



## Development of a simplified mathematical-model for a three-stage anaerobic digester stabilizing fruit and vegetable waste (FVW) under limiting-substrate condition

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The present study focused on the modeling of a three-stage hybrid anaerobic digester, stabilizing fruit and vegetable waste (FVW), under limiting-substrate condition. The digester consisted of a hydrolytic reactor operated under suspended-growth condition, an acidogenic/acetogenic reactor operated under hybrid-growth condition, and a methanogenic reactor also operated under hybrid-growth condition. The three reactors were connected in series. Monod's kinetics was used for modeling the substrate consumption in the suspended-growth part of all the three stages, whereas Fick's second law of molecular diffusion was followed while modeling the substrate consumption into the biofilm that comprised the attached-growth microbes. This is to say that the model considered the substrate mass-transfer external to the biofilm, and into the biofilm as per Fick's second law of molecular diffusion. Appropriate boundary conditions, which were relevant to limiting-substrate scenario, were incorporated while deriving the model and identical reaction kinetics were assumed for both the attached and suspended-growth systems. The step-by-step procedure to solving the mathematical model has also been suggested.

Keywords: Three-stage anaerobic digestion (AD), mathematical-modeling, biofilm reactor, Monod's kinetics, fruit and vegetable waste (FVW).

### Introduction

Stabilization of concentrated organic wastes viz. wastes with high COD (Chemical Oxygen Demand) or high percentage of biodegradable organic matter (such as fruit and vegetable waste, food waste, agricultural waste, plant residue, animal matter, food processing wastewater, slaughterhouse wastewater, etc.) via anaerobic digestion (AD) has long been seen by municipalities and industries as the go-to strategy, which aims to achieve the highest standards for pollution control. AD not only strives to efficiently stabilize almost every type of organic waste matter (solid and liquid), but it is also one of the viable strategies to techno-economically ensure the energetic valorization of biomass and different waste forms<sup>17</sup>. Since its introduction in the field of stabilizing the organic fraction of the municipal solid waste (OFMSW), the implementation in the technology of AD has seen several modifications, which have been aimed at improving the handling of the crucial operational steps and the overall process stability, besides improving the overall operational efficiency

in terms of biogas yield<sup>5</sup>. In the anaerobic conversion of solid organic waste to biogas, there are four major steps, which are mediated by a plethora of microbial communities. These are hydrolysis – where the conversion of the solid matter to long-chain fatty acids (LCFAs) occurs, acidogenesis – where the conversion of the LCFAs into short-chain fatty acids (SCFAs) occurs, acetogenesis – where the conversion of the SCFAs into acetates occurs, and lastly, methanogenesis – where the SCFAs, including the acetates, and the generated  $\text{CO}_2 + \text{H}_2$  get converted into methane ( $\text{CH}_4$ ). Stage-separation has been one such modification, where the major steps in the AD process (for the conversion of solid to gas) have been made to occur in two or three different reactors connected in series<sup>11</sup>.

In a three-stage AD system, the phases of hydrolysis, acidogenesis and acetogenesis, and methanogenesis are made to operate in three separate chambers connected in series<sup>6</sup>. Similarly, in a two-stage AD system, depending on the type of solid organic waste being stabilized, either of the

hydrolytic or the methanogenic phases are made to operate in conjunction with the acidogenic and the acetogenic phases in two separate chambers connected in series. Separating the hydrolytic phase enables the conversion of even the most complex type of solid organic waste types that are rich in lignin and cellulose (such as rice husk, wheat straw, vegetable waste, garden waste, etc.) without interfering the remaining phases<sup>7</sup>. One of the ways of achieving this is via enzymatic hydrolysis, where enzyme secreting microbes or extracellular are introduced into the hydrolysis reactor<sup>10,8</sup> for the efficient breakdown of the complex molecular structures. One other major advantage of separating the hydrolytic phase is the recovery of ethanol.

Further, if the operation of the acidogenic and acetogenic phases is done separately then not only the desirable pH-maintenance of all the phases are achieved easily, but at the same time, judicious utilization of the produced volatile fatty acids (VFAs)<sup>9</sup> in generating both H<sub>2</sub> and CH<sub>4</sub> is easily ensured. The application of three-stage AD systems in stabilizing OFMSW as well as other solid organic waste are, therefore, manifolds including the production and utilization of ethanol, biohythane, and a better quality solid digestate/residue<sup>4</sup>.

At the heart of the development and operation of any type of anaerobic treatment system there is process kinetics. It is to say that, process kinetics, by taking into account the microbiology and biochemistry of the anaerobic process<sup>28</sup>, play a significantly important role towards forming a sound base needed for the development of system/process control, design, and analysis of the AD system. The rates of waste utilization, the quantitative description of these rates, and the environmental and operational factors affecting these rates are explicitly dealt with process kinetics. As a result, a sound understanding of the process kinetics of an AD system allows for improved performance optimization and operational stability. The growth kinetics of any biological waste treatment process (anaerobic digestion, aerobic digestion) is based on two very elementary relationships, namely the growth rate, and the substrate utilization rate. Several mathematical models<sup>12–15,19,20</sup> that have been developed hitherto basically describe the effect of limiting substrate concentration on the microbial growth rate. In the case of AD, some of the crucial steps of the endogenous decay phase, such as biomass destruction, cell maintenance, predation,

cell death, and lysis, related to the decrease in microbial cell mass are usually found to operate at very low specific growth rates. The net microbial growth-rate is, therefore, modified by taking into consideration the microorganism decay-rate.

While studying the kinetics of the hydrolysis step, researchers usually observed it to be the rate-limiting step in the overall anaerobic conversion of especially complex substrates (e.g. organic solid waste) to biogas (methane). This is to say that during investigations when the acidogenesis or the methanogenesis step appeared to be rate-limiting, based on evidences, the importance of hydrolysis in ensuring the occurrence of the subsequent acidogenesis and the methanogenesis steps were more often than not overlooked. Pavlostathis and Giraldo-Gomez<sup>28</sup> did an extensive review of past literature and concluded that other than the hydrolysis step, all the other major processes involving the AD of all types of organic waste were possible to be modeled following Monod's kinetics<sup>17</sup>. Recently developed models on wastewater treatment and AD of organic waste (both liquid and solid), such as the International Water Association (IWA), Anaerobic Digestion Model 1 (ADM 1) and the IWA activated sludge models (ASMs)<sup>1,16</sup>, have also avoided the use of Monod's kinetics while modeling the hydrolysis step. In the present study, however, the modeling of the entire three-stage AD process, under suspended-growth condition, including the hydrolysis step has been via the use of Monod's kinetics.

In the present study, an attempt has been made to model the operation of a three-stage hybrid anaerobic digester, stabilizing fruit and vegetable waste (FVW), under limiting substrate condition. The three stages, which incorporated the hydrolysis, the acidogenesis/acetogenesis, and the methanogenesis steps, were operated in three distinct chambers. The hydrolytic phase was operated under suspended-growth condition, whereas the acidogenic/acetogenic and the methanogenic phases were operated under hybrid-growth condition. The advantages of the attached-growth or biofilm systems in treating complex organic matter (solid and liquid) are inimitable. In addition to rendering effective gas-liquid separation, some of the major advantages of using anaerobic biofilm reactors include handling of high organic loads, presence of high biomass concentration, resistance to shock loadings, and the improved substrate dispersion without the requirement of mechanical mixing<sup>18,24</sup>. Further, studies<sup>27,3</sup>

have also revealed that compared to conventional treatment systems, biofilm reactors tend to have reduced start-up time, shorter retention times, and up to five times increased organic loading speeds. As such, the evaluation of different types of biofilm reactors has been promising too at the industrial level<sup>21</sup>.

In biofilm systems, the transport of substrate has been thought to occur through a combination of convection (transport of solute by bulk flow of fluid) and diffusion (transport via random molecular motion). The transport of the substrates from the bulk-liquid to the outer surface of the biofilms is known as external mass-transfer and is a phenomenon usually governed by the turbulence of the fluid moving past the biofilm<sup>22</sup>. The hydrodynamics of a treatment system, therefore, has got an important role to play in deciding the extent of external mass-transfer. Modeling of biofilm reactors, dedicated to the anaerobic stabilization of both solid and liquid organic waste, has resulted in the development of numerous biofilm models and modeling platforms. These provide frameworks for “good practice in biofilm reactor modeling (GBMP)”<sup>22</sup>. While modeling the attached-growth systems for both the acidogenic and the methanogenic reactors, those frameworks mentioned by Rittmann *et al.*<sup>22</sup> were, therefore,

strictly followed.

*Development of the mathematical model:*

A simplified mathematical model of a three-stage hybrid anaerobic digestion (AD) system (as shown in Fig. 1), stabilizing FVW, under steady-state and limiting-substrate condition has been developed assuming similar reaction kinetics for both the suspended and the attached-growth microorganisms, and uniform bio-film thickness ( $L_f$ ). The model considered the three major phases of the AD process, viz. hydrolysis, acidogenesis, and methanogenesis, occurring separately under the suspended growth biomass. The solid substrate firstly gets broken into LCFAs, and thereafter the LCFAs are broken into SCFAs, from which ultimately biogas ( $CH_4$  and  $CO_2$ ) is generated. The filter media provided in the acidogenic and the methanogenic reactors cater to the attached-growth system. In the methanogenic reactor, the filter media also acts as a barrier, essentially for separating the methane from the combined matrix, and in the acidogenic reactor, the filter media results in the enhanced SCFA production. Moreover, the methanogenesis process occurring within this biomass is considered to follow the principle of Fixed Biofilm process, where there is no uniform mixing of the SCFA. Monod’s kinetic expression for substrate utiliza-

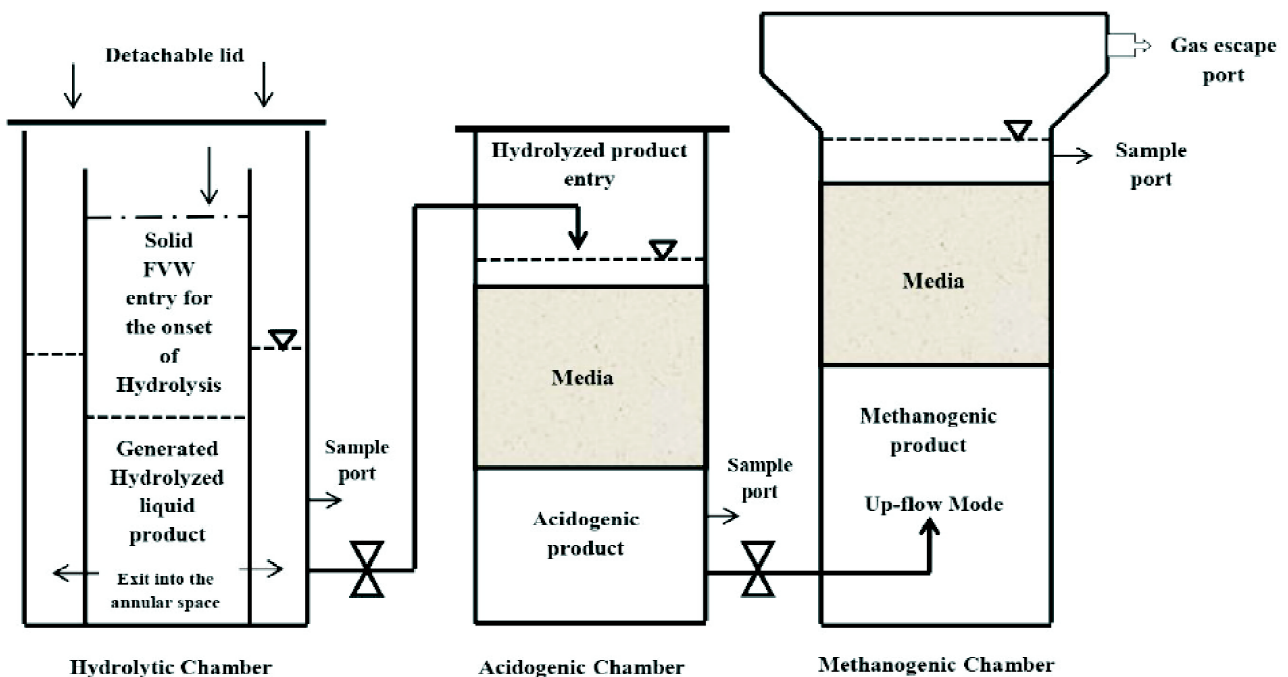


Fig. 1. Conceptual presentation of the three-stage hybrid anaerobic digester.

tion into the bio-film coupled with Fick's second law of molecular diffusion of substrate into the bio-film from bulk liquid<sup>23</sup> is used to derive the model. The model assumed identical reaction kinetics for both the attached- and the suspended-growth microbes in the case of the both the acidogenic and the methanogenic reactors<sup>2</sup>.

The consequences taking place in a three-stage hybrid AD system treating organic solid substrate can be identified as the following:

- (I) In the hydrolytic reactor/system, conversion of the solid substrates into particulate organic matter and LCFAs, expressed as mgCOD/L, occurs via hydrolysis. The phenomenon results in the gradual decrease of the solid substrate concentration. The detention time ( $t_H$ ) is considered as the time during which the solid-substrate is ultimately degraded to LCFAs in the same system.
- (II) In the acidogenic reactor/system, conversion of the LCFAs occurs into SCFAs, expressed as mgCOD/L. In this system, the detention time ( $t_A$ ) is considered as the time during which the LCFAs are ultimately converted into SCFAs. Hence, the decrease in LCFA concentrations (as mgCOD/L) is considered in this system.
- (III) In the methanogenic reactor/system, the formation of biogas from the SCFAs, entering from the acidogenic system, occurs. The detention time ( $t_M$ ) is considered as the time during which the SCFAs (mgCOD/L) are converted to gaseous products like methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ). The produced gas would remain dissolved. With the progression of time, and with the increase in its amount (on weight basis) per liter of the methanogenic content, it would come out of solution.

*Hydrolysis stage:*

In the case of the hydrolysis reactor, which is essentially a suspended-growth system, the following substrate removal kinetics can be written,

$$\frac{dS_H}{dt} = - \frac{k_H X_H S_H}{K_{SH} + S_H} \quad (1)$$

- $S_H$  = solid hydrolyzable substrate (mgCOD/L)
- $K_H$  = maximum specific rate of hydrolysis ( $\text{day}^{-1}$ )
- $X_H$  = concentration of hydrolytic microbes (mg/L)
- $K_{SH}$  = half-velocity constant for hydrolysis (mgCOD/L)

Under limiting substrate condition ( $K_{SH} \gg S_H$ ), eq. (1) can be modified as

$$\frac{dS_H}{dt} = - \frac{k_H X_H S_H}{K_{SH}}$$

or,  $\frac{dS_H}{S_H} = - \frac{k_H X_H S_H}{K_{SH}} dt$

Integrating both sides for boundary conditions  $t = 0, S_H = S_{H0}$  and  $t = t, S_H = S_H$

$$\int_{S_{H0}}^{S_H} \frac{dS_H}{S_H} = - \frac{k_H X_H}{K_{SH}} \int_0^t dt$$

or,  $\ln \left( \frac{S_H}{S_{H0}} \right) = - K'_H t$

where,  $K'_H = \frac{k_H X_H}{K_{SH}}$

or,  $S_H = S_{H0} e^{-K'_H t}$  (2)

*Acidogenesis stage:*

There are two different phases of biomass growth in the acidogenic reactor, firstly the attached growth, and thereafter the suspended growth.

*Attached growth system:*

In the attached-growth phase, the liquid substrate enters with a concentration equals to  $S_{LCFA}$ , which is same as  $S_{H0} - S_H$ . The mass rate of flow of the substrate through the attached-growth phase is denoted as,  $J_{LCFA}$ .

Now,  $J_{LCFA}$  can be expressed as,

$$J_{LCFA} = \frac{D_{fA}}{L_A} (S_{LCFA} - S_L) \quad (3)$$

where,  $J_{LCFA}$  = mass of LCFA diffused into the acidogenic biofilm per unit time per unit area ( $\text{mg}/\text{cm}^2/\text{day}$ )

$D_{fA}$  = molecular diffusion co-efficient of LCFA from bulk liquid into the acidogenic biofilm ( $\text{cm}^2/\text{day}$ )

$L_A$  = thickness of effective LCFA diffusion layer (cm),

$S_{LCFA}, S_L$  = LCFA concentration in the bulk liquid and at the acidogenic biofilm/liquid interface ( $\text{mg}/\text{cm}^3$ ), respectively.

Rearranging eq. (3),

$$S_L = S_{LCFA} - \frac{L_A}{D_{fA}} J_{LCFA}$$

Mass Balance of substrate between entry and exit yields,

$$S_L = S'_{LCFA} + a \cdot \theta_1 \cdot J_{LCFA} \quad (4)$$

where,  $S'_{LCFA}$  = final LCFA concentration in the effluent coming from the acidogenic biofilm (mg/cm<sup>3</sup>)

$a$  = specific surface area of acidogenic biofilm (cm<sup>2</sup>/cm<sup>3</sup>)

$\theta_1$  = hydraulic retention time (HRT) (day)

Also, transport of substrate into the biofilm would occur through molecular diffusion via Fick's second law,

$$r_{(LCFA)diff} = D_{fA} \frac{d^2 S'_{LCFA}}{dz_A^2} \quad (5)$$

where,  $r_{(LCFA)diff}$  = rate of LCFA diffusion (mg/cm<sup>3</sup>/day)

$Z_A$  = distance of the acidogenic biofilm layer from the biofilm support surface (cm).

Utilization of substrate (LCFA) at any position in the attached-growth system,

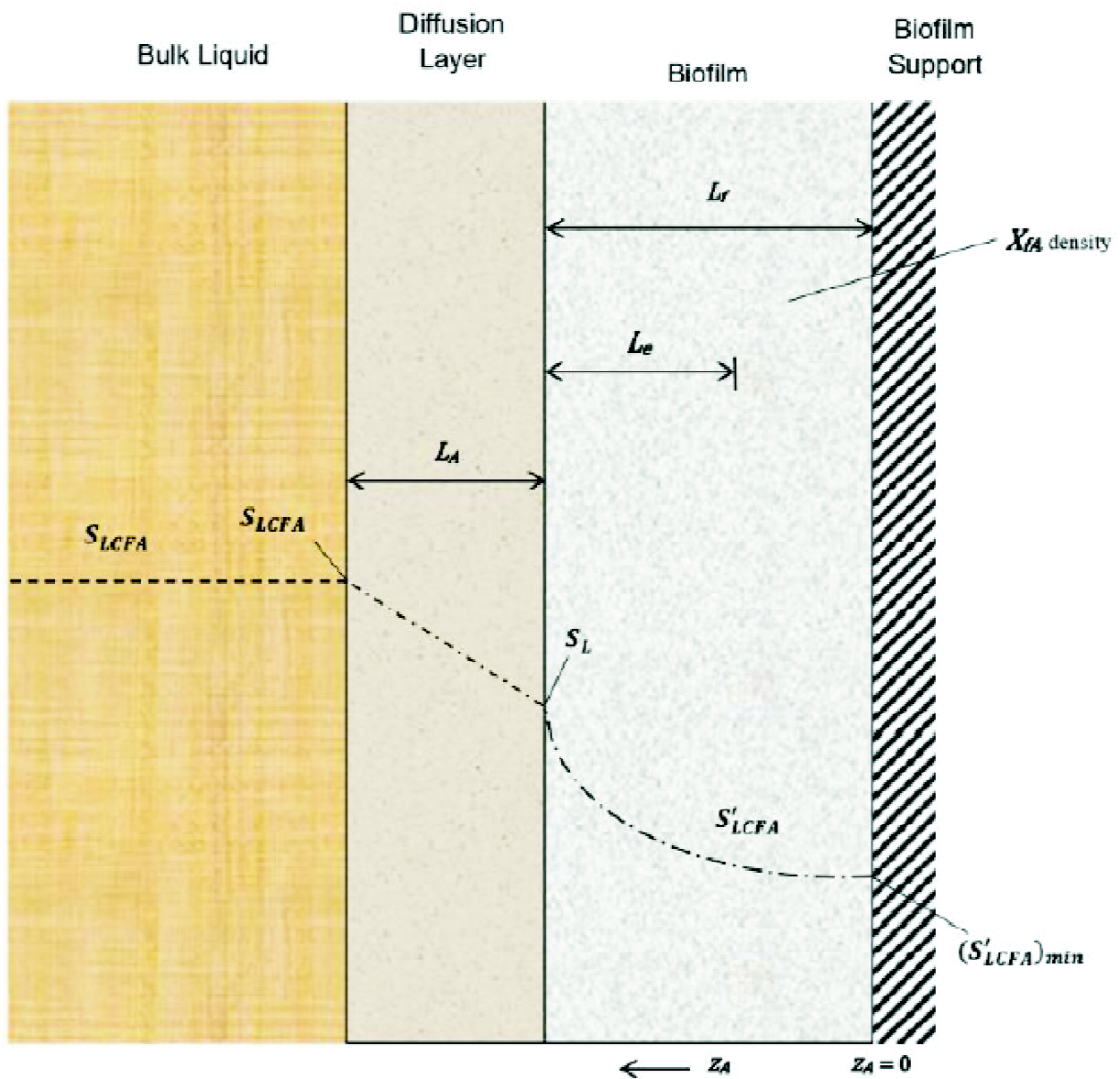


Fig. 2. Concentration profile of LCFAs through acidogenic biofilm.

$$r_{(LCFA)ut} = -\frac{k_A \cdot X_{fA} \cdot S'_{LCFA}}{K_{SA} + S'_{LCFA}} \quad (6)$$

where,  $X_{fA}$  is the attached acidogenic biomass concentration (in mg/cm<sup>3</sup>).

Since substrate utilization and diffusion would occur simultaneously, eqs. (5) and (6) can be combined to give the overall substrate mass-balance. Under steady-state condition, the substrate mass-balance in the biofilm can be represented as,

$$D_{fA} \frac{d^2 S'_{LCFA}}{dz_A^2} - \frac{k_A \cdot X_{fA} \cdot S'_{LCFA}}{K_{SA} + S'_{LCFA}} = 0$$

$$\text{or, } \frac{d^2 S'_{LCFA}}{dz_A^2} = \frac{k_A \cdot X_{fA} \cdot S'_{LCFA}}{D_{fA} (K_{SA} + S'_{LCFA})} \quad (7)$$

Under limiting substrate condition ( $K_{SA} \gg S'_{LCFA}$ ),

$$\frac{d^2 S'_{LCFA}}{dz_A^2} = \frac{k_A \cdot X_{fA} \cdot S'_{LCFA}}{D_{fA} \cdot K_{SA}}$$

$$\text{or, } \frac{d^2 S'_{LCFA}}{dz_A^2} = \left( \frac{k_A}{D_{fA} \cdot K_{SA}} \right) X_{fA} \cdot S'_{LCFA}$$

$$\text{or, } \frac{d^2 S'_{LCFA}}{dz_A^2} = K_1 \cdot X_{fA} \cdot S'_{LCFA} \quad (8)$$

$$\text{where, } K_1 = \frac{k_A}{D_{fA} \cdot K_{SA}}$$

Solution of eq. (8) requires two different boundary conditions,

(1) No substrate gradient in the attachment surface, i.e.

$$\text{At } Z_A = L_f, \frac{d^2 S'_{LCFA}}{dz_A} = 0$$

(2) At the biofilm-bulk liquid interface, where transportation of substrate from the bulk-liquid into the biofilm's outer surface occurs, the mass transport can be described via Fick's first law as

$$\text{At } Z_A = 0, J_{LCFA} = \frac{D_{fA}}{L_A} (S_{LCFA} - S_L) = D_{fA} \frac{dS'_{LCFA}}{dz_A}$$

Therefore, when the substrate from the biofilm/bulk-liq-

uid interface fully penetrates into the biofilm, the substrate flux  $J_{LCFA}$  and the LCFA concentration  $S'_{LCFA}$ , at any point in the biofilm from the biofilm support can be worked out as,

$$S'_{LCFA} = S_L \frac{\cosh\left(\frac{L_f - z_A}{D_{fA}/(X_{fA} \cdot K_1)}\right)}{\cosh\left(\frac{L_f}{\sqrt{\frac{D_{fA}}{X_{fA} \cdot K_1}}}\right)} \quad (9)$$

$$J_{LCFA} = \frac{D_{fA} \cdot S_L \tanh\left(\frac{L_f}{\sqrt{\frac{D_{fA}}{X_{fA} \cdot K_1}}}\right)}{\sqrt{\frac{D_{fA}}{X_{fA} \cdot K_1}}} \quad (10)$$

$\tanh(x)$  = hyperbolic tangent of  $x = (e^x - e^{-x})/(e^x + e^{-x})$

$\cosh(x)$  = hyperbolic cosine of  $x = \frac{1}{2}(e^x + e^{-x})$

*Suspended growth system:*

Rate of utilization of the substrate (LCFA) at any position in the suspended-growth system,

$$\frac{dS''_{LCFA}}{dt} = \frac{k_A X_A S''_{LCFA}}{K_{SA} + S''_{LCFA}} \quad (11)$$

where,  $k_A$  = maximum specific rate of LCFA utilization (day<sup>-1</sup>)

$K_{SA}$  = half-saturation constant for acidogenic system (mg/cm<sup>3</sup> or mgCOD/L)

$S''_{LCFA}$  = LCFA concentration in the acidogenic suspended phase (mgCOD/L)

$X_A$  = concentration of biomass in the acidogenic suspended phase (mg/L)

Under limiting substrate condition i.e.  $K_{SA} \gg S''_{LCFA}$

Hence, eq. (11) can be modified as follows.

$$\frac{dS''_{LCFA}}{dt} = -\frac{k_A X_A S''_{LCFA}}{K_{SA}}$$

$$\text{or, } \frac{dS''_{LCFA}}{dt} = -K'_A S''_{LCFA}$$

$$\text{where, } K'_A = \frac{k_A X_A}{K_{SA}}$$

$$\text{or, } \frac{dS''_{LCFA}}{S''_{LCFA}} = -K'_A dt$$

Integrating both sides under boundary conditions  $t = 0, S''_{LCFA} = S'_{LCFA}$  and  $t = t, S''_{LCFA} = S''_{LCFA}$

$$\int_{S'_{LCFA}}^{S''_{LCFA}} \frac{dS''_{LCFA}}{S''_{LCFA}} = -K'_A \int_0^t dt$$

$$\text{or, } \ln \left( \frac{S''_{LCFA}}{S'_{LCFA}} \right) = -K'_A t$$

$$\text{or, } \frac{S''_{LCFA}}{S'_{LCFA}} = e^{-K'_A t}$$

$$\text{or, } S''_{LCFA} = S'_{LCFA} e^{-K'_A t} \quad (12)$$

*Methanogenesis stage:*

There are two different phases of biomass growth in the methanogenic reactor, firstly the suspended-growth and thereafter attached-growth.

*Suspended growth system:*

Rate of utilization of substrate (SCFA) at any position in the suspended-growth system,

$$\frac{dS_{SCFA}}{dt} = - \frac{k_M X_M S_{SCFA}}{K_{SM} + S_{SCFA}} \quad (13)$$

$S_{SCFA}$  = concentration of SCFA (mgCOD/L)

$k_M$  = maximum specific rate of methanogenesis ( $\text{day}^{-1}$ )

$X_M$  = concentration of suspended methanogenic biomass (mg/L)

$K_{SM}$  = half-saturation constant for methanogenic system (mgCOD/L or  $\text{mg}/\text{cm}^3$ )

Under limiting substrate condition,  $K_{SM} \gg S_{SCFA}$

Hence, eq. (13) can be modified as follows,

$$\frac{dS_{SCFA}}{dt} = - \frac{k_M X_M S_{SCFA}}{K_{SM}}$$

$$\text{or, } \frac{dS_{SCFA}}{dt} = -K'_M S_{SCFA}$$

$$\text{where, } K'_M = \frac{k_M X_M}{K_{SM}}$$

$$\text{Therefore, } \frac{dS_{SCFA}}{S_{SCFA}} = -K'_M dt$$

Integrating both sides under boundary conditions  $t = 0, S_{SCFA} = (S_{SCFA})_{in}$ , and  $t = t, S_{SCFA} = S_{SCFA}$

$$\int_{(S_{SCFA})_{in}}^{S_{SCFA}} \frac{dS_{SCFA}}{S_{SCFA}} = -K'_M \int_0^t dt$$

$$\ln \left[ \frac{S_{SCFA}}{(S_{SCFA})_{in}} \right] = -K'_M t$$

$$\text{or, } \frac{S_{SCFA}}{(S_{SCFA})_{in}} = e^{-K'_M t}$$

$$\text{or, } S_{SCFA} = (S_{SCFA})_{in} e^{-K'_M t} \quad (14)$$

*Attached-growth phase:*

The substrate flux through the attached-growth biofilm in the methanogenic reactor can be expressed as,

$$J_{SCFA} = \frac{D_{fm}}{L_M} (S_{SCFA} - S_S) \quad (15)$$

where,  $J_{SCFA}$  = mass of SCFA diffused into the methanogenic biofilm per unit time per unit area ( $\text{mg}/\text{cm}^2/\text{day}$ )

$D_{fm}$  = molecular diffusion coefficient of SCFA from the bulk liquid into the methanogenic biofilm ( $\text{cm}^2/\text{day}$ )

$L_M$  = thickness of effective SCFA diffusion layer (cm)

$S_{SCFA}, S_S$  = SCFA concentration in the bulk liquid and at the methanogenic biofilm/liquid interface ( $\text{mg}/\text{cm}^3$ ), respectively

$$S_S = S_{SCFA} - \frac{L_M}{D_{fm}} J_{SCFA}$$

Mass Balance of substrate between entry and exit yields,

$$S_S = S'_{SCFA} + a' \cdot \theta_2 \cdot J_{SCFA} \quad (16)$$

where,  $S'_{SCFA}$  = final SCFA concentration in the effluent coming from the methanogenic biofilm ( $\text{mg}/\text{cm}^3$ )

$a'$  = specific surface area of methanogenic biofilm ( $\text{cm}^2/\text{cm}^3$ )



$\theta_2$  = hydraulic retention time (HRT) (day)

Utilization of substrate (SCFA) at any position in the biofilm would be same as that in a suspended-growth system,

$$r_{(SCFA)ut} = \frac{k_M \cdot X_{fm} \cdot S'_{SCFA}}{K_{SM} + S'_{SCFA}} \quad (17)$$

where,  $r_{(SCFA)ut}$  = rate of SCFA utilization (mg/cm<sup>3</sup>/day)

$X_{fm}$  = biomass density present in the attached

methanogenic biofilm (mg/cm<sup>3</sup>)

The SCFA concentration profile through the methanogenic biofilm is shown in Fig. 3.

Also, transport of substrate into the biofilm would occur through molecular diffusion via Fick's second law,

$$r_{(SCFA)diff} = D_{fm} \frac{d^2 S'_{SCFA}}{dz_M^2} \quad (18)$$

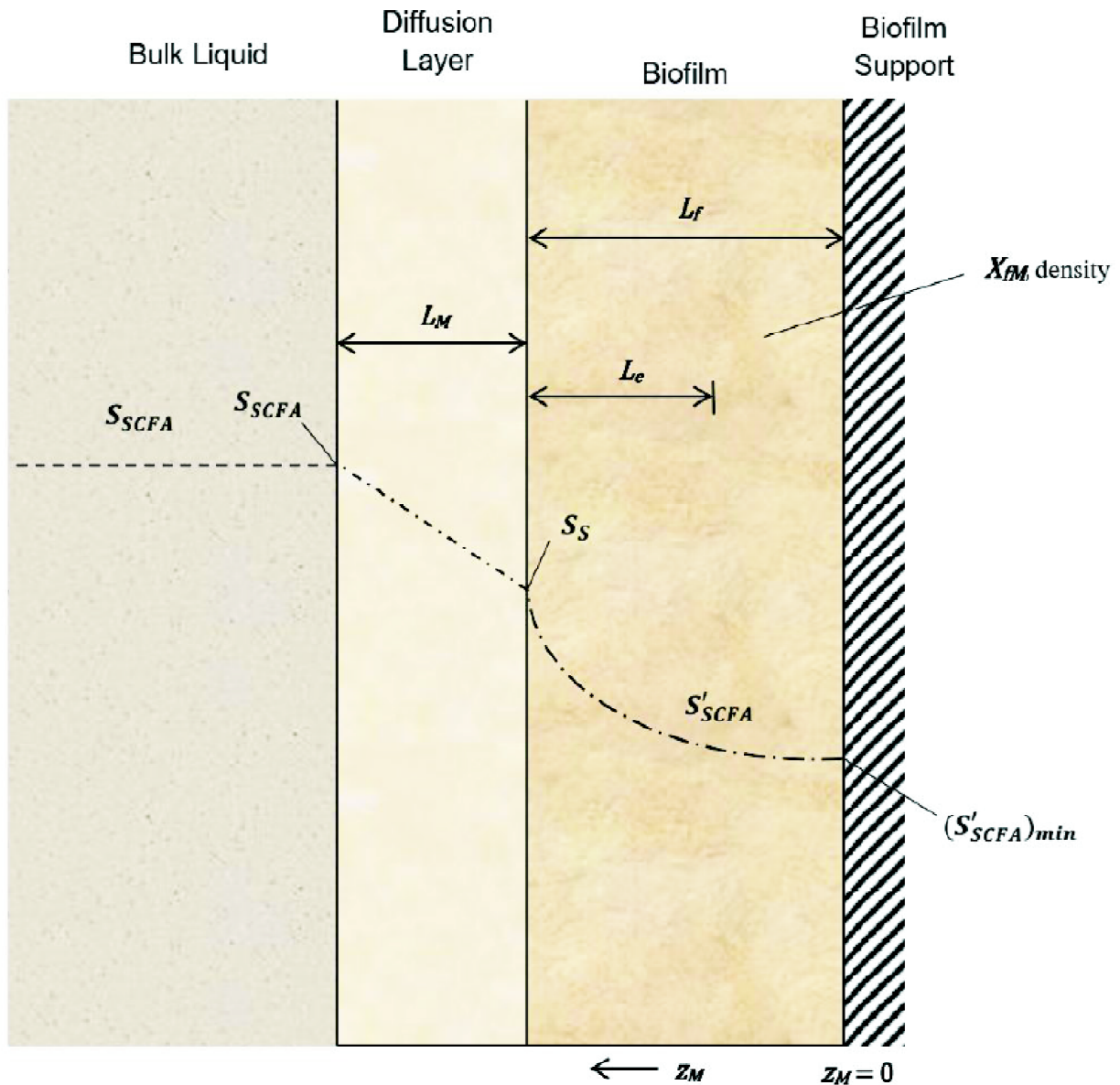


Fig. 3. Concentration profile of SCFAs through methanogenic biofilm.



where,  $r_{(SCFA)diff}$  = rate of SCFA diffusion (mg/cm<sup>3</sup>/day)

$Z_M$  = distance of methanogenic biofilm layer from the biofilm support surface (cm).

Since substrate utilization and diffusion would occur simultaneously, eqs. (17) and (18) can be combined to give the overall substrate mass-balance. Under steady-state condition, the substrate mass-balance in the biofilm can be represented as,

$$D_{fM} \frac{d^2 S'_{SCFA}}{dz_M^2} - \frac{k_M \cdot X_{fM} \cdot S'_{SCFA}}{K_{SM} + S'_{SCFA}} = 0$$

$$\text{or, } \frac{d^2 S'_{SCFA}}{dz_M^2} - \frac{k_M \cdot X_{fM} \cdot S'_{SCFA}}{D_{fM} (K_{SM} + S'_{SCFA})} = 0 \quad (19)$$

Under limiting substrate condition ( $K_{SM} \gg S'_{SCFA}$ ),

$$\frac{d^2 S'_{SCFA}}{dz_M^2} = \frac{k_M \cdot X_{fM} \cdot S'_{SCFA}}{D_{fM} K_{SM}}$$

$$\text{or, } \frac{d^2 S'_{SCFA}}{dz_M^2} = \left( \frac{k_M}{D_{fM} \cdot K_{SM}} \right) X_{fM} \cdot S'_{SCFA}$$

$$\text{or, } \frac{d^2 S'_{SCFA}}{dz_M^2} = K_2 \cdot X_{fM} \cdot S'_{SCFA} \quad (20)$$

$$\text{where, } K_2 = \frac{k_M}{D_{fM} \cdot K_{SM}}$$

Solution of eq. (20) requires two different boundary conditions,

(1) No substrate flux into the attachment surface,

$$\text{At, } Z_M = L_f, \frac{dS'_{SCFA}}{Dz_M} = 0$$

(2) At the biofilm/bulk-liquid interface, where transportation of the substrate from the bulk-liquid into the biofilm's outer surface occurs, the mass transport can be described via Fick's first law,

$$Z_M = 0, J_{SCFA} = \frac{D_{fM}}{L_M} (S_{SCFA} - S_S = D_{fM} dS'_{SCFA} dz_M)$$

Therefore, when the substrate from the biofilm/bulk-liquid interface fully penetrates into the biofilm, the substrate flux  $J_{SCFA}$  and the SCFA concentration  $S'_{SCFA}$ , at any point in the biofilm, from the biofilm support can be estimated as,

$$S'_{SCFA} = S_S \frac{\cosh\left(\frac{L_f - z_M}{D_{fM}/(X_{fM} \cdot K_2)}\right)}{\cosh\left(\frac{L_f}{\sqrt{\frac{D_{fM}}{X_{fM} \cdot K_2}}}\right)} \quad (21)$$

$$J_{SCFA} = \frac{D_{fM} \cdot S_S \tanh\left(\frac{L_f}{\sqrt{\frac{D_{fM}}{X_{fM} \cdot K_2}}}\right)}{\sqrt{\frac{D_{fM}}{X_{fM} \cdot K_2}}} \quad (22)$$

$\tanh(x)$  = hyperbolic tangent of  $x = (e^x - e^{-x})/(e^x + e^{-x})$

$\cosh(x)$  = hyperbolic cosine of  $x = \frac{1}{2}(e^x + e^{-x})$

*Solution of the developed mathematical model:*

The above developed mathematical model can be put to use to predict the effluent substrate concentration from the three different stages only after the relevant kinetic coefficients are known. For instance, in the case of the hydrolytic reactor, the value of  $S_H$  (in mgCOD/L) represents the COD of the solid substrate left in the hydrolytic reactor following the attainment of the steady-state. The time that elapses in order for the substrate, undergoing hydrolysis, to reach this equilibrium or steady-state is the hydrolytic batch period (or  $t_H$ ). Therefore, the various kinetic coefficients ( $k_H$ ,  $K_{SH}$ ), relevant to the hydrolysis step, that are needed to predict the COD equivalent of the final solid substrate left following the conclusion of a particular batch period can be found out graphically by conducting several batch studies. The average suspended hydrolytic biomass concentration or  $X_H$  (in mg/L) corresponding to the batch studies conducted would also have to be determined.

The hydrolyzed liquid product entering into the acidogenic reactor would undergo acidogenesis and acetogenesis. Since the production of SCFAs or VFAs is predominant in the acidogenic reactor, the hydrolyzed product entering into the

acidogenic reactor is assumed to primarily constitute LCFAs and the concentration of which is expressed as mgCOD/L. The LCFA concentration (as mgCOD/L) entering into the acidogenic can be found out by subtracting  $S_H$  from  $S_{H0}$  corresponding to a particular hydrolytic batch. This  $S_{H0} - S_H$  represents the influent LCFA concentration corresponding to the acidogenic reactor. Upon entry into the acidogenic reactor, the hydrolyzed product would firstly, pass through the anaerobic filter comprising the biofilm supported on some inert media, and thereafter through the suspended-growth part. To predict the substrate flux ( $J_{LCFA}$ ) diffusing into the acidogenic biofilm and the concentration of the substrate ( $S'_{LCFA}$ ) exiting the attached-growth system, the various parameters relevant to the acidogenic biofilm part ( $D_{fA}$ ,  $L_A$ ,  $S_L$ ), the acidogenic attached-growth biomass concentration ( $X_{fA}$ ), and the specific surface area of the acidogenic biofilm have to be found out first. Values of  $D_{fA}$  and  $L_A$  can be assumed by referring to the guidelines, pertaining to biofilm modeling, specified by Mendoza and Sáez<sup>18</sup>, Rittmann *et al.*<sup>22</sup>, Boltz *et al.*<sup>2</sup>, Stewart<sup>26</sup>, and Rittmann and McCarty<sup>23</sup>. The values of  $S_L$  and the biofilm specific surface area has to be determined experimentally. The  $S'_{LCFA}$  exiting the acidogenic attached-growth part would enter into the acidogenic suspended-growth part from where it would exit as  $S''_{LCFA}$ . The value of  $S''_{LCFA}$  can, therefore, be predicted by determining the acidogenic suspended-growth kinetic coefficients ( $k_A$ ,  $K_{SA}$ ) and the acidogenic suspended-growth biomass concentration ( $X_A$ ). This can be achieved by conducting suitable number of acidogenic batch studies under suspended-growth conditions similar to the hydrolytic operation.

In the case of the methanogenic reactor, the concentration of the final substrate ( $S'_{SCFA}$ ) exiting the reactor can be predicted in a similar manner, as specified in the case of the acidogenic reactor, with the exception that the flow of the substrate (VFA/SCFA) would firstly be through the suspended-growth part, and then through the attached-growth part. The influent for the methanogenic reactor would be the SCFAs/VFAs produced in the acidogenic reactor and its value would, therefore, be expressed as  $S'_{LCFA} - S''_{LCFA}$  (mgCOD/L). Methanogenic batch studies under suspended-growth conditions have to be conducted for determining the relevant methanogenic suspended-growth kinetic coefficients ( $k_M$ ,  $K_{SM}$ ). To determine the parameters relevant to the

methanogenic biofilm part ( $X_{fM}$ ,  $D_{fM}$ ,  $L_M$ ,  $S_S$ ), protocols as specified above (for the acidogenic biofilm modeling operation) would have to be followed. The solution of the proposed mathematical model can, therefore, be suitably done via the FORTRAN programming language similar to that suggested by Sarkar and Mazumder<sup>25</sup>.

## Conclusions

The importance of three-stage AD towards stabilization of OFMSW, as highlighted in the present study, is drawing rapid attention amongst researchers in the field of anaerobic stabilization of organic waste matter. Separation of the major phases (hydrolysis, acidogenesis/acetogenesis, and methanogenesis) has not only resulted in striking a much-needed balance between the generation and stabilization of the ever-increasing load of OFMSW, but also contributed to the yield of various types of liquid and gaseous biofuel, besides generating better quality digestate/bio-sludge. Just as the development of various mathematical models (ASMs, and ADM1) helped in the rapid improvement and implementation of anaerobic stabilization of liquid organic waste, the present study focused on the development of a simplistic mathematical model, under limiting-substrate condition, considering the crucial biotechnological aspects of a three-stage hybrid anaerobic digester meant for the stabilization of FVW. The developed mathematical model is flexible enough to be relevant to the operation of any three-stage anaerobic digester (comprising both suspended- and attached-growth system) stabilizing solid organic waste matter. The rendered flexibility is on account of the incorporation of the classical Monod's kinetics, while modeling the suspended-growth part, and Fick's 2nd law of molecular diffusion, while modeling the mass-transport inside the biofilm. Another theoretical consideration, which makes the proposed mathematical model even more flexible, is the simplistic assumption of the solid substrate conversion into LCFAs as the major process in the hydrolytic reactor, the LCFAs to SCFAs conversion as the major process in the acidogenic reactor, and the degradation of the SCFAs (into biogas) as the major process in the methanogenic reactor. In modeling the hybrid acidogenic and the methanogenic reactors, the developed mathematical model, therefore, considered the competition between the suspended- and the attached-biomass for the substrate-type atypical to the respective stages.

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