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MODELLING THE PERTURBATION EFFECTS OF THE CHICKEN LITTER OVERLOADING SHOCKS ON LONG-TERM SEMICONTINUOUS ANAEROBIC DIGESTERS

THESIS

In partial fulfillments of the requirements for the degree of:

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MODELLING THE PERTURBATION EFFECTS OF THE CHICKEN LITTER OVERLOADING SHOCKS ON LONG-TERM SEMICONTINUOUS ANAEROBIC DIGESTERS

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DEDICATION

To God for the health and protection in my journey through this world.

Blessed is the one who finds wisdom, and the one who gets understanding, for the gain from her is better than gain from silver and her profit better than gold. She is more precious than jewels, and nothing you desire can compare with her.

Proverbs 3:13-26

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RESUMEN GENERAL

MODELADO DE LOS EFECTOS DE PERTURBACIÓN DE CHOQUES DE SOBRECARGA DE POLLINAZA EN DIGESTORES ANAERÓBICOS EN SEMICONTINUO A LARGO PLAZO.

La composición química y el flujo másico de entrada, juegan un rol vital en el éxito de un proceso de digestión anaeróbica, si ambos se mantienen constantes en un proceso continuo, se puede lograr la producción de metano. Por lo tanto, en procesos de escala completa una de las principales preocupaciones es la sobrecarga orgánica. Esto puede desequilibrar las rutas tróficas, resultando en acumulación de ácidos grasos volátiles (AGV). Dependiendo de la severidad del disturbio, puede ocasionar la falla del digestor. Los modelos matemáticos aplicados a sistemas biológicos proveen información y alternativas para superar estos obstáculos. En este contexto, en el presente trabajo se implementó el modelo de digestión anaeróbica número 1 para simular choques de sobrecarga orgánica. El objetivo fue proponer valores de parámetros cinéticos que permitan describir y entender un sistema perturbado. Para la recolección de datos, dos digestores mesofílicos de 10 L A y B trabajando en modo semi-continuo, fueron tratados en las mismas condiciones de operación. Los digestores se sometieron a dos pulsos de sobrecarga orgánica con un periodo de recuperación entre ambos. para monitorear el desempeño de los digestores se usaron los AGV, pH, y la actividad metanogénica específica. Se usó un algoritmo de evolución diferencial estándar (DEA) para calibrar 28 parámetros bioquímicos. La calibración se obtuvo usando los datos de la primera perturbación en el digestor A. Los parámetros bioquímicos relacionados con la degradación de AGV mostraron los cambios más significativos (por ejemplo: $K_{m,c4}$ de 20 a 4.92; $K_{m,pro}$ de 30 a 2.17; $k_{m,ac}$ de 8 a 5.24; $k_{m,h2}$ de 35 a 10.60 $kg_{COD} \bullet m^{-3}$). Después de la calibración, las salidas del modelo mostraron un mejor ajuste a los datos experimentales en relación con la eficiencia del modelado (EF) y el índice de ajuste (index) comparado con parámetros bioquímicos estándar. Los resultados mostraron que DEA proporciona un método de calibración robusto para simular la respuesta de choques de sobrecarga de pollinaza en un proceso de producción de metano continuo.

Palabras clave: Modelado, ADM1, Disturbios

GENERAL ABSTRACT

MODELLING THE PERTURBATION EFFECTS OF THE CHICKEN LITTER OVERLOADING SHOCKS ON LONG-TERM SEMI-CONTINUOUS ANAEROBIC DIGESTERS.

Chemical composition and mass flow inlet play a vital role in a successful anaerobic digestion process; if both are kept constant in a continuous process, methane production can be achieved. Thus, one of the main concerns in full-scale processes is the overloading shock. That can unbalance trophic pathways, resulting in the accumulation of volatile fatty acids (VFA). Depending on the disturbance severity, it can lead to digester failure. Mathematical modelling applied to biological systems provides insights and alternatives for overcoming these hurdles. In this context, the Anaerobic Digestion Model number 1 was implemented in the present work to simulate organic overloading shocks. The objective was to propose kinetic parameter values which allow description and understanding of a perturbed system. Two 10 L mesophilic anaerobic digesters working in a semi-continuous mode, A and B, were treated under the same operational conditions for data collection. The digesters were submitted to two organic overloading pulses with a long time in between for recovery. VFAs, pH, and specific methanogenic activity (SMA) were used to monitor the digesters' performance. A standard differential evolution algorithm (DEA) was used for calibrating 28 biochemical parameters. Calibration was obtained using just the data of the first perturbation of digester A. Biochemical parameters related to the degradation of VFAs showed the most significant changes (i.e., $K_{m,c4}$ from 20 to 4.92; $K_{m,pro}$ from 30 to 2.17; $k_{m,ac}$ from 8 to 5.24; $k_{m,h2}$ from 35 to 10.60 $kg_{COD} \bullet m^{-3}$). After calibration, the model outputs showed a better fit with experimental data regarding modeling efficiency (EF) and the agreement index (index) than standard biochemical parameters. The result showed that DEA provides a robust calibration method for simulating the response of chicken litter overloading shocks in continuous methane production processes.

Key words: Modelling, ADM1, Disturbances

1. GENERAL INTRODUCTION

The urban solids residues generated worldwide are estimated at 2.01 billion tons, of which 40 % correspond to organic material (Kaza et al., 2018). The abovementioned might be a big drawback that generates environmental pollution if this is not managed adequately. One of the most important sustainable technologies in development for managing these issues is anaerobic digestion (AD). AD degraded organic matter to produce biogas used in stoves for domestic activities and to produce electricity (Bond & Templeton, 2011; Enzmann et al., 2018). Other useful byproducts obtained from AD are hydrogen and carboxylic acids (Feng et al., 2022; Koutrouli et al., 2009).

The AD approach as an alternative energy source (i.e., biogas and methane production) presents economic unfeasibility due to the high operation cost and low-rate production (Enzmann et al., 2018). These issues lead practitioners to press the digester with organic overloading to obtain more profits, which could disturb the digester's performance (Regueiro et al., 2015). Complete digester failure occurs and a period without OLR will be necessary to recover the initial condition (He et al., 2017). In the case of full-scale reactor, recovery implies time and monetary loss, for overcoming these problems, experimental designs should consider assessing organic overloading (Berninghaus & Radniecki, 2022). Mathematical models are another approach that allows understanding and predicting systems' behavior under different conditions (Donoso-Bravo et al., 2011). Anaerobic digestion model number 1 (ADM1) was proposed by the IWA task group for modeling biochemical and physicochemical processes (Batstone et al., 2002). This model has shown its robustness in simulating different conditions such as lab scale or full-scale anaerobic digesters, continuous or semicontinuous feed regimes also varying temperature (mesophilic or thermophilic), hydraulic retention time (HRT) and fed substrate (Jurado et al., 2016; Koutrouli et al., 2009; Ozkan-Yucel & Gökçay, 2010; Rivera-Salvador et al., 2014). However, few studies have applied ADM1 to model organic

overloading conditions. Some of these studies use ADM1 to explain the step-loading regime (Fatolahi et al., 2020).However, sudden organic overloading is more common in full-scale plants (Ozkan-Yucel and Gökçay, 2010).

Nevertheless, literature available in which ADM1 was applied to assess pulses disturbance was performed by volatile fatty acids (VFAS) and the soluble part of the substrate (Batstone et al., 2003; Jurado et al., 2016; Kalfas et al., 2006; Koutrouli et al., 2009). A problem with this approach is that it does not represent the system properly since it does not use a raw substrate. It also is addressed by knowing the kinetic of certain parts of the entire process. However, AD is comprised mainly of four linked processes (i.e., hydrolysis, acidogenesis, acetogenesis, and methanogenesis) that occur in cascade and simultaneously once a steady state is reached. In this sense, making a general analysis of the entire kinetic process can be more useful in full-scale plant design. ADM1 allows obtaining the aforesaid target through calibrating parameters from hydrolysis to methanogenesis using evolutionary algorithms (i.e., using differential evolution algorithm (DEA)) (Rivera-Salvador et al., 2014). For all these reasons, in this study, ADM1 was applied for modelling disturbance organic overloading pulses. In semicontinuous anaerobic digestion of chicken litter using DEA for calibrating parameters.

2. REVIEW OF THE LITERATURE

2.1 Brief description of the process

In recent years, anaerobic digestion (AD) has had an increasing relevance as a renewable energy source with benefits in the environmental field due to its capacity to utilize organic material residues (e.g., manure, food waste, and crop residues) for producing biogas that can be used to produce electricity, heat or as a vehicle fuel (Scarlat et al., 2018). AD is a complex multistage process performed by different groups of microorganisms in oxygen absence. These stages are commonly founded in literature as hydrolysis, acidogenesis, acetogenesis, and methanogenesis, and for correct performance of the entire process, these stages must be in equilibrium (Amin et al., 2021). **Figure 1** shows the main stages of anaerobic digestion.

Hydrolysis. It is a process where the organic material in the form of complex macromolecules is decomposed in their monomers or another simplest form. Carbohydrates such as starch can be decomposed in glucose molecules, and proteins are generally decomposed in peptides and amino acids; in the case of lipids, the most common is triglyceride which is decomposed in a molecule of glycerol and three molecules of long-chain fatty acids (Weinrich & Nelles, 2021). In AD, the process previously described is carried out by enzymes delivered to the pool from different groups of bacteria, which means that this is an extracellular process (Batstone et al., 2002).

Acidogenesis. This process involves fermentation of sugars, proteins and oxidation of long-chain fatty acids. The intermediate metabolites generated in this process are acetate, propionate, butyrate, and valerate, commonly known as VFA (Weinrich & Nelles, 2021). Also, other metabolites can be produced and accumulated for the metabolism of these bacteria, for instance, ethanol and lactate (Weinrich & Nelles, 2021).

Acetogenesis. In this process, acetate is generated by certain types of bacteria, which use propionate, butyrate, and valerate for their maintenance. The most common pathway for degrading propionate is the route of

methylmalonyl-CoA (Sieber et al., 2012). In the case of butyrate and valerate are degraded by the β-oxidation route (Batstone et al., 2003). It is essential to mention that acetate can be generated by other bacteria that use CO_2, H_2, and formate to grow in the commonly called Acethyl Co-A pathway (Pan et al., 2021). This process is known as homoacetogenesis; the bacteria of the abovementioned process compete with methanogen hydrogenotrophic for the same substrates (Pan et al., 2021). Both processes are essential for keeping an equilibria concentration of hydrogen in the media.

Methanogenesis. The last phase in AD is methanogenesis. This process is carried out by archaea mainly by three routes: acetoclastic, hydrogenotrophic, and metyltrophic. The first one uses acetate as a substrate, which is decarboxylated, releasing a methyl group and carbon dioxide; after that, the methyl group is reduced to methane (Madigan et al., 2011). On the other hand, the hydrogenotrophic route mainly uses carbon dioxide and hydrogen, which are released in the previous process; in this process, a series of reactions reduce carbon dioxide to methane (Madigan et al., 2011). The last route, known as methylotrophic, uses methylated compounds to produce methane; one example is ethanol (Madigan et al., 2011).

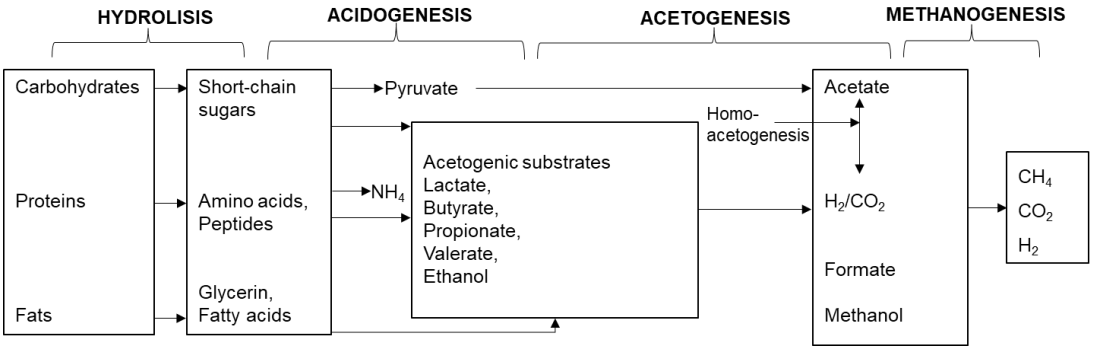

Figure 1. Biochemical process in AD. It is adapted with some modifications from (Deublein & Steinhauser, 2008).

It is important to stress that usually AD take place in a single digester; it has several implications for defining the operational conditions for methane production. The microorganisms involved in AD have different growing

requirements, mainly temperature and duplication time. This has the effect on biodigester operation conditions; being the temperature control the main variable to achieve. Feed chemical composition and mass flow play an important role in keeping a success AD process; if both of them are kept constant in a continuous process, microorganisms can be adapted to that feed, and consequently methane production can be maintain almost constant (Theuerl et al., 2019). However, if there is an unbalance in these operational conditions, methane production can be jeopardize (He et al., 2017).

It is necessary to distinguish between disturbance and perturbation. The former is understood as a sudden change in the environmental condition, and the latter is the system performance registered after disturbance (Todman et al., 2016). On the other hand, in terms of the microbiome of a biological system, Shade et al. (2012) discerned two kinds of disturbance: pulse and press disturbance; the first occurs in a short period meanwhile the second in a long-term.

2.2 Overloading condition on the organic loading rate (OLR)

The organic loading rate (OLR) considers the amount of organic fed matter per unit of reactor working volume; it can be found in terms of chemical oxygen demand (COD) or volatile solids (VS). Organic loading rate disturbance can be applied as pulse or press disturbance. These events can be conducted by modifying the quantity of organic matter in the input flow or either diminishing or increasing the hydraulic retention time (HRT). Increasing OLR in AD is very common, utilizing the abovementioned methods, also called organic and hydraulic overload (Regueiro et al., 2015).

In AD, press disturbance, also called step loading, is a stepwise, slowly increasing OLR that allows the microbiome adaptation to the new condition. One example of this is presented by He et al. (2017); these authors incremented organic loading by 1 $g_{VS}\bullet L^{-1}$ d^{-1} every 15 days until they reached the digester failure. Conversely, organic loading pulses are commonly carried out to assess a system's performance in a sudden shock. Since these events

are common in full-scale anaerobic digesters, they occur randomly and cause dangerous responses to digesters (Berninghaus & Radniecki, 2022).

2.3 ADM1 implementation

ADM1 compiled biochemical and physicochemical processes. The following equations describe the former according to the implementation realized by (Rosén & Jeppsson, 2006).

Enzymatic reactions and decayed biomass are described by first-order kinetic:

$$\rho_i = k \cdot X \quad (1)$$

Where k could be disintegration, hydrolysis, or decayed biomass rate [d^{-1}], X is either the concentration of substrate or microorganism [$kg_{COD} \bullet m^{-3}$].

Microorganism metabolism equations are given by:

$$\rho_i = km \frac{s}{ks + s} \cdot x_i \cdot I \quad (2)$$

Where km is the rate of consumption of substrate [d^{-1}], ks is the half-saturation constant [$k_{COD} \bullet m^{-3}$], s is the concentration of substrate [$k_{COD} \bullet m^{-3}$], x is the microorganism concentration [$k_{COD} \bullet m^{-3}$], and I is an inhibition factor given by the following equations.

Limiting nitrogen:

$$I_{IN,lim} = \frac{1}{1 + \frac{K_{s,IN}}{S_{IN}}} \quad (3)$$

Where $Ks_{,IN}$ is a parameter inhibition [M], and S_{IN} is the inhibition concentration of nitrogen [kmole $N \bullet m^{-3}$].

Hydrogen inhibition by long-chain chain volatile fatty acids, c4 (Butyrate and valerate), and propionate:

$$I_{h2} = \frac{1}{1 + \frac{S_{h2}}{K_I}} \quad (4)$$

Where S_{h2} is the hydrogen inhibition concentration [kg_{COD}], and kI is the inhibition parameter [kg_{COD}●m^{-3}] different for each component above mentioned.

Inhibition by low pH values.

$$I_{pH} = exp\left(-3\left(\frac{pH - pH_{uL}}{pH_{uL} - pH_{LL}}\right)^2\right) \quad (5)$$

Where pH_{LL} and pH_{uL} are the values of pH for the working threshold of a certain process. For instance, acidogenic reactions have these values in ADM1 implementation (4 – 5.5).

Meanwhile, the latter is described by:

Acid-based rates:

$$\rho A = k_{A,i}\left(S_i - \left(K_{va,i} + S_{H^+}\right) - K_{a,i}S_i\right) \quad (6)$$

Where s_i is the total concentration of component in question (i, e., VFA [kg_{COD} ●m^{-3}], carbonates [Kmonle C●m^{-3}] or ammoniacal nitrogen [Kmonle N●m^{-3}])

The gas mass transfer equation is described in the materials and methods section, as well as mass balance equations for the implementation in continuous mode.

2.4 Concerning present work

In the present work, ADM1 was implemented in the original form to model organic overloading pulses in semicontinuous anaerobic digestion of chicken litter. The objective was to propose insights for understanding the kinetics of perturbed systems. It is important to stress that four linked processes comprise AD (e.g., hydrolysis, acidogenesis, acetogenesis, and methanogenesis). Those processes occur in cascade and simultaneously once the steady state is reached. In this context, realizing the complete radiography of the system is a good approach. This objective can be achieved through parameter calibrations. This purpose becomes achievable since evolutionary algorithms have shown their simplicity of use and

robustness for estimating many parameters of the model. some of these are mentioned below.

2.5 Strategies adopted for simulating

For conducting a simulation, it is necessary to know realistically and accurately the inputs to the model. In this context, when ADM1 is used, knowing substrate characteristic is paramount. ADM1 uses COD units because it was proposed mainly for simulating wastewater. Nevertheless, in the case of a complex substrate such as animal manure, agricultural residues, or food waste, several approaches have been proposed in the literature, for instance, the correlation between VS and COD by means of regression analysis (Lübken et al., 2007; Wichern et al., 2009). Another way proposed for estimating theoretical COD in complex substrates is the conversions factors (Koch et al., 2010). **Figure 2** shows the use of these conversion factors for better understanding.

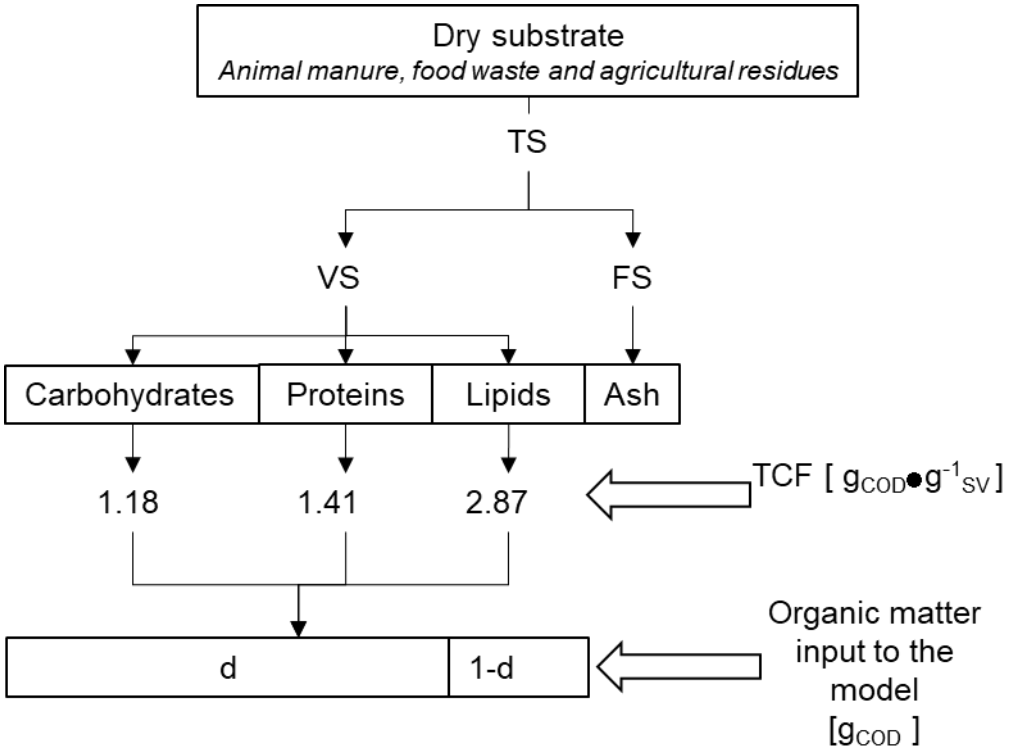

Figure 2. General dry substrate and theoretical conversion factors (TCF). FS: fixed solids, d: degradable part of organic matter, 1-d: nondegradable part.

2.6 Degradable part of organic material (d)

For ADM1 simulation, it is necessary to know the degradable part of organic matter (Batstone et al., 2002). and it can be determined by employing a long-term biochemical methane potential (BMP) in terms of VS or COD removed and can be estimated according to the specific methane potential, (Labatut et al., 2022).

$$fD = \frac{B_o}{B_u} = \frac{COD_D}{COD} = \frac{VS_D}{VS} \quad (7)$$

B_o and B_u are the observed biochemical methane potential and ultimate methane potential, respectively (mL $CH_4 \bullet g^{-1}_{VSfed}$), COD_D and VS_D are biodegradable chemical oxygen demand, and volatile solids also respect the total (COD and VS) quantified in the influent stream (Labatut et al., 2022).

2.7 Importance of kinetic calibration parameters

The digester performance is highly related to the structure of the microbiome inside the reactor, and these are different according to the type of substrate and operational condition (Theuerl et al., 2019). Also, two identical assembled reactors under disturbance might have distinct behavior, as reported by (Lv et al., 2019). According to the above reasons, calibration parameters to a specific AD system is essential. In this sense, minimizing the distance between experimental and simulated results (i.e., VFAS, biogas, or methane partial pressure) is used for calibrating parameters. This can be achieved by using straightforward or complex strategies. For instance, Wichern et al. (2009) used manual calibration and genetic algorithms (GA) for simulating fermentation grass silage and got a better fit using GA than manual calibration. Rivera-Salvador et al. (2014) also obtained a better simulation quality using a standard differential evolution algorithm (DEA) than the manual calibration coupled with non-linear square errors for AD of chicken litter with a modified ADM1. (Fatolahi et al., 2020) recently obtained good results using GA for calibrating parameters of ADM1 for simulating AD of organic fraction municipal solid waste at different OLRs. In addition, modelling systems with dynamic OLR can challenge the ADM1, but this describes more realistically what happens in full-scale plants (Ozkan-Yucel & Gökçay, 2010).

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3. MODELLING THE PERTURBATION EFFECTS OF THE CHICKEN LITTER OVERLOADING SHOCKS ON LONG-TERM SEMI-CONTINUOUS ANAEROBIC DIGESTERS.

3.1 Introduction

Manure management contributes to 10 % of greenhouse emissions in the livestock sector, estimated at 8.1 gigatonnes of CO_2-eq (FAO, 2022). Nitrogen is released mainly in the form of nitrous oxide and ammonia; which contributes to public health hazards (Malomo et al., 2018). Chicken litter management, having a high content of organic nitrogen, could have a critical impact on the environment (Meneses-Reyes et al., 2018). This fact takes more relevance since the USDA project a 2 percent demand annually growth through 2031 (USDA, 2022). Anaerobic digestion (AD) has had an increasing relevance in the recent years as a renewable energy source utilizing organic residues (e.g., manure, food waste, and crop residues) (Scarlat et al., 2018). AD is a complex multistage process performed by different groups of microorganisms in oxygen absence. These stages include hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The methane process performance depends on the dynamic equilibrium of the microbial communities of these stages (Amin et al., 2021). It is important to stress that usually AD take place in a single biodigester; it has several implications on defining the operational conditions for methane production. The microorganisms involved in AD have different growing requirements, mainly temperature and duplication time (Amin et al., 2021). This has the effect on biodigester operation conditions; being the temperature control the main variable to achieve. Under controlled temperature conditions, feed chemical composition and mass flow play an important role in keeping a success AD process; if both are kept constant in a continuous process, microorganisms can be adapted to that feed, and consequently methane production can be achieved successfully (Theuerl et al., 2019). However, if there is an unbalance in these operational conditions, methane production can be

jeopardized (He et al., 2017). Even the disturbance depends on the temporal and spatial scales, Shade et al. (2012) consider the press and pulse disturbances play an important role in the microbial community responses. Organic loading rate (OLR) disturbance can be observed when the bioreactor input is modified by either the organic matter concentration or the flow rate. AD Overloading is observed frequently in full-scale plants, Berninghaus & Radniecki. (2022) indicated that depending on the amount and duration of shock loads; the bioreactor can show resistance and resilience, for low shock events, or from disturbance to failure, for repeated large shocks.

Mathematical modelling applied to biological systems allows to provide insights and alternatives for overcoming these hurdles. (Batstone et al., 2002) proposed the Anaerobic Digestion Model No. 1 (ADM1); which has been widely used for different AD processes. García-Diéguez et al. (2011) used the ADM1 for optimizing a control strategy based on the disturbances in the feed. Spyridonidis et al. (2018) used ADM1 to simulate slaughterhouse byproducts treatment; the structure of the model was suitable for predicting the response of small or medium disturbances, but not for abrupt organic shocks. ADM1 was capable of simulate overloading shocks up to 6-times the original feed inlet Y. Huang et al. (2019). ADM1 has been applied for defining the substrate-feeding regime to satisfy specific requirements by means solving multi-objetive optimization using genetic algorithms (GA) (Ashraf et al., 2022).

The biodigester performance is highly related to the structure of the microbiome; which varies according to, among other factors, inoculum, feedstock and operational conditions (Theuerl et al., 2019). In fact, two identical assembled reactors, having a similar microbial structure at the beginning, under ammonia inhibition conditions might lead to differences in microbial communities (Lv et al., 2019). Taking in consideration the biodigester performance dependence on microbiome structure, the calibration of the parameters for simulating an specific AD system is essential. In this sense, minimizing the distance between experimental and simulated results (i.e., VFAS, biogas, or methane partial pressure) has being used for calibration. This can be achieved by using straightforward or

complex strategies. Wichern et al. (2009), simulating fermentation grass silage, observed a better fit using GA than manual calibration. For AD chicken litter process, Rivera-Salvador et al. (2014) reported a better simulation quality using a standard differential evolution algorithm (DEA) than the manual calibration coupled with non-linear square errors. GA was successfully used for simulating AD of organic fraction municipal solid waste at different OLRs (Fatolahi et al., 2020). Modelling systems with dynamic organic loading can challenge the ADM1, which is the situation in full-scale plants (Ozkan-Yucel & Gökçay, 2010). ADM1 has being able to simulate full-scale anaerobic digester under variable conditions, i.e. biogas flow rate varying from practically zero to 6000 m^3 d^{-1}, (Baquerizo et al., 2021). In this context, the ADM1 was implemented in the present work to simulate organic overloading shocks for parallel bioreactors under long adaptation period to chicken litter as feedstock. The objective was to propose kinetic parameter values, which allow a better description and understanding of a perturbed system. The experiments included two main disturbances, having a pertinent recovery time for the biodigesters. The model was calibrated using one disturbance of one biodigester; it was challenged to simulate a second disturbance as well as a parallel biodigester with two disturbances.

3.2 Material and methods

3.2.1 Experimental set-up and operation conditions

The present work used the experimental set-up reported by (Meneses-Reyes et al., 2018). Two digesters (**A** and **B**), 10 L working volume and 3 L head space each in a semi-continuous mode, were fed with a target of 3 % chicken litter solution in the period considered to have a low, 0.653 ± 1.04 $g_{VS}\bullet L^{-1}d^{-1}$ organic loading rate (OLR). Before this experiment, the digesters were fed with the same feed for 7 hydraulic retention time (HRT), i.e., 210 d using a HRT of 30 d. **Figure 3a** shows the evolution of pH and methane percentage of digesters **A** and **B**; it shows that both digesters performed in a very similar manner. In fact, when the overloading shocks were applied, the perturbation response was a reduction in methane percentage in a similar manner for

both digesters. Two overloading disturbances pulses were applied (**Figure 3b**), which included the increase of both concentration and volume fed. The first disturbance was between days 0 and 10, using overloading of 4.62 g_{VS}●L^{-1} d^{-1}; while the second one was between days 301 and 311, with 4.08 g_{VS}●L^{-1} d^{-1}. Thus, the shocks were close to sevenfold and six fold OLR, respectively.

The target HRT for the experiment was 30 d. Since the flow rate increased during the perturbations, the HRT for the first and second perturbations was 20 d, which lasted for 11 d. Along the experiments, the volatile fatty acids (VFAs) profile, methane percentage, VS, and TS were evaluated weekly, while the biogas was daily. The analytical methods is detailed in (Meneses-Reyes et al., 2017), and for biogas is detailed by (Meneses-Reyes et al., 2018).

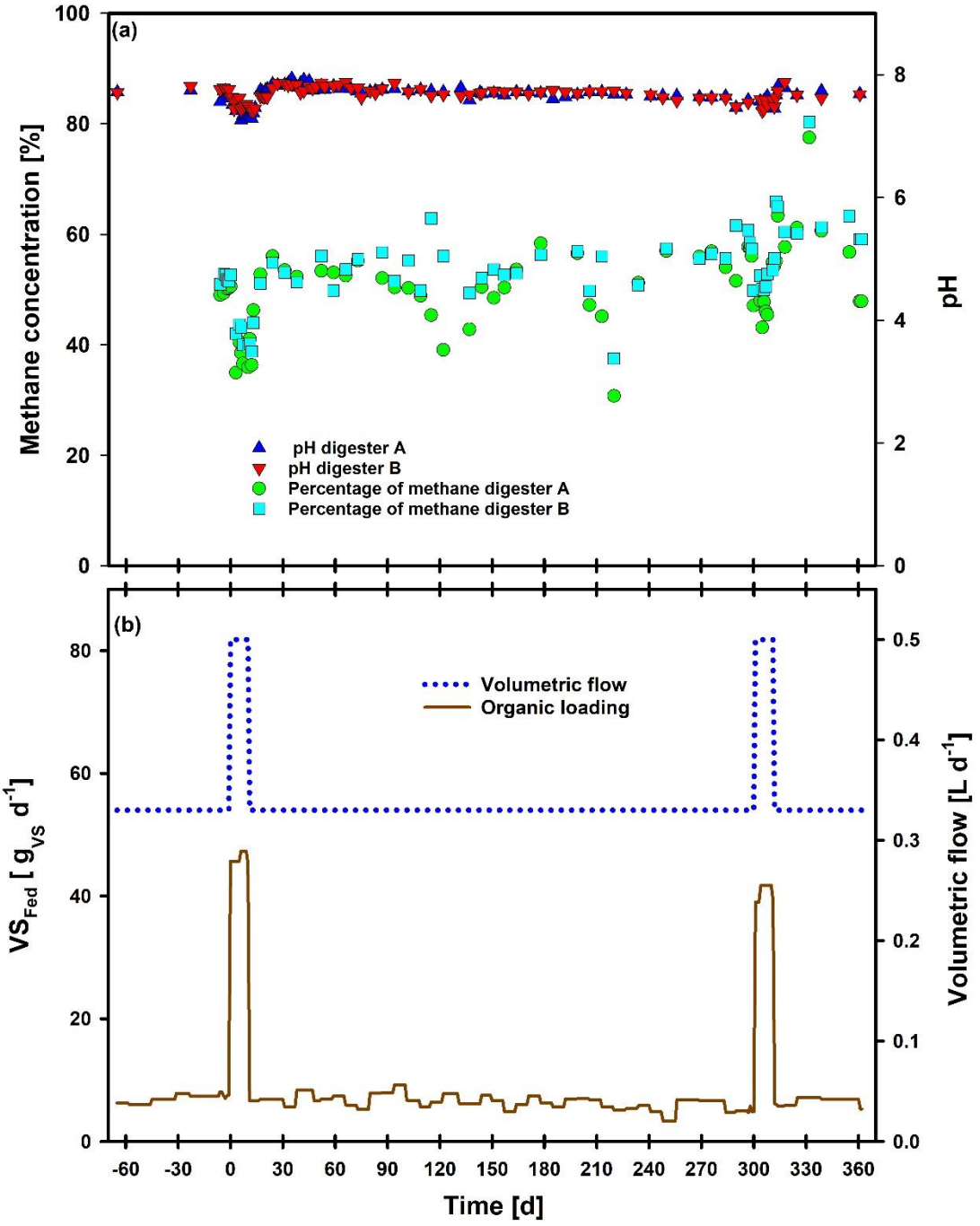

Figure 3. (a) Methane percentage and pH performance in both digesters assembled A and B. **(b)** Dynamic feed charged in the daily inflow during experiments for digesters A and B.

3.2.2. Substrate

Chicken litter was used as a substrate in the entire experiment. (Meneses-Reyes et al., 2017) Reported the chemical composition. Based on that information, **Table 1** shows the substrate characteristics as a function of TS, and the organic components in the sample.

Table 1. Chemical composition of chicken litter and the proportion of each component in VS as well as the distribution of the degradable fraction of VS used for modelling.

Component	TS [%]	VS [%]	Degradable part VS [%]
Total volatile solids (TVS)	69.61	-	
Crude protein (CP)	37.27	53.54	51.99
Ether extract (EE)	2.73	3.92	
Crude fiber (CF)	24.52	35.22	
Free nitrogen extract (FNE)*	5.10	7.32	7.32
Ash (Fixed solids)	30.39	-	

*FNE = TVS – (CP+EE+CF)

3.2.3 Model implementation

The model was implemented in MATLAB/Simulink® using the adaptation proposed by (Rosén & Jeppsson, 2006), which consist of 19 biochemicals process, 6 acid-based reactions, and 3 liquid-gas transfer process. The model includes 35 ordinary differential equation and 4 algebraic equations. The equations were solved by ODE 15s algorithm available in MATLAB. **Equation 8** describes the dynamic state variables in the liquid phase.

$$\frac{\mathrm{d}S_{\mathrm{liq},i}}{\mathrm{d}t} = \frac{q_{\mathrm{in},i}\mathrm{S}_{\mathrm{in},i}}{V_{\mathrm{liq}}} - \frac{S_{\mathrm{liq},i}q_{\mathrm{in},i}}{V_{\mathrm{liq}}} + \sum_{j=1-19} \rho_j \mathrm{V}_{i,j} \qquad (8)$$

Where $S_{in,i}$ and $S_{liq,i}$ are the concentration (kg_{COD}) of composite i in the influent stream and liquid phase, respectively. V_{liq} is the reactor working volume, the term $\sum_{j=1-19} \rho_j \mathrm{V}_{i,j}$ is the sum of the products between kinetic rates ρ_j and stoichiometric factors $V_{i,j}$. The interaction liquid gas transfer is described by **Equation 9.**

$$\rho\mathrm{T,i} = k_L a \left(S_{liq,i} - K_{H,i} P_{i,gas}\right) \qquad (9)$$

Where K_La is the overall mass transfer coefficient (d^{-1}), $K_{H,I}$ is the equilibrium constant from Henry's law to the gas i (M bar^{-1}). $P_{i,}$ gas is the partial pressure of gas i (Batstone et al., 2002).

Initial dynamic state variables were taken from Rosén and Jeppsson (2006). Excluding organics composites concentration in the liquid phase and hydrogen, carbon dioxide, and methane concentration in the gas phase were set at 0.

3.2.3 Model input matrix

Since the degradable fraction of substrate is a key factor for defining organic compounds that enter to the process, and it influences the model performance, in the present work the degradable fraction was taken as the degradable VS (DVS). The degradable fraction of substrate was 59.31 %; which was estimated based on biochemical methane potential study presented by our research group (Meneses-Reyes et al., 2017). It can be noted, in **Table 1**, that the major component of organic matter considered degradable was the protein; this criterion was based on the predominance of microorganism related to protein degradation in food waste during and after press disturbance (He et al., 2017). Li et al. (2017) showed the dominance of metabolic and transport of amino acids in high solids dewatered sludge systems. Huang et al. (2018) reported that the conversion of protein was the most relevant metabolic pathway in acid and alkali primary sludge fermentation. Additionally, lipids and crude fiber were taken as a non-degradable fraction of the organic matter. Lipids had a negligible concentration; additionally, it has been reported that lipids present a low water solubility that could form micelles, which makes difficult the degradation (Labatut, 2012). Also, crude fiber is composed mainly of recalcitrant composites (Usman Khan & Kiaer Ahring, 2021). All free nitrogen extract was taken as degradable. In the case of protein, the value was adjusted to the estimated DVS.

The amount of each composite in the model input was obtained by **Equation 10**.

$$S_{in,i} = \frac{S \bullet X_i}{q_{in}} \bullet COD_{th,i} \quad (10)$$

Where S is the total organic matter (g_{vs}), fed daily X_i is the mass fraction of each composite (i.e., carbohydrates, proteins, and lipids) concerning the total. $COD_{th,i}$ is the theoretical conversion factor ($g_{COD} \bullet g_{VS}^{-1}$) that varies according to the composite and can be obtained by **Equation 11** (Koch et al., 2010).

$$\mathrm{DQO_{th,i}} = \frac{16[2\mathrm{a} + 0.5(\mathrm{b} - 3\mathrm{d}) - \mathrm{c}]}{12.0107\mathrm{a} + 1.00784\mathrm{b} + 15.999\mathrm{c} + 14.0067\mathrm{d}} \quad (11)$$

Where a, b, c, and d are the number of carbon, hydrogen, oxygen, and nitrogen, respectively. The organic nitrogen in the entrance to the model was taken from experimental ammoniacal nitrogen in the substrate (Batstone et al., 2002); which was fitted as a function of TS to estimate daily ammoniacal nitrogen.

3.2.4 Parameters calibration

The calibration was performed using a standard differential evolution algorithm (DEA) as reported by (Rivera-Salvador et al., 2014). The parameters of the algorithm were set a as follows: crossover probability = 0.2; differential variation factor = 0.9; population size = 60, and accuracy = 1 x 10^{-6}. 28 parameters of ADM1 were calibrated that involve hydrolysis, acidogenesis, acetogenesis and methanogenesis as follows: K_{dis}, $K_{hyd,ch}$, $K_{hyd,pr}$, $K_{,hyd,li}$, $K_{m,su}$, $K_{S,su}$, Y_{su}, $k_{m,aa}$, $K_{S,aa}$, Y_{aa}, $k_{m,fa}$, $K_{S,fa}$, Y_{fa}, $k_{m,c4}$, $K_{S,c4}$, Y_{c4}, $K_{Ih2,c4}$, $k_{m,pro}$, $K_{S,pro}$, Y_{pro}, $K_{Ih2,pro}$, $k_{m,ac}$, $K_{S,ac}$, Y_{ac}, $k_{m,h2}$, $K_{S,h2}$, Y_{h2}, and $K_{I,nh3}$.

VFA in the first disturbance period from digester A (from day -65 to 102 d) was used to fit simulated data to the experimental. The experimental period comprising from (103 to 365 d) of the same digester (A), and the complete

experimental data from digester B (-65 to 365 d), were used to validate the model. The cost function used to fit the data has the form presented in **Equation 12**.

$$f(\mathrm{p}) = \sum_{\mathrm{j}=1-4} \left(\hat{\mathrm{y}}_{\mathrm{ij}} - \mathrm{y}_{\mathrm{ij}}\right)^2 \quad (12)$$

Where f is the objective function that depends on the vector parameter p, $\widehat{\mathrm{y}_{\mathrm{ij}}}$ is the value in the position i[th] by the j[th] VFA obtained from the simulation. Meanwhile, y_{ij} is the correspondingly observed value. DEA was run ten times; it was reported the average and standard deviation. Simulation quality was evaluated according to **Equations 13, 14, 15,** and **16** (Wallach, 2006).

$$\mathrm{RRMSE} = \frac{\mathrm{RMSE}}{\bar{\mathrm{y}}} \quad (13)$$

$$\mathrm{EF} = 1 - \frac{\sum_{\mathrm{i}=1}^{\mathrm{N}} (\mathrm{y}_{\mathrm{i}} - \hat{\mathrm{y}}_{\mathrm{i}})^2}{\sum_{\mathrm{i}=1}^{\mathrm{N}} (\mathrm{y}_{\mathrm{i}} - \bar{y})^2} \quad (14)$$

$$\mathrm{index} = 1 - \frac{\sum_{\mathrm{i}=1}^{\mathrm{N}} (\mathrm{y}_{\mathrm{i}} - \hat{\mathrm{y}}_{\mathrm{i}})^2}{\sum_{\mathrm{i}=1}^{\mathrm{N}} (|\hat{\mathrm{y}}_{\mathrm{i}} - \bar{\mathrm{y}}| + |\mathrm{y}_{\mathrm{i}} - \bar{\mathrm{y}}|)^2} \quad (15)$$

$$\mathrm{r} = \frac{\sum_{\mathrm{i}=1}^{\mathrm{N}} \left[(\mathrm{y}_{\mathrm{i}} - \bar{\mathrm{y}})(\hat{\mathrm{y}}_{\mathrm{i}} - \bar{\hat{\mathrm{y}}})\right]}{\sqrt{\sum_{1}^{\mathrm{N}} [(\mathrm{y}_{\mathrm{i}} - \bar{\mathrm{y}})^2] \sum_{1}^{\mathrm{N}} \left[(\hat{\mathrm{y}}_{\mathrm{i}} - \bar{\hat{\mathrm{y}}})^2\right]}} \quad (16)$$

Where RMSE is the root mean square error, $\bar{y}$ is the average of data observed, y_{i} is the i[th] experimental observed value, $\hat{\mathrm{y}}_{\mathrm{i}}$ is the i[th] value obtained by the simulation and $\bar{\hat{\mathrm{y}}}$ is the average of simulation data.

3.3 Results and discussion

3.3.1 Digesters´ performance

Two digesters were used for the experiments (**A** and **B**). As it was described in the previous section, both digesters had a similar performance, at daily bases, in terms of pH and methane percentage. The first disturbance, applied to digesters **A** and **B**, lasted for 11 d with sevenfold OLR, while the second one also lasted for 11 days with sixfold OLR. The changes in the specific methanogenic activity (SMA) and the VFA were registered throughout the entire experiment. **Table 2** shows the average and range of SMA as well as the average TVFA before the disturbance and the maximum value register after disturbance, which is known as resistance (Shade et al., 2012) of the microbial community to the organic shock. It is important to point out, that the first disturbance produced a perturbation that needed around 2 HRT to recover for digesters **A** and **B**; while in the second disturbance, in both digesters, had a lower influence on TVFA accumulation and a shorter recovery time, around 1.5 HRT. These facts suggest the digesters experienced a kind of adaptation to the organic shock; Berninghaus & Radniecki. (2022), working with stepwise overloading shocks, reported that the system had shorter recovery times as the overloading shock increases in the range of 2.5 to 9.0 $g_{VS}\bullet L^{-1}$ d^{-1}. It could be attributed to the effect on methanogenic archaea populations are jeopardized since their duplication time is usually longer than the one of the fermenters (Amin et al., 2021). (Sun et al., 2019), working with pig manure, have reported that when overloading take place from 6 to 9 $g_{VS}\bullet L^{-1}$ d^{-1} methane quality reduces from 65.0 to 28.0 %.

Table 2. Digesters' performances in present work before and after disturbances were applied.

Digester	Variable	The period from -65 to 102 d		The period from 103 to 362	
		Average before pulse (-65 to 0)	Values after pulse	Average before pulse	Values after pulse
A	**SMA [mL CH_4 ●g^{-1}_{SV}]**	173.6 ± 54.7	37.4 - 495.2	217.2 ± 93.3	115.6 - 849.4
	Percentage CH_4 [%]	50.0 ± 0.7	35.0	50.5 ± 6.8	43.1
	pH	7.7 ± 0.1	7.3	7.7 ± 0.1	7.5
	TVFA [mg●L^{-1}]	812.4 ± 498.4	15195.5	554.4± 341.571	7837.7
	Acetate [mg●L^{-1}]	636.0 ± 434.0	8161.7	327.3 ± 220.4	4204.4
	Propionate [mg●L^{-1}]	58.4 ± 37.2	4361.1	78.8 ± 58.9	2060.4
	iso-butyrate [mg●L^{-1}]	39.4 ± 21.6	608.7	38.9 ± 18.8	377.5
	Butyrate [mg●L^{-1}]	23.2 ± 8.2	1088.0	60.3 ± 32.5	485.6
	iso-valerate [mg●L^{-1}]	37.2 ± 18.3	820.4	50.7 ± 22.4	590.8
	Valerate [mg●L^{-1}]	18.0 ± 0.8	369.1	53.2 ± 27.6	189.0

Table 2 (*continued*).

Digester	Variable	The period from -65 to 102 d		The period from 103 to 362	
		Average before pulse (-65 to 0)	Values after pulse	Average before pulse	Values after pulse
B	**Methane [mL CH_4 ●g^{-1}_{SV}]**	195.7 ± 18.0	35.5 - 461.3	237.6 ± 109.7	142.1 – 1254.0
	Percentage CH_4 [%]	52.1 ± 0.7	38.8	54.3 ± 5.3	50.0
	pH	7.8 ± 0.1	7.4	7.7 ± 0.1	7.4
	TVFA [mg●L^{-1}]	222.8 ± 86.5	10011.6	507.158 ± 333.551	8620.5
	Acetate [mg●L^{-1}]	154 ± 67.4	5233.4	266.8 ± 187.9	4885.2
	Propionate [mg●L^{-1}]	21.8 ± 9.1	3048.0	94.9 ± 71.7	2296.0
	iso-butyrate [mg●L^{-1}]	13.0 ± 21.8	505.1	41.4 ± 17.0	411.9
	Butyrate [mg●L^{-1}]	13.6 ± 1.0	720.8	54.4 ± 41.6	558.2
	iso-valerate [mg●L^{-1}]	16.2 ± 1.1	778.0	53.9 ± 23.9	577.0
	Valerate [mg●L^{-1}]	17.4 ± 0.2	359.3	48.5 ± 34.5	191.9

As a response to both disturbances, for digesters **A** and **B**, the SMA showed a decrease at the beginning of the organic shocks, which remained low during the time that the overloading shock was applied; as soon as the overload was released SMA was recovered, showing even a peak above the previous average SMA.

After disturbance, VFA concentration increased up to a peak in both digesters. The maximum concentration, for digesters **A** and **B** expressed as g_{COD}●L^{-1}, registered for the first perturbation, respectively, is as follows: acetate (8.7) (5.6), propionate (6.6) (4.6), butyrate (3.1) (2.2), and valerate (2.4) (2.3). For the second perturbation, the trend was quite similar but with lower concentrations. The values for digesters **A** and **B** are**,** respectively, as follows: acetate (4.5) (5.2), propionate (3.1) (3.5), butyrate (1.6) (1.8), and valerate (1.6) (1.6). It is important to notice that during the overloading press, the pH reduces slightly even the VFA peaks registered, it can be attributed to the high NH_4^+ concentrations in chicken litter, which can have a buffer effect due to, either, NH_3/NH_4^+ or NH_3/CO_3^{2-}/VFAs (Meng et al., 2018). This trend has been reported for chicken manure disturbed digesters, in a semicontinuous digester subject to sudden changes with the adaptation period Bi et al. (2019) and to step-loading shocks (Wang et al., 2019). In the case of food residuals the same trend has been also observed (He et al., 2017).

3.3.2 Model calibration

For model calibration, the beginning of the disturbance was taken as time zero. Thus, the VFA data of digester **A** from day -65 to 102 were used for calibration. **Tables 3** and **4** show the parameters calibrated along with those reported in the literature. Some of the literature data reported in both tables were obtained under pulse, or press disturbance experiments for instance (Batstone & Keller, 2003) Worked with VFA pulse disturbance using cattle manure as feedstock, while Kalfas et al. (2006) working also with pulse VFA disturbance and soluble part of feedstock that was raw olive pulp. Koutrouli et al. (2009) Performed the first pulse VFA disturbance followed by a press stepwise with olive pulp. Fatolahi et al. (2020) calibrated the ADM1 by

applying step loading with the organic fraction of municipal solid waste (OFMSW).

18 kinetic, three inhibitory, and seven yield parameters were calibrated to describe the disturbance and perturbation processes comprehensively. For calibration, parameter $k_{,dis}$, was considered for the disintegration process. Also, it was considered just the composite of organic material (e.g., proteins, carbohydrates, and lipids) as input to the model based on the literature (Batstone et al., 2015).

DEA has shown its simplicity of use and robustness for estimating many parameters in dynamic crop models, especially DE/ran/1/bin (Cesar Trejo Zuniga et al., 2014). In ADM1, it was applied for calibrating 25 parameters; the simulation results showed a satisfactory fit to experimental data (Rivera-Salvador et al., 2014). Despite the advantage of using DEA for estimating model parameters, it is important to define the proper boundaries to obtain reasonable values related to the process. In the present work, the space of search for each parameter was defined according to the variation reported by (Batstone et al., 2002).

3.3.2.1 Parameters of desintegration, hydrolisis and acidogenesis

The $K_{dis,}$ $K_{hyd,ch}$, $K_{hyd,pr,}$ and, $K_{,hyd,li,}$ parameters are related to enzymatic reactions in the pool, as well as, the $K_{m,su}$ and $k_{m,aa}$ to the rate of fermentation of sugars and amino acids. As it can be seen in **Table 3,** these values were between one to three times larger than those reported in the literature. Fatty acids´ uptake rate, $k_{m,fa}$, took the lower limit in the algorithm set-up. $K_{S,su,}$ $K_{S,aa,}$ and $K_{S,fa}$, the half-saturation constant for sugars, amino acids, and long-chain fatty acids, took values of 98, 30, 295 % compared to the reference. $Y_{su,}$ $Y_{aa,}$ and Y_{fa} are the yield parameters in sugars, amino acids, and fatty acids uptake; the first two showed a decrease of 30 %; conversely, the last showed an increase of 19 %.

3.3.2.2 Parameters related to acetogenesis and methanogenesis

Acetogenesis comprises the uptake of propionate and c4 (ADM1 considers that butyrate and valerate are lumped (Batstone & Keller, 2003). For propionate, the calibrated $k_{m,pro}$, $K_{S,pro}$, *and* Y_{pro} parameters were smaller or slightly (28%) larger than the reference values. It can be seen in **Table 4** that the uptake rate is in accordance with the obtained by Koutrouli et al. (2009) and (Ozkan-Yucel & Gökçay, 2010). The $K_{S,pro}$ showed similarity with what was reported in the literature by pulses of VFA Koutrouli et al. (2009), by stepwise overloading (Fatolahi et al., 2020), and by a dynamic full-scale plant (Lübken et al., 2007) . $k_{m,c4}$ and Y_{c4} were smaller than the reference values. In the case of $K_{S,c4}$, the calibrated value was around two times larger than the reported value. The $k_{m,c4}$ in this work is in accordance with the reported by (Ozkan-Yucel & Gökçay, 2010). It is important to stress that in the case of the half-saturation constant Normak et al. (2015) reported a similar value to the one obtained in this work.

For acetoclastic and hydrogenotrophic methanogens, the parameters are as follows: $k_{m,ac,}$ $K_{S,ac,}$ Y_{ac}. and $k_{m,h2,}$ $K_{S,h2,}$ and Y_{h2}, respectively. The reduction of acetate uptake rate is in agreement with (Koch et al., 2010). These authors showed an accumulation of acetate after TS in the system increased. For the $K_{S,ac,}$ Kalfas et al. (2006) reported a similar value for VFAs pulses. Uptake rate and half saturation constant values for the hydrogenotrophic pathway, showed reduction; meanwhile, the calibrated yield value increased. Inhibition parameters ($K_{Ih2,c4,}$ $K_{Ih2,pro,\ and}$ $K_{I,nh3}$) varied by a factor of 30 % concerning reference; all are in accordance with the literature.

Figures 4 and **5** show the results of the calibration process. As it can be seen, the simulation with calibrated parameters has a better fit to the experimental data than the simulation with standard parameters.

Table 3. Values of kinetics parameters in disturbances systems along literature published compared with those were estimated in the present work.

Source	K_{dis} [d^{-1}]	$K_{hyd,ch}$ [d^{-1}]	$K_{hyd,pr}$ [d^{-1}]	$K_{,hyd,li}$ [d^{-1}]	$K_{m,su}$ [d^{-1}]	$K_{S,su}$ [kg_{COD}● m^{-3}]	Y_{su}	$k_{m,aa}$ [d^{-1}]	$K_{S,aa}$ [kg_{COD}● m^{-3}]	Y_{aa}	$k_{m,fa}$ [d^{-1}]	$K_{S,fa}$ [kg_{COD}● m^{-3}]	Y_{fa}	$k_{m,c4}$ [d^{-1}]
Reference value (Batstone et al., 2002)	0.50[c]	10[b]	10[b]	10[c]	30[b]	0.50[b]	0.10[a]	50[b]	0.30[a]	0.08[a]	6[c]	0.40[c]	0.06[a]	20[b]
Batstone et al. (2003)														12.0 ± 0.40
Lübken et al. (2007)		0.31	0.31	0.31										13.7
Wichern et al. (2009)	0.26													
Koch et al. (2010)		0.14		0.14										
Ozkan-Yucel and Gökçay (2010)		1	1	1	35	0.5								5
Normak et al. (2015)					11.9	4.5		19.8	0.3					12.2
Jurado et al. (2016)			3.0●10^{-3}	2.8●10^{-4}							0.93			13.1
Fatolahi et al. (2020)					6									13.95
Present work Average[1] ± standard deviation	1.99 ± 4.03●10^{-8}	19.99 ± 1.90●10^{-7}	20	39.03 ± 3.46	59.87 ± 0.02	0.01 ± 1.41●10^{-9}	0.07	100	0.21	0.06	0.01	1.58 ± 7.01●10^{-4}	0.07 ± 1.63●10^{-4}	4.92 ± 0.01

[a] Varies within factor of 30% by Bastone et al. (2002)
[b] Varies within factor of 100 % by Bastone et al. (2002)
[c] Varies within factor of 300% by Bastone et al. (2002)
[1] Average of ten replicants

Table 4. Values of kinetics parameters in disturbances systems along literature published compared with those were estimated in the present work.

Source	$K_{S,c4}$ [$kg_{COD} \bullet m^{-3}$]	Y_{c4}	$K_{Ih2,c4}$ [$kg_{COD} \bullet m^{-3}$]	$k_{m,pro}$ [d^{-1}]	$K_{S,pro}$ [$kg_{COD} \bullet m^{-3}$]	Y_{pro}	$K_{Ih2,pro}$ [$kg_{COD} \bullet m^{-3}$]	$k_{m,ac}$ [d^{-1}]	$K_{S,ac}$ [$kg_{COD} \bullet m^{-3}$]	Y_{ac}	$k_{m,h2}$ [d^{-1}]	$K_{S,h2}$ [$kg_{COD} \bullet m^{-3}$]	Y_{h2}	$K_{I,nh3}$ [$kmole \bullet m^{-3}$]
Reference value (Batstone et al., 2002)	0.20[c]	0.06[a]	$1 \bullet 10^{-5}$[a]	13[b]	0.10[b]	0.04[a]	$3.50 \bullet 10^{-6}$[a]	8[b]	0.15[b]	0.05[a]	35[b]	$7 \bullet 10^{-6}$[b]	0.06[a]	$1.80 \bullet 10^{-3}$[a]
Batstone et al. (2003)	0.29 ± 0.02													
Kalfas et al. (2006)				3.50 ± 0.32	0.06 ± 0.03			9.99 ± 1.2	0.31 ± 0.09					
Lübken et al. (2007)	0.357			5.5	0.392			7.1				$3 \bullet 10^{-5}$		
Koutrouli et al. (2009)				2.02 ± 0.07	0.03 ± 0.01			8.34 ± 1.02	0.96 ± 0.21					
Wichern et al. (2009)			$5.4 \bullet 10^{-8}$	13			$4.8 \bullet 10^{-8}$					$4.2 \bullet 10^{-5}$		$8.4 \bullet 10^{-3}$
Koch et al. (2010)			$5 \bullet 10^{-8}$				$4.6 \bullet 10^{-8}$	4.4				$5.6 \bullet 10^{-5}$		
Ozkan-Yucel and Gökçay (2010)				2.2				10	0.18				0.05	
Normak et al. (2015)	0.6			3.5	0.4			11.1	0.5					0.0223
Jurado et al. (2016)				6.56				45.02						
Fatolahi et al. (2020)					0.14				0.05			$7.79 \bullet 10^{-6}$		
Present work Average[1] ± standard deviation	0.64 ± $1.03 \bullet 10^{-3}$	0.04 ± $5.50 \bullet 10^{-35}$	$1.30 \bullet 10^{-5}$ ± $3.28 \bullet 10^{-42}$	2.17 ± $4.73 \bullet 10^{-3}$	0.20 ± $8.80 \bullet 10^{-34}$	0.05 ± $9.83 \bullet 10^{-7}$	$2.45 \bullet 10^{-6}$	5.24 ± $7.56 \bullet 10^{-5}$	0.3	0.06 ± $1.65 \bullet 10^{-8}$	10.60 ± 0.30	$1.39 \bullet 10^{-05}$ ± $4.39 \bullet 10^{-14}$	0.08	$2.34 \bullet 10^{-3}$

[a] Varies within factor of 30% by Bastone et al. (2002)
[b] Varies within factor of 100 % by Bastone et al. (2002)
[c] Varies within factor of 300% by Bastone et al. (2002)
[1] Average of ten replicants

3.3.3 Model validation

The calibrated parameters were validated in the period from 103 to 362 to digester A. The entire recorded data from digester B was also used for that purpose. **Figures 4** and **6** show the outputs of the model compared with experimental data in terms of TVFA (acetate + propionate + butyrate + valerate), pH, and SMA. During the first pulse and the period for recovery, TVFA is represented more satisfactorily by the calibrated parameters than the parameters suggested by (Batstone et al., 2002). A slight overestimation appears in data collected from digester B. Conversely, experimental response in the second pulse was overestimated by calibrated parameters. Both sets of parameters, reference and calibrated, underestimated pH but followed the same trend as data collected in both digesters. The outputs of the model overestimated the SMA during the first pulse and the period for recovery in both digesters. Conversely, SMA has underestimated the sharp increase after the second pulse in both digesters. **Figures 5** and **7** show the performance of individual volatile fatty acids; remarkably, the model output with parameters calibrated was better than the parameters suggested by (Batstone et al 2002). Nevertheless, overestimation occurred in the second pulse to both digesters A and B.

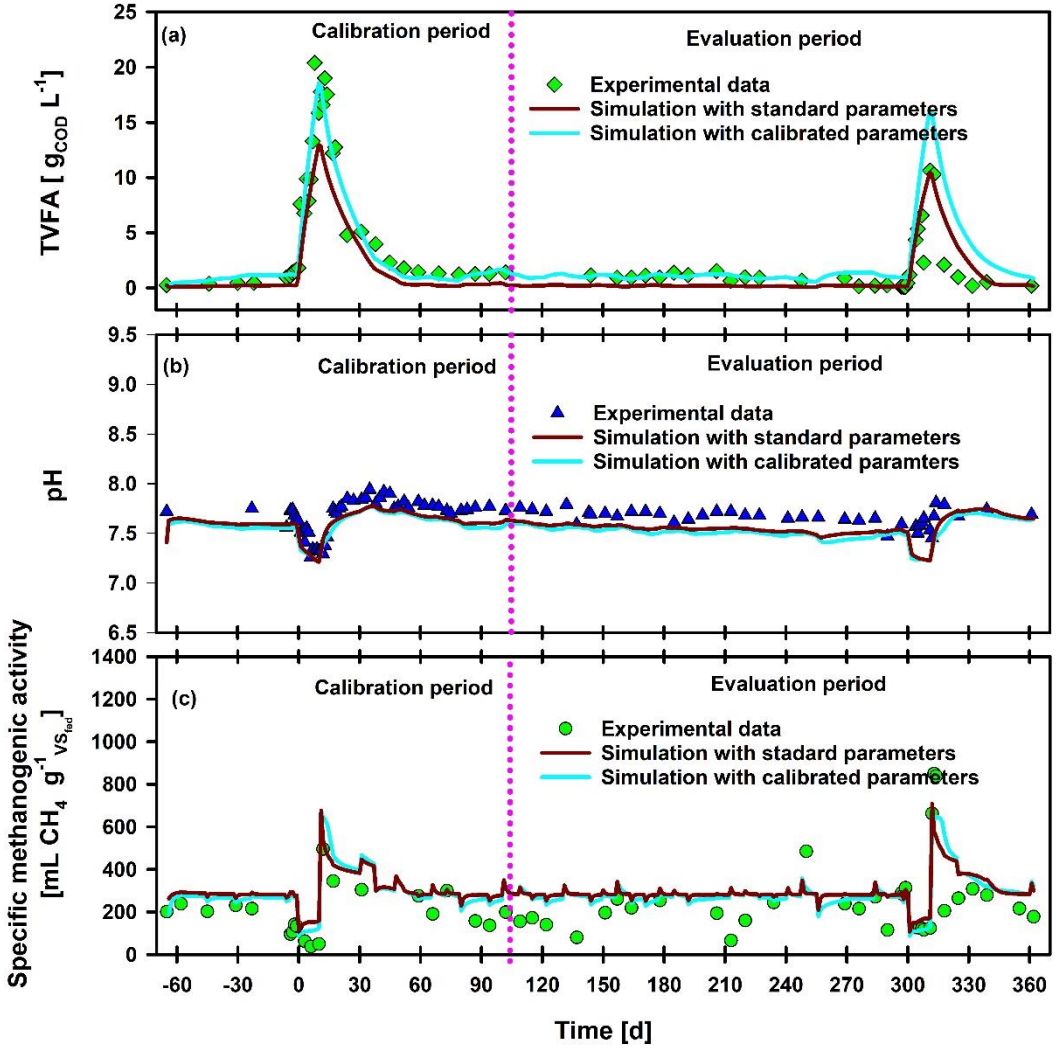

Figure 4. Comparison between experimental and simulated results of TVFA, pH, and specific methanogenic activity (SMA) from digester A.

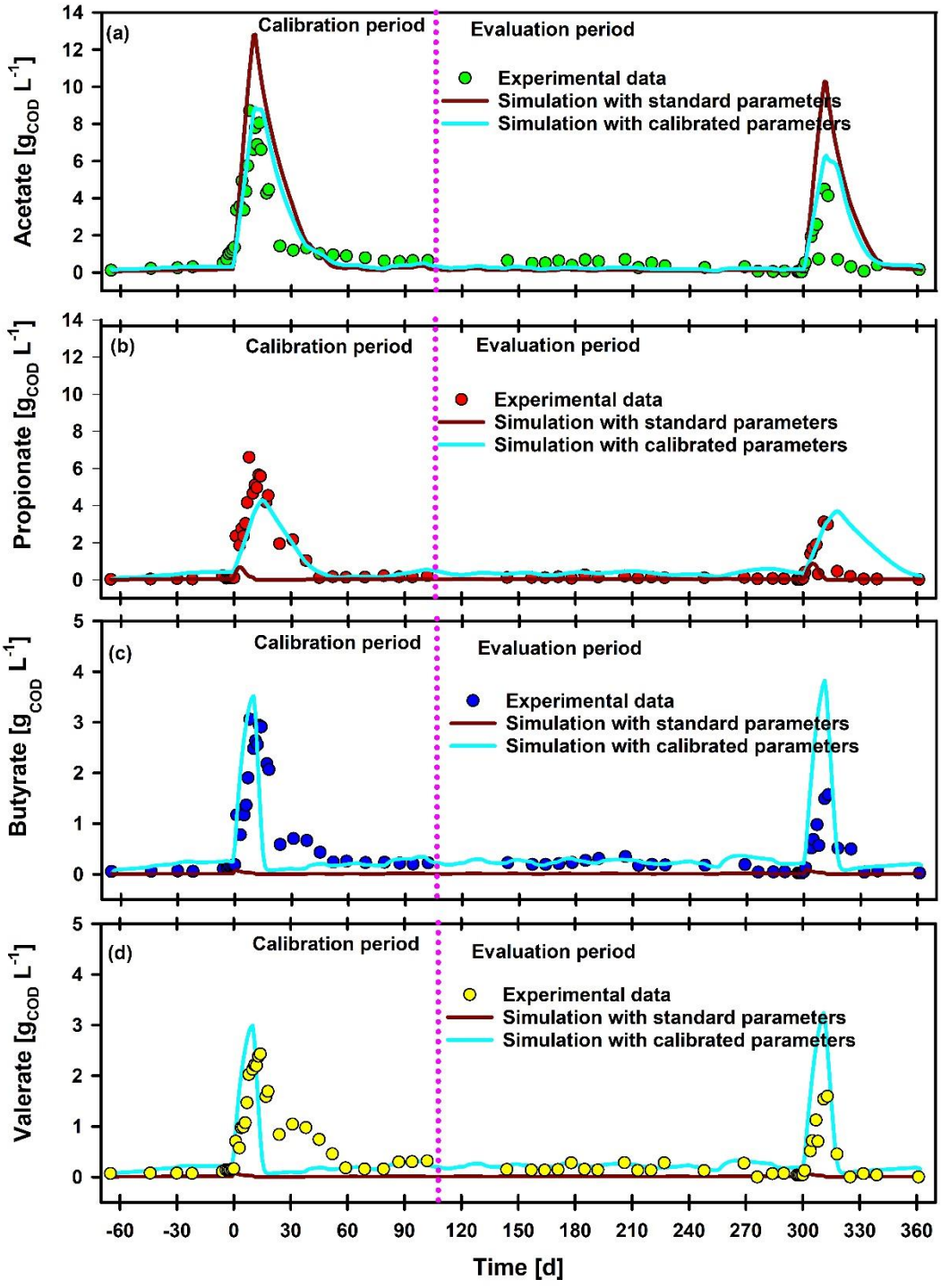

Figure 5. Comparison between experimental and simulated data of individual volatile fatty acids from digester A.

The model fit quality is shown in **Tables 5** and **6.** The RRMSE can be visualized as an error related to all data measured mean. In this context, digester A, that error was diminished by the calibration. In the case of Digester B, acetate, propionate, and SMA showed a decrease; butyrate, valerate, and TVFA showed an increase in this quality parameter. In both digesters, the pH did not change the trend.

The modelling efficiency parameter shows how the model is better at predicting rather than the average of experimental measurements (Wallach, 2006). The calibrated parameters improve the model prediction to digester A, except in cases of valerate and pH. For predicting acetate, propionate, and SMA of digester B, the calibrated model was better than the model that uses reference values. Another helpful parameter is the agreement index (*index*). For digester A, all the parameters that describe digester performance were improving with calibrated parameters except pH. To digester B, just TVFA and pH were not improved by calibrated parameters. In the case of the correlation coefficient, both digesters show the same trends; just the pH and SMA show a decrease in the positive linear correlation.

It is important to stress out that even TVFA was predicted satisfactorily by parameters suggested by Batstone et al (2002), the model did not describe the behavior of the individual VFA. The quality of the modelling for acetate, propionate and SMA was improved by calibrating parameters to both digesters. In the case of methane production, a similar conclusion is depicted by (Fatolahi et al., 2020), when stepwise disturbances were used, and for pulse shocks (Koutrouli et al., 2009). In the case of c4, the accumulation during disturbance was overestimated. Conversely, when low dynamic OLR was applied, the model predicted very satisfactorily, as seen in **Figures 5** and **7** for the VFAs mentioned above.

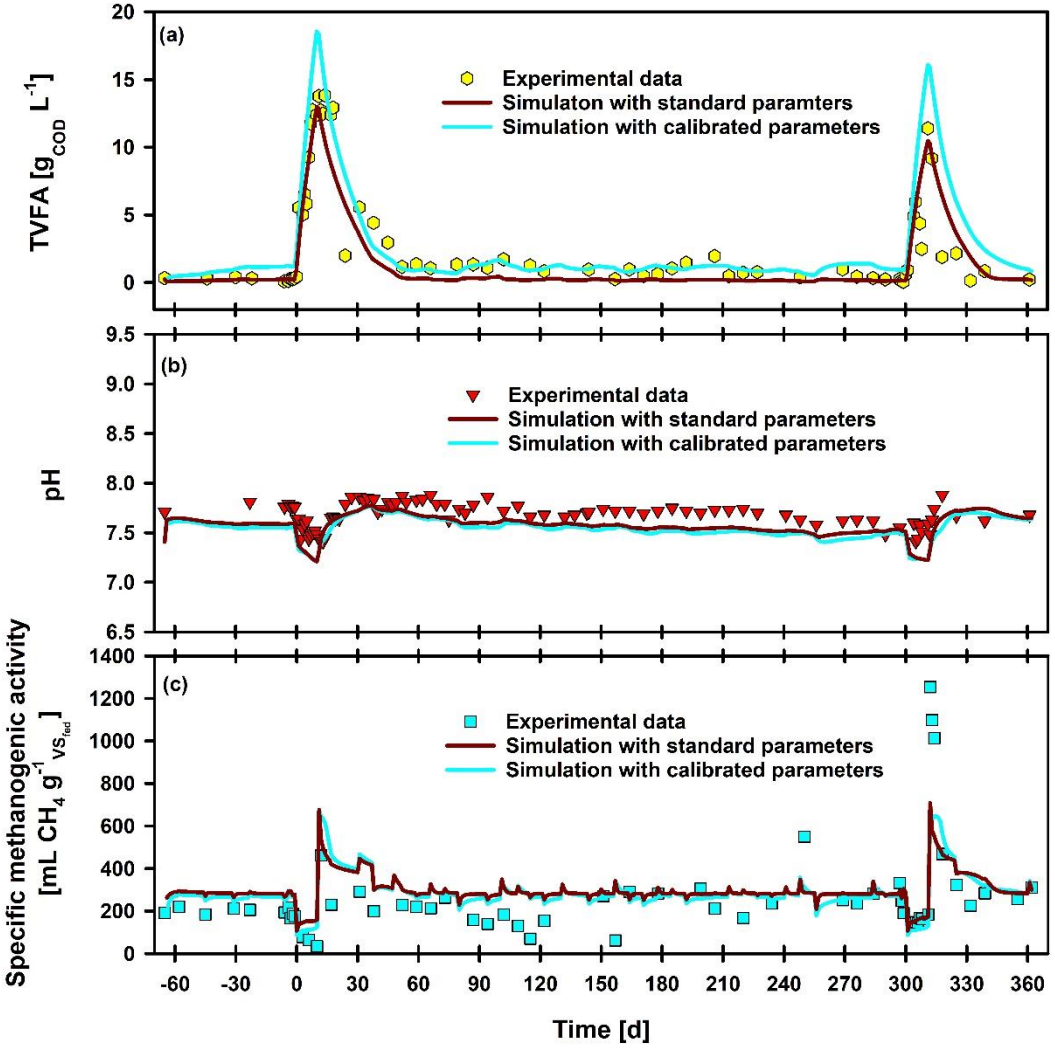

Figure 6. Comparison between experimental and simulated data of TVFA, pH, and SMA from digester B.

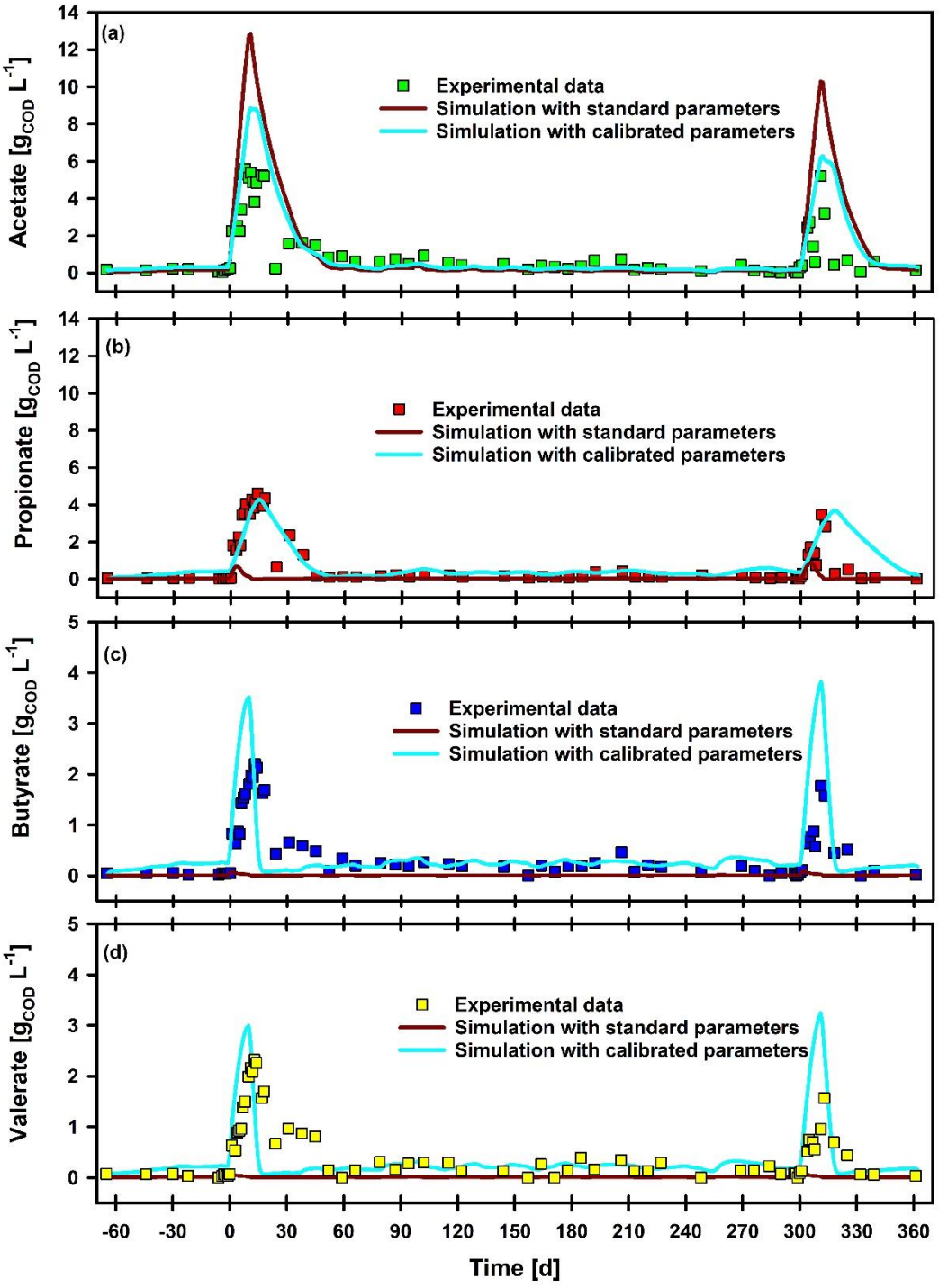

Figure 7. Comparison between experimental and simulated data of individual volatile fatty acids from digester B.

Table 5. Evaluation of simulation quality from digester A calibration and evaluation of parameters.

Goodness-of-fit parameter	Acetate		Propionate		Butyrate		Valerate		TVFA		pH		SMA	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
RRMSE	1.40	0.74	1.72	0.83	2.26	1.88	1.52	1.24	0.60	0.59	0.02	0.02	0.52	0.50
EF	-0.22	0.66	-0.32	0.69	-0.56	-0.09	-0.69	-0.12	0.79	0.80	-0.09	-0.43	0.44	0.49
Index	0.85	0.93	0.44	0.89	0.43	0.78	0.44	0.78	0.93	0.95	0.77	0.73	0.82	0.85
r	0.91	0.90	0.20	0.84	0.09	0.67	0.06	0.68	0.93	0.91	0.81	0.81	0.83	0.82

1: Simulation with standard parameters
2: Simulation with calibrated parameters

Table 6. Evaluation of simulation quality from digester B evaluation of parameters calibrated with data from digester A.

Goodness-of-fit parameter	Acetate		Propionate		Butyrate		Valerate		TVFA		pH		SMA	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
RRMSE	2.21	1.24	1.64	0.78	1.50	1.52	1.55	1.57	0.48	0.83	0.02	0.02	0.59	0.57
EF	-2.04	0.05	-0.34	0.70	-0.72	-0.77	-0.65	-0.69	0.85	0.57	-0.81	-1.32	0.53	0.55
Index	0.74	0.86	0.45	0.91	0.45	0.73	0.43	0.73	0.96	0.92	0.71	0.66	0.78	0.81
r	0.90	0.90	0.22	0.85	0.08	0.66	0.02	0.66	0.93	0.92	0.77	0.78	0.82	0.78

1: Simulation with standard parameters
2: Simulation with calibrated parameters

3.4 Conslusions

$K_{m,c4}$, $K_{m,pro}$, $k_{m,ac}$, *and* $k_{m,h2}$ showed the most significant changes during calibration. The model outputs, for digesters A and B, showed a better fit with experimental data regarding modelling efficiency (EF) and the agreement index (index) than the original ADM1 parameters. The result shows that DEAs provide a robust calibration method to estimate parameters. The calibration performed to the ADM1, along with the validation, allowed to predict the experimental data; thus, in the case of a disturbance, it has the advantage for taking control actions before perturbation takes place.

3.5 References

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