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ASSESSMENT OF ULTIMATE BIOGAS POTENTIAL OF CO-DIGESTED FRUITS, VEGETABLES AND MIXTURE OF FRUITS, VEGTABLES AND OIL SUBSTRATES

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ABSTRACT

Batch ensemble of co-digested vegetables (Potato, Carrot, and Spinach), fruits (Grape and Orange) and mixture of fruits, vegetables and cooked oil was carried out in two 6L laboratory anaerobic digestion reactors, under mesophilic condition, for 100 days. The organic loading rate for each experiment varied from 1.0 to 5.0 g VS/l. The degradation kinetics was considered as important factor in the comprehension of complex anaerobic mechanism processes. The study firstly concentrated on the kinetics constant "k" using first order Cone and Exponential models with the aim of analyzing the degradation performance and biogas production. The next modeling stage was based on two hypotheses: (i) the biogas process is a two-step reaction yielding VFA as intermediate products, and biogas as the final product, and (ii) the digestible substrate can be divided into a rapidly degradable and a slowly degradable fraction. The goodness of models fit to the observed data was evaluated by calculating the Pearson product-moment correlation coefficient (PCC) and the Residuals. The results showed

that all models perform well comparatively with the observed data. Estimated "k" values were similar for the vegetables and co-digestion with oil but significantly different in the case of fruits co-digestion.

Keywords: Anaerobic digestion; Kinetics; Modeling; Batch assays

I. INTRODUCTION

The generation of solid waste in the Middle East countries has crossed 150 million tons per annum. The sultanate of Oman amounts to about 1.6 million tons per annum which is the lowest quantity of solid wastes in the region (EcoMENA). The local government developed a multitude of solutions to overcome heuristic disposal of waste to protect the environment as well as the population health. It is a continuous efforts sustained by the Sultanate of Oman government willing to achieve a zero solid wastes dumping goal in the nearest future. Now days, there is still solid wastes are being sent to landfills, thus adding to the atmosphere emissions of thousands metric tons per annum of methane and carbon dioxide, the most important greenhouse gases. A possible way to dispose of these wastes is transform part of it into biogas. Anaerobic Digestion (AD) is considered one of the optimal medium that could be the alternative to solid waste direct dumping [9]. A technique that is considered a consolidated technology with more than 2200 high-rate reactors already implemented worldwide [18].

The mechanism of converting waste to energy under the anaerobic conditions is a biological process that is categorized by a high degree of waste stabilization, low production of waste biological sludge, low nutrient requirements, no oxygen requirements, and production of methane which is a useful end product. The AD technology, as a recognized robust and efficient technology, could be applied for the treatment of various types of organic wastes in a more sustainable way compared to alternative processes [2].

Interesting scientific results have been obtained in mixing simultaneously several solid as well as liquid organic wastes in order to produce biogas [5]. This process is commonly known as co-digestion (AcoD) and has been studied during the last 15-20 years [17]. For e.g., it has been reported, that mixing organic substrates can result in the production of a mixture with a C/N ratio included in the optimal range 20/1–30/1 [8]. The C/N ratio is known as a potential indicator for the digestion process performance. Furthermore, it has been showed that benefits of the co-digestion process can be resumed in: (1) dilution of the potential toxic compounds eventually present in any of the co-substrates involved; (2) adjustment of the moisture content and pH; (3) supply of the

necessary buffer capacity to the mixture; (4) increase of the biodegradable material content; (5) widening the range of bacterial strains taking part in the process [5].

Chemical reaction kinetics is significantly important to identify before starting the development and operation of any anaerobic treatment systems. The knowledge of AcoDs kinetics is useful for giving insights on biochemistry and microbiology phenomena going on in along the AcoD process. They are also important for process analysis, control, and design. Furthermore process kinetics deal with operational and environmental factors affecting the microbes growth rates. A sound knowledge of kinetics allows for the optimization of performance, a more stable operation as well as better control of the AcoD process [15]. However, determining reliable kinetic constants is complicated due to the AD process itself as a complicated multi-stage dynamic process that requires a combined effort of several bacterial groups [21].

The main objective of this study was to describe and implement three models to evaluate biogas production kinetics in batch biogas potential assays: first-order one block model (Model A), two-steps (Model B), and two-pool first-order (Model C).

II. SELECTED MODEL

Model (A)

The idea is to model the process evolving the biogas production. In fact, we assume that describing the time line of cumulative biogas production in batch digestion can be expressed as a function of time *F(t)* multiplied by a final gas volume B_f, which is the asymptotic experimental gas volume from digestion of a given quantity of substrate. The function *F(t)* should be non-negative, monotonic, and close to 1.0 as time approaches infinity [14].

It is not impossible that in an AD process, if no extensive accumulation of intermediary products is detected, the biogas production can represent alone the hydrolysis rate of particulate organic matter. Following the later approach and assuming first order kinetics for the hydrolysis of particulate organic matter, the cumulative biogas production can be described by one of the following equations:

1-*Exponential model* [20]

$$B_p = B_f(1-e^{-kt}) \qquad (1)$$

2-*Cone model* [14]

$$B_p = \frac{B_f}{1+(kt)^{-n}} \quad (2)$$

where B_p represents the biogas production as a function of time **t** (h); B_f ultimate biogas production (mL) and k first-order rate constant (h^{-1}).

It is important to mention that we considered by applying the **Eq.1** and **Eq.2** models that biogas production rate would increase with an increasing period of time until reaching the maximum and decrease exponentially to zero starting the decline phase.

Model (B)

Two-steps approach model

In this model approach we assumed that the complex anaerobic reaction is simply reduced to an ensemble of two sequenced intrinsic chemical reactions namely the acidification and methanation. In 2010, Shin and Song [17] limited the chemical transformation mechanism process by the terms linked to the substrate and kinetics that could be first order modeled. During the hydrolysis process the mass balance equation of the main substrates are as follow:

$$\frac{dS}{dt} = -k_H S \quad (3)$$

Eq.3 describes the substrate removal rate of the hydrolysis stage where S (mg COD/L) is the substrate concentration and k_H (h^{-1}) is hydrolysis and acidification constant.

$$\frac{dS_{VFAcumul}}{dt} = k_H S_{VFAcumul} \quad (4)$$

Eq.4 is the VFA cumulative rate where $S_{VFAcumul}$ (mg COD/L) is the cumulative corresponding to VFA produced by acidification.

$$\frac{dS_{VFAremoved}}{dt} = -k_{VFA} S_{VFAremoved} \quad (5)$$

Eq.5 is the VFA removed rate where $S_{VFAremoved}$ (mg COD/L) is the cumulative removed by methanation, k_{VFA} is the VFA degradation constant (h^{-1}) and S_{VFA}(mg COD/L) is the *VFA* concentration.

The solution to **Eq.3** is:

$$S = S_0 e^{-k_H t} \quad (6)$$

Assuming:

$S_{VFA} = S_{VFAcumul} + S_{VFAremoved}$, also combining **Eq.6** along with **Eq.4** & **Eq.5** and considering the total mass balance evolving both steps acidification and methanation, the final *Two-steps approach model* will be expressed as follow:

$$B_p = B_f\left(1 + \frac{k_H \times e^{-k_{VFA}t}}{k_{VFA} - k_H} - \frac{k_{VFA} \times e^{-k_H t}}{k_{VFA} - k_H}\right) \qquad (7)$$

k_H first-order kinetics constant of substrate degradation into VFA (first step)

k_{VFA} first-order kinetics constant of VFA degradation into methane (second step).

Model (C)

Two-pool first-order approach model

In 2000, Rao et al. [16] proposed an empirical model based on parallel pseudo-first-order reactions to determine the ultimate biogas production and ultimate biodegradable substrate concentration. The degradation process was subdivided into two fractions: a fast degradation fraction and a slowly degradation one. The modeled part is as follow:

$$B_p = B_f\left(1 - \lambda \times e^{-k_{Ra}t} - (1-\lambda) \times e^{-k_{Sl}t}\right) \qquad (8)$$

λ ratio of rapidly degradable substrate to total degradable substrate

k_{Ra} first-order kinetics constant for the degradation of rapidly degradable substrate

k_{Sl} first-order kinetics constant for the degradation of slowly degradable substrate.

III. ESTIMATION OF MODEL PARAMETERS

To estimate models parameters we applied a mathematical approach based on both sensitivity analysis and non-linear optimization. The main ides was to identify the best models fit parameters corresponding to the error between simulated values and measurements having the lowest value. Following the later statement, the model parameters were estimated using the *nlinfit* and *optimist* functions in Matlab software (R2011a).

A Levenberg-Marquardt algorithm [10-12] for best least-squares estimation of non-linear parameters was applied in our calculations. Levenberg-Marquardt algorithm usually starts using a steepest descent method and progressively becomes a Gausse-Newton method as it gets closer to the optimum value of the researched parameter. This way, the algorithm is more robust than Gausse-Newton but achieves better convergence than steepest descent. The literature review

showed that LMA has been commonly applied to parameter identification in AD models. In 1999, Garcia-Ochoa et al. [6] used LMA for the treatment of livestock manure, Aceves-Lara et al. used, in 2005, LMA for raw industrial wine distillery vinasses and in 2001, Deveci and Ciftci used LMA for baker's yeast effluents analysis[1,22-23]. Aceves-Lara et al. [1] combined LMA with an asymptotic observer to evaluate the parameters kinetics.

IV. METHODS AND EXPERIMENTAL SETUP

Substrates

The substrates were collected from Al Mawalah Central Market in Muscat (Sultanate of Oman). However, the cocked oil was collected from nearby restaurants. Before starting the experiments all solid substrates were shredded in small pieces and stored at 4 degree Celsius and characterized for total solids (TS), Suspended solids (SS) and Volatile suspended solids (VS) determination.

Inoculum

Granular sludge obtained from UASB (Upflow anaerobic sludge blanket) reactor treating sugar factory effluent was used to inoculate the 6L volume bioreactor. The reactor was fed with 600-700 g of settled sludge and mixed well at 35±5°C to break down the granules. The inoculum was tested for its methanogenic activity by addition of 2 ml of ethanol a sole source of carbon, in few batches.

Reactors operation

Two exact double-walled bio-reactors of 6L effective volume: B1 and B2, maintained at 35°C by a regulated water bath. The dynamical mixing process in the reactors was performed by using magnetic stirring located at the bottom part of the bio-reactor. An online Metler Toledo pH probe (Inpro 4260i) measuring system was set to continuously monitoring and maintained at 7.5±0.5. The reactor was operated in batch mode without withdrawal. The reactor B1 and B2 were fed with vegetable substrates at an OLR varying from 1.0 to 5.0 g VS/l, respectively.

Statistical analysis

The accuracy of the model parameters and confidence intervals of the model prediction were calculated. The 95% (α) confidence intervals for the non-linear least squares estimation of "k" were determined. In other terms, in case where the same population is sampled on large occasions and interval estimates are made on each occasion, the resulting intervals would have limits that cover the true population parameter in approximately 95 % of the cases. A confidence stated at a (1−α) level can be thought of as the inverse of a significance level, αThe Pearson product-moment

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correlation coefficient was determined to measure the correlation magnitude between the measured values and the predicted values.

V. RESULTS AND DISCUSSION

Models skills

As a model quality criteria statement, we accepted only predicted B_f that did not exceeded the experimental value by 10%. Otherwise, we assumed that the experimental data does not fit the model and hence the model parameters such "k or B_f" is invalid and the numerical results were rejected.

Fig. 1 and **Fig. 2** represent the time series (*h*) function of the cumulated biogas production (mL). The experimental data were plotted as solid lines, and model data as dots. A quick visual inspection demonstrates that both Exponential and Cone models perform well in reproducing the experimental data. The PCC values were very high ranging between 0.9909 and 0.9991 (see **Table 2**). For each validation, PCC values were estimated by the following equation:

$$PCC = \frac{\sum_{i=1}^{N} (x_{i,meas} - \bar{x}_{i,meas})^2 (x_{i,pred} - \bar{x}_{i,pred})^2}{\sqrt{(x_{i,meas} - \bar{x}_{i,meas})^2} \sqrt{(x_{i,pred} - \bar{x}_{i,pred})^2}} \quad (9)$$

where $x_{i,meas}$ is measured value of biogas production volume, $x_{i,pred}$ is predicted value of biogas production volume, and N is number of measurements.

Results of rMSPE (**Eq.10**) values calculated for each test – not shown - clearly demonstrate that test with high value of PCC had the lowest value of rMSPE.

Modelling Priority was given to the most critical value B_f which is the ultimate biogas production, i.e., the cumulated biogas produced at the batch termination. All models yielded a reasonable estimate of B_f.

$$rMSPE = \sqrt{\sum_{I=1}^{N} \frac{\left(x_{i,meas} - x_{i,pred}\right)^2}{N}} \quad (10)$$

"k" estimations

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Table 1 shows that estimated value of "*k*" for two the Exponential model and the Cone model were almost constant for each of the co-digestion of vegetables (**Exp.1**) and co-digestion of fruits, vegetables and cooked oil (**Exp. 3**) tests. In the other hand, the estimated "*k*" values for co-digestion of fruits (**Exp. 2**) for both models were observed to be the highest one. The same observation applies to models B and C results (**Table 2**). The later statement corroborating the fact that the biogas production value during the **Exp.1** and **Exp.3** were less than the biogas value produced during the **Exp.2** which would mean that not all **Exp.1** and **Exp.3** related substrates fed to the AcoD systems were converted into methane. It is reasonable to assume that, in **Exp.1** and **Exp.2** batches, part of the particulate matter hydrolyzed and turned into volatile fatty acids (VFA), but not converted into methane, remained in the system. The k_{VFA} values for **Exp.2** displayed in **Table 3** shows higher range than in case of **Exp.1** and **Exp.3**. This would mean that for the same amount of OLR the VFA degradation characterizing **Exp.2** batch is reasonably faster and unobstructed comparing to the other experiments.

Analysis of the residuals

Residuals are known as the difference between the observed value of experiments data and the predicted value of modeled data. A "good" model is the one that is good at predicting, that is, one that produce small prediction errors when applied to the observed data [11]. In addition, in an ideal case the residuals should display a random behavior distributed along time which meaning that the model error is only related to measurement uncertainty. In **Figs. 3**, **4** and **5** we plotted the models B and C residuals. The random pattern was not clearly observed for both models. This lead to the fact that both models may not reflect the reality but only estimate the complex process of the biochemical process of the AcoD system. Models B, and C yielded less residuals than model A (Exponential).

We might state at this point that the model complexity in some cases is very useful to reach a better fit on the data. In other terms, the more the model has complex design the more it approaches a better fit to the experiments data. Whereas residuals are important to evaluate the model results it should be taken carefully since alone they do not verify if a model is applicable for estimation purposes.

VI. CONCLUSION

In this work three models were tested for the quality control of biogas production assays. They showed good performances and strong positive PCC values (≥0.99). The models parameters were

calculated. These model parameters could indeed well represent a continuous anaerobic digestion process facing several dynamic changes. The model tool box could be a good medium to perform a systematic, executable, plug-and-play system. It could be run on a regular basis on real time data collected from laboratories assays. It will help better understanding of the biochemical process occurring during the AcoD process and it will assist in optimizing the reactors performances. The modeling approach was able to identify the slowly degradable substrates and helped us to provide plausible explanations. A primal information that will help researchers to decide whether or not to replace the substrates or/and inoculum or to extend the digestion period for more decisive results.

Model B is characterized by its ability to yield an estimation of transient VFA accumulation during the anaerobic digestion process. A useful information for researcher to know since VFA concentrations once kept at plausible levels could ensure an optimal performance of the bioreactor. Nonetheless, the modeling process remains an approximation of the reality complexity. The model validity will be based on the trade-off between the process complexity, the model flexibility and parsimony (determined by the number of state variables and parameters included).

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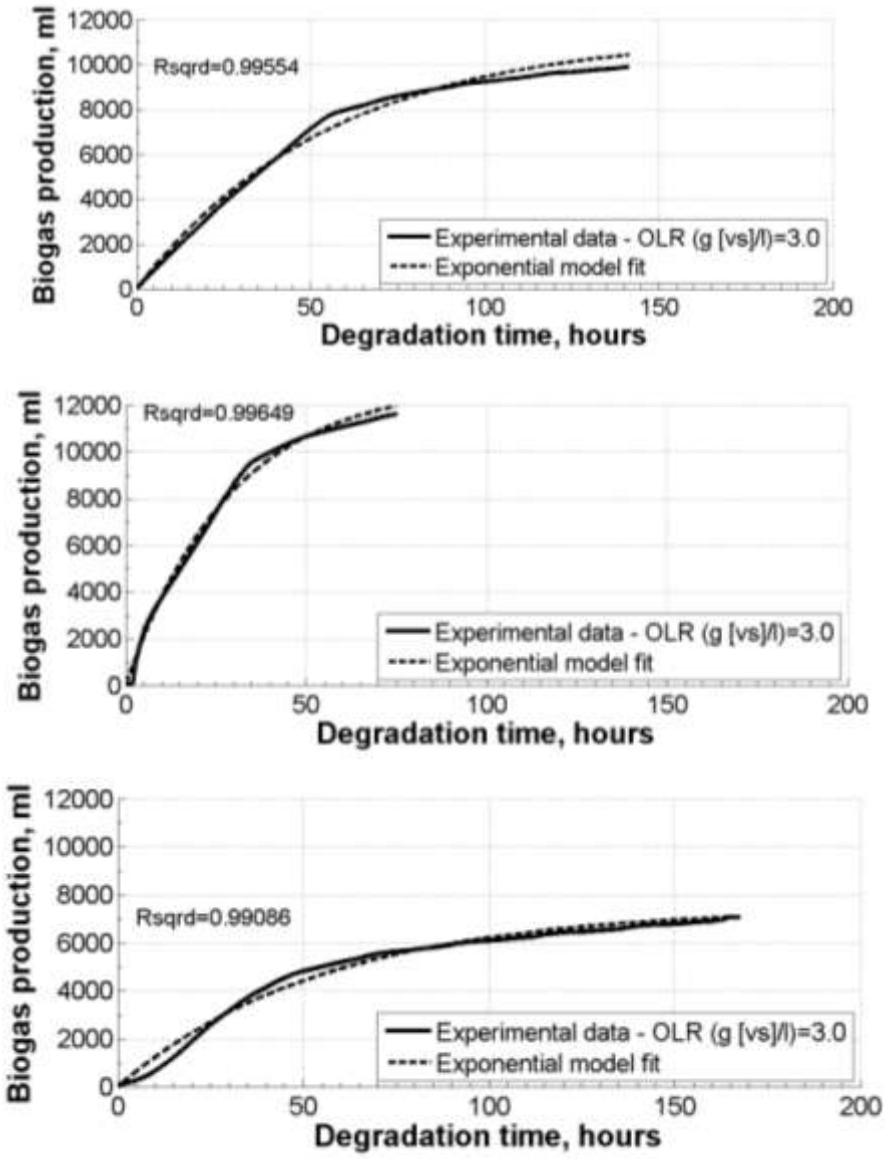

Fig. 1 Measures and *Exponential* model fitted values of biogas production from co-digestion test (OLR=3.0 g[VS]/l) as a function of digestion time. *(top): vegetables co-digestion**;** (medium): fruits co-digestion and (bottom):fruits, vegetables and cooked oil co-digestion**.***

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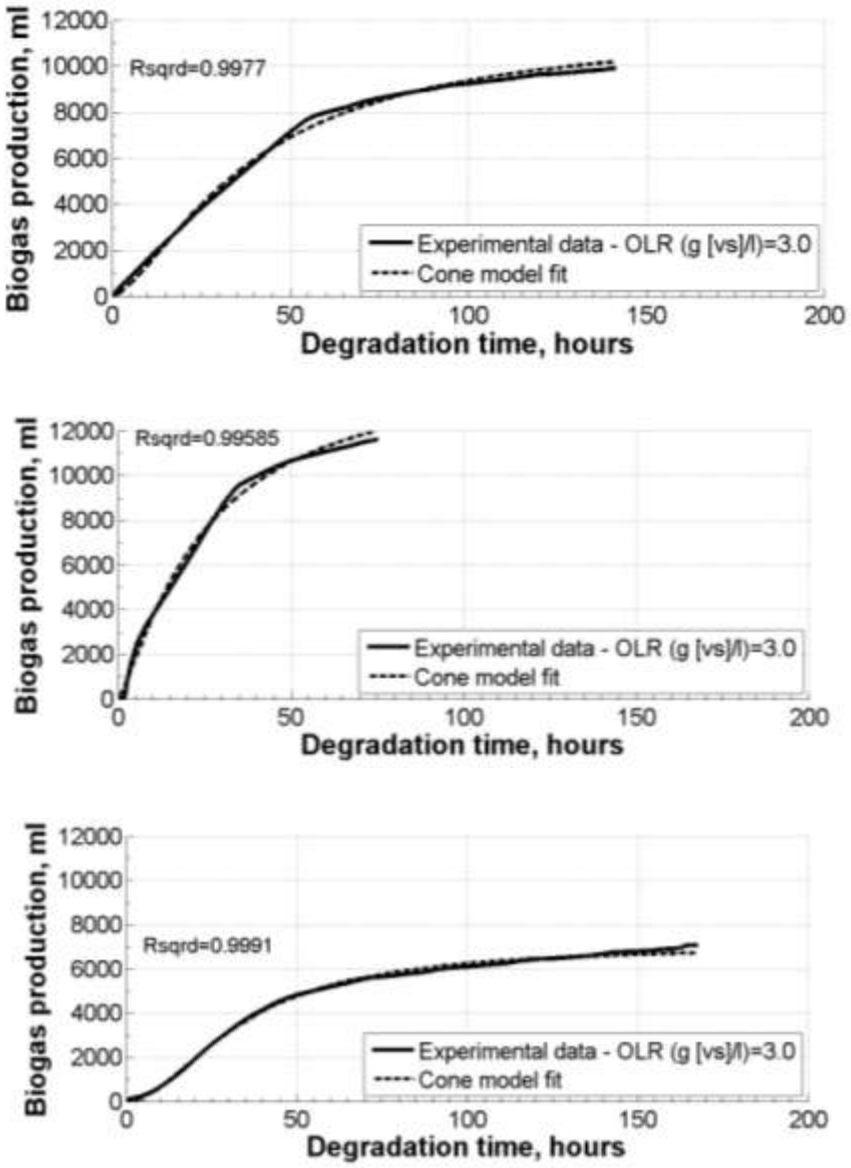

Fig. 2 Measures and *Cone* model fitted values of biogas production from co-digestion test (OLR=3.0 g[VS]/l) as a function of digestion time. *(top): vegetables co-digestion**;** (medium): fruits co-digestion and (bottom):fruits, vegetables and cooked oil co-digestion**.***

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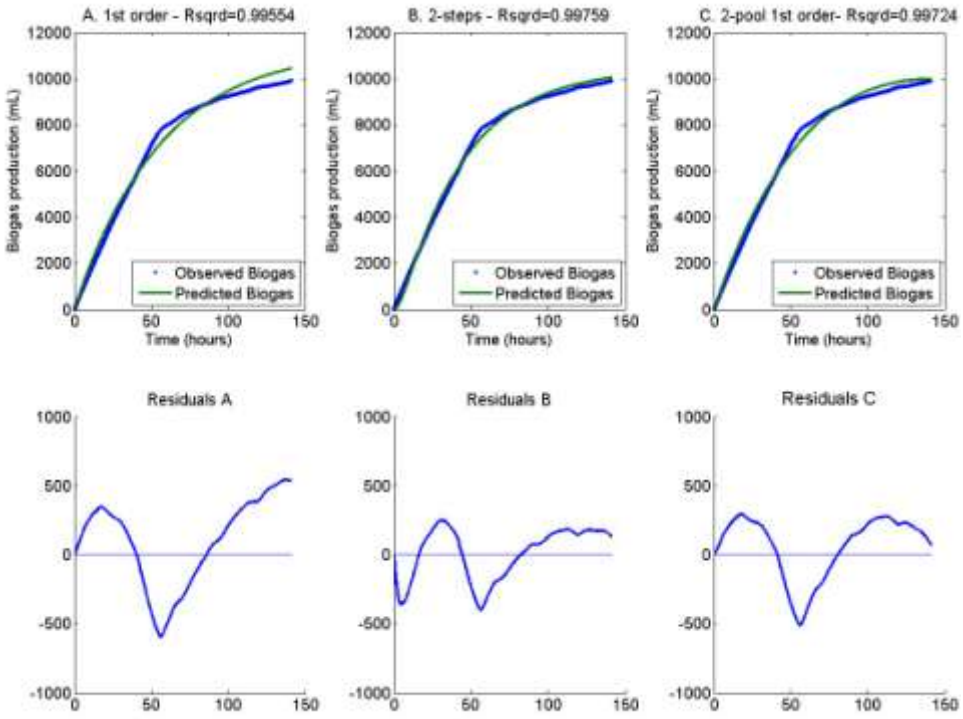

Fig. 3 (*top*) Measured data to model fitting data plots of biogas production from ***vegetables*** co-digestion test (model A, B and C). (*bottom*) Residuals.

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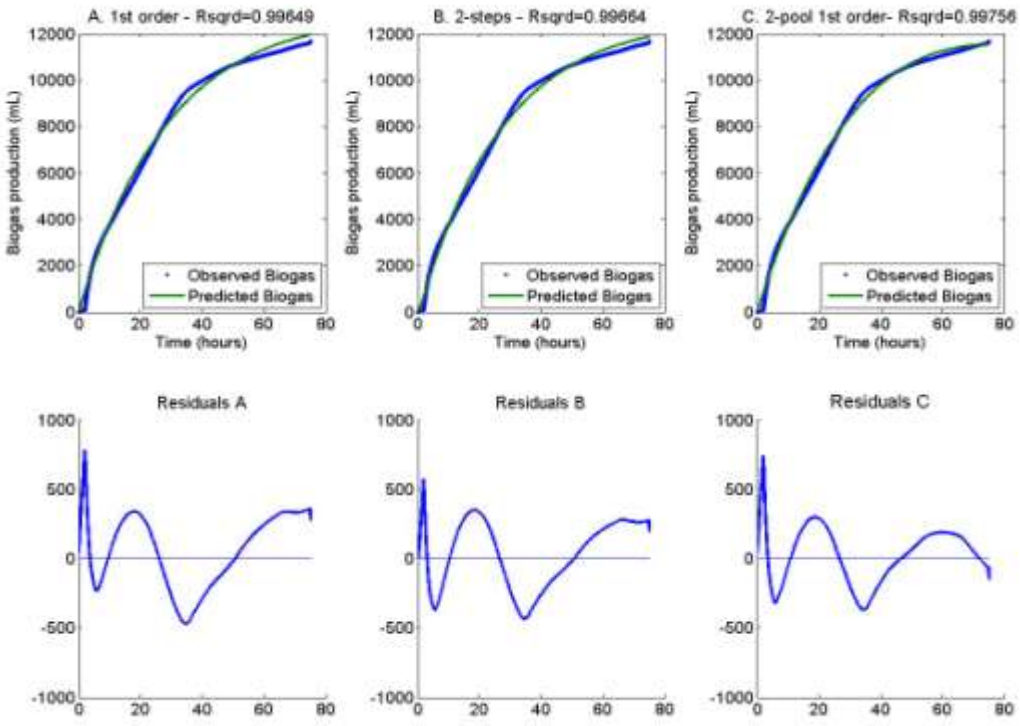

Fig. 4 (*top*) Measured data to model fitting data plots of biogas production from ***fruits*** co-digestion test (model A, B and C).(*bottom*) Residuals.

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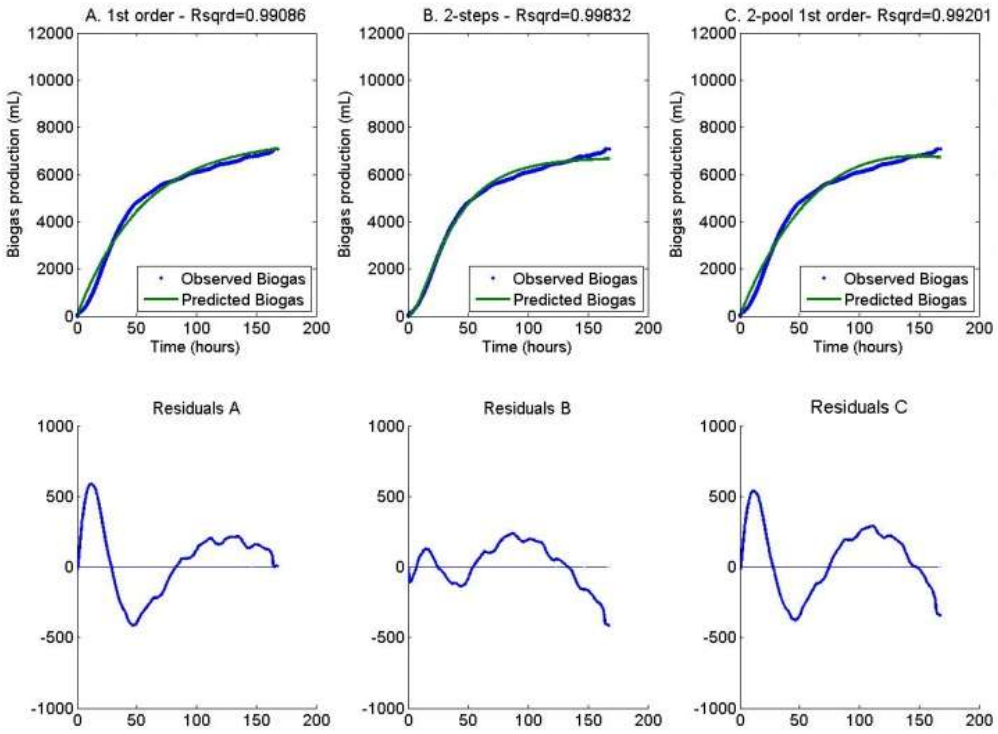

Fig. 5 (*top*) Measured data to model fitting data plots of biogas production from ***fruits***, ***vegetables and cooked oil*** co-digestion test (model A, B and C). (*bottom*) Residuals.

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Table1. Estimated "*k*" of the studied models (the 95% confidence intervals for the non-linear least squares parameter estimates "k" are between parentheses).

	Degradation kinetics rate (h^{-1})	
	k Exponential	*k* Cone
Exp.1	$0.018(3x10^{-4})$	$0.026(5.0x10^{-4})$
Exp.2	$0.035(5x10^{-4})$	$0.040(1.5x10^{-4})$
Exp.3	$0.018(3x10^{-4})$	$0.030(2.0x10^{-4})$

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Table2. Pearson correlation coefficients (PCC) of different models.

	Pearson Correlation Coefficients	
	Exponential Curves	Cone Curves
Exp.1	0.9955	0.9977
Exp.2	0.9965	0.9959
Exp.3	0.9909	0.9991

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Table 3. Estimated "*k*" of the studied models B and C. (the 95% confidence intervals for the non-linear least squares parameter estimates "k" are between parentheses).

	Degradation kinetics rate (h^{-1})			
	Model B		Model C	
	k_H	k_{VFA}	k_{Ra}	k_{SI}
Exp.1	0.024($3x10^{-4}$)	0.215($3x10^{-4}$)	0.009($3x10^{-4}$)	0.006($3x10^{-4}$)
Exp.2	0.037($4.5x10^{-4}$)	1.738($5x10^{-4}$)	0.017($4x10^{-4}$)	0.012($4x10^{-4}$)
Exp.3	0.031($1.5x10^{-4}$)	0.108($2x10^{-4}$)	0.008($2x10^{-4}$)	0.006($2.5x10^{-4}$)

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