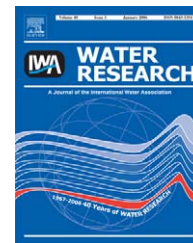


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# Consecutive reaction kinetics involving a layered structure of the granule in UASB reactors

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## ABSTRACT

A consecutive-reaction kinetic model for the sucrose-fed upflow anaerobic sludge bed (UASB) reactor that accounts for a layered structure of the granule and the mass fraction of methanogens ( $f$ ) is proposed. When the UASB reactor was maintained at the volumetric loading rates (VLR) of 7.9–13.8 kg chemical oxygen demand (COD)/m<sup>3</sup> d, the accumulated volatile fatty acids (VFAs) increased with increasing VLR, whereas the experimental  $f$  decreased with increasing VLR. This was primarily because methanogenesis was the rate-limiting step and the sucrose-fed granule was a layered structure. The calculated residual concentrations of sucrose and the intermediates VFAs using the layered-structure model are less deviated from the experimental measurements than those using the homogeneous-structure model. The calculated effectiveness factors for sucrose uptake and intermediates VFAs uptake ( $\eta_1$ ;  $\eta_2$ ) ranged from 0.18 to 0.35 and 0.65 to 0.96, respectively, indicating that the overall substrate (sucrose or intermediates VFAs) removal in the UASB reactor was diffusion-controlled, especially at the VLRs of 7.9–10.6 kg COD/m<sup>3</sup> d. This finding was also confirmed by the simulated concentration profiles of sucrose and VFAs in the UASB-granule. From the simulation results, the effect of internal mass transfer resistance on overall substrate (sucrose) removal should not be neglected, especially for a granule size of greater than 2.0 mm.

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## 1. Introduction

Since their introduction approximately 25 years ago, UASB reactors have been widely used to treat various kinds of wastewaters. Anaerobic bacteria are immobilized in UASB reactors by a process of spontaneous aggregation of the bacteria, resulting in dense sludge granules (Lettinga et al., 1984). In UASB reactors, the anaerobic degradation of a complex substrate should exhibit two primary reaction steps, that is, the substrate is first biodegraded to volatile fatty acids (VFAs), and the VFAs formed are further biodegraded to methane and carbon dioxide by methanogens. By using the

scanning and transmission electron microscopy, MacLeod et al. (1990) observed that the granular aggregates in sucrose-fed UASB reactors were three-layered structures; the external layer mostly consists of acidogens, the second layer consists of syntrophic association, and the core consists of acetoclastic methanogens. Layered structure of the UASB-granule was also reported by Guiot et al. (1992), Fang et al. (1994) and Zhu et al. (1997), who utilized either carbohydrates or brewery waste as fed-substrate. In addition, Arcand et al. (1994) pointed out that the activity of acidogens decreased markedly if the disintegration of the external layer of the UASB-granule (fed by sucrose) occurred.

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## Nomenclature

$a$	specific surface area ( $\text{mm}^{-1}$ )
$Bi_1, Bi_2$	Biot number (dimensionless)
$C_{in}$	tracer concentration in the influent (mg/l)
$C_t$	tracer concentration in the effluent at time $t$ (mg/l)
$d_p$	average diameter of granules based on surface area (mm)
$D_{f1}$	diffusion rate of sucrose within granule ( $\text{m}^2/\text{d}$ )
$D_{f2}$	diffusion rate of acetate within granule ( $\text{m}^2/\text{d}$ )
$D_{w1}$	diffusion rate of sucrose in diffusion layer ( $\text{m}^2/\text{d}$ )
$D_{w2}$	diffusion rate of acetate in diffusion layer ( $\text{m}^2/\text{d}$ )
$f$	mass fraction of methanogens (dimensionless)
$k$	maximum specific sucrose utilization rate constant ( $\text{d}^{-1}$ )
$k_1$	maximum specific sucrose utilization (acidogenesis) rate constant ( $\text{d}^{-1}$ )
$k_2$	maximum specific acetate utilization rate constant of enrichment culture ( $\text{d}^{-1}$ )
$k'_2$	maximum specific acetate utilization rate constant of mixed culture ( $\text{d}^{-1}$ )
$K_s$	half-saturation constant of sucrose (mg/l)
$K_{s1}$	half-saturation constant of sucrose (acidogenesis) (mg/l)
$K_{s2}$	half-saturation constant of acetate (mg/l)
$L_1, L_2$	thickness of diffusion layer (mm)
$M_x$	biomass in UASB reactor (g)
$Q$	inflow rate (l/d)
$r$	radial distance from center of granule (mm)
$r^*$	dimensionless radial distance from center of granule = $r/R$
$R$	granule radius (mm)
$R_1, R_2$	thickness distribution of acidogens and methanogens (mm)
$Re$	Reynolds number (dimensionless)
$S_{B,-1}, S_{B,0}, S_{B,+1}$	acetate bulk concentration in three consecutive samples (mg/l)

$S_{b1}, S_{b2}$	sucrose and VFAs concentrations in bulk liquid (mg/l)
$S_{b1}^*, S_{b2}^*$	dimensionless sucrose and VFAs concentrations in bulk liquid = $S_{bi}/K_{si}$
$S_{f1}, S_{f2}$	sucrose and VFAs concentrations within granule (mg/l)
$S_{f1}^*, S_{f2}^*$	dimensionless sucrose and VFAs concentrations within granule = $S_{fi}/K_{si}$
$S_{in}$	sucrose influent concentration (mg/l)
$S_{s1}, S_{s2}$	sucrose and VFAs concentrations at liquid/granule interface (mg/l)
$S_{s1}^*, S_{s2}^*$	dimensionless sucrose and VFAs concentrations at liquid/granule interface = $S_{si}/K_{si}$
$Sc_i$ ( $i = 1, 2$ )	Schmidt number (dimensionless)
$\Delta t$	time interval (h)
$u_s$	superficial velocity (m/h)
$V_R$	reactor volume (l)
$X_B$	average MLVSS concentration in batch reactor (mg/l)
$X_b$	biomass concentration in sludge-bed zone (mg VSS/l)
$X_f$	microbial density in sludge-bed zone (mg VSS/l)
$\beta$	yield coefficient for acetate formation (dimensionless)
$\varepsilon$	porosity in sludge-bed zone (dimensionless)
$\phi_1, \phi_2$	Thiele modulus (dimensionless)
$\nu$	dynamic viscosity ( $\text{m}^2/\text{s}$ )
$\eta_1, \eta_2$	effectiveness factor for sucrose and acetate uptake in sludge bed (dimensionless)

## Subscripts

1	substrate sucrose
2	intermediates VFAs
b	bulk
f	granule

According to the theory of external mass transfer and internal diffusion and substrate utilization kinetics, [Canovas-Diaz and Howell \(1988\)](#) developed a two-layer anaerobic biofilm model, based on the assumption that an acidogenic biofilm forms the outer layer and a methanogenic biofilm the inner one. However, in their model calculations, the experimental mass fractions of acidogens and methanogens were not used, they used the assumed values instead. In addition, [Tartakovsky and Guiot \(1997\)](#) formulated a multi-layered biofilm model, taking into account three different microbial groups (i.e., acidogens, syntrophic association and methanogens were distributed in the outer layer, second layer and core, respectively). Similarly, they also used the assumed mass fractions of various microbial groups. In fact, the assumed mass fraction of methanogens ( $f = 0.5$ ) used by [Tartakovsky and Guiot \(1997\)](#) are somewhat deviated from the experimental values determined by [Huang et al. \(2003\)](#) ( $f = 0.13\text{--}0.43$ ).

In this work, a laboratory-scale UASB reactor was used to treat complex substrate sucrose to generate experimental data. Independent batch experiments were also conducted to determine biokinetic parameter values of acidogenesis and methanogenesis. The mass fraction of methanogens ( $f$ ) in the UASB reactor operated at different volumetric loading rates (VLRs) was experimentally determined. In addition, a kinetic model that accounts for a layered structure of the granule and  $f$  was formulated and validated by experiments. The validated model was then used to simulate the effects of granule size on the effectiveness factor and treatment efficiency of the UASB reactor. Moreover, to clarify the role of mass transfer playing in the overall sucrose/intermediates VFAs removal in the UASB reactor, the calculated effectiveness factors for sucrose uptake and intermediates VFAs uptake ( $\eta_1, \eta_2$ ) and the simulated concentration profiles of sucrose and intermediates VFAs in the UASB-granule are presented as well.

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