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Kinetic prediction of biochemical methane potential of pig slurry

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Abstract

Empirical Kinetic Models have been used to describe and establish the Anaerobic Digestion kinetics of pig slurry's (8% TS) Biochemical Chemical Potential. A wide selection of Empirical Kinetic Models were fitted to the experimental data collected in batch assays of different Substrate to Inoculum ratios, 0.65 (BMP1) and 1 (BMP2). For the selection of the most suitable model for each BMP assay, the statistical tools R^2 and the RMSE, along with the Information Criterion AIC and BIC, were taken into consideration. From all the studied models, the Weibull model proved to be the most suitable for kinetic parameter prediction for both BMP1 and BMP2 assays. This model presented the lowest values of AIC and BIC, along with the highest value of R^2 and the lowest RMSE. In this regard, a R^2=0.998, and a RMSE=0.004, was obtained for BMP1, and a R^2=0.999 and a RMSE=0.008 for BMP2.

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Keywords: Anaerobic digestion; Biomethane potential test; Kinetic evaluation; Kinetic study; Numerical computation; Pig slurry

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1. Introduction

Anaerobic Digestion (AD) is a natural process that allows microorganisms to decompose organic matter in the absence of oxygen. This process can be divided into four stages, hydrolysis, where the long carbon chains are shortened; acidogenic when bacteria convert the sugars and amino acids into carbon dioxide, hydrogen and ammonia; acetogenesis, in which the short chains are converted into acetic acid; and methanogenesis, where the acetic acid is converted into methane [1]. To evaluate the biodegradability of a given substrate, the Biochemical Methane Potential (BMP) assay is widely employed. It is defined as a simple batch procedure that decomposes the substrate anaerobically. The biogas produced during the experimental period is measured and the methane content

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is evaluated [2]. This test can only provide the maximum production of a given substrate. However, using Empirical Kinetic Models (EKM), other parameters such as the adaptation time of the substrate or the rate that the substrate is converted into biogas can be predicted.

AD process, being a biological system, can be modeled as a cellular growth process. First, an adaptation period is required to allow microorganisms to acclimate to the substrate and flourish, designated as the Lag Phase period. The next phase, known as the growth phase, contemplates a rapid growth, where the methane production increases each day until reaching a stationary phase. The former phase will last until the organic matter in the substrate is depleted, leading then to a decrease in biogas production until, eventually, the production stops, corresponding to the so-called death phase. Hence, the Empirical Kinetic models for AD are based on microbial growth, including statistical distribution and enzymatic or chemical kinetics [1,3].

The Empirical Kinetic Models are in constant development and adjustment to promote an adaptation to a given operation or experimental data observation. For AD analysis, the curve of the methane accumulation over time obtained from the BMP is the crucial point for the kinetic evaluation. Once the BMP curve describes an exponential function, a mathematical equation is frequently used to describe the AD kinetics under different models such as the Exponential model, Transference or Transfer function of the First-Order kinetic [3]. For instance, the Gompertz model used to describe the human demography was modified to adjust to all phases of the AD process [1]. Some probability distributions, such as in the Weibull and Cauchy models, are also applied to describe the AD process, along with the Cone model that was primarily used to evaluate the gas production in ruminates digestive system [4].

This study presents an evaluation of the kinetic performance of AD for BMP assays of Pig Manure (PM) at 8% concentration (on a Total Solid (TS) basis), aiming for the determination of kinetic parameters for this substrate. The experimental BMP assay was performed in two tests at two different Substrate to Inoculum Ratios (SIR), 0.65 (BMP1), and 1.0 (BMP2).

2. Materials and methods

2.1. Experimental data collection

The experimental set of data was acquired from a BMP assay at Lab-scale. The BMP assay was conducted at mesophilic conditions (37 ± 1 °C and 1 atm), using pig slurry as substrate at 8% TS and inoculum from a municipal wastewater treatment station. The two Substrate to Inoculum Ratio (SIR) employed were 0.65 and 1.0 named as BMP1 and BMP2, respectively. The experimental data allowed for determining the experimental accumulated methane production as a function of time.

2.2. Kinetic models for data fit

The kinetic performance of the BMP was evaluated using the EKM presented in Table 1.

Where, $BMP(t)$ is the Cumulative methane yield (L CH_4/gVS), BMP_0 the Methane potential of the substrate (L CH_4/gVS), k is Methane production rate (1/d), t is the hydraulic retention time (d), R_{max} the maximum methane production rate (L CH_4/gVS .d), λ the lag phase (1/d), e is the Euler's number, μ_{max}. The maximum specific growth rate (1/d).

2.3. Model comparison and selection

The evaluation of the most suitable model requires not only an assessment of the coefficient of determination, denoted R^2 and the Root-Mean-Square Error (RMSE), but also the second-order Akaike Information Criterion (AIC) test [7], Eq. (1), along with the Bayesian Information Criterion (BIC) test, Eq. (2) [8]. The reason behind this assumption is based on the fact that a good R^2 fitting does not translate into a valid model. The determination of AIC and BIC between the models allows inferring if the estimation of a given error and thereby the relative quality of the statistical models are adequate for the data set [9]. Both R^2 and RMSE parameters were determined by nonlinear regression, applying the "fitnlm" function on MATLAB®.

$$AIC = \begin{cases} N \ln\left(\frac{RSS}{N}\right) + 2K, & when \frac{K}{N} \geq 40 \\ N \times \ln\left(\frac{RSS}{N}\right) + 2K + \frac{2K(K+1)}{N-K-1}, & when \frac{K}{N} < 40 \end{cases} \quad (1)$$

Table 1. Empirical-Kinetic models for Anaerobic Digestion tested in this work.

Model Name	Model Equation	Reference
First-order Kinetic	$BMP\left(t\right)=BMP_0\times\left[1-e^{-k\left(t-t_{lag}\right)}\right]$	[1,3,5,6]
Modified Gompertz	$BMP\left(t\right)=BMP_0\times e^{-e^{-\frac{e\times\mu_{max}}{BMP_0}\left(t_{lag}-t\right)+1}}$	[3–5]
Logistic	$BMP\left(t\right)=\frac{BMP_0}{1+e^{2-\frac{\mu_{max}}{BMP_0}\left(t-t_{lag}\right)}}$	[1,3,5,6]
Feller	$BMP\left(t\right)=\frac{2BMP_0}{\pi}\arctan\left(e^{k\left(t-t_{lag}\right)}\right)$	[1,3–5]
Cone	$BMP\left(t\right)=\frac{BMP_0}{1+\left(k\times\left(t\right)\right)^{-n}}$	[1,3,5,6]
Chen–Hashimoto	$BMP\left(t\right)=BMP_0\times\left(1-\frac{k_{CH}}{\mu_{max}\times\left(t-t_{lag}\right)+k_{CH}-1}\right)$	[2,3]
Weibull	$BMP\left(t\right)=BMP_0\times\left[1-e^{-\left(k\left(t-t_{lag}\right)\right)^{\gamma}}\right]$	[3,4]
France	$BMP\left(t\right)=BMP_0\times\left[1-e^{k_1\left(t_{lag}-t\right)+k_2\left(\sqrt{t_{lag}}-\sqrt{t}\right)}\right]$	[3,6]
Cauchy	$BMP\left(t\right)=\frac{2BMP_0}{\pi}\arctan\left(k\left(t-t_{lag}\right)\right)$	[3,4]

$$BIC=N\times\ln\left(\frac{RSS}{N}\right)+K\ln\left(N\right) \tag{2}$$

Where the RSS is the Residual Sum of Squares, N is the number of data points and K is the number of parameters estimated by the model.

3. Results and discussion

3.1. Model fitting

Using the "fitnlm" function of MATLAB®, it is possible to obtain the estimated parameter for every model along with the statistical tool to evaluate the model when adjusted to the experimental data. Fig. 1 represents the fitting of all models for BMP1, likewise, the fitting of allmodels for BMP2 is presented in Fig. 2.

The graphic representation allows to conclude that most models attain a good fitting with the data. In the exponential zone Logistic, Cone, France, and Cauchy models presented a better fitting. Still, only France and Weibull models follow the experimental data behavior when the stationary region is achieved. To better understand the model fitting, Table 2 presents the predicted parameters by each model and the statistical tools, R^2 and RMSE.

Table 2. Predicted parameters for each model and statistical tools obtained for BMP1.

Model	First-Order	Gompertz	Logistic	Feller	Cone	Chen and Hashimoto	Weibull	France	Cauchy
BMP_0 *(LCH₄/gVS)*	0.381	0.375	0.373	0.374	0.397	0.454	0.374	0.378	0.419
μ_{max} *(LCH₄/gVS.d)*	N.A.	0.060	0.052	N.A.	N.A.	−1.11E+09	N.A.	N.A.	N.A.
T_{lag} *(d)*	N.A.	−0.538	−0.875	2.698	N.A.	N.A.	−0.696	0.028	0.285
K (1/d)	0.286	N.A.	N.A.	0.457	0.389	N.A.	0.236	0.348	0.414
K_{CH}	N.A.	N.A.	N.A.	N.A.	N.A.	−3.33E+09	N.A.	N.A.	N.A.
R^2	0.993	0.997	0.994	0.994	0.988	0.956	0.998	0.996	0.984
RMSE	0.007	0.005	0.008	0.006	0.010	0.017	0.004	0.006	0.011
Diff (%)	2.40	0.737	0.191	0.538	6.66	21.9	0.538	1.61	12.6

From Table 2, the Weibull model adjusted better to the data, since it presented the lowest value of RMSE and the highest value of R^2, which can be translated into a lower deviation between the predicted values and the experimental data. It is also represented the difference between the experimental value of BMP_0 and the one predicted by each model, divided by the experimental value of BMP_0 (Diff %). Additionally, it is possible to notice that only Chen and Hashimoto, and Cauchy models presented a deviation higher than 10%. For this reason, those were not considered as valid kinetic models for BMP1 [10].

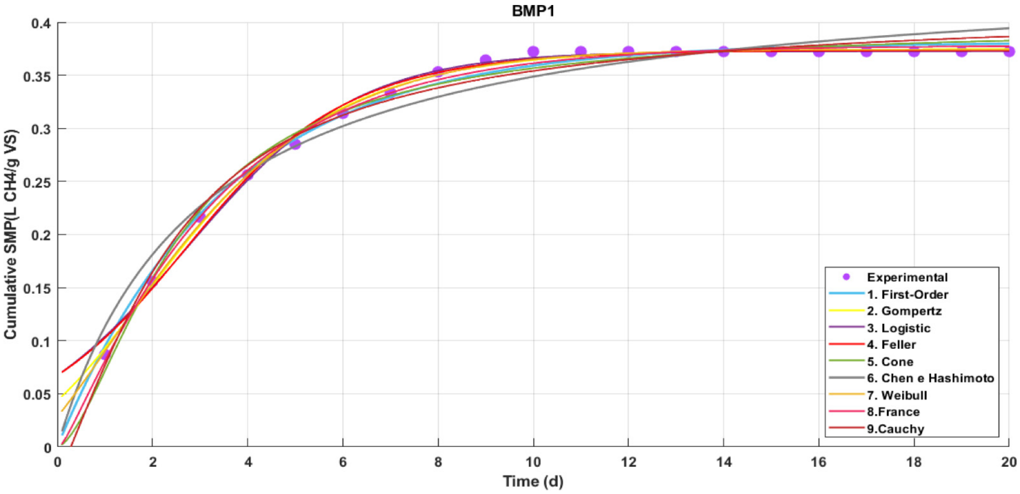

Fig. 1. Models fitting for BMP1.

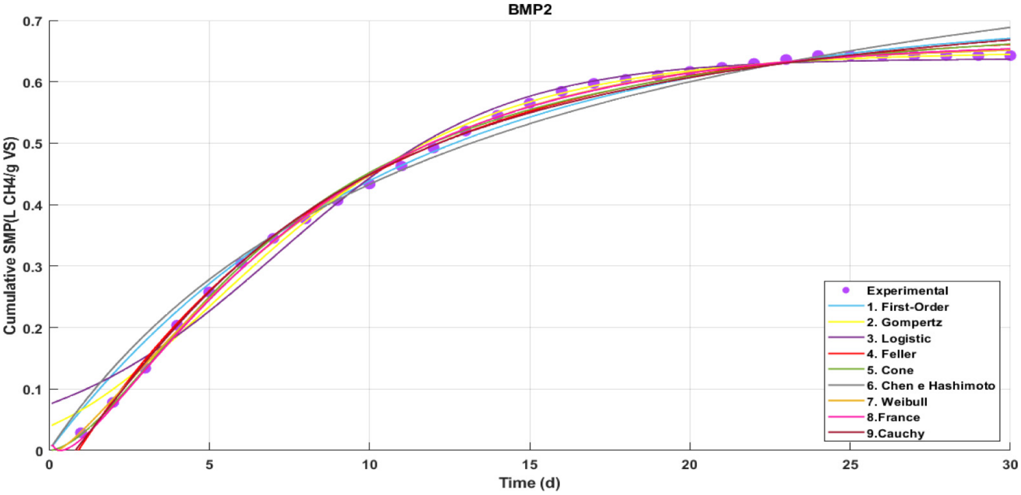

Fig. 2. Model fitting for BMP_2.

Once the stationary phase is achieved, only the France model kept adjusting to the data. Contrary to what was observed in the BMP1, the Logistic and the Gompertz models also fitted the stationary phase. Table 3 describes the predicted parameters by each model and the corresponding statistical coefficients, R^2 and RMSE.

This second experiment, carried out under a higher Substrate to Inoculum Ratio, confirmed that the Weibull model was the model that better fits the experimental data since it presents the highest determination coefficient, R^2 (0.999), and the lowest RMSE of all tested models. Similar to the behavior detected in BMP1, in Table 3, can be observed that Gompertz, Logistic, Feller, Weibull, and France models were considered valid for this assay, because First-order, Cone Chen, and Hashimoto, and Cauchy presented once more a deviation higher than 10%.

When comparing the experimental BMP_0 (0.643 L CH4/g VS) with the predicted one, both Gompertz and Logistic models predicted the BMP_0 with the same deviation (0.937%). However, Gompertz achieved the closest BMP_0 to the experimental value with the highest R^2.

Velázquez-Martí et al. [1] employed Gompertz, first-order kinetic, transference, and Cone models to evaluate the kinetic models to be used in AD under mesophilic conditions. The authors found that all provided high R^2, but presented significant differences in the RMSE. Regarding their studies, the transfer model and the first-order kinetic model generally produce higher RMSE, so the modified Gompertz model and the Cone model make more accurate

Table 3. Predicted parameters for each model and statistical tools obtained for BMP2.

Model	First-Order	Gompertz	Logistic	Feller	Cone	Chen and Hashimoto	Weibull	France	Cauchy
BMP_0 *(LCH_4/gVS)*	0.710	0.649	0.637	0.683	0.727	0.977	0.658	0.665	0.795
μ_{max} *($LCH_4/gVS.d$)*	N.A.	0.048	0.045	0.079	N.A.	−1.68E+06	N.A.	N.A.	N.A.
T_{lag} *(d)*	N.A.	0.165	0.048	0.918	N.A.	N.A.	0.269	0.361	0.823
K *(1/d)*	0.096	N.A.	N.A.	N.A.	0.135	N.A.	0.114	0.171	0.133
K_{CH}	N.A.	N.A.	N.A.	N.A.	N.A.	−1.34E+05	N.A.	N.A.	N.A.
R^2	0.989	0.996	0.988	0.997	0.997	0.978	0.999	0.998	0.995
RMSE	0.020	0.013	0.021	0.012	0.011	0.028	0.008	0.009	0.013
Diff (%)	10.4	0.933	0.933	6.22	13.1	51.9	2.33	3.42	23.6

estimations. In this study, the previous was not verified, with the R^2 value being conformable with the RMSE. This means that to the highest R^2 corresponds the lowest RMSE achieved. The former occurs due to the limitations of the EKM, which are only valid under specific operational conditions [11]. For the same substrate, as soon as the SIR is changed, the previous valid model might not be applied in the new SIR. The same occurs when the reactor configuration is different, with the kinetic parameters changing as well.

3.2. Model selection

Table 4 presents the criteria analysis for BMP1 and BMP2, allowing for the selection of the most suitable model.

Table 4. Criteria analysis of the best fit for BMP1 and BMP2.

	Model	RSS	AIC	Δ AIC	Akaike weight	BIC	Δ BIC
BMP_1	First-Order	0.000959	−137.44	−20.09	2.40E+07	−136.15	−20.06
	Gompertz	0.000369	−153.74	−3.79	1.80E+04	−152.25	−3.96
	Logistic	0.000777	−138.86	−18.67	1.46E+07	−137.37	−18.84
	Feller	0.000740	−139.84	−17.70	9.40E+06	−138.35	−17.87
	Cone	0.001572	−124.77	−32.76	8.28E+09	−123.28	−32.94
	Chen e Hashimoto	0.005336	−100.32	−57.21	4.96E+14	−98.84	−57.38
	Weibull	0.000261	−157.53	0.00	3.84E+03	−156.21	0.000
	France	0.000542	−142.90	−14.64	2.78E+06	−141.58	−14.64
	Cauchy	0.002124	−118.74	−38.79	1.25E+11	−117.26	−38.96
BMP_2	First-Order	0.011569	−146.24	−56.19	1.37E+14	−143.88	−54.54
	Gompertz	0.004557	−171.71	−30.72	1.03E+09	−168.43	−29.99
	Logistic	0.012372	−141.75	−60.68	1.21E+15	−138.46	−59.96
	Feller	0.003358	−180.87	−21.55	1.43E+07	−177.59	−20.83
	Cone	0.003216	−182.17	−20.25	7.78E+06	−178.89	−19.53
	Chen e Hashimoto	0.022453	−123.87	−78.56	5.10E+18	−120.59	−77.83
	Weibull	0.001497	−202.42	0.00	6.68E+02	−198.42	0.000
	France	0.002069	−192.72	−9.70	6.18E+04	−188.72	−9.70
	Cauchy	0.004628	−171.24	−31.18	1.27E+09	−167.96	−30.46

As reported in Pererva et al. [3], understanding the information criteria allows avoiding overfitting. The authors performed a critical review of various BMP tests of various publications. The main conclusion is that a general model cannot be established, with each model being unique for each situation. Therefore, there is no mathematical model capable of describing the biomethane formation kinetics precisely.

To select the best model, the lower value of the AIC and BIC must be considered. The Weibull model presents the lowest AIC and BIC values for both essays, providing the perspective that this model produced the best fit. Regarding BMP2, the Weibull model showed the lowest AIC and BIC. Consequently, it is the best model to fit the BMP2 data. Thus, the criteria validated the efficiency of the statistical tool R^2 as a good indicator of the model fitting.

4. Conclusion

A kinetic performance of a BMP assay for Pig Slurry was studied using two different Substrate to Inoculum Ratios (0.65 and 1). In this study, a wide variety of Empirical Kinetic Models (EKM) are tested, such as the ones based on microbial growth, enzymatic or chemical kinetic and statistical distribution.

The Empirical Kinetic Models proved to be very useful tools to predict the kinetic parameters of a specific growth profile in biological systems. The low deviations obtained between the theoretical and experimental values (nearly equal to or lower than 10%) were achieved for the First-Order, Modified Gompertz, Logistic, Feller, Cone, Weibull, and France models in the BMP1 test. For the BMP2, low deviations were observed in the Modified Gompertz, Logistic, Feller, Weibull, and France models. Statistical tools, such as the R^2 and the RMSE, along with the Information Criteria AIC and BIC are employed to select the most suitable model for each BMP assay.

The Weibull model is shown to be the most suitable model to predict the kinetic parameters for both essays, presenting the lowest AIC and BIC values. Regarding the statistical tools, this model in the BMP1 presented the highest value of R^2 (0.998) and the lowest RMSE (0.004). It was estimated a methane production rate of 0.088 L CH_4/ g VS.d. Likewise, in the BMP2, this model was the one reaching the highest value of R^2 (0.999) and the lowest RMSE (0.008), with an estimated $\mu_{\max}$ of 0.075 LCH_4/gVS.d.

CRediT authorship contribution statement

Andreia D. Santos: Investigation, Data curation, Conceptualization, Formal analysis, Validation, Writing - original draft. **João R. Silva:** Data curation, Writing – review & editing. **Luis M. Castro:** Conceptualization, Supervision, Validation, Writing – review & editing. **Rosa M. Quinta-Ferreira:** Conceptualization, Supervision, Writing – review & editing, Project administration, Funding acquisition.

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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