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Gamma distribution function to understand anaerobic digestion kinetics: Kinetic constants are not constant

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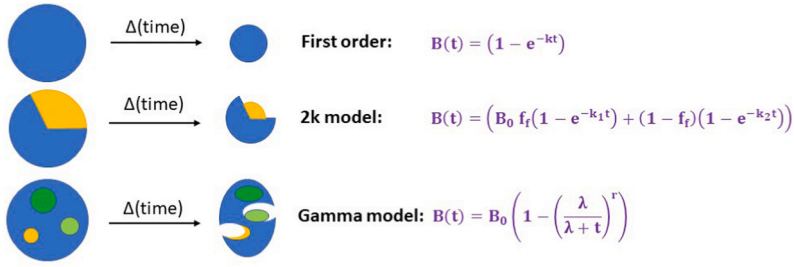
HIGHLIGHTS

- Gamma model as a new way to explore anaerobic digestion kinetics.
- Gamma model allows mathematising the hidden variability of kinetic constants.
- Each substrate displayed a characteristic distribution function.
- Gamma model could model kinetic changes related to anaerobic co-digestion.

GRAPHICAL ABSTRACT



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ABSTRACT

The Gamma model is a novel approach to characterise the complex degradation dynamics taking place during anaerobic digestion. This three parameters model results from combining the first-order kinetic model and the Gamma distribution function. In contrast to conventional models, where the kinetic constant is considered invariant, the Gamma model allows analysing the variability of the kinetic constant using a probability density function. The kinetic constant of mono-digestion and co-digestion batch tests of different wastes were modelled using the Gamma model and two common first-order models: one-step one-fraction model and one-step two-fraction model. The Gamma distribution function approximates three distinct probability density functions, i.e. exponential, log-normal, and delta Dirac. Specifically, (i) cattle paunch and pig manure approximated a log-normal distribution; (ii) cattle manure and microalgae approximated an exponential distribution, and (iii) primary sludge and cellulose approximated a delta Dirac distribution. The Gamma model was able to characterise two distinct waste activated sludge, one approximated to a log-normal distribution and the other to an exponential distribution. The same cellulose was tested with two different inocula; in both tests, the Gamma distribution function approximated a delta Dirac function but with a different kinetic value. The potential and consistency of Gamma model were also evident when analysing pig manure and microalgae co-digestion batch tests since (i) the mean k of the co-digestion tests were within the values of the mono-digestion tests, and (ii) the profile of the density function transitioned from log-normal to exponential distribution as the percentage of microalgae in the mixture increased.

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1. Introduction

Anaerobic digestion is a reliable biotechnology for the management and valorisation of organic-rich waste such as sewage sludge, animal manure, food waste and agri-industrial residues (Chowdhury et al., 2019; Mata-Alvarez et al., 2014; Stamatelatou and Tsagarakis, 2015; van Lier et al., 2008; Varjani et al., 2021). Mathematical models have been extensively used to design and control full-scale digesters (Weinrich and Nelles, 2021). Most of these models are based on empirical or semi-empirical equations (i.e. they reflect the cumulative effect of a multistep process) such as the first-order kinetics and the Monod kinetics (Batstone et al., 2002; Kythreotou et al., 2014). The anaerobic digestion model no. 1 (ADM1) is the common platform to model anaerobic digestion systems (Batstone et al., 2002). However, the ADM1 is acknowledged to be a highly complex model due to the large number of state variables, rate and equilibrium expressions, stoichiometric coefficients, and kinetic parameters (Batstone, 2006). Furthermore, the ADM1 requires extensions to explain certain phenomena such as sulphate reduction, syntrophic acetate oxidation and mineral precipitation (Ahmed and Rodríguez, 2018; Batstone, 2006; Capson-Tojo et al., 2021; Flores-Alsina et al., 2016; Zhang et al., 2015). In other cases, the complexity of the ADM1 needs to be reduced; for instance, to be implemented in control systems (Giovannini et al., 2018). Several authors have highlighted the importance of improving anaerobic digestion models (Batstone et al., 2015; Mata-Alvarez et al., 2014) since there is no reliable strategy to unify theoretical simulations and lab-scale studies with full-scale application.

It is known that kinetic constants of chemical reactions are independent of the reactor scale (Fogler, 2005). However, Batstone et al. (2009) and Jensen et al. (2011) reported significant discrepancies between the first-order hydrolysis constants obtained in batch and continuous anaerobic digestion reactors. In anaerobic digestion, these differences could be attributed to the handling of heterogenous influents, which chemical and microbial composition is dynamic over time, different operation regimes (e.g. hydraulic and organic loading), and hydrodynamic differences (Sadino-Riquelme et al., 2018). Segura et al. (2017) introduced the idea that inhibition constants in mathematical models of microbially-driven processes are not necessarily constant over time. Segura et al. (2017) proposed a time-dependent inhibition equation to model the dynamic acclimation of microalgae activity to ammonia inhibition. Similarly, Capson-Tojo et al. (2020) showed that the ammonia inhibition constant of anaerobic digesters depends on the archaeal community. These observations align with the use of semi-empirical equations to model biological systems (unlike the mechanistic Michaelis-Menten enzymatic model). Accordingly, the assumption that kinetic constants are invariant is not justified for semi-empirical models.

Modelling complex systems is a common challenge in different fields of knowledge. Continuous-distribution kinetic models have been successfully used to facilitate the mathematisation of complex systems. Kodera et al. (2000) used a continuous-distribution kinetic model to evaluate the kinetics of asphaltene hydrocracking at three different temperatures, and Yianatos et al. (2010) used the Gamma distribution function to model the flotation rate of minerals in flotation cells. The ability of the Gamma distribution function to describe the variability of biological kinetic constants has been reported by Haglund et al. (2012), who used the Gamma distribution function to describe the folding times of the leptin gene. The advantage of continuous-distribution kinetic models is their ability to simulate systems with a certain degree of stochasticity including the distribution of a reaction mixture and mixing characteristics during the reaction (Kodera et al., 2000; Yianatos et al., 2010). However, to the best of the authors' knowledge, a continuous-distribution kinetic model has not been used to model microbially-driven processes.

The combination of the first-order kinetic model (the simplest and most widely used kinetics to model anaerobic digestion) with the Gamma distribution function results in a semi-phenomenological model with the advantage that the first-order kinetic constant can follow a range of values (distribution) instead of being defined by an invariant value. The advantage of the Gamma distribution function over other distributions (e.g. Gaussian, Poisson, Weibull) relies on its capability to change its shape (from exponential to symmetric probability distribution) with only two parameters (i.e. λ and r) (Montgomery and Runger, 2014). This capability is particularly interesting to model anaerobic digesters fed with complex substrates and/or subjected to strategies aiming to improve their performance such as anaerobic co-digestion or waste pre-treatments. The probability density functions allow studying the variability of kinetic constants without changing the model that predicts the maximum methane potential. The use of simple models with parameters that can follow a probability distribution is a new approach to model complex microbially-driven processes such as anaerobic digestion.

The objective of this work is to propose a new approach to model the complex and diverse biochemical reactions occurring in anaerobic digesters. This approach uses the first-order kinetic model, where the first-order kinetic constant model is redefined by adding a Gamma distribution function. The goodness of fit of this approach (namely Gamma model) is compared with two commonly used first-order approaches: (i) one-step one-fraction model (namely 1k model), and (ii) one-step two-fraction model (namely 2k model). These three models have been tested on a range of biomethane potential tests results used as case study.

2. Materials and methods

2.1. BMP tests

Biochemical methane potential (BMP) tests were carried out at mesophilic conditions following the procedure described by Angelidaki et al. (2009) and Holliger et al. (2016). BMP tests were performed in triplicate in 160 mL serum bottles sealed with butyl rubber septa and aluminium crimp caps. Serum bottles contained inoculum and the amount of substrate required to achieve an inoculum-to-substrate ratio (ISR) of 2 on volatile solids (VS) basis. Blank assays, containing only inoculum, were used to correct for the background methane production of the inoculum. The headspace of each bottle was flushed with 99.99% N_2 for 1 min at 4 l/min. Finally, the bottles were placed in a temperature-controlled incubator set at 37 °C. The bottles were manually mixed by swirling before each sampling event. At each sampling event, the accumulated volumetric methane production was calculated using the headspace gas pressure and biogas composition. Methane yields (ml CH_4/g VS) are reported as the average of the triplicates at standard conditions (i.e. 0 °C, 1 atm, and dry). BMP calculations were cross-validated with the OBA web application (Hafner et al., 2018).

Ten different BMP tests using common anaerobic digestion substrates have been used in this research. The substrates include (i) cattle manure (this study), (ii) cattle paunch waste (cattle stomach content comprised of partially digested feed) (this study), (iii) primary sludge (Peces et al., 2020), (iv) two waste activated sludge (WAS_1 and WAS_2) from different municipal wastewater treatment plants (Peces et al. (2020), this study), (v) microcrystalline cellulose tested two independent times with inoculum from the same full-scale digester (Hafner et al., 2020), and (vi) a co-digestion experiment including pig manure mono-digestion, microalgae mono-digestion and three co-digestion mixtures between pig manure and microalgae (Astals et al., 2015).

2.2. Mathematical models for anaerobic digestion

2.2.1. One-step one-fraction first-order model (1k model)

The biochemical conversion of an organic substrate to methane can be described by a single first-order kinetic model (one-step one-fraction, Equation (1)) (Angelidaki et al., 2009; Gavala et al., 2003; Li et al., 2016); where k is the first-order kinetic constant (d^{-1}), S is the organic

substrate concentration (g COD/l), and t is time (d).

$$Substrate\ (S) \rightarrow Methane(B)$$

$$\frac{dS}{dt} = -kS \quad \text{Eq. 1}$$

For a batch reactor, such as BMP tests, the substrate mass balance is shown in Equation (2).

$$S = S_0 e^{-kt} \quad \text{Eq. 2}$$

In BMP assays, methane production (B) is the measured variable instead of substrate consumption. Therefore, Equation (2) is commonly expressed in terms of methane production (Equation (3)).

$$B(t) = \alpha V_{reactor}(S_0 - S) \quad \text{Eq. 3}$$

where α is the yield of the volumetric methane produced by the mass of substrate consumed (e.g. 350 ml CH_4/g COD at 0 °C and 1 atm), $V_{reactor}$ is the volume of liquid phase (l), and S_0 is the initial substrate concentration (g COD/l). When all the substrate is consumed, Equation (3) expresses the maximum amount of methane that can be produced (B_0) (Equation (4)).

$$B_0 = \alpha V_{reactor} S_0 \quad \text{Eq. 4}$$

Combining Equations (2)–(4), the first-order model equation for methane production is obtained (Equation (5)).

$$B(t) = B_0\left(1 - e^{-kt}\right) \quad \text{Eq. 5}$$

where B is the methane production (ml CH_4/g VS), B_0 is the maximum methane potential (ml CH_4/g VS), k is the first-order kinetic constant (d^{-1}), and t is time (d).

2.2.2. One-step two-fractions first-order model (2k model)

Some authors have modified Equation (5) by dividing the substrate into two fractions, a rapidly and slowly biodegradable fraction, a.k.a. one-step two-fraction model (Equation (6)) (Astals et al., 2015; García-Gen et al., 2015; Wang et al., 2013; Weinrich et al., 2020).

$$Substrate\ (S_1 + S_2) \rightarrow \left\{ \begin{array}{l} S_1 \rightarrow Methane_1 \\ S_2 \rightarrow Methane_2 \end{array} \right\} \rightarrow Methane(B)$$

$$B(t) = B_0\left(f_{fraction}\left(1 - e^{-k_1 t}\right) + \left(1 - f_{fraction}\right)\left(1 - e^{-k_2 t}\right)\right) \quad \text{Eq. 6}$$

In the 2k model, the substrate is characterised by two fractions ($f_{fraction}$) and a distinct first-order kinetic constant for each fraction, i.e. k_1 and k_2. In Equation (6), B is the methane production (ml CH_4/g VS), B_0 is the maximum methane potential (ml CH_4/g VS), $f_{fraction}$ splits the substrate into rapidly and slowly biodegradable fraction, k_1 and k_2 are the first-order kinetic constants for each fraction (d^{-1}), and t is time (d).

2.2.3. Gamma model

Most anaerobic digestion mathematical models consider kinetic parameters a constant value, i.e. a delta Dirac distribution (Batstone et al., 2002; Donoso-Bravo et al., 2010; Gavala et al., 2003). For the first-order kinetic model, the delta Dirac distribution is written as $\delta_{k\text{-}value}(k\text{-}k_{value})$ (Yianatos et al., 2010).

Equation (7) shows the general equation to express the expected value (mean) of a mathematical function [h(x)] for any given random variable (x) with a probability density function [f(x)] (Montgomery and Runger, 2014). For the methane production function (B) with the random variable as kinetic constant (k), Equation (7) is expressed as Equation (8).

$$E[h(x)] = \int_{-\infty}^{\infty} h(x) f(x) dx \quad \text{Eq. 7}$$

$$E[B(k,t)] = B(t) = \int_{-\infty}^{\infty} B(k,t) f(k) dk \quad \text{Eq. 8}$$

When the kinetic constant (k) follows a Dirac distribution, the first-order model is obtained (Equation (9)).

$$B(t) = \int_{-\infty}^{\infty} B_0\left(1 - e^{-kt}\right) \delta_{k_{value}}(k - k_{value})\, dk = B_0\left(1 - e^{-k_{value} t}\right) \quad \text{Eq. 9}$$

To include a probabilistic behaviour to the first-order kinetic constant, a different probability distribution must be used. Among the different probability distribution functions, the Gamma distribution function (Equation (10)) offers greater flexibility without a complex mathematical expression (Montgomery and Runger, 2014). The Gamma distribution function can approximate other probability density functions depending on the values taken by its characteristic parameters (i.e. λ and r).

$$f(x) = \frac{\lambda^r x^{r-1} e^{-\lambda x}}{\Gamma(r)}; x > 0 \quad \text{Eq. 10}$$

When the Gamma distribution parameters are determined, the expected value (mean) of the random variable can be calculated using Equation (11). In this study, the random variable is the first-order kinetic constant (k, units of d^{-1}). The variance of the first-order kinetic constant is calculated using Equation (12) (units of d^{-2}).

$$E(k) = mean\ k = \frac{r}{\lambda} \quad \text{Eq. 11}$$

$$variance\ k = \frac{r}{\lambda^2} \quad \text{Eq. 12}$$

Combining Equation (8) and the Gamma distribution function (Equation (10)), a new methane production model is obtained (Equation (13)); hereafter referred as the Gamma model. Equation (13) development is provided in the supplementary material Note S1.

$$B(t) = B_0\left(1 - \left(\frac{\lambda}{\lambda + t}\right)^r\right) \quad \text{Eq. 13}$$

In the Gamma model (Equation (13)), B is the methane production (ml CH_4/g VS), B_0 is the maximum methane potential (ml CH_4/g VS), λ (d) and r (–) are the characteristic constants of the Gamma distribution, and t is time (d).

2.3. Parameters estimation

The model parameters were obtained by the least squares method implemented in Matlab® (R2016a). The function *lsqcurvefit* using the 'trust-region-reflective' optimisation algorithm was used to carry out the non-linear regression of the 1k model, 2k model, and Gamma model. This function minimises the mean squared differences between the experimental data and the model predictions. The function *nlparci* was used to calculate the 95% confidence interval of each parameter. This function retourn the confident interval using the residuals and jabobian matrix reported by *lsqcurvefit* (details about both functions are freely available at MathWorks webpage). The m-scripts are available in the supplementary data Note S2. The goodness of fit was evaluated by the coefficient of determination (R^2), the adjusted coefficient of determination (R^2_{adj}), and the root mean squared error (RMSE). The mean and variance of the Gamma distribution function are also reported (Equations (11) and (12), respectively).

3. Results

3.1. Mono-digestion BMP modelling

Fig. 1 shows the experimental cumulative methane production curves of the mono-digestion experiments, the methane production curves predicted by each model, and the probability density function of the first-order constant from the Gamma distribution function (Equation (10)). All experimental methane production curves showed an exponential behaviour without lag-time, except for cellulose. Table 1 summarises the estimated parameters from the 1k model, the 2k model, and the Gamma model. The 2k model and the Gamma model provided a

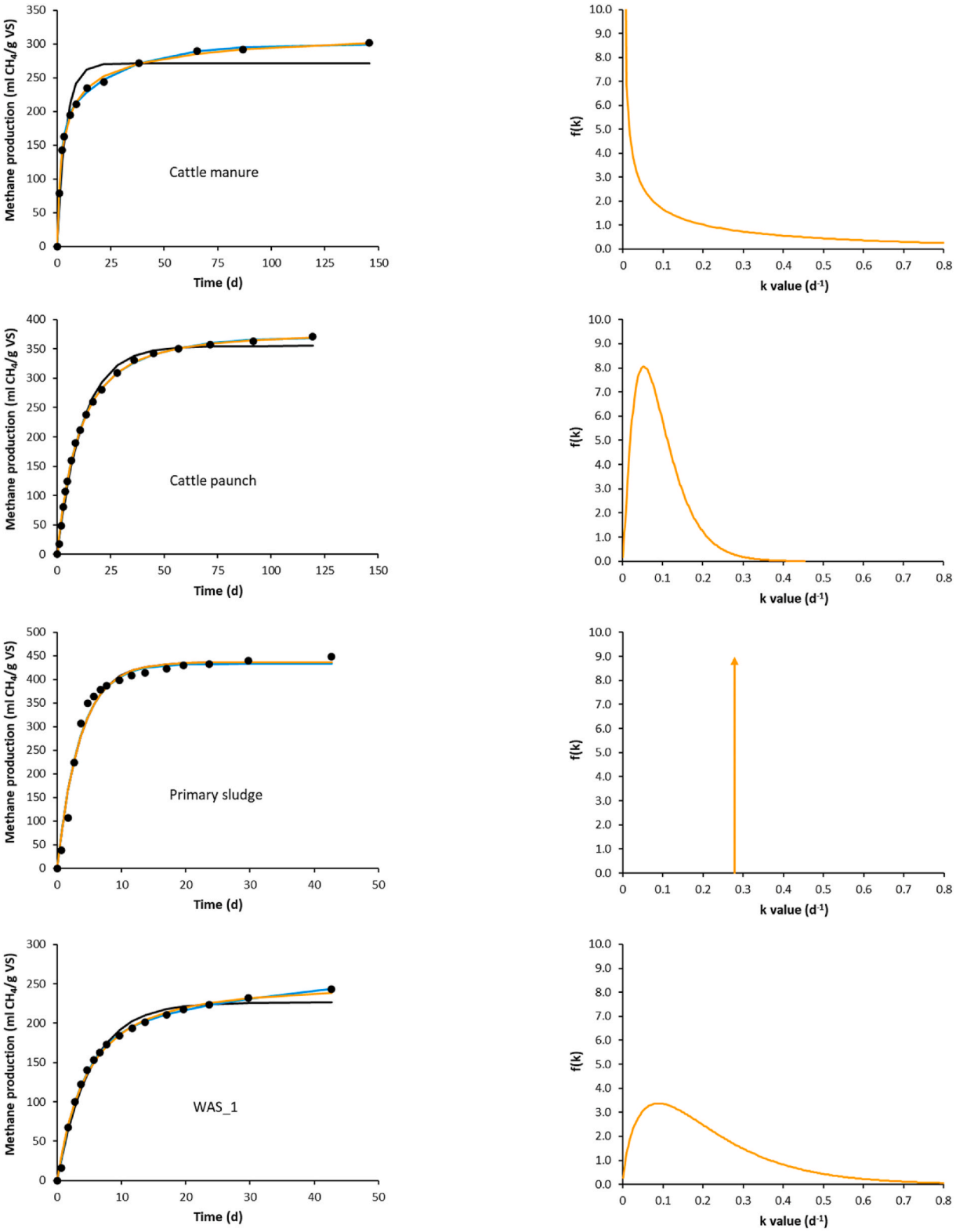

Fig. 1. (right column) Mono-digestion cumulative methane production curves: experimental data (dots), 1k model (black line), 2k model (blue line), and Gamma model (orange line). (left column) Gamma distribution function. The delta Dirac distribution is plotted as an arrow.

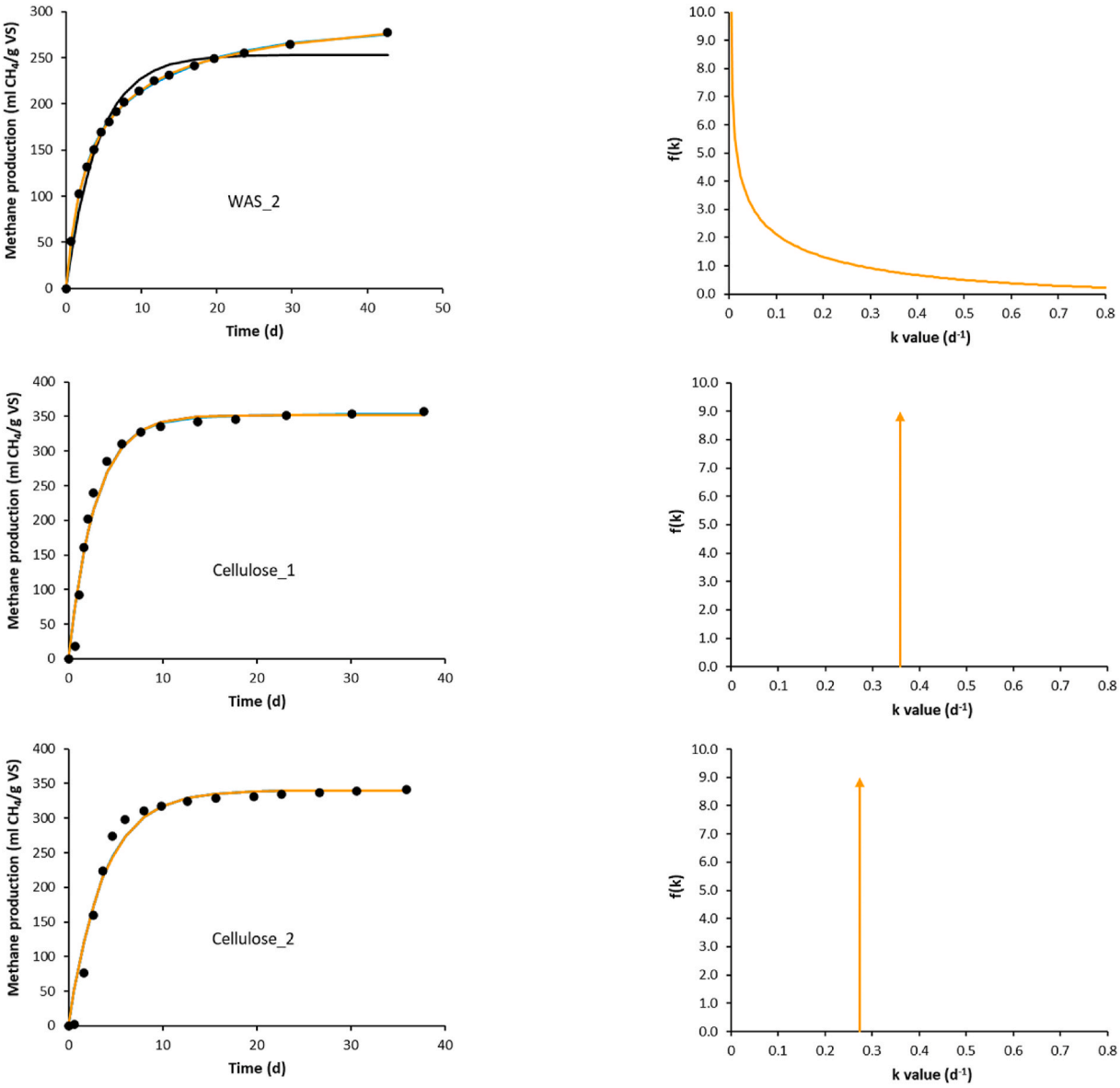

Fig. 1. (*continued*).

Table 1
Model parameters and their 95% confidence interval (in brackets), and goodness of fit parameters (R^2, R^2_{adj}, RMSE) for mono-digestion BMP curves using the 1k, 2k, and Gamma models.

	Parameters	Cattle manure	Cattle paunch	Primary sludge	WAS_1	WAS_2	Cellulose_1	Cellulose_2
1k model	B_0 (ml CH_4/g VS)	271.0 (44.1)	354.9 (15.5)	436.2 (38.1)	226.2 (15.8)	252.9 (21.9)	352.2 (35.3)	340.1 (35.5)
	k (d^{-1})	0.25 (0.17)	0.08 (0.01)	0.28 (0.09)	0.19 (0.04)	0.23 (0.07)	0.36 (0.13)	0.27 (0.11)
	R^2	0.941	0.996	0.978	0.989	0.978	0.977	0.972
	R^2_{adj}	0.936	0.996	0.976	0.989	0.976	0.975	0.971
	RMSE	24.92	8.76	23.25	8.11	12.41	20.81	22.13
2k model	B_0 (ml CH_4/g VS)	299.8 (19.6)	370.1 (14.3)	432.8 (0.1)	272.2 (237.1)	280.7 (12.8)	420.5 ($7.7{\cdot}10^5$)	442.3 ($6.0{\cdot}10^9$)
	$f_{fraction}$ (−)	0.60 (0.12)	0.55 (0.38)	0.83 ($1.2{\cdot}10^7$)	0.65 (0.25)	0.50 (0.09)	0.83 ($1.5{\cdot}10^3$)	0.77 ($1.1{\cdot}10^7$)
	k_1 (d^{-1})	0.54 (0.22)	0.14 (0.06)	0.28 ($3.0{\cdot}10^3$)	0.27 (0.16)	0.53 (0.14)	0.36 (0.01)	0.27 (0.01)
	k_2 (d^{-1})	0.04 (0.03)	0.04 (0.03)	0.28 ($1.3{\cdot}10^4$)	0.03 (0.15)	0.08 (0.03)	$1.2{\cdot}10^{-3}$ (10)	0.01 (0.01)
	R^2	0.998	0.999	0.977	0.997	0.999	0.977	0.972
	R^2_{adj}	0.997	0.999	0.972	0.996	0.999	0.971	0.966
	RMSE	4.68	3.06	23.36	4.41	1.89	20.80	22.13
Gamma model	B_0 (ml CH_4/g VS)	339.9 (95.8)	375.2 (15.2)	436.0 (0.1)	248.8 (43.7)	324.1 (25.9)	352.0 (0.1)	340.0 (0.1)
	λ (d)	1.06 (1.44)	24.33 (14.00)	$5.5{\cdot}10^4$ ($1.9{\cdot}10^8$)	7.96 (13.33)	2.07 (0.09)	$3.6{\cdot}10^4$ ($1.7{\cdot}10^8$)	$3.3{\cdot}10^4$ ($1.9{\cdot}10^8$)
	r (−)	0.44 (0.47)	2.28 (1.22)	$1.5{\cdot}10^4$ ($5.4{\cdot}10^7$)	1.71 (2.68)	0.62 (0.18)	$1.3{\cdot}10^4$ ($6.1{\cdot}10^7$)	$9.1{\cdot}10^3$ ($5.3{\cdot}10^7$)
	mean k (d^{-1})	0.418	0.094	0.278	0.215	0.300	0.359	0.273
	variance k (d^{-2})	0.395	0.004	0.001	0.027	0.145	0.001	0.001
	R^2	0.996	0.999	0.978	0.996	0.999	0.977	0.971
	R^2_{adj}	0.996	0.999	0.975	0.995	0.999	0.973	0.968
	RMSE	6.78	3.13	23.25	5.30	1.34	19.99	21.32

better fit of the experimental data than the 1k model as shown by the R^2, R^2_{adj} and RSME values. The estimated first-order kinetic constant (1k model) and the mean k (Gamma model) were quite similar (Table 1), except for cattle manure and WAS_2. This difference can be related to the tailing present in their methane production curves, i.e. a non-asymptotic deviation from the first-order exponential ideal behaviour (see discussion in Section 4.2).

The Gamma distribution function of cattle manure and WAS_2 followed an exponential distribution (Fig. 1) which is characterised by a large variance of the kinetic constant (Table 1). In contrast, the Gamma distribution function of primary sludge, cellulose_1 and cellulose_2 approximated a delta Dirac distribution which is characterised by a variance of the kinetic constant close to zero (i.e. the methane production curves display an almost ideal first-order exponential behaviour). For cattle paunch and WAS_1, the Gamma model approximated a log-normal distribution.

3.2. Co-digestion BMP modelling

Fig. 2 illustrates the cumulative methane production curves of pig manure and microalgae mono- and co-digestion as well as the probability density function of the first-order constant from the Gamma distribution function. The mono-digestion of these two substrates was characterised by a distinct probability density function. Pig manure approximated a log-normal distribution, while microalgae followed an exponential distribution. The probability density functions from co-digesting pig manure and microalgae transitioned from log-normal to exponential distribution as the percentage of microalgae in the mixture

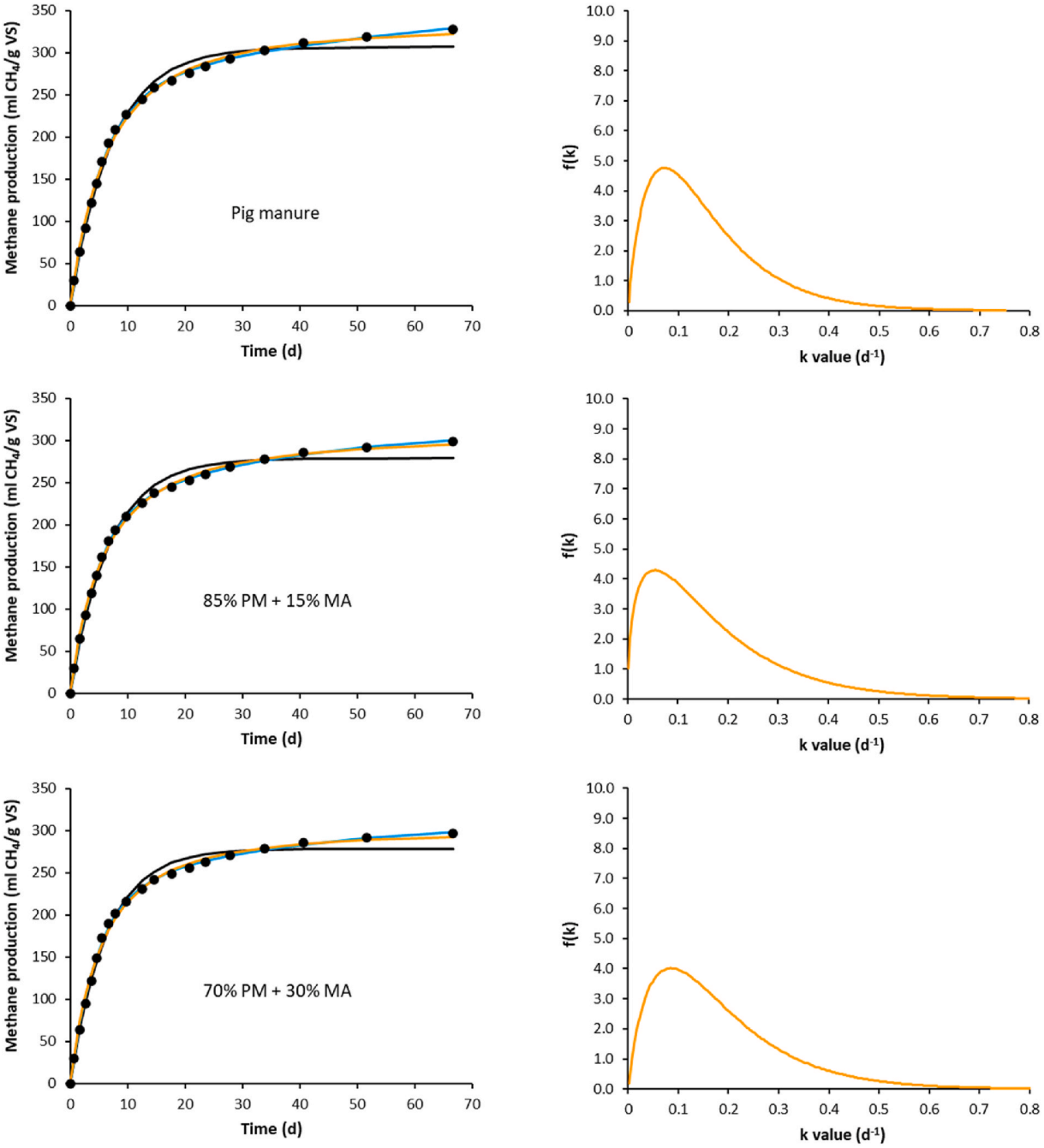

Fig. 2. (right column) Pig manure and microalgae mono- and co-digestion cumulative methane production curves: experimental data (dots), 1k model (black line), 2k model (blue line), and Gamma model (orange line). (left column) Gamma distribution function.

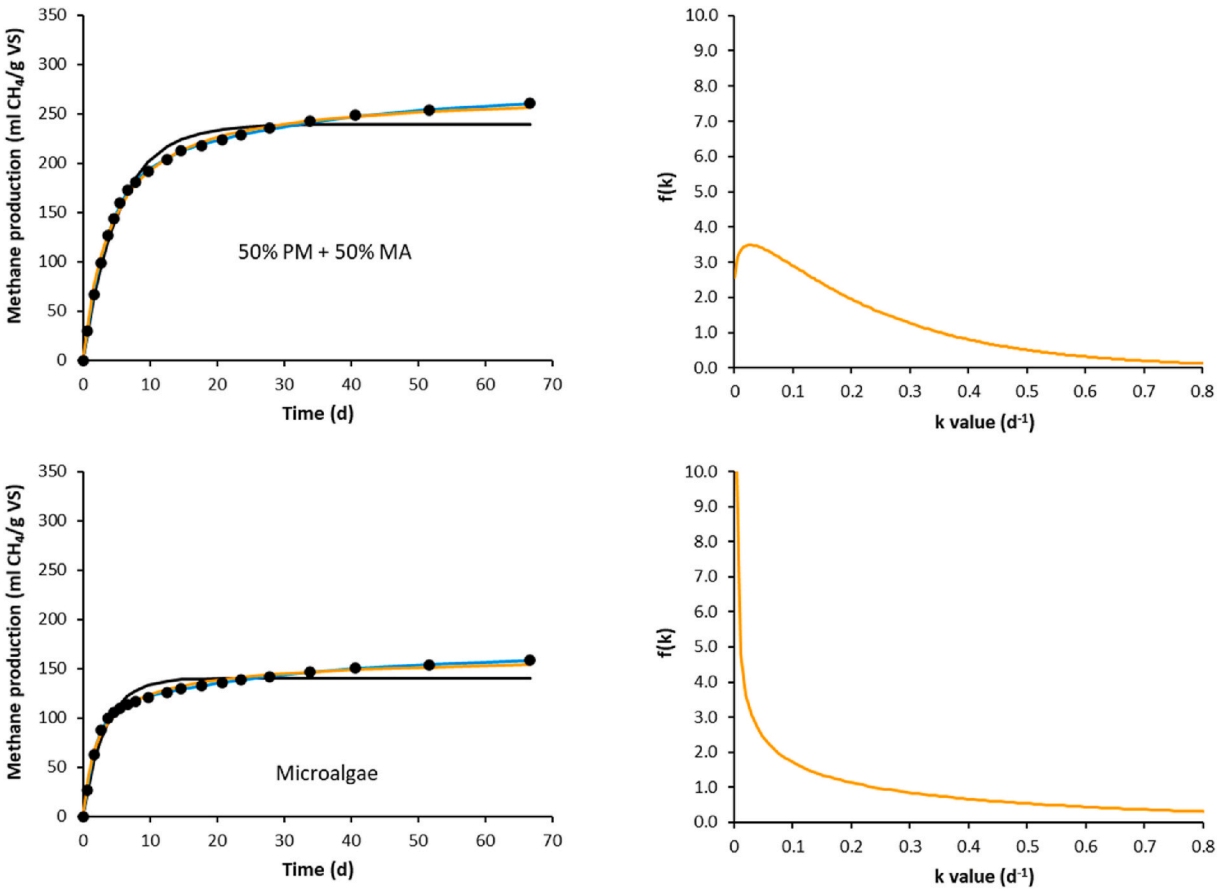

Fig. 2. (*continued*).

Table 2
Model parameters and their 95% confidence interval (in brackets and goodness of fit parameters (R^2, R^2_{adj}, RMSE) for the pig manure (PM) and microalgae (MA) mono- and co-digestion BMP curves using the 1k, 2k, and Gamma models.

	Parameters	Pig manure (PM)	85%PM + 15%MA	70%PM + 30%MA	50%PM + 50%MA	Microalgae (MA)
1k model	B_0 (ml CH_4/g VS)	306.8 (16.2)	278.8 (15.6)	278.4 (14.6)	239.2 (15.1)	140.4 (12.1)
	k (d^{-1})	0.14 (0.02)	0.15 (0.03)	0.16 (0.03)	0.19 (0.04)	0.31 (0.12)
	R^2	0.992	0.990	0.991	0.984	0.954
	R^2_{adj}	0.992	0.990	0.990	0.984	0.953
	RMSE	9.57	9.53	9.19	10.08	9.39
2k model	B_0 (ml CH_4/g VS)	358.0 (141.7)	313.2 (39.1)	311.1 (68.2)	269.6 (17.9)	164.3 (12.1)
	$f_{fraction}$ (−)	0.69 (0.12)	0.66 (0.11)	0.71 (0.14)	0.66 (0.06)	0.64 (0.04)
	k_1 (d^{-1})	0.18 (0.05)	0.21 (0.05)	0.22 (0.07)	0.29 (0.04)	0.54 (0.04)
	k_2 (d^{-1})	0.02 (0.06)	0.03 (0.04)	0.03 (0.07)	0.03 (0.02)	0.03 (0.02)
	R^2	0.999	0.999	0.998	0.999	0.999
	R^2_{adj}	0.999	0.999	0.998	0.999	0.999
	RMSE	3.66	2.50	3.82	1.64	1.40
Gamma model	B_0 (ml CH_4/g VS)	334.4 (33.9)	308.3 (26.6)	299.2 (27.1)	268.9 (26.1)	170.3 (37.8)
	λ (d)	11.32 (11.74)	8.68 (6.61)	10.36 (11.40)	4.87 (3.72)	1.24 (1.54)
	r (−)	1.76 (1.70)	1.47 (1.04)	1.88 (1.89)	1.13 (0.76)	0.59 (0.58)
	mean k (d^{-1})	0.155	0.170	0.182	0.232	0.475
	variance k (d^{-2})	0.014	0.020	0.018	0.048	0.383
	R^2	0.998	0.998	0.997	0.998	0.993
	R^2_{adj}	0.997	0.998	0.997	0.998	0.992
	RMSE	5.30	3.78	5.19	3.66	3.75

increased. The mean k of the Gamma model for the co-digestion mixtures progressively increased from 0.17 to 0.23 d^{-1} as the percentage of microalgae in the mixture increased (Table 2). These values are between the calculated mean k from pig manure (0.15 d^{-1}) and microalgae (0.47 d^{-1}), which shows the consistency of the Gamma model.

4. Discussion

4.1. Models fitting quality

All the methane production curves modelled in this study had an R^2_{adj} close to one. The R^2_{adj} and the R^2 were very similar, indicating that the

models were not over-parametrised (Montgomery, 2012). Therefore, the three models were suitable to describe the methane production of BMP tests. However, the highest R^2 of the Gamma model (3 parameters) and the 2k model (4 parameters) shows that they provide a better fit of the experimental data than the 1k model (2 parameters). The advantage of the Gamma model and the 2k model is particularly evident in the methane production curves that showed tailing (e.g. cattle manure, WAS_2 and microalgae mono-digestion) since the first-order model is not able to follow the non-asymptotic deviation from the first-order exponential behaviour. This deviation causes the 1k model to underestimate the maximum methane potential (Figs. 1 and 2).

4.2. Advantages of the Gamma model

The Gamma model provides a good estimate of ultimate methane production (Figs. 1 and 2) regardless of the distribution of k (f(k)), a minimum requirement for any BMP test modelling approach. In contrast to the 1k model, the Gamma model and the 2k model can represent the tailing of the methane production curve frequently observed in BMP tests. However, this limitation does not apply for those substrates where the Gamma distribution function approximated a delta Dirac distribution (e.g. primary sludge and cellulose). A delta Dirac distribution indicates that the methane production curve can be described by an ideal first-order model (i.e. there is no k distribution). The Gamma distribution function (Equation (10)) is not able to plot a probability function distribution with zero variance (i.e. delta Dirac distribution). However, when the Gamma function approximates a delta Dirac distribution (i) the mean k is very similar to the kinetic constant obtained by the 1k model, (ii) the variance of k is close to zero, and (iii) the λ and r parameters show large confidence intervals (see primary sludge or cellulose in Table 1). The large confidence intervals make sense since the methane production curve is represented by a single k value. Therefore, one advantage of the Gamma distribution function is its ability to mathematically differentiate between substrates that follow an ideal first-order behaviour (the process is represented by a single kinetic constant) from those that deviate from the ideal behaviour (the process is represented by a kinetic constant distribution).

Most waste are complex and heterogeneous, therefore, it is expected that the Gamma distribution function will not approximate a delta Dirac distribution. Indeed, primary sludge was the only waste that approximated a delta Dirac distribution (microcrystalline cellulose is a pure substrate used as a positive control in BMP tests (Holliger et al., 2016)). When the calculated variance is not close to zero, the Gamma distribution function does not approximate a delta Dirac distribution; instead, the kinetic constant follows a distribution density function. The shape of the Gamma distribution function varies from an exponential distribution (e.g. cattle manure, WAS_2, microalgae) to an approximated log-normal distribution (e.g. cattle paunch, WAS_1, pig manure). An exponential distribution indicates that the substrate comprises a wide range of kinetic constants from easily to slowly biodegradable, while a log-normal distribution indicates that there is a cluster of kinetic constants around a mean k value but with a marked bias. Another advantage of the Gamma distribution function is its capability to represent the distribution of the first-order kinetic constants of a waste instead of the traditional invariant value. This represents a new approach to characterise the heterogeneous degradation of organic waste during anaerobic digestion (Figs. 1 and 2).

The 2k model, where the substrate degradation is defined by two kinetic constants, could be inferred as an in-between solution between the 1k model (one kinetic constant) and the Gamma model (multiple kinetic constants). However, the phenomenological representation of the 2k model is debatable when analysing the BMP results from the cellulose tests. The 2k model predicts that about 80% of the cellulose is easily biodegradable (k_1) and that the other 20% is slowly biodegradable (k_2). However, microcrystalline cellulose is a pure substrate. Accordingly, the estimation that about 20% of cellulose is slowly biodegradable does not seem logical and it may be related to an improvement of the data fitting. The advantage of the 2k model relates to its capability to model methane production curves with tailing (e.g. cattle manure and microalgae) where the slowly biodegradable fraction is able to describe the slow but steady methane production after the first days. Despite its limitations, the 2k model could be used to describe the methane production curves of substrates where the Gamma distribution function follows an exponential distribution. The 2k model approximates the exponential distribution to two invariant kinetic constants, k_1 representing the easily biodegradable fraction and k_2 representing the slowly biodegradable fraction. However, the Gamma distribution function is more flexible and represents the distribution of the first-order kinetic constants with higher definition.

4.3. Consistency of the Gamma model: Co-digestion as a case study

The Gamma model allowed a detailed evaluation of the impact of co-digestion on anaerobic digestion performance. The Gamma distribution function for pig manure and microalgae mono-digestion tests were very different, which facilitated studying the kinetics distribution changes due to co-digestion (Table 2, Fig. 2). Specifically, pig manure had a mean k of 0.155 d^{-1} and a log-normal distribution, while microalgae had a mean k of 0.475 d^{-1} and an exponential distribution. The mean k for the co-digestion tests were within the values of the mono-digestion tests (Table 2), which indicates that the Gamma model results are consistent. These results support the conclusions from Astals et al. (2015), who despite using a 2k model, observed that the co-digestion experiments could be modelled using the kinetic constants obtained from modelling the mono-digestion experiments (i.e. the change in degradation rate could be explained by the change in substrate composition). It is hypothesised that by analysing the shape and mean k of probability density distribution, the Gamma model could be used to identify mixtures where there is a synergistic kinetic improvement, i.e. an improvement of the degradation kinetics compared to the proportional one.

The probability density functions (f(k)) of pig manure and microalgae co-digestion transitioned from log-normal to exponential distribution as the percentage of microalgae in the mixture increased (Fig. 2). This is particularly evident in the probability density function of the 50% manure +50% microalgae mixture, where (i) there is higher frequency (f(k)) of kinetic constants closer to 0 than in the other mixtures, and (ii) there is a higher frequency of kinetic constants above 0.4 d^{-1} than in the other mixtures (similar to the microalgae probability density function). The probability density function of the 70% manure +30% microalgae and 85% manure +15% microalgae mixtures resembled the pig manure log-normal distribution, which is consistent with the higher percentage of pig manure in these mixtures (mixtures were performed on a VS basis).

4.4. Implications of the Gamma model and future research

The growing importance of anaerobic digestion in circular economy and biorefinery schemes makes anaerobic digestion modelling a valuable task despite its complexity. A major constraint for anaerobic digestion models is the inability to quantify the amount of active biomass for each reaction rate (van Lier et al., 2008). This constraint could explain the lack of reproducibility in BMP kinetics and the kinetic discrepancy between anaerobic digestion experiments carried out with different reactor types (Batstone et al., 2009; Hafner et al., 2020; Jensen et al., 2011). In consequence, full-scale digesters sizing is typically based on heuristic values such as hydraulic retention time and organic loading rate. Therefore, it is necessary to continue developing mathematical strategies that allow improving the complex task of sizing biological reactors.

For the first time in the field of study, a model that considers the distribution of the first-order kinetic constant has been evaluated. This is

a new approach compared to conventional empirical and semi-empirical models where kinetic constants are invariant (e.g. first-order kinetics, Gompertz, Monod, Cone). The main advantage of the Gamma model is its capability to describe the distribution of the kinetic constant using a probability density function. Several phenomena could explain the distribution of the kinetic constant. For instance, it could be related to the heterogeneous composition of the substrate where each fraction is characterised by a different degradation kinetic constant. This distribution could also be related to organic particles with the same composition but with different geometries since the observed kinetic constant is affected by the bioavailable surface area (Aldin et al., 2011; Elmitwalli et al., 2001; Levenspiel, 1999). Changes in surface area do not affect the maximum methane yield but they change the methane production dynamics (Krause et al., 2018). Finally, the distribution of the kinetic constant could be related to changes in microbial structure and composition during the BMP test (Li et al., 2015; Vrieze et al., 2015; Zhang et al., 2009). Lv et al. (2020) showed the dynamic behaviour of the microbial communities during BMP tests. The impact of the microbial community in the Gamma distribution function can be observed by comparing the two independent BMP tests using cellulose since these tests were carried out with the same substrate but two different inocula. Both tests approximated a delta Dirac function, but the mean k was 0.36 and 0.27 d^{-1} for cellulose_1 and cellulose_2, respectively.

The Gamma model is a novel and complementary approach to describe and to understand the complex biochemical degradation dynamics taking place during anaerobic digestion. In co-digestion experiments, the distribution function allowed visualising how mixing substrates affects the degradation dynamics (Table 2 and Fig. 2). Similarly, the Gamma model could be used to analyse the impact of other strategies to improve anaerobic digesters performance, e.g. pretreatments, bioaugmentation, additives. Future research should investigate how to combine the Gamma model (and stochastic model) with the deterministic model ADM1, which is the most used model in application and research.

5. Conclusions

The Gamma model (a three parameters model) was able to describe the variability of the first-order kinetic constant of ten BMP tests, including mono-digestion and co-digestion experiments. This opposes conventional model approaches where the kinetic constant is considered invariant. The Gamma distribution function can approximate three distinct probability density functions, i.e. exponential, log-normal, and delta Dirac. Specifically, (i) cattle paunch, WAS_1, and pig manure approximated a log-normal distribution function; (ii) cattle manure, WAS_2, and microalgae approximated an exponential distribution function, and (iii) primary sludge and cellulose approximated a delta Dirac distribution function. In contrast to the common first-order kinetic model, the Gamma model could represent the tailing of the methane production curve frequently observed in BMP tests. The consistency of Gamma model was evident when analysing pig manure and microalgae co-digestion BMP tests since (i) the mean k for the co-digestion tests were within the values of the mono-digestion tests, and (ii) the profile of the density function transitioned from log-normal to exponential distribution as the percentage of microalgae in the mixture increased.

Authors contribution statement

Cristopher Da Silva: Conceptualization, Methodology, Formal analysis, Data curation, Writing - original draft, Visualisation. **Miriam Peces:** Investigation, Data curation, Writing -review & editing, Visualisation. **Martín Faúndez**: Methodology, Formal analysis, Writing - review & editing. **Henrik Hansen:** Conceptualization, Writing - review & editing. **José Luis Campos:** Conceptualization, Writing -review & editing, Funding adquisition. **Joan Dosta:** Writing - review & editing, Supervision, Funding adquisition. **Sergi Astals**: Conceptualization, Methodology, Investigation, Writing - review & editing, Supervision, Funding adquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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