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Improving the biogas performance of selected waste materials by substrate ratio optimization and microalgae addition

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Abstract. Biogas production has become a common practice for obtaining renewable energy, being implemented or expanded in many countries due to a large number of advantages. The organic material conversion to biogas may be improved and optimized by co-digestion that ensures a better supply of nutrients and oligo-minerals for the microbial population. Comparative assays were conducted on the co-digestion of selected waste under different mixing ratio to identify the optimal feedstock composition for a better biomethane production. Also, experiments investigated the influence of 5% microalgal biomass addition to the selected organic mixtures on biogas production and showed that the microalgal biomass slightly increased the biogas quantity and quality without causing any delay on the mass biodegradability. The anaerobic digestion of microalgae-additivated substrates may be used as optimization method to increase the economic profitability of the biogas plants. Further research is required to establish at which extent different percentages of microalgae may induce changes in the substrates biomethane potential.

Keywords: biogas, microalgal biomass, co-digestion, optimization.

1. Introduction

Biogas technology has received special attention in the past decades as it is a promising alternative to disposal organic waste and produce green energy for electricity supply, heating, cooling, transport and fuel gas, with additional

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economic, environmental and climate benefits [1]. Biogas from waste and residues can play a critical role in the energy future and increase the security of the energy supply [2]. Renewable energy sources will reduce the need to import fossil fuels and will ensure heating, gas and power supply for isolated consumers [3], while the fertilizers generated as by-products from the biogas units can sustain the ecological agriculture. However, the performance of waste conversion into biogas still remains a crucial issue and this has caused many research initiatives to improve the process efficiency.

During the anaerobic digestion process of organic materials, particular attention need to be given to certain parameters known to directly affect the process efficiency and the biogas production rate [4]; they should be carefully monitored to avoid major imbalances that would significantly slow down or even stop the biogas production.

Anaerobic digestion is carried out by a complex consortium of bacteria which is sensitive to parameters such as temperature, pH, minerals, nature of substrate, organic loading rate, volatile fatty acids, design of digester etc. [5]. The inoculum to substrate ratio is also very important as it can determine higher or lower biogas and methane yields [6]. The chemical degradation of biopolymers such as cellulose, starch and other polysaccharides was studied by some scientists who proposed reliable mathematical models describing the dynamics of hydrolysis of polysaccharides from a vegetal material, to help in a better understanding the experimental data obtained for the biomass decomposition through biochemical processes [7]. Many experimental studies have shown that for an optimal anaerobic digestion, C/N ratio should be 20-30/1 [6,8,9,10].

Despite many advantages that the biogas technology may bring to environment and energy sectors, the efficiency of anaerobic digestion is questionable and may be limited by many factors such as inadequate amount and diversity of waste from a single resource, which is insufficient for large-scale bioreactors, as well as the limitations of using single substrates, such as improper carbon-nitrogen ratios, low pH of the substrate high concentrations of ammonia etc. Therefore, co-digestion of mixture substrates for biogas production has recently attracted more interest [10]. Co-digestion is a process optimization option that utilizes nutrients and bacterial diversity in selected wastes to ensure a better nutrient balance and improve the efficiency of the substrate biotransformation [6,11].

In their research, Callaghan et al. showed that increasing the proportion of fruit and vegetable waste from 20% to 50% as co-substrate to cattle slurry in a mesophilic anaerobic digester improved the methane yield from 0.23 to 0.45 m^3 CH4 kg^{-1}VS added [12]. Maragkaki et al. found that food waste, cheese whey and olive mill wastewater addition to sewage sludge can boost biogas yields by 1.2–2.7 times [13]. Ara et al. shown that the mixture of organic fraction of municipal solid waste, thickened waste activated sludge and primary sludge generated up to 135.6% more biogas than the calculated expected biogas yield from the corresponding individual substrates [14].

Numerous researchers demonstrated that using micro- and macroalgal biomass as co-substrates in AD may improve the biogas yields because of positive synergisms formed in the anaerobic digestion medium and the source of nutrients (mainly nitrogen) from the algal co-substrates [15]. Co-digestion of algal biomass with other waste substrates have various benefits such as improved C/N ratio, buffer capacity, dilution of inhibitory compounds, enhanced nutrient balance and digestion [6,15].

Even a small improvement in the process leading to a better biogas yield is considered to be highly beneficial at industrial level in terms of commercial prospective [16]. Hence, adjusting the proportions of mixture substrates in anaerobic co-digestion to obtain suitable feed characteristics, such as the C/N ratio, pH and nutrients, is an effective way to achieve desired digestion performance [10].

The main objectives of the present study were to comprehensively analyze the influence of the microalgae biomass addition to various mixtures of vegetal substrate and to evaluate the process stability towards biogas production in a batch laboratory scale anaerobic co-digestion. This experimental research is a preliminary assessment of the energy potential of vegetal and algal residuals and is useful for the development of efficient functional models to be implemented at organic waste generators.

2. Materials and methods

For this experimental work, several types of agro-industrial residuals were used to prepare the substrates for anaerobic digestion. They were provided by INCDCSZ Brasov and consisted of: beet root waste (BW), potato waste (PW), corn silage (CS), cow dung (CD) and chicken manure (CM). Dry powder of microalgal biomass was supplied by INCDCP-ICECHIM Bucharest. Inoculum was acquired from an industrial biogas plant using as feedstock various organic waste and wastewaters. Samples were grounded to get a granulation less than 10 mm using a stainless steel-bladed chopper, after which representative samples were subjected to physico-chemical analysis to determine total solids (TS), volatile solids (VS), carbon (C) and nitrogen (N). The organic residuals were stored in the freezer before substrate preparation for anaerobic digestion.

The anaerobic digestion experiments were conducted using a laboratory experimental set-up consisting of 8 dark glass fermentation bottles of 240 mL, being connected via Teflon tubes to 5 L gas collecting bags. The bottles were sunk to the neck in a thermostatic water bath to insure constant temperature of 37±1°C during the experiment. Fig. 1 presents the experimental set-up used for the anaerobic digestion tests.

The reaction bottles were fed with the substrate mixtures and anaerobic conditions were created by flushing argon for 3 min. in the bottles headspace. The fermentation bottles were tightly closed and sealed to ensure no gas leaks, then placed in the water bath. The substrate homogenisation was done manually, by gently shaking the fermentation bottles twice a day.

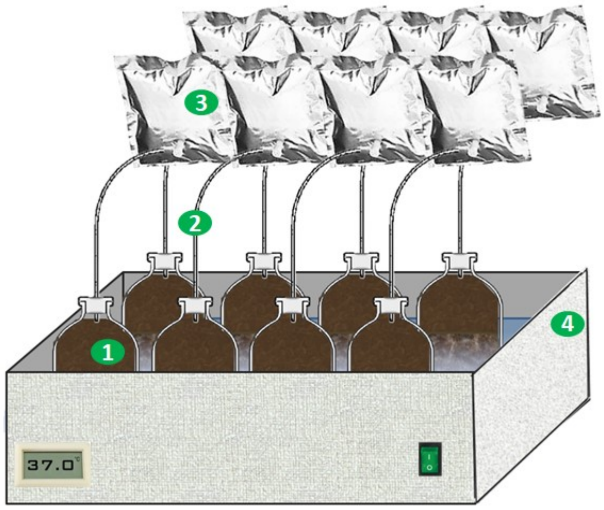

Fig. 1. Laboratory experimental set-up for the anaerobic digestion tests (1- dark glass fermentation bottle; 2-connection tube; 3-gas collecting bag; 4-thermostatic water bath).

Co-digestion experiments were aimed at identifying the optimal feedstock composition for enhanced biomethane production, as well as investigating the influence of 5% microalgal biomass addition on the substrate digestibility. For this purpose, the biomethane potential tests (BMP) were carried out for the following 8 samples: 4 samples of different mixtures of BW, PW, CS, CD and CM, inoculum and water (tests no. 1, 2, 3 and 4) and 4 microalgae-additivated samples of the same mixtures as 1, 2, 3 and 4 but enriched with 5% (relative to substrate TS) microalgal biomass (tests no. 1A, 2A, 3A and 4A). The mixing ratio for each substrate was decided in order to obtain a C/N value in the range of 20-25 which is indicated in the literature as being the optimum range to maximize the biomethane yield by ensuring proper growth of the anaerobic bacterial community [10,17]. The TS concentration of the substrate in the total fermentation mass was set to 10% and the seeding inoculum was 1/3 from the total fermentation mass. Water was added to fill up to the total reaction volume of 150 mL. The substrate composition for each test is given in Table 1. After 2-3 days of anaerobic digestion, the substrates started to produce biogas in noticeable quantities. The generated biogas was periodically sampled and qualitatively analysed for biomethane composition using a Varian GC-450 gas chromatograph coupled with flame ionization detector (FID), after preliminary calibration with methane standard, on a low polarity capillary column (100% polydimethylsiloxane, 15 m x 0.25 mm; 0.25 mm film thickness).

Table 1 Tests for anaerobic co-digestion optimization

Test no.	Substrate composition					Substrate characteristics			Additive
	BW (%)	PW (%)	CS (%)	CD (%)	CM (%)	TS (g/L)	VS (g/L)	C/N	Microalgal biomass (%)
1	10	10	30	20	20	99.99	83.72	24.90	-
1A	10	10	30	20	20	99.99	83.72	24.90	5
2	10	20	10	40	20	100.08	81.49	24.31	-
2A	10	20	10	40	20	100.08	81.49	24.31	5
3	10	10	20	30	30	100.13	79.05	22.92	-
3A	10	10	20	30	30	100.13	79.05	22.92	5
4	5	10	20	40	25	99.86	78.99	21.57	-
4A	5	10	20	40	25	99.86	78.99	21.57	5

The quantification of biogas production was achieved by the water displacement method, according to Moletta and Albagnac [18], knowing that the volume of water displaced by the biogas pumped into the upper space of the inverted measuring cylinder is the same with the biogas volume.

3. Results and discussions

Biogas production for the 4 mixtures of samples prepared for anaerobic co-digestion, representing a total of 8 samples with and without the addition of microalgal biomass, is shown in Fig. 2a, b.
It can be noticed that for all 8 samples undergoing anaerobic co-digestion, biogas production started relatively quickly, this allowing that biogas production and composition be quantified starting with the second day of fermentation. The inoculum source likely played an important role in the accelerated start of substrate degradation, being previously used for the anaerobic digestion of similar organic residuals at the industrial biogas plant [19]. The microbial community in the inoculum was thus easily adaptable to the new substrate compositions and experimental process operating conditions [20]. Moreover, the growth profile in biogas and biomethane production indicates, on the one hand, very rapid accommodation of fermentative microorganisms with the organic substrate and, on the other hand, very optimal conditions of microbial growth, without the presence of inhibitory substances.

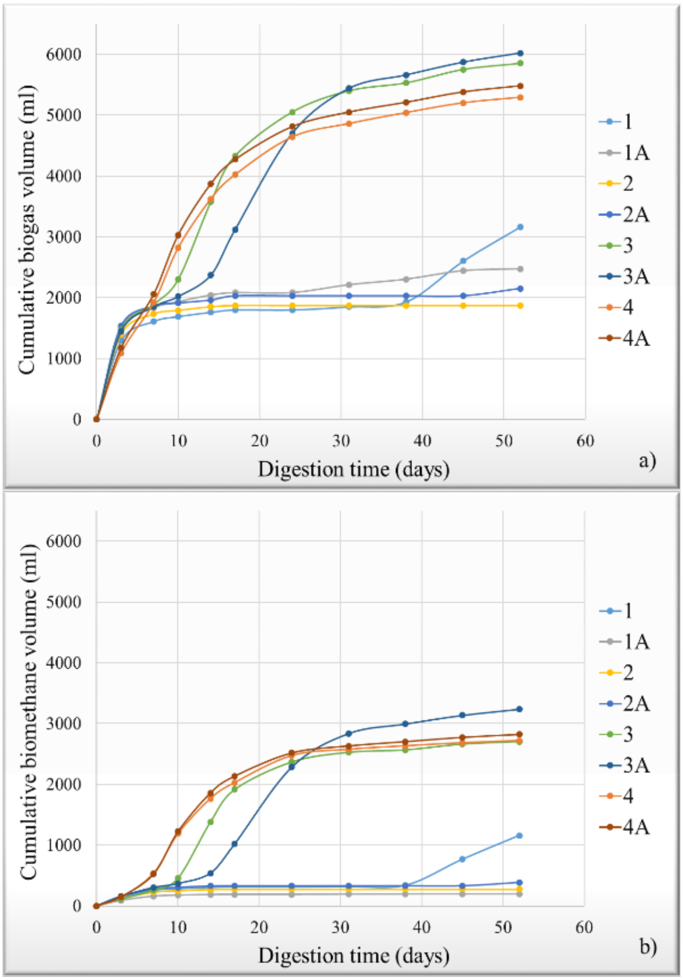

Fig. 2. Biogas (a) and biomethane (b) total production (mL).

It is generally observed that a proper composition of the feedstock is required so as to keep the C/N ratio in the optimal range of 20-30/1. Vegetable materials usually have a high carbon content and a C/N ratio above the recommended level for optimal anaerobic digestion, which causes methane production process inhibition due to excess organic acids. On the other side, the excess protein content of algal biomass leads to a low C/N ratio (< 10) and this would be a critical issue for algae mono-digestion since the anaerobic degradation of protein-rich compounds produces excess ammonia that is a strong inhibitor for methanogens. In this context, adjusting C/N ratio and mixing the vegetal substrate with nitrogen-rich materials is an option that increases the quality of the generated biogas and makes the process efficient, practicable and economical. The production of biogas and biomethane, respectively, increased steadily and rapidly in the first 5 days of anaerobic digestion, both for the organic mixtures without microalgal biomass and for the additivated samples. Samples 1, 1A, 2 and 2A have shown a sudden slowdown in biogas production after the first week of fermentation, indicating either a rapid exhaustion of organic matter or more likely biochemical imbalance that negatively affected the fermentation microbiota. The high complexity of the organic biopolymers in the substrate, coupled with the very diverse microbial species that require different growth conditions could explain the significant oscillations of the biomethane concentrations over the digestion experiments [21]. For samples 1 and 1A this behavior can be attributed to the larger amount of corn silage (CS) from the mixture, which probably caused an increase in volatile fatty acid concentration in the fermentation slurry and acidic inhibition. However, sample 1 demonstrated an increase in biogas and biomethane production after 40 days of fermentation, indicating a restoration of the biochemical balance. For samples 2 and 2A, the reduction of biogas and biomethane production can be attributed to the CD to CM ratio, many studies showing that a higher CD:CM ratio may produce better biogas yields than in the case of a higher percentage of nitrogen-rich CM, which can lead to ammonia inhibition [22, 23,24]. The sample mixtures 3, 3A, 4 and 4A recorded an accelerated and continuous increase in biogas production even after the first week of fermentation but gas production slowed down after approx. 30 days of experiment. Also, it can be observed that biomethane production increased more vigorously after 7 days of fermentation for samples 4 and 4A, but samples 3 and 3A showed a slight delay in the production of biomethane, which was accelerated after 10 and 14 days of fermentation, respectively, and decreased after 25 days of experiment. Figure 3 shows the biomethane potential (BMP) of the 8 samples, expressed in mL CH_4/gVS.

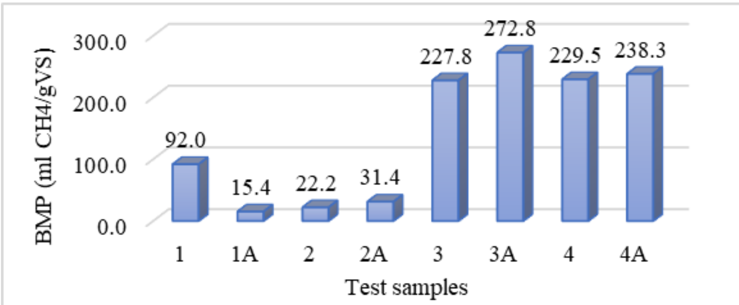

Fig. 3. Biomethane production of the test samples.

The highest BMP of 272.8 mL CH_4/g VS was recorded for the sample 3A consisting of BW, PW, CS, CD, CM in the ratios of 1:1:2:3:3, additivated with 5% microalgal biomass, while the lowest BMP of 15.4 mL CH_4/gVS was obtained for the sample 1A consisting of BW, PW, CS, CD, CM in the ratios of 1:1:3:2:2, additivated with 5% microalgal biomass. In fact, samples 3 and 4 with and without the addition of microalgal biomass have proven a much better fermentation efficiency than samples 1, 1A and 2, 2A.

The highest biomethane concentrations (HC) in biogas as daily measurement for the 8 samples of the substrate subjected to the experiments, and the maximum biomethane concentrations as the average of the measurements over the entire fermentation time length (AC) are shown in Table 2.

Table 2. Biomethane concentrations in biogas.

Sample	HC (%CH_4)	AC (%CH_4)
1	69.8	36.6
1A	21.2	7.8
2	39.0	14.5
2A	50.8	17.8
3	72.9	46.2
3A	79.7	53.7
4	72.3	51.3
4A	75.8	51.4

Hence, it is obvious that the mixture of components but also the contribution of micronutrients are essential factors in attaining a favorable fermentation environment, implicitly in the production of biogas and biomethane. Although the microalgae have relatively high nitrogen inputs, the large biogas and biomethane yields of samples 3, 3A, 4 and 4A indicate that the addition of microalgal biomass is not able to produce ammonia inhibition. It can be presumed that mixture synergies within the fermentation mass could more strongly influence the biogas production than some soft variations in the substrates C/N [17,25]. Basically, these experimental results revealed that the influence of the microalgal extract on mixtures of organic materials selected for fermentation has been shown to softly stimulate biogas production and increase biomethane yield, except for the mixture 1 represented by BW, PW, CS, CD, CM in the ratios of 1:1:3:2:2 for which the addition of microalgae has been process inhibitory. These relatively inconclusive results indicate that research should continue on samples with other mixing ratios between residual materials and microalgae, many previous research results published in scientific literature demonstrating that up to a certain concentration microalgal biomass may have a stimulating or inhibitory effect on a particular mixture, but might have the opposite effect at higher concentrations of algae.

The significant differences noticed in the biomethane concentrations in biogas for the selected mixtures tested in this research are clearly indicating the high importance of the chemical and microbial interactions which are influenced by the specific substrate composition. Therefore, the preliminary experimental researches are essential to determine the optimal mixing ratios of raw materials used to prepare the digestion substrates for a profitable waste treatment and energy generation in large-scale applications.

4. Conclusions

One of the most cost-effective and reliable technologies for organic waste sustainable management is anaerobic digestion which may bring multiple environmental and economic benefits. Numerous laboratory researches address the identification of process optimization options that aim at increasing the economic profitability of the large-scale biogas units.

The purpose of this research was to determine the biogas and biomethane potential of several mixing ratios of beet root waste (BW), potato waste (PW), corn silage (CS), cow dung (CD) and chicken manure (CM) and to assess the contribution of 5% microalgal biomass addition in improving the process performances and the biomethane production by co-digestion batch experiments.

The experimental results proved that the ratio of different materials is an important factor in creating an optimal nutrient balance to facilitate the activity of methanogens; the biomethane concentration and the biogas volume were strongly influenced by the quality of the fermentation substrate, specifically by the organic wastes mixing ratio. Also, the experiments showed that microalgal biomass slightly enhanced the biogas production of the selected substrate mixtures, although one sample mixture exposed the opposite effect. The highest biomethane potential of 272.8 mL CH_4/g VS was recorded for the sample consisting of BW, PW, CS, CD, CM in the ratios of 1:1:2:3:3, additivated with 5% microalgal biomass, while the lowest BMP of 15.4 mL CH_4/gVS was obtained for the sample consisting of BW, PW, CS, CD, CM in the ratios of 1:1:3:2:2, additivated with 5% microalgal biomass.

This preliminary research opens the way for further more in-depth experimental studies to involve different concentrations of microalgal biomass as a co-digestion additive in order to certify the microalgal biomass effect on biogas production.

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