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Analogous study of biogas production by anaerobic digestion of sewage treatment plant sludge, proposal of universal dimensionless models

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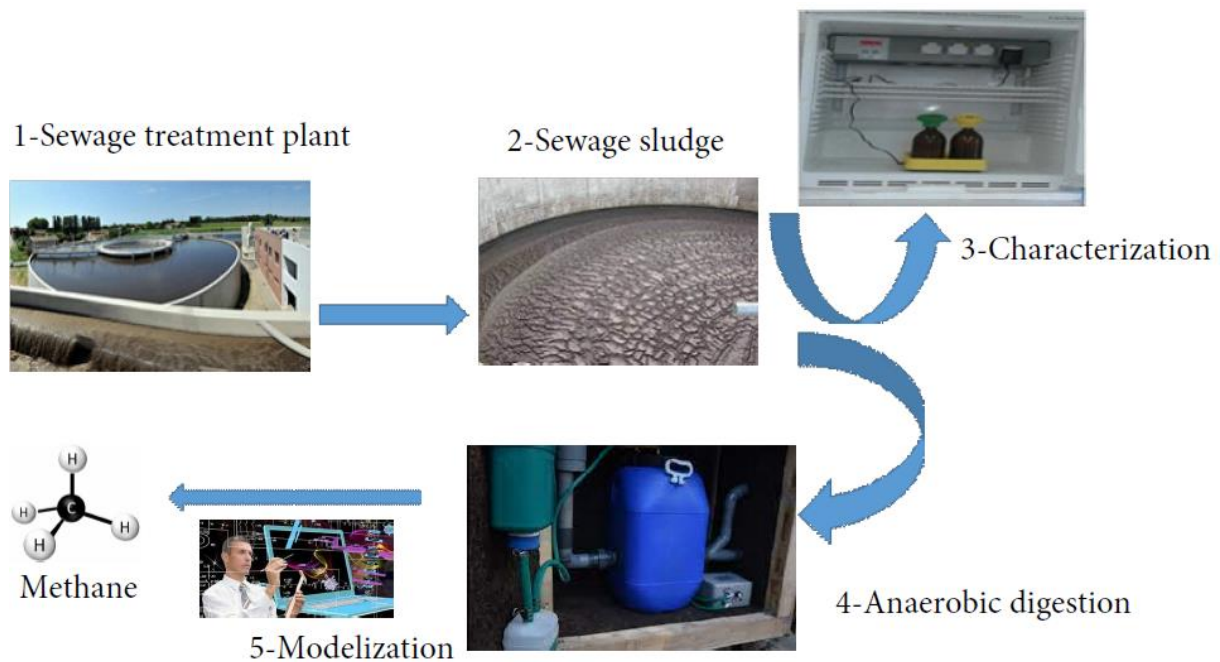
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Abstract

In this study, a characterization protocol of sewage sludge in Algeria was carried out. Their objective was to study the process of anaerobic digestion for the production of biogas by analogy to experiments which have already been made in the literature on sludge have the same characteristic as our own product. Five models have been proposed to simulate the anaerobic digestion process; three for the production of biogas and two models for the degradation of organic matter. The performance of the proposed models have been validated with experimental data from the literature.

The modeling of the volume of biogas produced was carried out by that of Gompertz and models proposed for different products. We observed a good agreement of the models proposed with the experimental data with a maximum value in $r^2 = 0.9996$ and minimum in $ESM = 6.34 \cdot 10^{-4}$. The modeling of the degradation of organic matter was carried out by the first order model (eq IV.19), and dimensionless models proposed. The latter gave a good agreement with the experimental data better than the model of the literature with a maximum value in $r^2 = 0.9985$ and minimum in $ESM = 8.91 \cdot 10^{-4}$.

Graphical Abstract



Statement of Novelty

This manuscript aims to:

- A characterization protocol for sewage sludge in Algeria was carried out
- Study on the anaerobic digestion process for biogas production has been made
- The volume of biogas produced was modeled by that of Gompertz and the models proposed
- Degradation of organic matter was made by the first order model, and models proposed
- Proposed models give better smoothing curves compared to those in the literature

Keywords: Anaerobic co-digestion, Biogas, Dimensionless models, Organic matter, Sewage sludge.

Nomenclature

r^2 : coefficient of determination

RMSE: root mean square error

T: air temperature ($^{\circ}\text{C}$)

WS: wastewater sludge

χ^2 : reduced chi-square

COD : chemical oxygen demand

BOD : biochemical oxygen demand

X_B : cumulative production of biogas (mL) as a function of time t (h)

$X_{B,r}$: cumulative production of biogas

t_L : latency time (h)

X_P : ultimate potential of biogas (mL)

R_{max} : peak biogas production rate (mL h^{-1})

Y_t : organic matter content at time t

1. Introduction

Increasing concern of safe disposal of different wastes generated in the society necessitates the scientific community to collect and treat the wastes effectively. Significant developments have taken place in treating the wastewaters during the last two decades. This has resulted in increasing sludge production, which is consuming 50% of the current operating costs of wastewater treatment plants (**Wim 2008**). Sludge is a by product obtained from different unit operations of wastewater treatment plants during different physical, chemical and biological processes which includes clarifier, biological reactor, centrifuge, etc (**Venkateswara Rao and Baral 2011**). The problem of disposal of sludge from sewage treatment plants is more delicate given the increased production of wastewater and regulations that is becoming more demanding (**Ameri et al. 2018**). The use of sewage sludge in agriculture has been widely practiced in most developed countries (**Laube and Vonplon 2004**). Sludge processing pathways have always had goals; reduction of volume and fermentability, namely their stabilization (**Bennouna and Kehal 2001**). Different strategies for the treatment and final disposal are possible but the general opinion is that sewage sludge is a valuable source of energy and materials (**Đurđević et al. 2019**). Sewage sludge treatment has relied on three main processes: dewatering and drying, stabilisation by anaerobic digestion and thermal treatment (**Mills et al. 2014**). Anaerobic digestion is the preferred stabilisation method as it produces biogas, a valuable energy source (**Đurđević et al. 2018**).

Biogas production is influenced by the amount of added organic material, the pH of the digester, any toxic substances, and the anaerobic condition C/N ratio. Additionally, biogas production is affected by the proximate composition and characteristics of the initial organic material, which have significant effects on the decomposition efficiency of the anaerobic organic material and methane production (**Chynoweth et al. 1993; Walker et al. 2009**). **Min-Jee et al. (2017)** studied effect of proximate composition ratios for biogas production. Have found that, biogas production can be improved by mixing of agricultural by-products that have a low biogas production rate to achieve the same proximate composition as an agricultural by-product that has a high biogas production rate. **Laskri et al. (2015)** found that, the volume of biogas produced during the digestion of sludge of waste water (5 000 mL)) is greater than 10 times compared with the digestion of organic matter in the landfill waste (500 mL) in the time of digestion 30 days. A large part of works deals with the effect of sludge thermal treatments on biogas production enhancement during anaerobic digestion (**Haug et al.1978; Tanaka et al. 1997; Valo et al. 2004; Bougrier et al. 2006**). On the other hand, **Pérez Garcia et al. (1986)** studied the agronomic value of sewage sludge from Tenerife. Influence of drying methods on thermodynamic parameters and Comparative approach to the performance of sludge drying were studied by **Ameri et al. (2018)** and **Ameri et al. (2020)**.

Numerous works have studied the production of biogas from sewage treatment plant sludge by anaerobic digestion, but few studies which have addressed the simulation of this process. Anaerobic digestion and biogas potential: simulations of industrial and laboratory processes have been studied by **Hamawand and Baillie (2015)**. The simulation showed the ability to overcome the uncertainty and discrepancy of measured biogas from an industrial digester. In the case of the lagoon digester, it was shown that the discrepancy in the measured biogas is around 250%. The measured biogas was higher by 2.5-fold than that predicted by simulation. Successful simulation studies were carried out on the anaerobic co-digestion process to find the optimal ratios of substrates in the suspension introduced into the digester by **Inayat and al. (2019)**. The optimal substrate composition found is 50% wastewater, 25% livestock manure and 25% biomass. The development of a process modeling simulation by aspen plus for the anaerobic digestion process was investigated by **Al-Rubaye et al. (2018)**. The AD model developed at Aspen aims to find the optimum temperature, reactor size and substrate flow rate to achieve an optimum process. The percentage of methane gas has dropped from about 70% to about 90% (**Al-**

Rubaye ans al. 2017). Concerning biogas from anaerobic co-digestion of food waste and primary sludge. The system efficiency using the heat generated increase to 75.25 % and 78.43% for thermophilic and mesophilic conditions respectively. However, despite the biogas production is higher at thermophilic conditions ($137.4 \text{ m}^3 \text{ hr}^{-1}$) compared to mesophilic scenario ($67.74 \text{ m}^3 \text{ hr}^{-1}$) (**Calispa Aguilar et al. 2017**).

The main objective of this study was to characterize the sludge and on this characterization we take the results of biogas production from a similar sludge to our own product for the validation of five new universal and dimensionless models with the experimental production data. of biogas and the degradation of organic matter. The five new universal and dimensionless models were evaluated and compared to different models from the literature to select the model that best suits the experimental data of biogas production and organic matter degradation. The latter was evaluated with other methane and hydrogen production data from the literature.

2. Materials and methods

2.1. Methanization

Methanization or anaerobic digestion is the decomposition of organic material by microorganisms in the absence of oxygen, which is to say in anaerobic. This is a process that involves several bacterial species that simultaneously transform organic waste into biogas (Fig. 1). Anaerobic fermentation can take place in three temperature ranges: Psychrophiles: 15 to 25 °C, Mesophiles: 25 to 45 °C, Themophiles: 55 to 65 °C (**Umotte and Leduc 1981**).

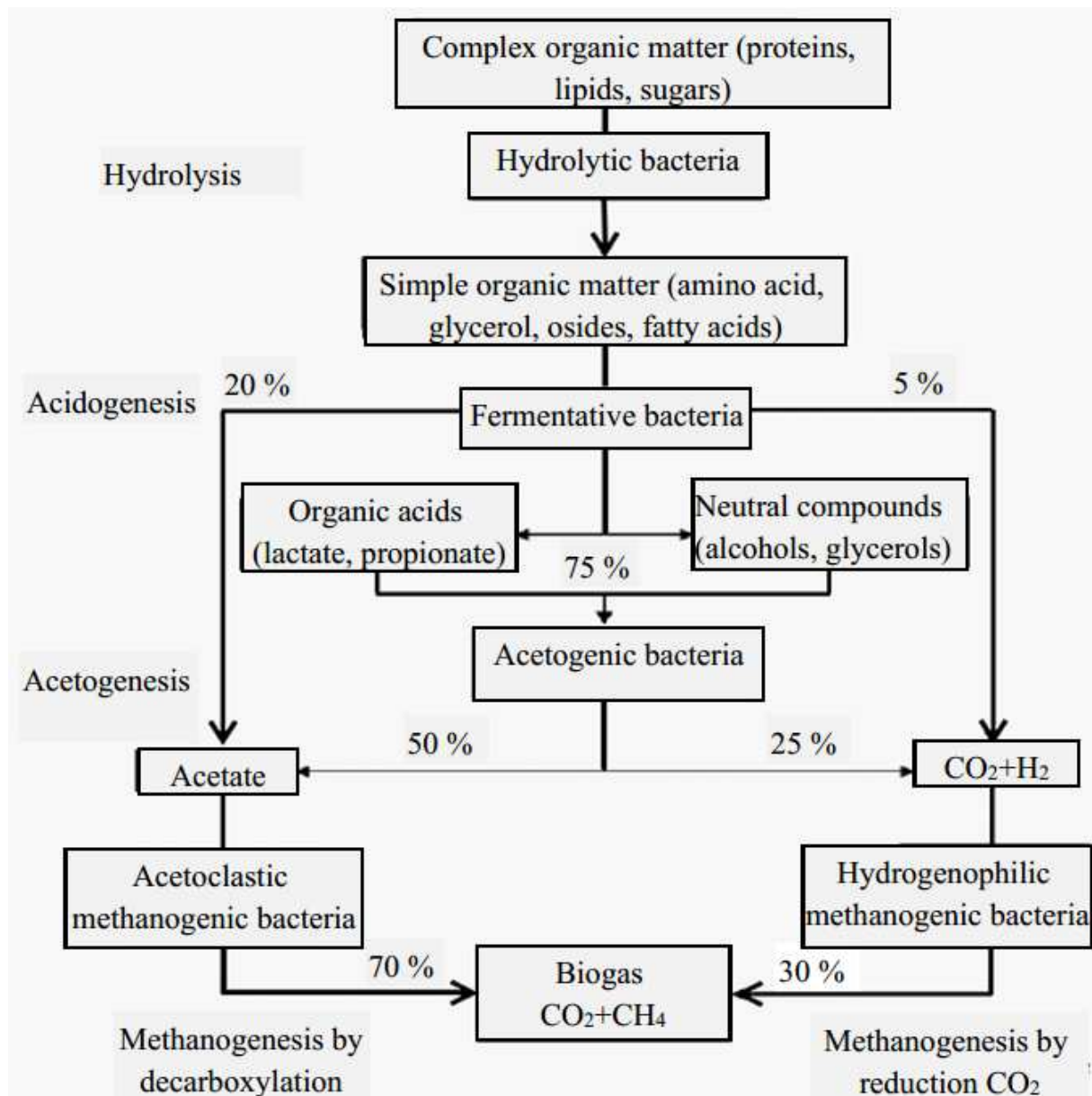


Fig. 1. Main phases of the anaerobic digestion process (Ladjel and Abbou 2016)

The result of anaerobic digestion includes both biogas and digestate, the latter requires solar drying for its stabilization as what **billal et al. (2018)** did on mud, **Djebli et al. (2020)** on potatoes, **Badaoui et al. (2019)** on tomato waste, vacuum drying as **Keskes et al. (2020)** did on pharmaceutical powders.

The composition of the biogas is shown in Table 1 below

Table 1. Composition of biogas (Lagrange 1979)

Component	Percentage of content (%)
Methane	40-80
Carbon dioxide	20-55
Water vapour	0-10
Nitrogen	0-5
Oxygen	0-2
Hydrogen	0-1
Ammonia	0-1
Hydrogen sulfide	0-1

2.2. Anaerobic digestion of waste from a wastewater treatment plant

To study this step, we took the results obtained on a sample of sludge taken from the treatment plant by lagoon to carry out an anaerobic digestion of this type of waste. This sample is placed in the digester with a dilution rate: 80%. Tables (2 and 3) give the physicochemical characteristics of our sludge and the sludge which has undergone anaerobic digestion respectively.

The factors that influence the production of biogas are mainly based on the operating conditions as well as the type of feed to the digester. Operating conditions such as pH and temperature directly influence microorganisms. The composition and the concentration of sludge are also important, without forgetting the toxic compounds and the inhibitors of the methanogenic phase. Sometimes the toxic compounds are not initially present in the feed, but they are produced inside the reactor from the degradation of the substrate (for example VFAs (volatile fatty acids) and ammonia.

Table 2. Average composition of sludge (ONA Boumerdes)

Characteristic	Concentration
Total dry matter (%)	10-16
Volatile matter (%)	50-70
Nitrogen (N, %)	1.25-4.8
Phosphorus (P, %)	0.16-7

COD (mg L ⁻¹)	500-1000
BOD (mg L ⁻¹)	160-500

Table 3. Average composition of sludge (**Laskri 2016**)

Characteristic	Concentration
Total dry matter (%)	5-18
Volatile matter (%)	60-80
Nitrogen (N, %)	1-4
Phosphorus (P, %)	0.1-1.2
COD (mg L ⁻¹)	500-1500
BOD (mg L ⁻¹)	160-750

Due to the impossibility of carrying out an experimental study on methanization. We have taken the results of a study conducted on a sludge with the same characteristics as our own product, as they show in Tables (2 and 3). Based on this analysis, we notice that there is a great convergence of results; this indicates that our sludge will produce a quantity of gas close to the results of Table 4.

Table 4. Anaerobic digestion of WWTP sludge (**Laskri 2015**)

Residence time (d)	Nature of gas formed	T (°C)	pH	COD (mg L ⁻¹)	V of biogas (mL)
0	-	36	7.17	760	0
1	Flammable	36	6.99	540.45	500
2		-	6.75	356	840
5		-	6.68	350	1225
6		-	6.70	331.45	1567
7		-	6.74	244	2069
8		-	6.91	220	2457
16		-	7.12	168	3560
19		33	7.11	154	3890
23		36	7.18	133	4050
25		-	7.25	119.34	4568

Tables (2 and 3) show that the two substrates are rich in organic matter and therefore they could easily promote anaerobic digestion. The results are given in Table 4.

The biodegradability of the sludge from the wastewater made it possible to recover flammable biogas after 24 hours of digestion and the production of the biogas reached almost 5 liters for an initial concentration of 70 g L⁻¹. The reduction in COD is very significant and the purification efficiency reaches 80% (Fig. 2).

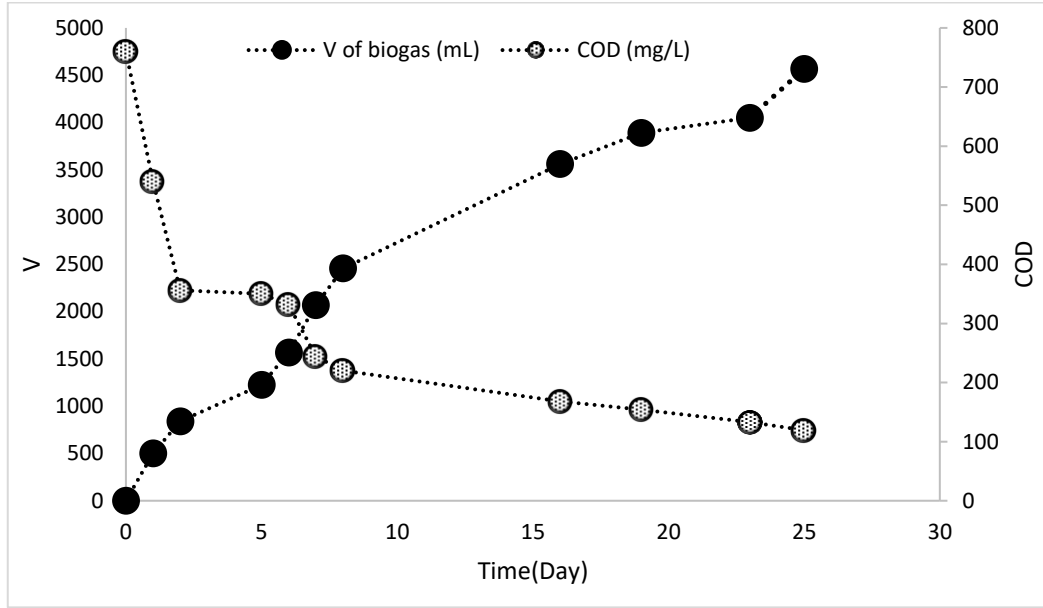


Figure. 2. Temporal evolution of volume of biogas produced and COD from anaerobic digestion of residual sludge

3. Modeling of results

3.1. Modeling of cumulative biogas production

The biogas production curves were modeled using the modified Gompertz equation (Lay et al. 1999). This equation (IV.1) was used to analyze the cumulative production of biogas.

$$X_B(t) = X_P \cdot \exp \left\{ -\exp \left[-\frac{R_{\max} \cdot e}{X_P} (t - t_L) + 1 \right] \right\} \quad (\text{IV.1})$$

$X_B(t)$ represents the cumulative production of biogas (mL) as a function of time t (h);

t_L latency time (h) ;

X_P , the ultimate potential of biogas (mL);

$R_{\max}$, the maximum speed of biogas production (mL h⁻¹).

Roeland (2017) cited in his article a set of Gompertz models in Growth Analyzes and New Approach Gompertz Model: An Addition to the Unified Richards Family. Some of the parameterizations of the Gompertz model found in the literature are more useful than others, because they have parameters that are easy to interpret. A valuable and commonly found re-setting is:

$$X_B(t) = A \exp(-\exp(-K_G(t - t_i))) \quad (IV.2)$$

Such that: K_G is a growth rate coefficient (which affects the slope), and t_i represents the inflection time.

In growth curve analyzes of bacterial (or microbial) counts, in particular the adaptation of a four-parameter Gompertz model, as suggested by **Gibson et al. (1987)**, the model becomes:

$$X_B(t) = B + A \exp(-\exp(-K_G(t - t_i))) \quad (IV.3)$$

- The modification of Zwietering

The reparameterization proposed by **Zwietering et al. (1990)** is often referred to as a "modified Gompertz" is generally applied to bacterial growth data, particularly in food. It can be given as:

$$X_B(t) = A \exp\left(-\exp\left(\frac{e K_Z}{A}(t_{lag} - t) + 1\right)\right) \quad (IV.4)$$

Where K_Z is the absolute growth rate (i.e. tangent to the curve) at T_{Lag} time, called the "lag time".

- The re-setting of Zweifel and Lasker

The parameterization of **Zweifel and Lasker (1976)** was copied by **Ricker (1979)** in his book and found its place in the study of fish growth. Today, we often talk about the Ricker model. This model is mainly used for the growth of fish, but it is also fitted to the growth data of other animals, for example crustaceans. It can be expressed as:

$$X_B(t) = W_0 \exp(m(1 - \exp(-K_G t))) \quad (IV.5)$$

Where k_G is the value of the growth coefficient, W_0 is specified as the initial value (number, density, mass, length, etc.). It gives the starting point of the growth curve.

- The Gompertz-Laird

Another very common type II parameterization is the version of the Gompertz model originally proposed by **Laird (1964)** to describe the growth in tumor size, but it is often adapted to the growth in number (populations) of cells and microbes. With **Aggrey's (2002)** notation (often encountered in growth studies in domestic animals), the Gompertz-Laird model becomes:

$$X_B(t) = W_0 \exp\left(\left(\frac{L}{K}\right) (1 - \exp(-kt))\right) \quad (IV.6)$$

We can consider this model as a variant of the model (eq.IV.5) (or vice versa), but in reality their parameters behave very differently. The W_0 parameter is comparable to that of the model (eq.IV.5), but the other parameters are not. Interpretations of the K and L parameters vary in the literature and are often ambiguous or poorly explained.

- W_0 -simpler shapes

Another re-parameterization is that suggested by **Norton (1988)**. It is sometimes mistakenly considered a Gompertz-Laird model and looks like this:

$$X_B(t) = W_0 \exp\left(\ln\left(\frac{A}{W_0}\right) (1 - \exp(-K_G t))\right) \quad (IV.7)$$

This model has very different parameters than Laird's. It has the same growth rate coefficient and the same parameter for the initial value (or starting point) as the model (IV.5).

- Absolute growth rate

Previous authors have also noted, more or less explicitly, that it is possible to re-parameterize the Gompertz model so that the growth parameter returns a relative or absolute growth rate.

$$X_B(t) = A \exp\left(-\exp\left(-\frac{e K_U (t-t_i)}{A}\right)\right) \quad (IV.8)$$

- The Unified Gompertz

The traditional three-parameter Gompertz model, as in the version shown in Eq (IV.1), is a special case of the four-parameter Richards model, for example:

$$X_B(t) = A \left(1 - \left(\frac{1}{d}\right) \exp(-K_R(t - t_i))\right)^d \quad (IV.9)$$

Where k_R is the growth constant specific to the model controlling the maximum growth rate and the parameter determining the inflection value. This model (Eq.IV.9) presents the same problem as the traditional Gompertz models. Namely, the growth parameter (k_G) is not comparable to the growth coefficients of versions of other traditional models. In addition, these growth parameters (or growth coefficients) are more difficult to interpret because they do not constitute the absolute or relative growth rate. Therefore, we recommended two forms of the Richards model, which we called the Unified-Richards (or U-Richards). The first of them, the t_i shape of U-Richards (**Sugden et al. 1981**), is given by:

$$X_B(t) = A \left(1 + (d - 1) \exp \left(\frac{-k_U(t-t_i)}{d^{1-d}} \right) \right)^{\frac{1}{1-d}} \quad (IV.10)$$

Where d is the fourth parameter (shift of the inflection value). The second, the W_0 form of U-Richards (**Tjørve and Tjørve 2010**) then becomes:

$$X_B(t) = A \left(1 + \left(\left(\frac{W_0}{A} \right)^{1-d} - 1 \right) \exp \left(\frac{-k_U t}{d^{1-d}} \right) \right)^{\frac{1}{1-d}} \quad (IV.11)$$

We find two general expressions that group together almost all models in the literature:

The first (concerns the equations from Eq.IV.1 to Eq.IV.8) is made up of two exponential contributions grouping nine parameters (Eq IV.12).

$$X_B(t) = E + A \exp\{B + (C - 1)\exp - [K(t - t_i) + D]^\alpha\}^F \quad (IV.12)$$

The second expression (concerns the equations from Eq.IV.9 to Eq.IV.11) is made up of a single exponential contribution grouping nine parameters (Eq IV.13):

$$X_B(t) = A \left\{ B + (C - 1)\exp - \left[\frac{K}{E}(t - t_i) + D \right]^\alpha \right\}^F \quad (IV.13)$$

The parametric matrix of the two models (Eqs. IV.12 and IV.13) is given in Table 5.

Table 5. Parametric matrix of the two models

Model	Model parameters									Number of parameters
	A	B	C	D	E	F	K	α	t_i	
Eq.IV.1	X_P	0	0	1	0	1	$(eR_m)/X_P$	1	t_i	3
Eq.IV.2	A	0	0	0	0	1	K_G	1	t_i	3
Eq.IV.3	A	0	0	0	B	1	K_G	1	t_i	4
Eq.IV.4	A	0	0	1	0	1	$(eK_Z)/A$	1	t_i	3
Eq.IV.5	W_0	m	1-m	0	0	1	K_G	1	0	4
Eq.IV.6	W_0	L/K	$1-L/K$	0	0	1	K	1	0	4
Eq.IV.7	W_0	$\ln(A/W_0)$	$1-\ln(A/W_0)$	0	0	1	K_G	1	0	4
Eq.IV.8	W_0	0	0	0	0	1	eK_u/A	1	t_i	3
Eq.IV.9	A	1	$1-1/d$	0	1	d	K_R	1	t_i	5
Eq.IV.10	A	1	d	0	$d^{\frac{d}{1-d}}$	$\frac{1}{1-d}$	K_U	1	t_i	6
Eq.IV.11	A	1	$\left(\frac{W_0}{A}\right)^{1-d}$	0	$d^{\frac{d}{1-d}}$	$\frac{1}{1-d}$	K_U	1	0	5

To avoid the dimensional problem of the variables of the equations, we follow the following steps:

$$X_{B,r} = \frac{X_B}{X_{B,max}}, X_{P,r} = \frac{X_P}{X_{B,max}}, K = k \cdot t_{\infty} = \frac{R_{max} \cdot t_{\infty} \cdot e}{X_P} \text{ et } \tau = \frac{t}{t_{\infty}} \text{ soit: } \frac{t}{t_{\infty}} - \frac{t_i}{t_{\infty}} = \tau - \tau_L$$

Equation IV.1 becomes:

$$X_{B,r}(t) = X_{P,r} \cdot \exp\{-\exp[-K \cdot (\tau - \tau_L) + 1]\} \quad (IV.14)$$

Knowing that: $X_{B,r}$; $X_{P,r}$; K ; τ are dimensionless

In the same way, one does with the other equations and the results of modeling for the eleven equations according to the two dimensionless general models proposed are cited in Table 6.

Table. 6. Kinetic parameters of the proposed models and the models in the literature by analogy

Models	Parameters	r^2	RMSE
$X_{B,r}(t) = A \exp\{-\exp[-K(\tau - \tau_L) + 1]\}$	$A = 0.967, K = 4.323$ $\tau_L = 1.02 \cdot 10^{-3}$	0.9844	$1.84 \cdot 10^{-2}$
$X_{B,r}(t) = A \exp(-\exp(-K(\tau - \tau_L)))$	$A = 0.968, K = 4.320$ $\tau_L = 0.232$	0.9844	$1.84 \cdot 10^{-2}$
$X_{B,r}(t) = B + A \exp(-\exp(-K(\tau - \tau_L)))$	$A = 2.324 ; B = -1.187$ $K = 2.1263, \tau_L = -0.199$	0.9880	$1.41 \cdot 10^{-2}$
$X_{B,r}(t) = A \exp(-\exp(K(\tau_L - \tau) + 1))$	$A = 0.967, K = 4.322$ $\tau_L = 9.932 \cdot 10^{-3}$	0.9844	$1.84 \cdot 10^{-2}$
$X_{B,r}(t) = A \exp((B - (1 - C) \exp(-K\tau)))$	$A = 0.554, B = 0.557$ $C = -1.73, K = 4.323$	0.9844	$1.84 \cdot 10^{-2}$
$X_{B,r}(t) = A \exp((B - (1 - C) \exp(-K\tau)))$	$A = 0.554, B = 0.557$ $C = -1.73, K = 4.323$	0.9844	$1.84 \cdot 10^{-2}$

$X_{B,r}(t) = A \exp((B - (1 - C) \exp(-K\tau)))$	A= 0.554, B= 0.557 C= -1.73, K= 4.323	0.9844	1.84 10 ⁻²
$X_{B,r}(t) = A \exp(-\exp(-K(\tau - \tau_L)))$	A=0.968, K=4.320 $\tau_L=0.232$	0.9844	1.84 10 ⁻²
$X_{B,r}(t) = A (1 - (1 - C) \exp(-K(\tau - \tau_L)))^F$	A= 1.226, C= 0.199 K= 1.565, $\tau_L=0.130$ F= 1.033	0.9879	1.42 10 ⁻²
$X_{B,r}(t) = A \left(1 + (C - 1) \exp\left(\frac{-K(\tau - \tau_L)}{E}\right) \right)^F$	A= 1.505, C= 0.513 K= 0.858, $\tau_L= 0.789$ E= 0.943, F= 0.838	0.9875	1.47 10 ⁻²
$X_{B,r}(t) = A \left(1 + (C - 1) \exp\left(\frac{-K \tau}{E}\right) \right)^F$	A= 1.225, C= 0.017 K= 0.506, E= 0.323 F= 1.034	0.9879	1.42 10 ⁻²
$X_{B,r}(t) = E + A \exp\{B + (C - 1)\exp - [K(\tau - \tau_L) + D]^\alpha\}^F$	E =-0.656, A= 0.651 B =0.858, C= 0.289 K =2.500, L =0.401 I= 1.109, D= 0.903 F=1.121	0.9892	1.27 10 ⁻²
$X_{B,r}(t) = A \left\{ B + (C - 1)\exp - \left[\frac{K}{E}(\tau - \tau_L) + D\right]^\alpha \right\}^F$	A =0.923, B =1.228 C =-0.244, K =0.041 E =0.029, L =-0.647 I =1.768, D= -0.824 F=0.599	0.9885	1.36 10 ⁻²

The values of the coefficient of determination (r^2), and the mean systematic error RMSE vary from 0.9844 to 0.9892, 1.27 10⁻² to 1.84 10⁻² respectively.

The two models proposed (Eq.IV.12, Eq.IV.13), and the Gompertz model give the highest values of the determination coefficient with the lowest mean systematic error values RMSE.

The two models offered have the following advantages:

- Gives the best smoothness for the cumulative gas production curves
- By analogy facilitate the use of equations existing in the literature

Considering the efficiency of two proposed models, we will try to improve them by proposing three models represented on the equations (IV.15, IV.16, IV.17).

$$X_{B,r}(t) = A \exp\{-\exp[-K(\tau - \tau_L)^\alpha + a(\tau - \tau_L)^\beta]\} \quad (IV.15)$$

$$X_{B,r}(t) = E + A \exp\{B + (C - 1)\exp - [K(\tau - \tau_L)^\alpha + D(\tau - \tau_L)^\beta]\}^F \quad (IV.16)$$

$$X_{B,r}(t) = A \left\{ B + (C - 1)\exp - [K(\tau - \tau_L)^\alpha + D(\tau - \tau_L)^\beta] \right\}^F \quad (IV.17)$$

Table 7. Kinetic parameters of the improved proposed models

Models	Parameters	r ²	RMSE
$X_{B,r}(t) = A \exp\{-\exp[-K(\tau - \tau_L)^\alpha + a(\tau - \tau_L)^\beta]\}$	A=1.034, K=3.254 $\tau_L=1.36 \cdot 10^{-2}$, $\alpha=0.90866$ $\beta=-0.05806$, a=0.7836	0.9891	$1.28 \cdot 10^{-2}$
$X_{B,r}(t) = E + A \exp\{B + (C - 1)\exp - [K(\tau - \tau_L)^\alpha + D(\tau - \tau_L)^\beta]\}^F$	E=-0.185, A= 0.533 B= 0.601, C= -0.139 K= -0.139, $\tau_L=2.232 \cdot 10^{-5}$ $\alpha=1.041$, D= 1.975 $\beta=-1.336$, F= 1.522	0.9893	$1.27 \cdot 10^{-2}$
$X_{B,r}(t) = A \{B + (C - 1)\exp - [K(\tau - \tau_L)^\alpha + D(\tau - \tau_L)^\beta]\}^F$	A=0.430, B=0.930 C=-0.629, K=0.046 $\tau_L=-0.831$, $\alpha=15.445$ D= 1.026, $\beta=2.658$ F= 0.450	0.9877	$1.45 \cdot 10^{-2}$

The models proposed (Eqs IV.15, IV.16, IV.17) gave better smoothing of the cumulative gas production curves by comparing with the equations ((IV.1, IV.12, IV.13). The proposed model (Eq IV.16) with a single exponential and nine parameters gave a highest coefficient of determination value with a lowest mean systematic error value RMSE. Figure (3 and 4) represent the smoothing results of the cumulative gas production curves.

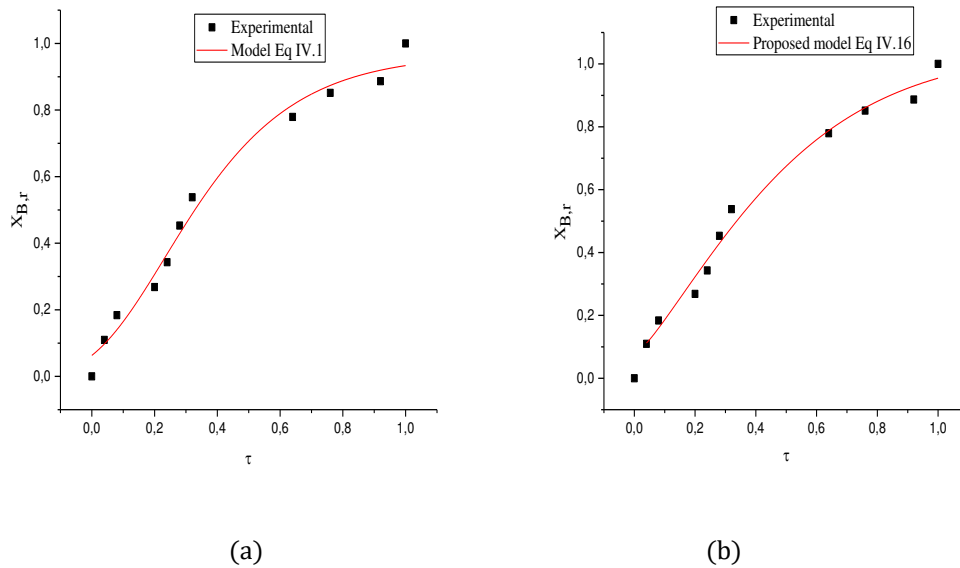


Figure. 3. Validation of models: (a) Gompertz model Eq IV.1; (b) Proposed model Eq IV.16

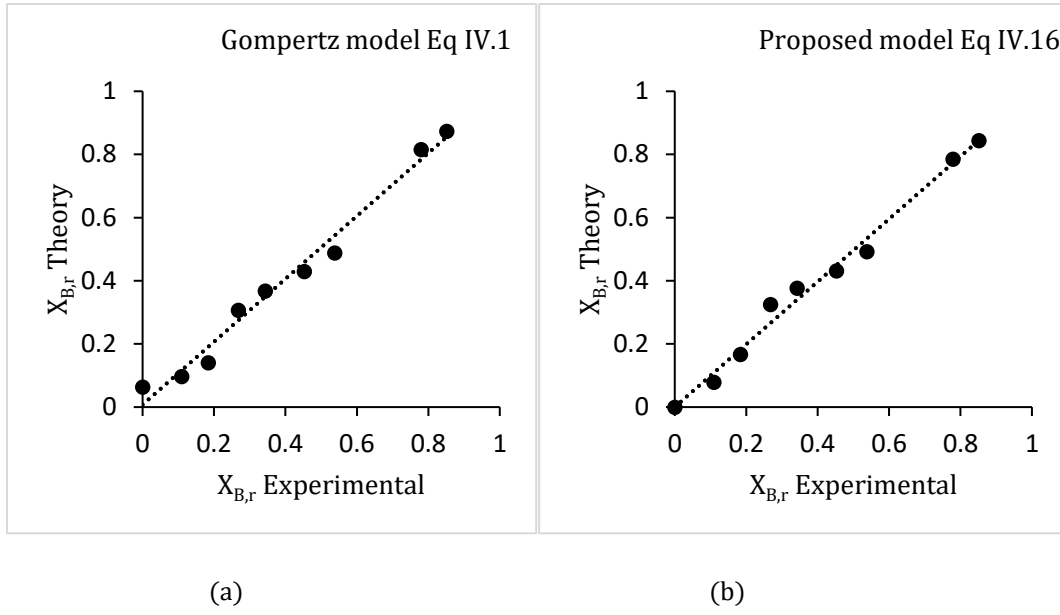


Figure. 4. Comparison of the rate of experimental biogas with the volume predicted by the models: (a) Gompertz model Eq IV.1; (b) Proposed model Eq IV.16

3.1.1. Validation of proposed models with experimental data from the literature

The aim of this section is to evaluate the new models (Eqs IV.16, IV.17) which best match the biogas production data with other experimental data from the literature. They are of different types and structures.

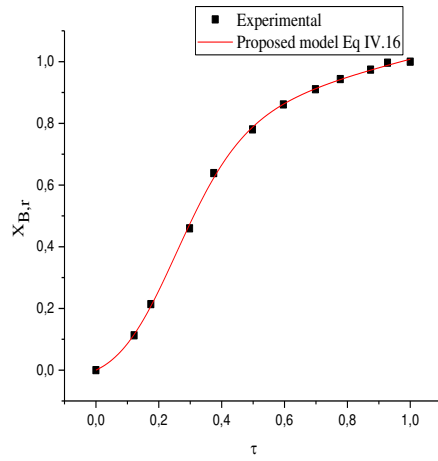
We also propose a model which combines the two contributions (Eqs IV.16, IV.17), the expression of the proposed model becomes:

$$X_{B,r}(t) = \gamma \{E + A \exp\{B + (C - 1) \exp - [K(t - t_i) + D]^\alpha\}^F\} + (1 - \gamma) \{A \{B + (C - 1) \exp - [K(t - t_i) + D]^\alpha\}^F\} \quad (IV.18)$$

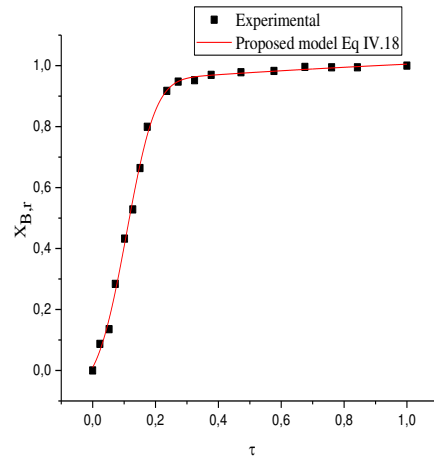
If $\gamma = 1$, we fall back on equation IV.16

If $\gamma = 0$, we fall back on equation IV.17

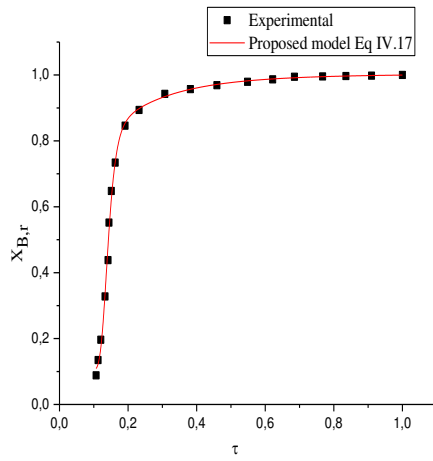
If $\gamma \neq 1, \gamma \neq 0$, we fall back on equation IV.18 (IV.16 + IV.17)



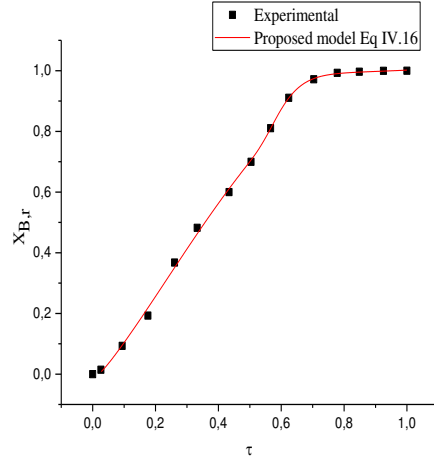
(a)



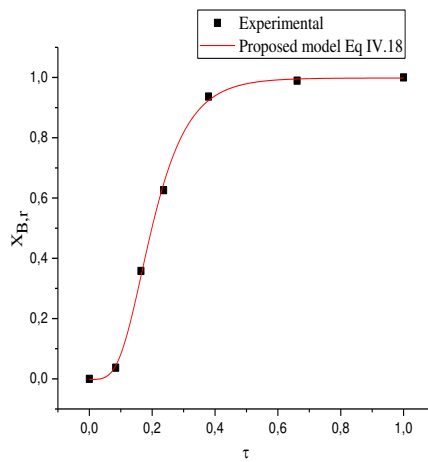
(b)



(c)



(d)



(e)

Figure. 5. Variation of the biogas production rate of the models proposed with the experimental production rate of the literature, Methane production: (a) Sludge and plant waste; (b) Residues from vegetable crops; (c)

Waste from *Bougainvillea spectabilis*; (d) Animal manure mixed with straw, Hydrogen production: (e) Food waste and sewage sludge.

A comparison was made between the proposed models (Eqs IV.16, IV.17, IV.18) and the best model found for each product selected in the literature, using the coefficient of determination and the mean square error are indicated. in Table 8. Consequently, the proposed models have high values of (r^2) and low values of RMSE compared to those obtained with the models of modified Gompertz, BPK, logistic function, transfer function, and exponential for both cases (production of Methane and Hydrogen).

Table 8. Results obtained from the models proposed for the production of biogas from products in the literature

Reference	Product	Model	Coefficients	r^2	RMSE
(Pham Van et al. 2018)	Sludge and plant waste (Methane: CH ₄)	Proposed model Eq IV.16	E=0.109, A=0.547, B=-17.566, C=11.712, K=-0.069, τ_L = -0.289, α = -2.765, D=0.128, β =-2.220, F= -0.086	0.9992	1.15 10 ⁻³
		Proposed model Eq IV.17	A=0.543, B=-0.287, C=0.852, K=0.872, τ_L =-0.017, α =-1.266 D=1.375, β =0.058, F=23.786	0.9996	7.23 10 ⁻⁴
		Proposed model Eq IV.18	E=0.750, A=0.297, B=0.321, C=-0.555, K=0.624, τ_L =-1.339, α =3.176, D=0.789, β = 0.055, F=10.934, γ = -0.037	0.9996	6.34 10⁻⁴
		Modèle de BPK	---	0.9988	0.19
(Pengfei et al. 2019)	Plant crop residues (Methane: CH ₄)	Proposed model Eq IV.16	E=-0.111, A= 0.656, B=0.576, C=0.977, K=29.666, τ_L =-0.187, α =1.409, D= 13.644, β =0.356, F=0.892	0.9972	6.13 10 ⁻³
		Proposed model Eq IV.17	A=100.407, B=2.425, C=943.463, K=1.718, τ_L =-1.410, α =3.603, D=0.141, β =-0.485, F=-4.990	0.9973	5.98 10 ⁻³
		Proposed model Eq IV.18	E=-0.602, A=1.060, B=0.936, C=0.994, K=22.705, τ_L =-0.576, α =3.229, D=17.847, β =0.948, F=0.298, γ =0.901	0.9978	4.79 10⁻³
		Gompertz equation	---	0.997	---
(Xiyan et al. 2015)	Bougainvillea spectabilis waste (Methane: CH ₄)	Proposed model Eq IV.16	E=0.119, A=0.657, B=0.552, C=-6.847, K=-0.475, τ_L =0.055, α =-0.905, D= -5.827, β =-0.011, F=0.545	0.9956 5	8.76 10 ⁻³
		Proposed model Eq IV.17	A=0.002, B=2.325, C=2.042, K=0.086, τ_L =-0.836, α =-67.519, D=-0.108, β =-6.284, F=5.123	0.9978	4.4 10⁻³
		Proposed model Eq IV.18	E=-0.210, A=0.797, B=1.379, C=0.997, K=-0.157, τ_L =-0.027, α =-1.884, D= 3.335, β =0.118, F=0.259, γ =0.712	0.9963 6	7.33 10 ⁻³
		Gompertz equation	---	0.9967	---
		Logistic function	---	0.9964	---
		Transfer function	---	0.9359	---
(Heui Kwakb et al., 2013)	Animal manure mixed with straw	Proposed model Eq IV.16	E=100.407, A=2.425, B=0.899, C=-1.003, K=-1.039, τ_L =0.026 α =0.408, D=-5.597, β =1.227, F=0.626	0.9955	9.49 10 ⁻³

	(Methane: CH ₄)	Proposed model Eq IV.17	A=0.830, B=0.857, C=-0.744, K=2.362, τ_L =-0.267, α =5.836 D=0.867, β =-0.012, F=0.351	0.9974	5.33 10 ⁻³
		Proposed model Eq IV.18	E=-0.748, A=1.206, B=1.213, C=2.432, K=0.109, τ_L =0.026, α =- 5.924, D=0.653, β =-2.575, F=-0.433, γ =-0.217	0.9992	1.15 10⁻³
		Modified Gompertz model	---	0.908	6.810 ⁻²
		Exponential model	---	0.870	7.210 ⁻²
(Kim et al., 2004)	Food waste and sewage sludge (Hydrogen: H ₂)	Proposed model Eq IV.16	E=-0.004, A=0.01, B=0.1, C=-0.2, K=0.007, τ_L =-0.099, α =1628, D=- 11.492, β =0.8, F=46.145	0.9990	1.14 10⁻³
		Proposed model Eq IV.17	A=0.6, B=0.323, C=-4, K=11 τ_L =-0.24, α =4, D=3, β =-0.235 F=0.431	0.9976	2.69 10 ⁻³
		Proposed model Eq IV.18	E=-0.004, A=0.01, B=0.1, C=-0.2, K=0.007, τ_L =-0.099, α =1628, D=- 11.492, β =0.8, F=46.145, γ =1	0.9990	1.14 10⁻³
		Modified Gompertz model	---	0.993	9.80 10 ⁻³

The data obtained, presented in Table 8, confirms that the new models are universal and allow to describe the production curves of methane and other gases such as hydrogen of different products.

3.2. Biodegradation kinetics

According to **Chynoweth et al. (1993)** and **Nikolaeva et al. (2009)**, the anaerobic digestion of most substrates follows first order degradation kinetics. The production of biogas is proportional to the amount of COD consumed during the fermentation process. The rate of substrate removal is described by equation (IV.18).

$$-\frac{dY_t}{dt} = kY_t \quad (IV.18)$$

By integration of equation (IV.18) and with $Y_t = L_u$ at $t = 0$

$$Y_t = L_u \cdot e^{-kt} \quad (IV.19)$$

Where: Y_t , the organic matter content at time t ;

L_u , the initial amount of biodegradable organic matter.

By analogy to equation (IV.18), we propose the following dimensionless model:

$$Y = \frac{y}{y_0} \text{ et } \tau = \frac{t}{t_\infty} \text{ that implies } \frac{y_0 dy}{t_\infty d\tau} = -ky_0^n Y^n$$

We define a degradation kinetics of order (n)

$$\frac{dy_t}{dt} = -k_n y^n \quad (IV.20)$$

The solution of eq. IV.20, gives the kinetics of order (n)

$$Y = [1 + k_n^* \tau]^{\frac{1}{1-n}} \quad (IV.21)$$

With $k_n^* = (n - 1)k_n t_{\infty} y_0^{n-1}$, $n \neq 1$

Where: y, the organic matter content at time t (COD); Y, unitless ratio

The expression IV.21 can be modified, by articulating the fractional differentiation:

$$Y = [1 + k_n^* \tau^\alpha]^{\frac{1}{1-n}} \quad (IV.22)$$

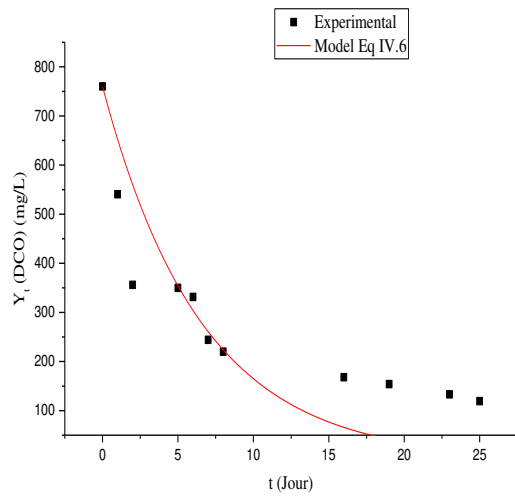
Where: α is the fractional coefficient of the model

Table 9. Parameters of the kinetic model

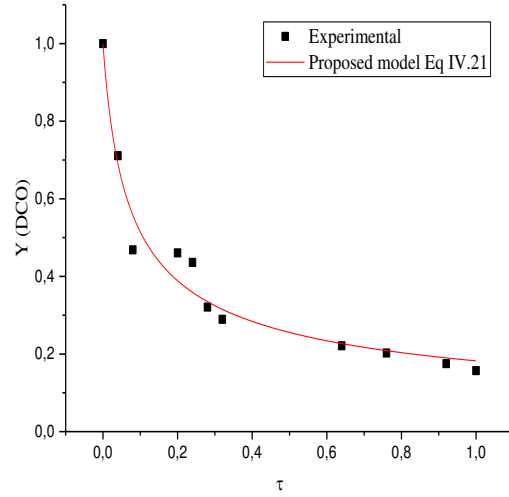
Models	Settings	r ²	RMSE
Eq IV.19 (Chynoweth et al. 1993)	K=0.153 (J ⁻¹)	0.737	2.4 10 ⁻²
Proposed model Eq IV.21	K _n [*] =26.445 [k _n =0.545(J ⁻¹)] n=2.94626	0.967	2.1 10 ⁻²
Proposed model Eq IV.22	K _n [*] =1 .016 n=1 .387 α =0 .552	0.9706	1.95 10 ⁻²

The values of the coefficient of determination (r²), and the mean systematic error RMSE are 0.737, 0.967, 0.9706 and 2.4 10⁻², 2.1 10⁻², 1.95 10⁻² for the model (Eq IV.19) and the proposed models (Eq IV.21, Eq IV.22) respectively.

The proposed model (Eq.IV.22) gives the value of the highest coefficient of determination with the lowest mean systematic error value RMSE. So, it is he who best describes the behavior of COD degradation during anaerobic digestion (Figure. 6).



(a)



(b)

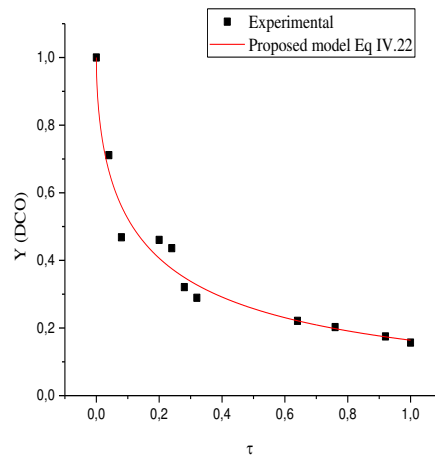
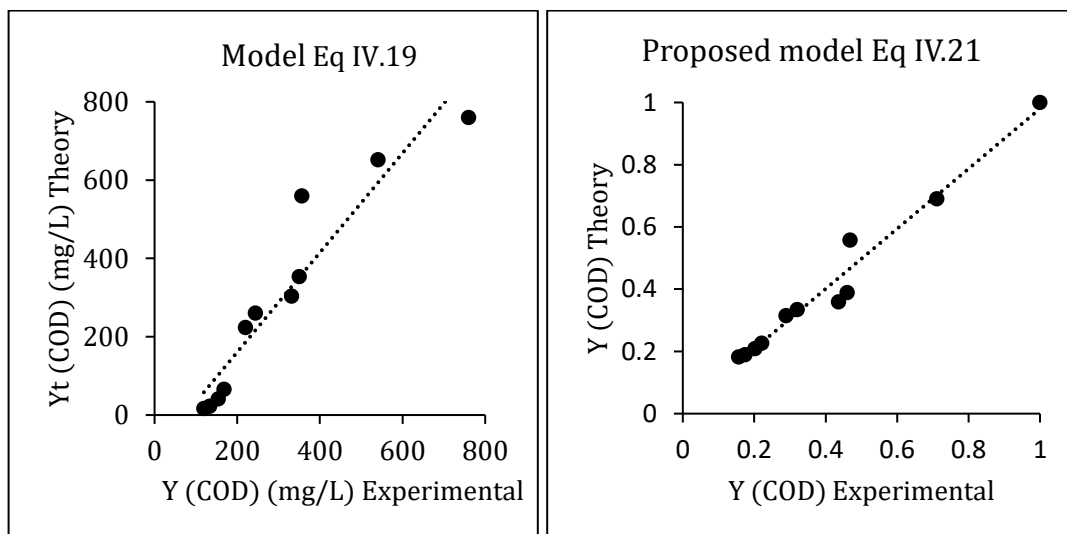


Figure. 6. Model validation



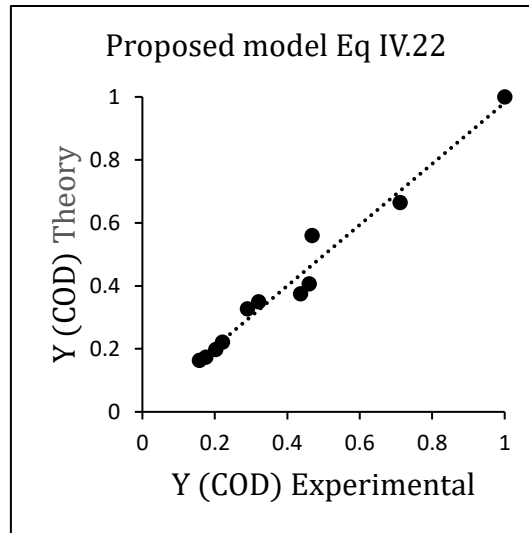


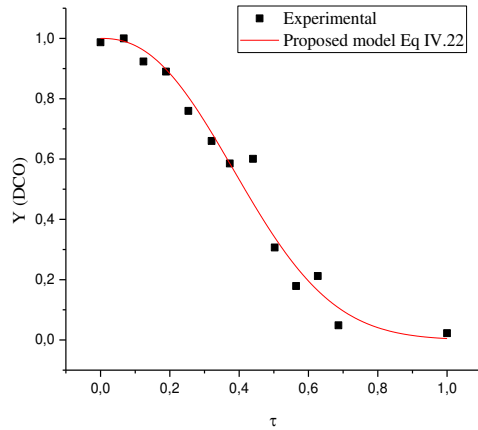
Figure. 7. Comparison of the experimental biodegradation rate with the data predicted by the models

To ensure the performance of the proposed models, we will validate them with the experimental data from the literature.

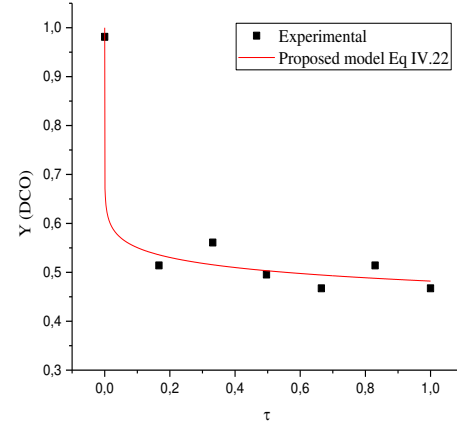
Table 10. Results obtained from the proposed models of the COD biodegradability of products from the literature

Reference	Product	Model	Coefficients	r^2	RMSE
(Schneider 2015)	Gelatin	Proposed model Eq IV.21	$K = -1.519, n = -0.598$	0.9652	$5.37 \cdot 10^{-2}$
		Proposed model Eq IV.22	$K = 0.038, n = 1.006, \alpha = 2.352$	0.9759	$3.73 \cdot 10^{-2}$
		Eq IV.19 (Chynoweth et al. 1993)	---	0.84	---
(Arras 2017)	Residual organic matter	Proposed model Eq IV.21	$K = 3.32 \cdot 10^5, n = 18.478$	0.9770	$4.64 \cdot 10^{-3}$
		Proposed model Eq IV.22	$K = 0.032, n = 1.043, \alpha = 0.088$	0.9773	$4.59 \cdot 10^{-3}$
		Eq IV.19 (Chynoweth et al. 1993)	---	0.9500	---
(Liu et al. 2017)	Sludge	Proposed model Eq IV.21	$K = -0.782, n = 0.380$	0.9978	$1.30 \cdot 10^{-3}$
		Proposed model Eq IV.22	$K = -0.613, n = 0.601, \alpha = 1.150$	0.9985	$8.91 \cdot 10^{-4}$
		Eq IV.19 (Chynoweth et al. 1993)	---	0.9747	---

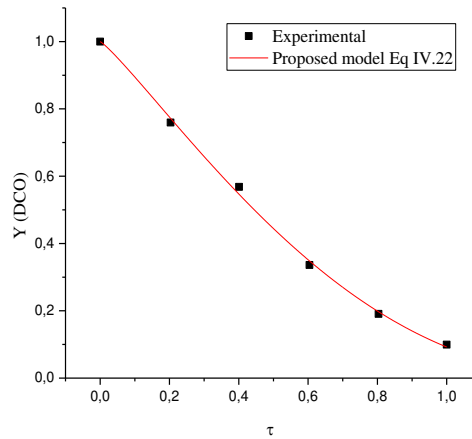
The data obtained, presented in (Table 10 and Figure. 8), confirm that the new models are universal and make it possible to describe the COD biodegradation curves of different products.



(a)



(b)



(c)

Figure. 8. Variation of the COD biodegradation rate of the models proposed with the experimental biodegradation rate from the literature: (a) Gelatin; (b) Residual organic matter; (c) Sludge

4. Conclusion

The first purpose of this chapter is to give an energy value to the mud by identifying the following points:

The modeling of the volume of biogas produced was carried out by that of Gompertz and the models proposed. We observed a good agreement of the proposed models with the experimental data.

The modeling of the degradation of organic matter was carried out by the first order model (eq IV.19), and proposed dimensionless models. The latter gave a good agreement with the experimental data better than the model in the literature.

Availability of Data and Material The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code Availability Not applicable.

Declarations

Conflict of interest On behalf of all authors, the corresponding author

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