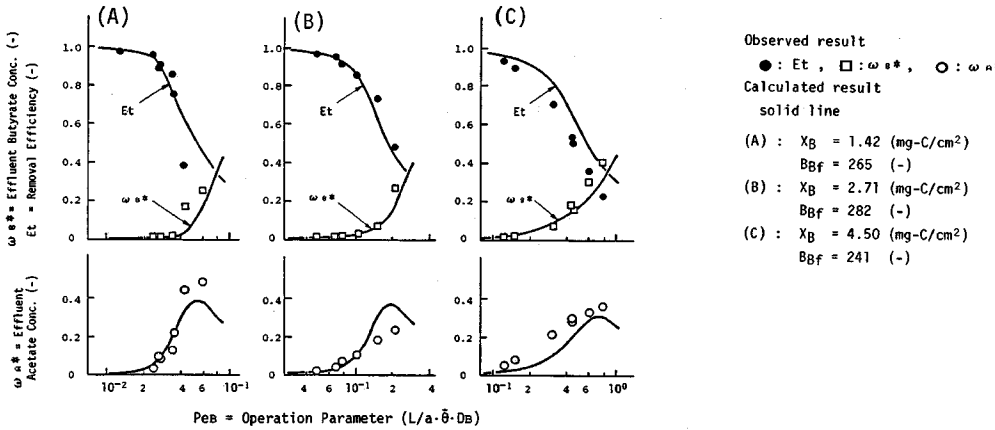

Fig. 6 Comparison of calculated and observed results of treatment characteristics for various attached biomasses in butyrate acclimated biofilm reactor.

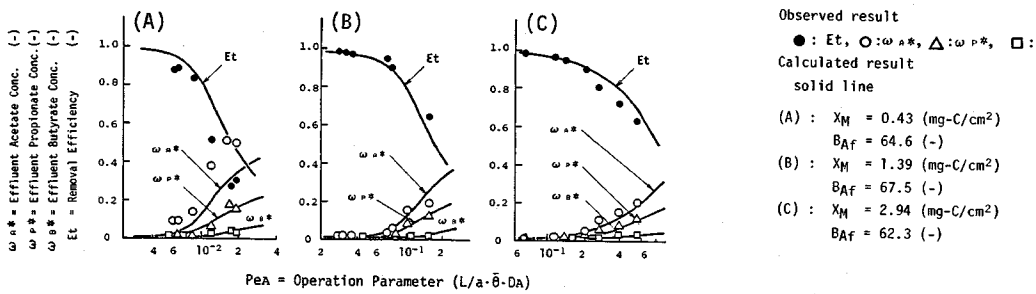

Fig. 7 Comparison of calculated and observed results of treatment characteristics for various attached biomasses in acid mixture acclimated biofilm reactor.

reactor. In the calculation, K_B=4 mg-C/l and K_A=16 mg-C/l were given, and biofilm properties of M_B and M_A were obtained according to Eq. (20). As shown in Fig. 6, the calculated results of effluent acid concentrations (ω_B^*, ω_A^*) and removal efficiencies (Et) fitted well with observed values.

From Figs. 5, 6, it is shown that treatment characteristics of propionate and butyrate in a consecutive decomposition regime were accurately evaluated by using the biofilm property and the operation parameter for each reaction step.

Fig. 7 shows the comparison in the acid mixture acclimated biofilm reactor. In the calculation, M_P and M_B in Eq. (7) and M_A in Eq. (6) were also obtained according to Eq. (20), and the values of K_A=16 mg-C/l, K_P=12 mg-C/l, K_B=4 mg-C/l and the influent substrate compositions of $\omega_{Af} : \omega_{Pf} : \omega_{Bf}$=0.56 : 0.32 : 0.12 were given. The calculated results of effluent concentrations (ω_A^*, ω_P^*, ω_B^*) and removal efficiencies (Et) fitted well with the observed values for each attached biomass (X_M), therefore it is shown that treatment characteristics in the methane production phase were evaluated well by using the biofilm properties (M_A, M_P, M_B) and the operation parameters (Pe_A, Pe_P, Pe_B) for the individual reaction step.

5. DISCUSSION

The relationships between biofilm properties and attached biomasses are important to evaluate the substrate diffusion rates at any thickness. In this study, the biofilm properties were approximated to a linear relation with the attached biomass. The linearity can be applied to the biofilms in which population balances of consortia are maintained in a stable condition. In the butyrate and acid mixture acclimated biofilms, the maximum specific removal rates of the individual volatile acids were relatively constant (Table 1), therefore, the population balances of these biofilms are considered to be stable.

In the propionate acclimated biofilms, treatment characteristics were not simulated well for X_P= 1.11 mg-C/cm^2 (Fig. 5). In this condition, which was obtained after about a year of operation, the specific removal rate of acetate was considerably small, but in the other conditions after 2-3 years of operation, the specific rates were nearly maintained at a constant value (Table 1). Koch et al.[6] reported that about a year was needed to establish a propionate-degrading enrichment culture with a stable bacterial population. According to this report, it may be supposed that, up to a year of operation, microbial population balances in the biofilm were unstable, and a stable balance was attained with further years of operation. However, as population balances in the biofilms can be affected by the corresponding microbial properties of acetogens, acetate-utilizing methanogens and H_2-utilizing methanogens, and also affected by interactions among these bacteria[7], detailed study on biofilm consortia in about a year of operation will be needed.

The operation parameters of Pe_A, Pe_P and Pe_B were approximated by a linear relation with the attached biomass (Eq. (22)). However, the proportionality coefficient (γ) differed with the biofilm reactor or with the feed acid composition (Table 2). Although the proportionality coefficient (γ_A) in the acid mixture acclimated biofilm reactor corresponded to the value of the methanogen attached biofilm reactor[2], the coefficients in the propionate or butyrate acclimated biofilm reactors were smaller. These differences seem to be mainly due to differences of predominant species in biofilms, and the fact that changes of effective diffusion coefficients or attached biomass densities may occur with shifts of predominant species. As the main component of the acid mixture used in the study was acetate (amounted to 56 % of total organic carbon), and propionate and butyrate were comparatively small, the acid mixture acclimated biofilms were considered to be similar to the methanogen attached biofilms. But, in the propionate or butyrate acclimated biofilms, one of predominant species is a propionate-using or butyrate-using acetogen unlike the methanogen attached biofilms. Since syntrophic associations between H_2-consuming methanogens and acetogens have been reported[7)~9)], it can be considered that microorganisms of methanogen and acetogen in the biofilms grow closely in juxtapositions[8] or clamping forms[9]. Therefore biomass densities of propionate or butyrate acclimated biofilms may be larger than methanogen attached biofilms, and the proportionality coefficients (γ) of operation parameter may decrease because of a smaller biofilm thickness.

6. SUMMARY

According to the steady-state mathematical biofilm model considering consecutive decompositions and diffusions of substrates, removal rates of propionate, butyrate and the volatile acid mixture within anaerobic biofilm reactors were analized, and biofilm parameters which specified treatment characteristics were studied. The following results were obtained.

(1) The normalized biofilm parameters, i.e. biofilm properties (M_A, M_P, M_B) and operation parameters (Pe_A, Pe_P, Pe_B), were represented as a function of the attached biomass (Table 2).

(2) Half-velocity coefficients of the volatile fatty acids in the methane production phase increase with increasing attached biomass because of the increments of substrate diffusion resistances.

(3) Treatment rates of propionate or butyrate dominant wastewaters depend on the diffusion and decomposition rates of propionate and acetate or butyrate and acetate, respectively.

Nomenclature

a : Specific area of biofilm (1/L)
C_j : Concentration of j-substrate within biofilm (M/L^3)
C_{jf} : Influent concentration of j-substrate (M/L^3)
C_j^* : Concentration of j-substrate at biofilm surface (M/L^3)
C_{Tf} : Influent concentration of total substrate (M/L^3)
D_j : Effective diffusion coefficient of j-substrate within biofilm (L^2/T)
K_j : Half-velocity coefficient of j-substrate decomposition (M/L^3)
K_j^* : Biofilm half-velocity coefficient based on the bulk concentration of j-substrate (M/L^3)
L : Biofilm thickness (L)
N_{jflux} : Removal rate of j-substrate at steady state (M/L^{2}T)
$(N_j)_{max}$: Maximum removal rate of j-substrate (M/L^{2}T)
X_j : Attached biomass acclimated with j-substrate (M/L^2)
y : Distance from support surface (L)
β : Proportionality coefficient of the biofilm property to attached biomass (L^2/M)
γ : Proportionality coefficient of the operation parameter to attached biomass (LT/M)
$\overline{\theta}$: Hydraulic retention time (T)
$\hat{v}_j$: Maximum specific decomposition rate of j-substrate (1/T)
ρ : Biofilm density (M/L^3)

Dimensionless parameters

B_j : Normalized concentration of j-substrate ($=C_j^*/K_j$)
B_{jf} : Normalized influent concentration of j-substrate ($=C_{Tf}/K_j$)
Et : Removal efficiency of total substrate
M_j : Biofilm property on the decomposition step of j-substrate ($=L\cdot(\hat{v}_j\cdot\rho\cdot a_j/K_j\cdot D_j)^{1/2}$)
Pe_j : Operation parameter on the decomposition step of j-substrate ($=L/(a\cdot\overline{\theta}\cdot D_j)$)
Y : $Y=y/L$
a_j : Mass fraction of j-substrate decomposer in biofilm
λ_{kj} : Normalized half-velocity coefficient ($=K_j^*/K_j$)
ω_j : $\omega_j=C_j/C_{Tf}$
ω_{jf} : $\omega_{jf}=C_{jf}/C_{Tf}$
ω_j^* : $\omega_j^*=C_j^*/C_{Tf}$

Subscript definition for j

A : Intermediate substrate or acetate
B : Butyrate
P : Propionate
S_i : I-th compornent of primary substrate
M : Acid mixture of acetate, propionate and butyrate

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