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Development, identification and validation of a mathematical model of anaerobic digestion of sewage sludge focusing on H_2S formation and transfer

F. Carrera-Chapela[a,b,*], A. Donoso-Bravo[b,c], D. Jeison[c,d], I. Díaz[e], J.A. Gonzalez[a], G. Ruiz-Filippi[b,c]

[a] Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, 15782 Santiago de Compostela, Spain
[b] Escuela de Ingeniería Bioquímica, Pontificia Universidad Católica de Valparaíso, General Cruz 34, Valparaíso, Chile
[c] INRIA-Chile, Communication and Information Research and Innovation Center (CIRIC), Avenida Apoquindo 2827, Piso 12, Las Condes, Santiago, Chile
[d] Chemical Engineering Department, Universidad de La Frontera, Av. Francisco Salazar 0145, Temuco, Chile
[e] Department of Chemical Engineering and Environmental Technology, Escuela de Ingenierías Industriales, Sede Dr. Mergelina, University of Valladolid, Dr. Mergelina s/n, 47011 Valladolid, Spain

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ABSTRACT

Nowadays, there are plenty of models of the anaerobic digestion process, however the impact of this odor emission on these models has received very little attention. Hydrogen sulfide (H_2S) has been used as odor trace marker for odor dispersion studies which is formed by microbial action of sulfate reducing bacteria under anaerobic conditions. A mathematical model with focus on the H_2S generation with a reduce number of parameters of five stages was developed. The model and parameters were calibrated and validated with experimental data from two pilot scale anaerobic reactors treating sewage sludge. The developed model is able to describe properly the dynamic behavior of this system, particularly, its gas phase composition with an accuracy of 90%, for hydrogen sulfide and carbon dioxide, and 60% for methane, within 99% of confidence.

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1. Introduction

In bioprocesses, the application of mathematical models allows representing and predicting the system's dynamic behavior and therefore, the establishment of control strategies and operational management measures. Unfortunately and despite the significant progress of the modeling practice in anaerobic digestion (AD), a proper application of mathematical modeling for control strategies remains a complex and an unsolved issue, which is caused, among other things by the lack of reliable, informative and affordable on-line measurement of the state variables [1]. The anaerobic digestion model n1 (ADM1) is a widely used model in AD, which provides a good tool to illustrate the complex system behavior of the AD [2]. However, in order to represent this complexity entails a high number of state variables as well as the physicochemical and biochemical processes, consequently a high number of parameters that need to be properly identified [3]. It is therefore that, simpler, although still mechanistic, models have been developed. That is the case of the AM2 model developed by Bernard et al. [1] and several modifications [3,4], which simplifies the whole anaerobic process in two stages, acidogenesis and methanogenesis. When the hydrolysis is the limiting step of the whole reaction, for instance when particulate substrate are treated, it is necessary to include the hydrolysis stage, previous to the acidogenesis [5].

The main odor emissions released to the atmosphere from the operation of WWTP come from several organic gases, but they can be characterized in terms of odor nuisance produced by sulfur reduced compounds, with H_2S as the main compound [6–9]. The H_2S generation is mainly based on the action of sulfate reducing bacteria (SRB) that can compete with methanogenic archaea for the intermediate carbon source [10,11]. However, the H_2S generation has been barely considered when using simplified models [12,13] despite, as previously mentioned, the importance of this compound on the global performance of the sludge management and treatment system as well as odor generation in WWTP [9].

* Corresponding author at: Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, 15782 Santiago de Compostela, Spain.
E-mail address: fabio.carrera@usc.es (F. Carrera-Chapela).

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Nomenclature

X_0	particulate organic matter (gCOD L^{-1})
S_1	soluble organic matter (gCOD L^{-1})
S_2	acetic acid equivalent (gCOD L^{-1})
S_3	sulfate (mg L^{-1})
K_{s1}	affinity constant of fermentative bacteria (gCOD L^{-1})
K_{s2}	affinity constant of methanogens (gCOD L^{-1})
K_{s3}	affinity constant of SRB (gCOD L^{-1})
K_{a1}	equilibrium constant H_2S (mol L^{-1})
K_j	stoichiometric coefficient
X_1	fermentative bacteria (gCOD L^{-1})
X_3	sulfate reducing bacteria (SRB) (gCOD L^{-1})
μ_{m1}	maximum specific rate acidogenic bacteria (d^{-1})
μ_{m2}	maximum specific rate methanogenic archaea (d^{-1})
ρ_{a_1}	acid–base equilibrium rate (mmol L^{-1} d^{-1})
D	dilution rate (d^{-1})
$\xi_{in,i}$	state variable value in the inlet
ξ_i	state variable
q_c	molar flow CO_2 (mmol L^{-1} d^{-1})
ρ	liquid–gas desorption rate (mmol L^{-1} d^{-1})
B	bicarbonate (mmol L^{-1})
IC	inorganic carbon (mmol L^{-1})
Z	cations (mmol L^{-1})
$r_{i,j}$	reaction rate for state variable i
X_2	methanogens bacteria (gCOD L^{-1})
k_h	hydrolysis coefficient (d^{-1})
μ_{m3}	maximum specific rate SRB (d^{-1})
K_{Hcc}	dimensionless Henry constant

The aim of this study is to develop a simplified mathematical model for the anaerobic digestion process that takes into account the hydrolysis and sulfate reducing action for hydrogen sulfide formation such that this model can afterward be used to asses the odor impact of the anaerobic digestion emissions.

2. Methodology

2.1. Model assumptions and considerations

A general scheme of the bioreaction pathways is shown in Fig. 1. The same stoichiometry and reaction kinetics presented by Donoso-Bravo et al. [14] were used in this study but adding the sulfate reducing stage. It must to keep in mind that any model is a mathematical projection of the actual process. For this reason, some reasonable and affordable assumptions, within the scope and objective of the model application, must be done.

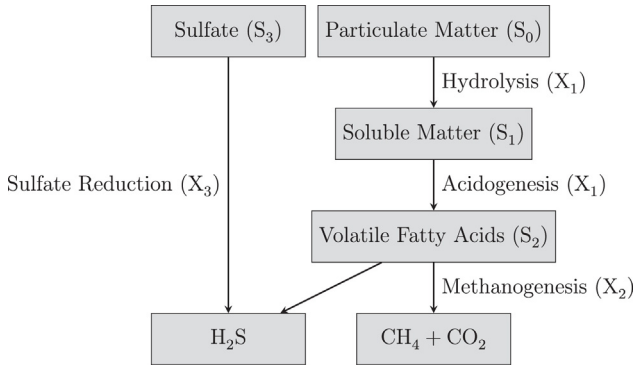

Fig. 1. Scheme of the anaerobic digestion for hydrogen sulfide production.

- There is no biomass death decay.
- The volatile fatty acids (VFA) are represented as acetic equivalents.
- Three microbial populations are involved in the hydrolysis, acidogenesis, methanogenesis and sulphate reduction.
- Hydrogen production/accumulation is negligible. Therefore, SRB use the VFA as electron donor and the sulfate as electron acceptor, instead of hydrogen.
- Only bicarbonate/carbon dioxide, hydrogen sulfide/bisulfide, sulphate and proton contribute to pH according to ion balance.
- There is no metal precipitation, such as FeS.
- Biogas release is carried out by the two-film theory according to the global mass transfer coefficient K_LA for hydrogen sulfide and carbon dioxide, whereas methane solubilization in water is assumed to be negligible.

2.2. Biological model

The first stage corresponds to the solubilization or hydrolysis of the particulate substrate, afterwards the soluble complex substrate is transformed into volatile fatty acids (VFA) which are represented as acetic equivalent, during the acidogenesis reaction, followed by he methanogenic step where the VFA are converted into biogas. Sulfate reduction process is carried out in parallel by the SRB using the VFA as electron donor and the sulfate as electron acceptor. The stoichiometric reactions considered in this model follow:

$$\text{Hydrolysis: } S_0 \xrightarrow{r_0} K_0S_1 \quad (1)$$

$$\text{Acidogenesis: } K_1S_1 \xrightarrow{r_1} X_1 + K_2S_2 + K_4CO_2 \quad (2)$$

$$\text{Methanogenesis: } K_3S_2 \xrightarrow{r_2} X_2 + K_5CO_2 + K_6CH_4 \quad (3)$$

$$\text{Sulphate reduction: } K_7S_3 + K_9S_2 \xrightarrow{r_3} X_3 + K_{10}CO_2 + K_8H_2S \quad (4)$$

The hydrolysis was modeled as a Contois function because hydrolysis is considered an enzymatic reaction carried out by hydrolytic/acidogenic bacteria and assumes that a high amount of extra-cell enzyme is a consequence of an increase amount of the biomass, which leads to an increase of the reaction kinetics. Otherwise, it has been shown the Contois function works better than classic first-order kinetics [15]. FB and SRB bacteria are well described their growth function by Monod kinetic, while MB can experiment uncompetitive inhibition for VFA accumulation which is best described by Haldane kinetic [1,11]. Thus, the kinetics for specific growth rate equation for FB, SRB, MB and hydrolysis are described by the following equations,

$$\text{Hydrolysis: } r_0 = k_h \cdot \frac{S_0}{K_{s0} \cdot X_1 + S_0} \cdot X_1 \quad (5)$$

$$\text{Acidogenesis: } r_1 = \mu_{m1} \cdot \frac{S_1}{K_{s1} + S_1} \cdot X_1 \quad (6)$$

$$\text{Methanogenesis: } r_2 = \mu_{m2} \cdot \frac{S_2}{K_{s2} + S_2 + \frac{S_2^2}{K_{I2}}} \cdot X_2 \quad (7)$$

$$\text{Sulphate reduction: } r_3 = \mu_{m3} \cdot \frac{S_2 \cdot S_3}{(K_{s3} + S_2) \cdot (K_{s4} + S_3)} \cdot X_3 \quad (8)$$

The mass balance for a continuous stirred reactor for each state variable is expressed by the following equation,

$$\frac{d\xi_i}{dt} = D \cdot (\xi_{in,i} - \xi_i) + \sum_{j=1}^{4} (K_{ij} \cdot r_j) - \rho_i \quad (9)$$

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