Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Modelling inhibitory effects of long chain fatty acids in the anaerobic digestion process

Ž. Zonta [a,b], M.M. Alves [c], X. Flotats [a,b], J. Palatsi [a,*]

[a] IRTA, GIRO Joint Research Unit IRTA-UPC, Torre Marimon, E-08140 Caldes de Montbui, Barcelona, Spain

[b] Dept. of Agrifood Engineering and Biotechnology, Universitat Politècnica de Catalunya (UPC), Parc Mediterrani de la Tecnologia, Edifici D-4, E-08860 Castelldefels, Barcelona, Spain

[c] IBB – Institute for Biotechnology and Bioengineering, Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-57 Braga, Portugal

ARTICLE INFO

Article history:
Received 30 July 2012
Received in revised form
3 December 2012
Accepted 5 December 2012
Available online 19 December 2012

Keywords:
Anaerobic digestion
LCFA inhibition
Mathematical modelling
ADM1

ABSTRACT

Mathematical modelling of anaerobic digestion process has been used to give new insights regarding dynamics of the long chain fatty acids (LCFA) inhibition. Previously published experimental data, including batch tests with clay mineral bentonite additions, were used for parameter identification. New kinetics were considered to describe the bio-physics of the inhibitory process, including: i) adsorption of LCFA over granular biomass and ii) specific LCFA substrate (saturated/unsaturated) and LCFA-degrading populations. Furthermore, iii) a new variable was introduced to describe the state of damage of the acetoclastic methanogens in order to account for the loss of cell-functionality (inhibition) induced by the adsorbed LCFAs. The proposed model modifications are state compatible and easy to be integrated into the International Water Association's Anaerobic Digestion Model N°1 (ADM1) framework. Practical identifiability of model parameters was assessed with a global sensitivity analysis, while calibration and model structure validation were performed on independent data sets. A reliable simulation of the LCFA-inhibition process can be achieved, if the model includes the description of the adsorptive nature of the LCFAs and the LCFA-damage over specific biomass. The importance of microbial population structure (saturated/unsaturated LCFA-degraders) and the high sensitivity of acetoclastic population to LCFA are evidenced, providing a plausible explanation of experimental based hypothesis.

1. Introduction

Long chain fatty acids (LCFAs) are the main intermediate by-product of the lipid degradation process, and their accumulation in anaerobic digesters has been related with problems of sludge flotation, biomass washout and inhibition of the microbial activity (Rinzema et al., 1994). The cell-membrane seems to be the prime common target for most of the described LCFA inhibitory effects over anaerobic biomass. According to Kim and Gadd (2008), cell-membrane exposure to high concentrations of LCFA promotes macromolecular crowding and disruption of mechanisms such as proton-motive-force, DNA-docking and ATP-chemosynthesis. Impairment in nutrient uptake or inhibition of specific enzyme activity was also reported (Desbois and Smith, 2010). Pereira et al. (2004, 2005) have proven that the LCFA inhibition

* Corresponding author. Tel.: +34 938654350x1336; fax: +34 938650954.
E-mail address: jordi.palatsi@irta.cat (J. Palatsi).

0043-1354/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2012.12.007

was reversible and also that the LCFA inhibition was related to physical transport limitation effects. The irreversible cell-damage, due to the adsorption of LCFA, was discarded after this evidence and new technological perspectives emerged for the high-rate anaerobic treatment of wastewater containing lipids (Alves et al., 2009).

Several studies have discussed the addition of competing adsorbents into systems treating grease and fats as a possible strategy to limit LCFA inhibitory effects (Angelidaki et al., 1999; Beccari et al., 1999; Nielsen and Ahring, 2006; Palatsi et al., 2009). However, the dynamics of the solid–liquid adsorption process were not included in those studies and approximations to the LCFA-inhibition process (ratio inhibitor/biomass) were considered only (Pereira et al., 2004; Palatsi et al., 2010).

Up to day, Hwu et al. (1998) have proposed one of the most detailed descriptions of the LCFA's bio-sorption, degradation and inhibition processes. The LCFA inhibitory process was described based on a four-phase theoretical model. First, after a LCFA-pulse or biomass exposure, the LCFA rapidly disappears from the aqueous phase and is adsorbed onto the solid phase. Because of the LCFA-toxicity effect, the methane production is negligible during this phase. Second, depending on the initial LCFA-pulse concentration, the LCFA-concentration could increase in the aqueous phase, as a consequence of desorption mediated by the initial methane produced. Third, the LCFA-concentration decreases in the aqueous phase as a consequence of the biological degradation of the adsorbed LCFA. Finally, methane is ultimately recovered once the remaining LCFA-adsorbed concentration is low. Also, recent advances in molecular microbial ecology have brought new insights on the specific microorganisms that are involved in the ß-oxidation process and the syntrophic methanogens interactions (Hatamoto et al., 2007; Sousa et al., 2007). Those microorganisms are not always abundant in non-adapted systems and their dynamics are not easy to follow. In this context, mathematical models are a valuable tool to be used to interpret collected data and to test new hypotheses.

Despite the fact that LCFA-inhibition is well documented and has a significant impact on the anaerobic digestion process, this phenomenon has not been included still in the ADM1 reference model (Batstone et al., 2002). In other developed models, LCFA inhibition is mainly modelled as a non-competitive process on the lipolytic, acidogenic or methanogenic activities (Angelidaki et al., 1999; Salminen et al., 2000; Lokshina et al., 2003). The commonly used non-competitive inhibition functions (Angelidaki et al., 1999; Palatsi et al., 2010) implicitly assume that, after a LCFA-shock, the time to restore cell-functionality is negligible. It has been demonstrated that methanogens can adapt in several ways the structure and dynamics of their damaged membranes after an inhibitory effect (Valentine, 2007), but not immediately. Consequently, those classical model approximations may result inappropriate to simulate heavily LCFA-inhibited systems. Furthermore, the physical adsorption of LCFA and its inhibitory effect, or the microbiological aspects of LCFA-degradation, remain poorly characterized for modelling purposes. To the best of our knowledge, a mathematical model that includes adsorption-inhibition-degradation processes remains still to be defined and tested.

This paper aims to propose a LCFA-inhibition sub-model with the condition to be easily integrated into the ADM1-model. This new approach tries to integrate all the previously reported knowledge about LCFA inhibitory process, regarding the adsorptive nature and transport limitations of LCFA, the new insights on microorganisms involved in ß-oxidation process and the possible membrane damage caused by LCFA exposure. Proposed model will be tested with two independent data sets obtained in previous batch experiments (Palatsi et al., 2012).

2. Material and methods

2.1. Experimental observations

Previously published experimental data were used for parameter identification. The experimental set-up consisted of several specific batch tests performed with two different anaerobic granular sludges (sludge-A and sludge-B, or independent data sets), including bentonite addition as a synthetic adsorbent, and synthetic sodium oleate as substrate. The experimental set-up and analytical methods are extensively described in Palatsi et al. (2012). The experimental observations were grouped in three main data-sets, summarized as follows:

Data set D_1: LCFA-adsorption batch tests with chemically inactivated biomass (sludge-A) and bentonite, monitoring the time evolution of soluble-LCFA concentrations ($LCFA_l$).

Data set D_2: Methanogenic activity test (SMA) with sludge-A ($D_{2,A}$) and sludge-B ($D_{2,B}$) with acetate (Ac) and hydrogen (H_2) as biogas formation substrates, monitoring the accumulated methane production in vials head-space (CH_4). In addition, blank assays with sludge-A and sludge-B (vials with biomass but without added substrates) were also monitored.

Data set D_3: Batch-tests with increasing LCFA-concentrations and specific batch-tests including preventing/recovering LCFA inhibition strategies, where bentonite was added as an exogenous adsorbent. The experiments with sludge-A ($D_{3,A}$) included vials with bentonite addition after the LCFA-pulse (T_A vials). The experiments with sludge-B ($D_{3,B}$) included vials with a bentonite-LCFA mixed compound added to the LCFA-free biomass (T_B vials), to prevent inhibition. Control vials with LCFA, but without bentonite, were also considered for both tested biomass (C_A and C_B vials). Solid-LCFA ($LCFA_s$), liquid-LCFA ($LCFA_l$), volatile fatty acids (VFA) and methane production (CH_4) measurements were adopted for system monitoring.

2.2. Model development

The developed models were based on a simplification of the anaerobic digestion process as described in the ADM1 model. The same structure, nomenclature and units of the ADM1 model were used (Batstone et al., 2002). The first proposed model, LCFA-M1, included the LCFA-adsorption process and non-competitive inhibition functions. The second model, LCFA-M2, also included a new variable called *healthy-state* that considers the LCFA-inhibitory stage of methanogenic biomass. The models were implemented in MatLab (The Mathworks,