

## ORIGINAL RESEARCH ARTICLE

# Efficient reuse of *Sargassum* spp. biomass and organic fraction of municipal solid waste by anaerobic co-digestion in the Dominican Republic: Evaluation of biochemical methanogenic potential and reaction rates

Rosy Paletta<sup>1</sup>, Pierpaolo Filippelli<sup>2</sup>, Sebastiano Candamano<sup>2</sup>, Luana Galluccio<sup>2</sup>, Angelo Macilietti<sup>2</sup>, Yessica A. Castro<sup>3</sup>, Antonio Tursi<sup>4</sup>, Eurípides Amaro<sup>3</sup>, J. Atilio de Frias<sup>3,\*</sup>

<sup>1</sup> Department of Computer Engineering, Modeling, Electronics and Systems, University of Calabria, 87036 Rende, Italy

<sup>2</sup> Department of Mechanical, Energy and Management Engineering, University of Calabria, 87036 Rende, Italy

<sup>3</sup> Department of Science and Engineering, Universidad Federico Henríquez y Carvajal (UFHEC), Santo Domingo 10106, Dominican Republic

<sup>4</sup> Department of Chemistry and Chemical Technologies, University of Calabria, 87036 Rende, Italy

\* Corresponding author: J. Atilio de Frias, atilio.defrias@ufhec.edu.do

## ABSTRACT

Anaerobic digestion (AD) is a potential solution to valorize invasive pelagic *Sargassum* spp. *Sargassum* spp. (SP) biomass is characterized by a low carbon/nitrogen (C/N) ratio, which, in addition to the presence of indigestible fiber, sulfide, salt, ash, and polyphenol content, are inhibitors to the AD process. Furthermore, its chemical composition depends on the season and region of harvesting. To increase biogas yields, biomass must be subjected to pre-treatment or an anaerobic co-digestion process with other waste biomass. In this paper results of co-digestion of *Sargassum* spp. and municipal solid waste (OFMSW) batches with different weight ratios are reported and compared with the mono-digestion of the two organic matrices. The objective is to provide an optimized SP to OFMSW ratio for the sustainable production of biogas in the Dominican Republic. Mono-digestion of *Sargassum* spp. showed the longest reaction time and the lowest biomethane yield as it lasted 30 days and provided a cumulative volume of biomethane equal to 79.68 NmLg<sup>-1</sup>vs. The addition of OFMSW led to the shortening of the reaction time to 10 days and to the increase of the yield and cumulative volume of biomethane. It can be attributed to the more favorable C/N ratio, to the presence of more readily digestible compounds and lower ash content of those batches. The reaction kinetics of all the investigated batches is properly fitted by the Modified Gompertz model. The system with a *Sargassum* spp.-OFMSW weight ratio of 33:67 allows to obtain a notable bio-methane volume of 327.27 ± 15.93 NmLg<sup>-1</sup>vs, ten times higher than from *Sargassum* spp. alone.

**Keywords:** *Sargassum* spp.; organic fraction of municipal solid waste; anaerobic co-digestion; kinetic models

## ARTICLE INFO

Received: 7 September 2023

Accepted: 12 December 2023

Available online: 9 April 2024

## COPYRIGHT

Copyright © 2024 by author(s).

*Applied Chemical Engineering* is published by Arts and Science Press Pte. Ltd. This work is licensed under the Creative Commons Attribution-NonCommercial 4.0 International License (CC BY 4.0).

<https://creativecommons.org/licenses/by/4.0/>

## 1. Introduction

*Sargassum* spp. is a genus of macroalga, phylum Heterokontophyta, belonging to the Phaeophyceae class. It gives its name to the Sargasso Sea, where these algae are particularly widespread. The increasingly abundant presence of *Sargassum* spp. is reflected in negative consequences at an environmental and economic level. One of the strategies for the valorization of *Sargassum* spp. is to produce biogas via anaerobic digestion (AD).

Anaerobic digestion is a biological process of degradation of the organic substrate in the absence of free oxygen<sup>[1]</sup>. Biogas is composed of 60%–70% methane and 30%–40% carbon dioxide, with traces of ammonia, hydrogen, hydrogen sulfide, nitrogen, oxygen, and water

vapor<sup>[2]</sup>. It is useful as an alternative to dispose the organic waste and to produce green energy. The AD process is widely used to treat organic waste<sup>[2]</sup>, such as sludge<sup>[3]</sup>, agricultural production waste<sup>[4-6]</sup>, waste water<sup>[7]</sup>, macroalgae<sup>[8-10]</sup>, in order to produce renewable energy. Waste biomass co-digestion represents an emerging technology to improve AD performance.

Researchers' interest in energy production from macroalgae has been growing recently. *Sargassum* spp. is the object of numerous studies. The presence of this brown macroalga has grown exponentially since 2011 from western Africa to the Gulf of Mexico, known as the Great Atlantic *Sargassum* Belt (GASB)<sup>[11]</sup>. *Sargassum* spp. is invading the beaches of South Africa, the Gulf of Mexico, the Atlantic Ocean, and the Caribbean causing various problems for local communities<sup>[12]</sup>. The presence of this biomass on beaches leads to adverse effects on tourism and fishing. Furthermore, its decomposition produces hydrogen sulphide (H<sub>2</sub>S), a toxic gas with a bad smell<sup>[13]</sup>. Therefore, the recovery of this waste biomass arouses considerable interest since it would not only allow production of renewable energy but also solve the problems related to its abundant presence. Although the applications of *Sargassum* spp. are not limited to AD biogas production alone, this application is the most promising. However, there are insufficient studies on *Sargassum* spp. seasonally and regionally-dependent characterization and biochemical conversion to support significant advances toward finding solutions,

The AD process of *Sargassum* spp. chiefly breaks down the cellulose fraction with yields lower than 50% in terms of biochemical methane potential (BMP) compared to theoretical. Low yields are attributed to the lignocellulose barrier, a low carbon/nitrogen (C/N) ratio, indigestible fiber, sulfide, salt, ash, and polyphenol content<sup>[12,14]</sup>.

To increase yields, *Sargassum* spp. must be subjected to pre-treatment. The pretreatments break down the lignin barrier<sup>[12]</sup> and increase accessibility to cellulose for downstream hydrolysis into glucose and towards methanogenesis. However, they also impact the overall energy balance as they increase the required energy to carry out the entire process<sup>[15]</sup>.

Anaerobic co-digestion with organic waste biomass represents a valid and cost-efficient method to increase yields without any pretreatment and it allows an environmentally sustainable exploitation of these renewable energy sources, otherwise landfilled. The organic waste biomass increases the content of lipids, redistributes metal elements and raises the buffering capacity of the digester thus boosting the digestion performance<sup>[15]</sup>.

Recent literature has explored pretreatment techniques on pelagic *Sargassum* spp. followed by co-digestion with the organic fraction of municipal solid waste (OFMSW). They reported that the maximum cumulative biomethane yields, equal to 293 NmLg<sup>-1</sup>vs, was obtained by co-digestion of *Sargassum* spp. with OFMSW at a 25:75 weight ratio, after mechanical pre-treatment (size reduction) and heat-treatment at 353.15 K for 15 h of *Sargassum* spp., followed by hydrothermal pre-treatment of SP and OFMSW in a pressurized batch reactor operating at 30 bars under N<sub>2</sub> gas at temperature 413.15 K for 30 min. and at stirring speed of 300 rpm<sup>[16]</sup>.

Oliveira et al. conducted a co-digestion study of *Sargassum* spp. with glycerol and waste frying oil. The co-digestion with glycerol and waste frying oil increased the BMP by 56% and 46%, respectively<sup>[17]</sup>. Rivera-Hernández et al. conducted a study in Mexico on the synergistic effect of the co-digestion of pig manure (PM) and *Sargassum* spp. (S) by testing five different ratios (100S-0PM, 65S-35PM, 50S-50PM, 30S-70PM, and 0S-100PM). The highest BMP of 441.47 mLg<sup>-1</sup>vs was obtained in 50S-50PM treatment<sup>[18]</sup>.

The arrival of *Sargassum* spp. in the Caribbean shores of the Dominican Republic has reached unsustainable levels. Even though efforts towards valorization and remediation exist across all levels, there are insufficient studies on *Sargassum* spp. characterization and biochemical conversion to support significant advances toward finding solutions.

The objective of this work is the valorization of *Sargassum* spp. species from the shores and beaches of the Dominican Republic via anaerobic digestion (mono-digestion and co-digestion) with OFMSW sourced from the area, , thus promoting the sustainability of AD implementation. From this point of view, this work is aimed to provide the optimized SP to OFMSW ratio in view of a potential year-round scale-up. During the months of non-accumulation of *Sargassum* spp. a plant would produce biogas from OFMSW only, and during the period of *Sargassum* spp. accumulation, it would work with a *Sargassum* spp.-OFMSW mix.

## 2. Materials and methods

### 2.1. Sample preparation

A sample of the macroalgae *Sargassum* spp. was provided by the Punta Cana Foundation group. Samples were washed with deionized water. Excess water was removed with blotting paper. Samples were air-dried for several days until constant weight was achieved. After drying, the *Sargassum* spp. samples were subjected to mechanical pre-treatment using a Philips-ProBlend Tech (Milan, Italy) mixer for 1 min at maximum speed.

The OFMSW sample was obtained from door-to-door municipal solid waste collection and was also subjected to the same mechanical pre-treatment.

The experiment was modeled by a modified experimental design methodology<sup>[19,17]</sup>.

The *Sargassum* spp. OFMSW organic matrix was prepared by mixing the previously prepared samples, according to **Table 1**.

**Table 1.** *Sargassum* spp.-OFMSW organic matrix preparation ratios (% wt as-is).

Sample ID	% <i>Sargassum</i> spp.	% OFMSW
S1	0	100
S2	10	90
S3	20	80
S4	25	75
S5	33	67
S6	50	50
S7	67	33
S8	75	25
S9	90	10
S10	100	0

### 2.2. Inoculum preparation

Inoculum was obtained by mixing water with cow manure (ratio 1:1). After being prepared it was kept at 384.15 K, a mesophilic temperature used subsequently for AD of the biomass, to acclimate it. After 30 days the volume of biogas produced by the inoculum was stable<sup>[20]</sup>.

### 2.3. Elemental analysis of *Sargassum* spp. and OFMSW

Both samples, *Sargassum* spp. and OFMSW, were characterized for carbohydrate, lipid, protein, C/N ratio, total solids (TS), volatile solids (VS), ash, and humidity content, following known procedures<sup>[21]</sup>.

Furthermore, for the sample of *Sargassum* spp. the content of metals and metalloids was determined using a Microwave Digestion System following the methodology used in a previous study<sup>[20]</sup>.

The content of metals and metalloids of the analyzed samples, expressed as mg kg<sup>-1</sup> S.S., is calculated according to the following Equation 1 where *B* is the concentration (mg L<sup>-1</sup>) expressed by the ICP-MS analysis,

$V$  (mL) is the volume of the solution obtained from the mineralization and brought to volume to 50 mL,  $m$  the mass of the mineralized sample.

$$\frac{mg}{Kg} S.S = \frac{BV}{m} \quad (1)$$

## 2.4. Determination of the experimental and theoretical methane potential

The experimental Biochemical Methane Potential ( $BMP_{ex}$ ) was determined with the Automatic Potential System Test II (AMPTS-II®) reactor system manufactured by BPC instruments (Lund, Sweden). The tests were conducted in duplicate. Operating conditions: inoculum/substrate ratio equal to 3, mesophilic temperature conditions at 384.15 K<sup>[20]</sup>.

The theoretical methane potential was calculated following the  $BMP_{thCOD}$  model<sup>[22]</sup> (Equation 2), based on the Chemical Oxygen Demand (COD) layer in the substrate.

$$BMP_{thCOD} = \frac{nCH_4 \times RT}{p \times VS} \quad (2)$$

where  $BMP_{thCOD}$  is the theoretical methane production from COD ( $LCH_4g^{-1}VS$ ), COD is the chemical oxygen demand,  $nCH_4$  are the amount of molecular methane (mol),  $R$  is the gas constant ( $82 \text{ atm mLmolK}^{-1}$ ),  $T$  the temperature of the reactor (310 K),  $p$  is the atmospheric pressure (1 atm) e  $VS$  the volatile solid of the substrate (g).

## 2.5. Kinetics of methane production

The kinetics of methane production was evaluated with two kinetic models: first order kinetic (Equation 3)<sup>[22]</sup> and Modified Gompertz model (Equation 4)<sup>[22]</sup>.

$$y(t) = A \times (1 - e^{-kt}) \quad (3)$$

$$y(t) = A \times e^{-\exp\left[\frac{u \times e}{A}(m-t)+1\right]} \quad (4)$$

where  $y(t)$  presents the biogas product during the AD process ( $NmLg^{-1}VS$ ),  $A$  represents the amount of biogas that should be produced ( $NmLg^{-1}VS$ ),  $k$  represents the reciprocal value of time when  $y(t)$  reaches the value of  $0.632A$ ,  $u$  represents the daily amount of biogas ( $NmLg^{-1}day^{-1}VS$ ),  $e$  it is a constant value (2.718282),  $m$  represents the lag phase period (days), and  $t$  is the time of AD process (days).

# 3. Results and discussion

## 3.1. *Sargassum* spp. and OFMSW characterization

The chemical-physical composition of the samples of *Sargassum* spp. and OFMSW is reported in **Table 2**. In the sample of *Sargassum* spp. several metallics and metalloids are present. Some of them are present in negligible quantities. The contents of metals and metalloids are reported for those with content greater than 1%: Na 1.22%, K 3.35%, Ca 1.92%. The characterization of the prepared samples is reported in **Table 3**. In our previous study the chemical composition of *Sargassum* spp. was analyzed in detail, which varies according to geographical location and seasons. The ranges of lipid, protein, carbohydrates and ash content for the *Sargassum* spp. is 0.6%–2.7%, 5.8%–14.1%, 13.4%–46.1%, 24.6%–76.4% respectively.

The content of  $VS$  (%),  $TS$  (%),  $ash$  (%) and  $moisture$  (%) of the samples under analysis are shown in **Table 3**. OFMSW sample (S1) was characterized by a low ash content while sample *Sargassum* spp. sample (S10) shows a much higher ash content that can be attributed to the bioaccumulation of minerals (e.g. Na, Ca, K, Mg) and trace elements (e.g. Fe, Zn, Ni, Cu) from the surrounding seawater<sup>[14]</sup>. The volatile solids content of OFMSW samples (S1) and *Sargassum* spp. sample (S10) was almost equal. The values of  $VS$ ,  $TS$ , moisture and ash for the OFMSW sample are in line with what has been reported in other studies<sup>[23–26]</sup>. As regards the sample of *Sargassum* spp., since it is a very heterogeneous biomass, the content of  $VS$  (%),  $TS$  (%),  $ash$  (%) and  $moisture$  (%) varies depending on the collection site and the period<sup>[12]</sup>.

**Table 2.** Characterization of *Sargassum* spp. and OFMSW samples.

	<i>Sargassum</i> spp.	OFMSW	
Compound	Content [%]	Content [%]	
Carbohydrates	51.9 ± 0.23	23.47 ± 0.09	Percentage of open-air pre-dried sample
Lipids	1.65 ± 0.03	2.32 ± 0.04	Percentage of open-air pre-dried sample
Proteins	0.62 ± 0.06	9.78 ± 0.11	Percentage of open-air pre-dried sample
C/N	8 ± 0.12	28 ± 0.15	Percentage of open-air pre-dried sample
Na	1.22 ± 0.02	-	Percentage of total solids after oven drying
K	3.36 ± 0.02	-	Percentage of total solids after oven drying
Ca	1.93 ± 0.02	-	Percentage of total solids after oven drying

**Table 3.** Characterization of the prepared samples.

Sample ID	VS (%)	TS (%)	ASH (%)	MOISTURE (%)
S1	44.51 ± 0.01	46.17 ± 0.01	1.66 ± 0.01	53.83 ± 0.01
S2	38.40 ± 0.05	47.01 ± 0.01	8.61 ± 0.06	52.98 ± 0.01
S3	34.30 ± 0.13	50.65 ± 0.04	16.35 ± 0.08	49.35 ± 0.04
S4	25.66 ± 0.26	45.71 ± 0.01	20.05 ± 0.27	54.28 ± 0.01
S5	26.20 ± 0.01	45.97 ± 0.06	19.77 ± 0.05	54.02 ± 0.06
S6	23.90 ± 0.01	48.64 ± 0.70	24.74 ± 0.72	50.85 ± 0.01
S7	33.07 ± 0.10	61.47 ± 0.06	28.40 ± 0.16	38.52 ± 0.01
S8	35.67 ± 0.08	68.64 ± 0.06	32.97 ± 0.02	31.36 ± 0.07
S9	43.75 ± 0.09	77.41 ± 0.04	33.66 ± 0.06	22.59 ± 0.04
S10	46.55 ± 0.11	76.16 ± 0.04	29.61 ± 0.15	23.85 ± 0.04

The ash and moisture contents in the samples increase with the increase of the percentage of *Sargassum* spp. present in the sample while the moisture content with the increase of the percentage of OFMSW present in the sample. It is worth noting that the VS/TS ratios of PS and OFMSW are 0.49 and 0.95 respectively. They highlight that the latter contains more readily digestible compounds. The finding can be attributed to the high amount of total indigestible fiber content in SP and higher lipid/protein fraction in OFMSW.

The C/N ratios of PS and OFMSW are 8 ± 0.12 and 28 ± 0.15, respectively. While the C/N ratios of OFMSW is within the suggested optimal range of 20:1 to 30:1 for stable bio-digester performance<sup>[27]</sup>, the low C/N ratio of PS can lead to the formation of ammonium ions that increase the pH in the digester negatively affecting the methanogens bacteria.

### 3.2. Biochemical methane potential test

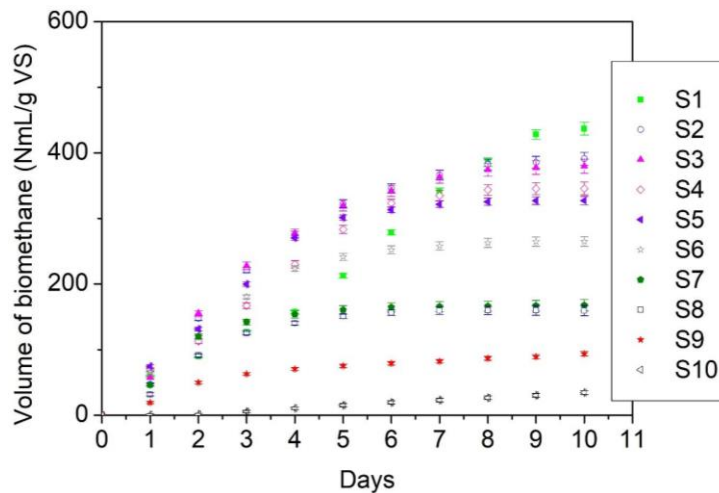
The  $BMP_{ex}$  evaluation test lasted 30 days. However, only the sample of *Sargassum* spp. (S10) took 30 days to reach the stationary state while all other samples reached it in just 10 days. The average cumulative values of  $BMP$  obtained after 10 days are shown in **Table 4**.

**Table 4.** Cumulative volume of biomethane ( $NmLg^{-1}vs$ ).

Sample ID	VS (%)	BMP ( $NmLg^{-1}vs$ )
S1	44.51 ± 0.01	436.71 ± 29.33
S2	38.40 ± 0.05	391.08 ± 4.69
S3	34.30 ± 0.13	379.78 ± 17.43
S4	25.66 ± 0.26	345.64 ± 35.41
S5	26.20 ± 0.01	327.27 ± 15.93

S6	23.90 ± 0.01	264.83 ± 16.36
S7	33.07 ± 0.10	159.40 ± 33.39
S8	35.67 ± 0.08	167.66 ± 11.23
S9	43.75 ± 0.09	99.73 ± 15.88
S10	46.55 ± 0.11	34.52 ± 2.15

The maximum total biomethane yield of  $436.71 \pm 29.33 \text{ NmLg}^{-1}\text{vs}$  was achieved with the OFMSW sample (S1), in line with what has been found in other studies<sup>[27,28]</sup>. The minimum total biogas yield of  $79.68 \pm 2.38 \text{ NmLg}^{-1}\text{vs}$  was achieved with the *Sargassum* spp. sample (S10) sample. Intermediate values were obtained for samples composed of a mix of *Sargassum* spp. and OFMSW at different percentages. It is possible to observe that the yield decreases with increasing amount of *Sargassum* spp. In fact, increasing the concentration of OFMSW also increases the C/N ratio, therefore the results are in line with what was expected. Thompson et al.<sup>[16]</sup> analyzed three different samples A1 (75% *Sargassum* spp. and 25% OFMSW), A2 (50% *Sargassum* spp. and 50% OFMSW) and A3 (25% *Sargassum* spp. and 75% OFMSW) for 21 days at 35 °C and identified the optimal mix in the A3. The results can be compared with those obtained for samples S4–S6–S8 in the present investigation. The yield of sample S4 is equal to  $345.64 \pm 35.41 \text{ NmLg}^{-1}\text{vs}$  after 10 days while the yield of sample A3 is equal to  $201.67 \pm 6.36 \text{ NmLg}^{-1}\text{vs}$ . The yield of sample S6 is equal to  $264.83 \pm 16.36 \text{ NmLg}^{-1}\text{vs}$  while the yield of sample A2 is equal to  $182.33 \pm 2.61 \text{ NmLg}^{-1}\text{vs}$ . The yield of sample S8 is equal to  $167.66 \pm 11 \text{ NmLg}^{-1}\text{vs}$  the yield of sample A1 is equal to  $97.46 \pm 1 \text{ NmLg}^{-1}\text{vs}$ . In all three cases the yield obtained in the present investigation is higher. The results can be ascribed to several factors such the different operating condition and the different composition of OFMSW. Furthermore, the fact that the *Sargassum* spp. was collected in a different region and period can affect the overall results. However, also in our case, taking into account only the S2–S4–S6 samples, the highest yield is obtained for the 25:75 *Sargassum* spp.-OFMSW sample.



**Figure 1.** Average cumulative volume of biomethane ( $\text{NmLg}^{-1}\text{vs}$ ) produced during anaerobic digestion of the samples.

The **Figure 1** shows the average cumulative volume of biomethane ( $\text{NmLg}^{-1}\text{vs}$ ) produced during anaerobic digestion of the samples. From the curves it is possible to note that the *Sargassum* spp. sample (S10) has a growing trend. Indeed, for this sample a stable production level was reached only after 30 days. The sample of OFMSW alone instead has a higher production speed and therefore the AD process reaches a stable trend in 10 days.

### 3.3. Determination of the theoretical potential

The data reported in **Table 5** show the yield of the samples compared to the theoretical yield. It is important to underline that for *Sargassum* spp. the experimental yield is always lower than the theoretical yield. Analyzing the data obtained, it is possible to observe that the yield increases with the increase of the percentage of OFMSW present in the samples.

**Table 5.** Cumulative volume of biomethane (NmLg<sup>-1</sup>vs).

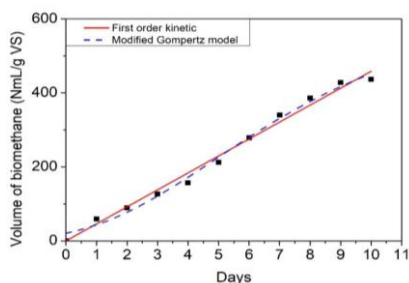
Sample ID	VS (g)	COD (g)	nCH4 (mol)	T (K)	R (atm mLmolK <sup>-1</sup> )	p (atm)	BMP <sub>thCOD</sub> (NmLg <sup>-1</sup> vs)	BMP <sub>ex</sub> (NmLg <sup>-1</sup> vs)
S1	0.44	0.59	0.009	310	82	1	519.95	436.71
S2	0.38	0.51	0.008	310	82	1	535.15	391.08
S3	0.34	0.45	0.007	310	82	1	523.35	379.78
S4	0.25	0.34	0.005	310	82	1	508.40	345.64
S5	0.26	0.35	0.005	310	82	1	488.84	327.27
S6	0.23	0.32	0.005	310	82	1	552.60	264.83
S7	0.33	0.44	0.007	310	82	1	539.21	167.66
S8	0.35	0.47	0.007	310	82	1	508.40	159.40
S9	0.43	0.58	0.009	310	82	1	532.04	99.73
S10	0.46	0.62	0.010	310	82	1	552.60	79.68

A comparison between the values of  $BMP_{th}$  and  $BMP_{ex}$  shows that for *Sargassum* spp. sample (S10) it is very far from the theoretical yield and that by decreasing the percentage of *Sargassum* spp. present in the samples the two values get closer. Actually, the *Sargassum* spp. sample (S10) reaches only the 14.41% of the theoretical yield. When the sample of *Sargassum* spp. OFMSW is added, the value of the experimental yield increases. In this way the gap between experimental yield and theoretical yield is reduced. Thus, the sample containing 10% *Sargassum* spp. and 90% OFMSW (S2) reaches 73.07% of the theoretical yield. The sample of OFMSW (S1) reaches 84% of the theoretical yield. This indicates that the OFMSW sample is more easily degradable than *Sargassum* spp.

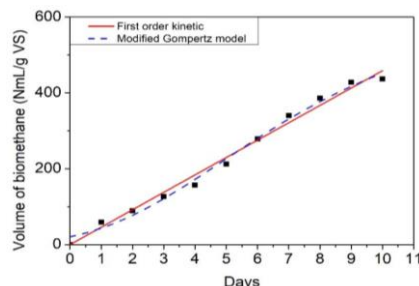
### 3.4. Kinetic production

First order kinetic model and Modified Gompertz model were used in order to find the kinetic parameters. **Figure 2** shows the curves. From the curves it is evident that the AD process develops in three phases. The first phase, called lag phase, represents the period necessary for the first quantity of biogas to be produced. The second phase coincides with exponential growth while the third phase represents the stationary phase.

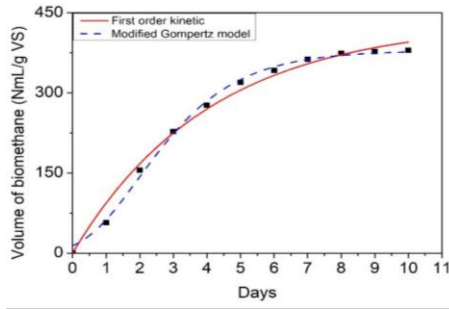
The parameters estimated using the two fitted kinetic are reported in **Table 6** and **Table 7**.



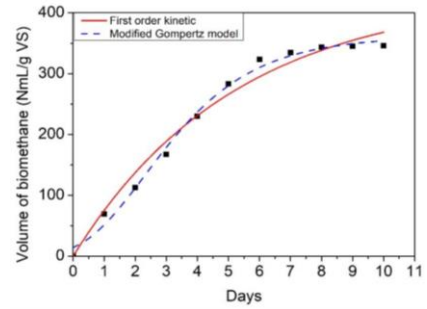
(a) sample S1



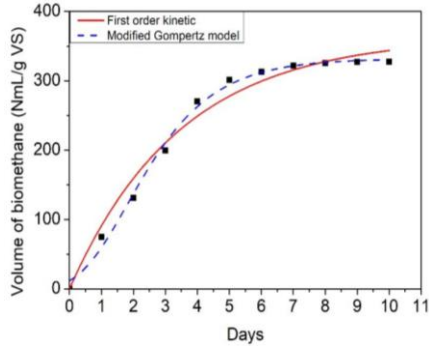
(b) sample S2



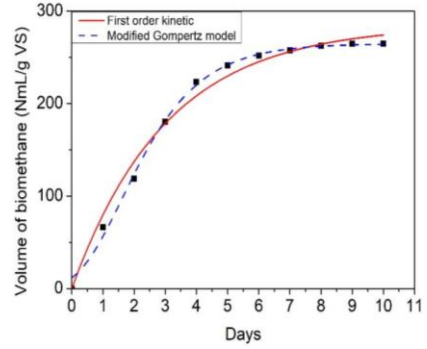
(c) sample S3



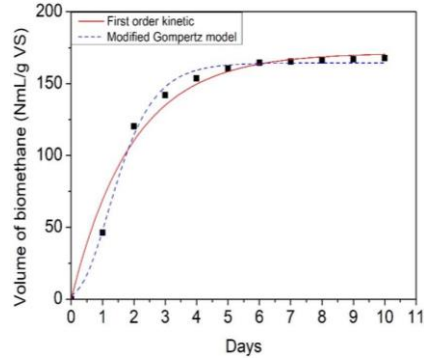
(d) sample S4



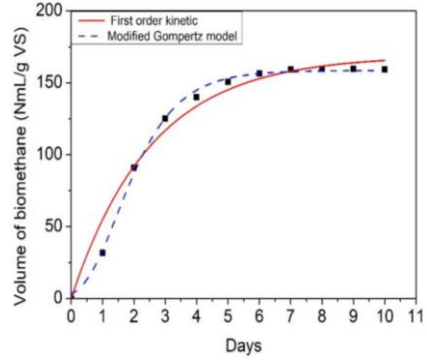
(e) sample S5



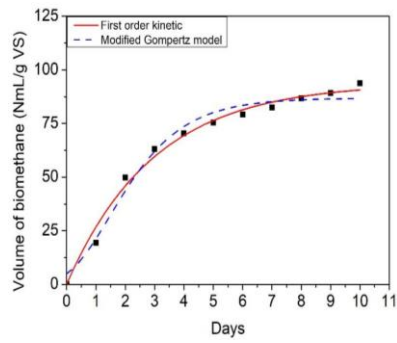
(f) sample S6



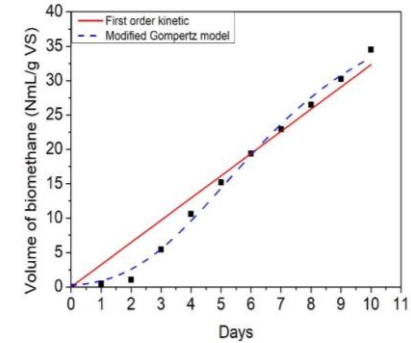
(g) sample S7



(h) sample S8



(i) sample S9



(j) sample S10

**Figure 2.** Experimental data fitted by the first order kinetic model and modified Gompertz model.

**Table 6.** Kinetic parameters of the first kinetic model.

Sample	$A$ (NmLg <sup>-1</sup> vs)	$k$ (day <sup>-1</sup> )	$R^2$
S1	72,139.588	0.0006	0.988
S2	458.786	0.217	0.985
S3	432.823	0.244	0.987
S4	432.051	0.191	0.980
S5	364.166	0.287	0.979
S6	282.850	0.329	0.987

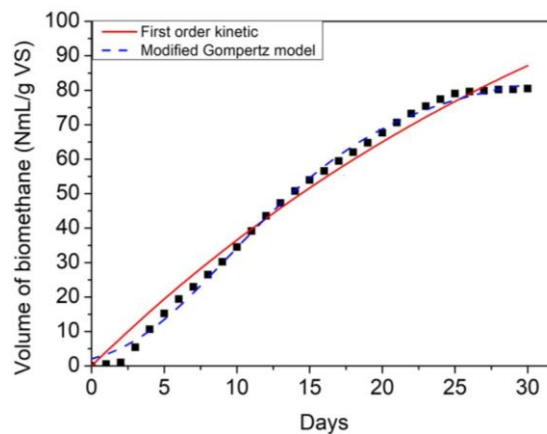


S7	171.349	0.516	0.977
S8	168.864	0.392	0.976
S9	93.947	0.335	0.988

**Table 7.** Kinetic parameters of the modified Gompertz model.

Sample	A (NmLg <sup>-1</sup> vs)	u (NmLg <sup>-1</sup> vsday <sup>-1</sup> )	m (day)	R <sup>2</sup>
S1	598.145	54.985	0.855	0.992
S2	389.583	85.832	0.425	0.997
S3	379.523	86.161	0.330	0.997
S4	360.996	68.232	0.349	0.994
S5	331.916	81.782	0.309	0.996
S6	264.980	69.496	0.203	0.997
S7	164.415	74.451	0.354	0.995
S8	158.544	55.683	0.409	0.997
S9	85.859	22.939	0.075	0.979

The data obtained from the fitting indicate that the Gompertz model fits the data better than the First order kinetic model. For all samples the values of A obtained using the Gompertz model deviate slightly from the experimental value, the values obtained for samples S1, S2, S3, S4, S5, S6, S7, S8, S9, deviate by 26.98 %, 0.38%, 0.07%, 4.44%, 1.42%, 0.56%, 3.15%, 5.44%. 13.90%, respectively from the experimental values. The *m* (day) parameter indicates the delay time, for all the samples it is less than one day. The parameter *u* (NmL g<sup>-1</sup>vsday<sup>-1</sup>) indicates the daily production of biomethane. The value of *R*<sup>2</sup> indicates how well the model fits the data. Furthermore, for sample S10 in **Figure 3** the fitting is reported not only at 10 days but also at 30 since the biogas production of this sample reaches a stable value after 30 days.



**Figure 3.** Experimental data fitted by the first order kinetic model and modified Gompertz model for the sample S10 after 10 days and 30 days of anaerobic digestion process.

The parameters estimated using the two fitted kinetic for the *Sargassum* spp. sample (S10) after 30 days are reported in **Table 8**.

**Table 8.** Kinetic parameters of the First kinetic model and Gompertz model for sample S10 after 30 days.

Sample	A (NmLg <sup>-1</sup> vs)	k (day <sup>-1</sup> )	u (NmLg <sup>-1</sup> vsday <sup>-1</sup> )	m (day)	R <sup>2</sup>
First order	165.057	0.025	-	-	0.984
Gompertz	86.450	-	4.466	2.267	0.997

## 4. Conclusions

The anaerobic digestion of *Sargassum* spp. leads to low biomethane yields, and this work demonstrated the significant increase in methane production when *Sargassum* spp. is co-digested with the organic fraction of municipal solid waste (OFMSW), with or without pretreatment. In this work, we determined the experimental biochemical methane potential ( $BMP_{ex}$ ) and the theoretical methane potential followed the  $BMP_{thCOD}$  model of *Sargassum* spp. alone and as part of an organic matrix with OFMSW. Results show that biomethane production decreases with higher *Sargassum* spp. concentration. In fact,  $BMP_{ex}$  values increased from  $79.68 \pm 2.15 \text{ NmLg}^{-1}_{VS}$  for *Sargassum* spp. only to  $436.71 \pm 29.33 \text{ NmLg}^{-1}_{VS}$  for OFMSW only. A comparison between the values of  $BMP_{th}$  and  $BMP_{ex}$  shows that for *Sargassum* spp. only, results are very far from the theoretical yield. This indicates that the biodegradation process of algal matrix is complex. By adding OFMSW to the *Sargassum* spp. sample the gap between  $BMP_{th}$  and  $BMP_{ex}$  decreases. The combination that allows to obtain a high biomethane volume and yield while using a large fraction of *Sargassum* spp. is *Sargassum* spp.-OFMSW 33:67. It provided a cumulative biomethane volume of  $327.27 \pm 15.93 \text{ NmLg}^{-1}_{VS}$ , ten times higher than by *Sargassum* spp. alone. An evaluation of experimental kinetic parameters shows that the modified Gompertz kinetic model provides a better data fit than first-order kinetics.

## Author contributions

Conceptualization, RP and JAdF; methodology, RP and AT; software, RP and SC; validation, RP, SC and YAC; formal analysis, RP; investigation, RP; resources, RP; data curation, RP and SC; writing—original draft preparation, RP; writing—review and editing SC, RP, PF, LG, JAdF, and AM; visualization, RP; supervision, JAdF; project administration, JAdF; funding acquisition, JAdF, PF, EA and AM. All authors have read and agreed to the published version of the manuscript.

## Acknowledgments

This research was supported by *Fondo Nacional de Innovación y Desarrollo Científico y Tecnológico (FONDOCyT)* of Dominican Republic, under *Ministerio de Educación Superior, Ciencia y Tecnología (MESCyT)* for the Project: *Innovación en los Procesos de Tratamiento de los Sargazos: evaluación de PBM (Potencial Bioquímico de Metano) y análisis de nuevas tecnologías para la generación de biogás*. Research Award No. 2018-2019-3C2-341

## Conflict of interest

The authors declare no conflict of interest.

## References

1. Angelidaki I, Ellegaard L, Ahring BK. Applications of the anaerobic digestion process. *Adv. Biochem. Eng. Biotechnol.* 2003, 82: 1–33.
2. Calbry-Muzyka A, Madi H, Rüschi-Pfund F, et al. Biogas composition from agricultural sources and organic fraction of municipal solid waste. *Renewable Energy.* 2022, 181: 1000-1007. doi: 10.1016/j.renene.2021.09.100
3. Appels L, Baeyens J, Degreè J, et al. Principles and potential of the anaerobic digestion of waste-activated sludge. *Progress in Energy and Combustion Science.* 2008, 34(6): 755-781. doi: 10.1016/j.pecc.2008.06.002
4. Merlin G, Boileau H. Anaerobic digestion of agricultural waste: state of the art and future trends. *Anaerobic digestion: types, processes and environmental impact.* Nova Science Publishers; 2013.
5. Macias-Corral M, Samani Z, Hanson A, et al. Anaerobic digestion of municipal solid waste and agricultural waste and the effect of co-digestion with dairy cow manure. *Bioresource Technology.* 2008, 99(17): 8288-8293. doi: 10.1016/j.biortech.2008.03.057
6. Li Y, Han Y, Zhang Y, et al. Anaerobic digestion of different agricultural wastes: A techno-economic assessment. *Bioresource Technology.* 2020, 315: 123836. doi: 10.1016/j.biortech.2020.123836
7. Monroy O, Fama G, Meraz M, Meraz M, et al. Anaerobic digestion for wastewater treatment in Mexico: state of the technology. *Water Research.* 2000. 34(6): 1803-1816.
8. McKennedy J, Sherlock O. Anaerobic digestion of marine macroalgae: A review. *Renewable and Sustainable*

- Energy Reviews. 2015, 52: 1781-1790. doi: 10.1016/j.rser.2015.07.101
9. Akila V, Manikandan A, Sahaya Sukeetha D, et al. Biogas and biofertilizer production of marine macroalgae: An effective anaerobic digestion of *Ulva* sp. *Biocatalysis and Agricultural Biotechnology*. 2019, 18: 101035. doi: 10.1016/j.bcab.2019.101035
  10. AP Y, Farghali M, Mohamed IMA, et al. Potential of biogas production from the anaerobic digestion of *Sargassum fulvellum* macroalgae: Influences of mechanical, chemical, and biological pretreatments. *Biochemical Engineering Journal*. 2021, 175: 108140. doi: 10.1016/j.bej.2021.108140
  11. Wang M, Hu C, Barnes BB, et al. The great Atlantic *Sargassum* belt. *Science*. 2019, 365(6448): 83-87. doi: 10.1126/science.aaw7912
  12. Lopresto CG, Paletta R, Filippelli P, et al. *Sargassum* Invasion in the Caribbean: An Opportunity for Coastal Communities to Produce Bioenergy Based on Biorefinery—An Overview. *Waste and Biomass Valorization*. 2022, 13(6): 2769-2793. doi: 10.1007/s12649-021-01669-7
  13. van Tussenbroek BI, Hernández Arana HA, Rodríguez-Martínez RE, et al. Severe impacts of brown tides caused by *Sargassum* spp. on near-shore Caribbean seagrass communities. *Marine Pollution Bulletin*. 2017, 122(1-2): 272-281. doi: 10.1016/j.marpolbul.2017.06.057
  14. Acid A, Milledge JJ, Maneein S, et al. *Sargassum* Inundations in Turks and Caicos. *Methane*; 2020.
  15. Fan YV, Klemeš JJ, Lee CT, et al. Anaerobic digestion of municipal solid waste: Energy and carbon emission footprint. *Journal of Environmental Management*. 2018, 223: 888-897. doi: 10.1016/j.jenvman.2018.07.005
  16. Thompson TM, Young BR, Baroutian S. Enhancing biogas production from caribbean pelagic *Sargassum* utilising hydrothermal pretreatment and anaerobic co-digestion with food waste. *Chemosphere*. 2021, 275: 130035. doi: 10.1016/j.chemosphere.2021.130035
  17. Oliveira JV, Alves MM, Costa JC. Optimization of biogas production from *Sargassum* sp. using a design of experiments to assess the co-digestion with glycerol and waste frying oil. *Bioresource Technology*. 2015, 175: 480-485. doi: 10.1016/j.biortech.2014.10.121
  18. Rivera-Hernández Y, Hernández-Eugenio G, Balagurusamy N, et al. *Sargassum*-pig manure co-digestion: An alternative for bioenergy production and treating a polluting coastal waste. *Renewable Energy*. 2022, 199: 1336-1344. doi: 10.1016/j.renene.2022.09.068
  19. Prakoso T, Rustamaji H, Yonathan D, et al. The Study of Hydrothermal Carbonization and Activation Factors' Effect on Mesoporous Activated Carbon Production From *Sargassum* sp. Using a Multilevel Factorial Design. *Reaktor*. 2022, 22(2): 59-69. doi: 10.14710/reaktor.22.2.59-69
  20. Paletta R, Candamano S, Filippelli P, Lopresto CG. Influence of Fe<sub>2</sub>O<sub>3</sub> Nanoparticles on the Anaerobic Digestion of Macroalgae *Sargassum* spp. *Processes*. 2023, 11(4): 1016. doi:10.3390/pr11041016.
  21. Sluiter, A. et al. Determination of total solids in biomass and total dissolved solids in liquid process samples. *National Renewable Energy Laboratory*; 2008. pp. 3–5.
  22. Mohamed MA, Nourou D, Boudy B, et al. Theoretical models for prediction of methane production from anaerobic digestion: A critical review. *International Journal of Physical Sciences*. 2018, 13(13): 206-216. doi: 10.5897/ijps2018.4740
  23. Campuzano R, González-Martínez S. Characteristics of the organic fraction of municipal solid waste and methane production: A review. *Waste Management*. 2016, 54: 3-12. doi: 10.1016/j.wasman.2016.05.016
  24. Sailer G, Eichermüller J, Poetsch J, et al. Characterization of the separately collected organic fraction of municipal solid waste (OFMSW) from rural and urban districts for a one-year period in Germany. *Waste Management*. 2021, 131: 471-482. doi: 10.1016/j.wasman.2021.07.004
  25. Awasthi MK, Pandey AK, Bundela PS, et al. Co-composting of organic fraction of municipal solid waste mixed with different bulking waste: Characterization of physicochemical parameters and microbial enzymatic dynamic. *Bioresource Technology*. 2015, 182: 200-207. doi: 10.1016/j.biortech.2015.01.104
  26. Montingelli ME, Tedesco S, Olabi AG. Biogas production from algal biomass: A review. *Renewable and Sustainable Energy Reviews*. 2015, 43: 961-972. doi: 10.1016/j.rser.2014.11.052
  27. Derba K, Bencheikh-Lehocine M, Meniai AH. Study of Biodegradability of Organic Fraction of Municipal Solids Waste. *Energy Procedia*. 2012, 19: 239-248. doi: 10.1016/j.egypro.2012.05.203
  28. Rodríguez A, Ángel J, Rivero E, et al. Evaluation of the Biochemical Methane Potential of Pig Manure, Organic Fraction of Municipal Solid Waste and Cocoa Industry Residues in Colombia. *Chemical Engineering Transactions*; 2017. pp. 55-60.