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Valorization of food waste leachates through anaerobic digestion.

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Abstract: According to European Union data, on average 173 kg per person of total food waste (organic waste) are produced annually, of which 92 kg per person come from households (organic waste). Food waste is defined the waste from household, restaurants, canteens, food industries as well as markets. The importance of food waste stretches from environmental pressures to economic and social impacts. An Environmental technology for the biodegradation of food waste is anaerobic digestion. Is a very attractive technique and combines waste treatment and renewable energy recovery. This study investigates the characteristics of food waste leachates from composting buckets and their valorization as substrate for anaerobic digestion process.

A complete characterization of different food waste leachates was conducted (pH, COD, VFAs, heavy metals etc.). Food waste leachates proved to be an ideal feedstock for anaerobic digestion. In this direction, batch tests were performed to evaluate the methane yield of food waste leachates under different operating conditions. Three different SIR ratios were tested (0,5, 1,0 and 1,5). A SIR equal to 0.5 proved to be the as the higher methane yield was achieved. The removal of COD under all operating conditions was higher than 70% with the higher removal (85,18%) for an SIR equal to 1.5.

Keywords: food waste leachates ; Anaerobic digestion ; SIR ; VFA ; heavy metals ;

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1. Introduction

Anaerobic digestion is an environmentally favourable technology and the most widespread good practice for the biodegradation of household waste. Anaerobic Digestion is a complex biochemical process in which organic material is decomposed by several groups of microorganisms in the absence of oxygen while renewable energy such as biogas is generated.

This technique is very attractive, combines waste treatment and renewable energy recovery. In addition to these two benefits, anaerobic digestion also reduces the odor of waste material while the digestate is rich in nutrients that can be used as fertilizer after the process of fermentation.

It is important to mention that, for this technology, monitoring of significant factors [1] is essential, such as: pH, Total Solids (TS), Volatile Solids (VS), Ammonium (NH_4^+), Chemical Oxygen Demand (COD), Alkalinity, Volatile Fatty Acids (VFAs), Total Organic Carbon (TOC) and Total Nitrogen (TN).

2. Materials and Methods

2.1 Sampling and pretreatment

Compost leachates were collected during the period May 2020 to May 2021. They are mainly consisting of fruits and vegetables, and their sampling procedure were from different stages of the composting process.

Specifically, collected samples before their composting for analysis as raw materials and leachate of compost samples in a pre-compost phase. The samples were collected from specific sampling spots. Composting containers were placed in public markets for the collecting of the food waste. In the period during October 2020 to May 2021 the samples were leachates from mechanical composting plant and waste transfer stations. They came from different cities of the Region of Western Macedonia, in Greece. Sample codes, their origin and dates of sampling are presented in the following Table 1. For each sample, 1,5 L of compost leachates were collected and delivered to the laboratory of CERTH in Ptolemais, within 24h. Depending on the test method, samples were filtered through membrane filter (glass fiber, 0,45 syringe filter etc.), acidified and centrifuged (HPLC analysis). A portion of the filtrated liquid was freeze-dried, and the remaining was stored at $4^{o}C$ before further analysis.

Table 1. Description of the Samples

Date of Sampling	Sample Name	Description of Sample
1/6/2020	S1	Raw material from bucket of public market
12/6/2020	S2	Raw material from bucket of public market
22/6/2020	S3	Raw material from bucket of public market
22/6/2020	S4	Raw material from bucket of public market
3/11/2020	S5	Leachate from mechanical composting plants
22/12/2020	S6	Leachate from mechanical composting plants
17/3/2021	S7	Leachate from waste transfer station
17/3/2021	S8	Leachate from waste transfer station
28/4/2021	S9	Leachate from waste transfer station
28/5/2021	S10	Leachate from waste transfer station

2.2 Analytical methods

The measurements of TS, VS, COD, NH_4^+, Alkalinity, TOC and TN were carried out according to APHA Standard Methods [2], The pH was measured using a digital pH-meter (Hanna, HI2260). The quantification of major and trace metals was carried out according to APHA Standard Methods and ISO 15586 and a Graphite Furnace Atomic Absorption Spectrophotometer was used (Shimadzu GFA-EX7i AA-6300). For the quantifications of TOC and TN, a TOC analyzer (Shimadzu, TOC-L) was used.

Finally, the quantification of VFAs was carried out by an HPLC. A portion of 100 ml filtered sample was acidified with 30 μL of H_3PO_4 (HPLC grade) and centrifuged at 10.000 rpm for ten minutes Also, VFAs from anaerobic digestion process, were determined according to the Kapp method [3].

2.3 High performance liquid chromatography

The used separation module Ecom, ECB2000, was equipped with pump and degasser (Ecom, ECP2000), oven (Ecom, ECO2000), diode array detector (Ecom, ECDA) and coupled with a RP-C18 column (Fortis Technologies, 250X4,6mm, 5um). Spectra were obtained between 200 and 230 nm. Isocratic elution procedure applied to the mobile phase (0,02mol/l KH_2PO_4/methanol) stable at 98:2 for 50 min. The mobile phase was acidified with H_3PO_4 to reach pH 2,88. The flow rate was 0,6 ml/min at 35 ^{o}C and 20μl injection volume [4]. Standard stock solution containing 100mg/l of the organic acids (Acetic, propionic and butyric acids) prepared in ultrapure water.

2.4 Inoculum and Substrate

Anaerobic sludge was used as inoculum (microbial culture) for the biomethane potential test arrays and obtained from a commercial mesophilic anaerobic digester plant in the area of Eordea (Western Macedonia).

The substrate for the digestion process was the sample S9 (Table 1) because of the C/N ratio (Table 2). Three ratios SIR (Substrate to Inoculum Ratio) were monitored for biomethane potential, 1,5, 1,0 and 0,5. The calculation for the SIR ratios were determined according to the VS of the substrate and the inoculum. . During start-up, flushing with N_2 took place and all samples were incubated at mesophilic conditions (35 +/-2°C) throughout the experimental process. All batch tests were performed in triplicate.

2.5 Biomethane Potential Test

BMP tests are a technique to determine the methane potential and the biodegradability of any type of waste [5]. Batch experiments carried out using the Automated Methane Potential Test System II (AMPTS II). Each of the AMPTS' bioreactors had 500 ml bottles with 400ml working volume and 100 ml headspace, was equipped with an individual mechanical stirrer and operated as a bench scale anaerobic glass bioreactor. The produced biogas from each glass bioreactor passed through a 3 M NaOH solution which retained CO_2 and H_2S. The upgraded biogas passed through a flow cell (one for each glass bioreactor) which measured gas productivity through water displacement. The digital impulse was registered by a computer [6, 7]. The results of BMP test experiments are expressed as normalized mL.

3. Results

The results of complete characterization of samples S1 to S10, are summarized below in Tables 2 to 3. The significant variation of leachate characteristics could be attributed to the impact of factors that affect quality and quantity, including waste composition, age of the waste and the composting technology used [8]. The leachate obtained was brown with an unpleasant odor that could be attributed to the organic acids and volatile fatty acids produced from composting food waste. Other volatile nitrogen and sulfur compounds could also have contributed to this odor [9].

The accumulated biomethane yields and the production flows of the three SIRs are shown in Fig.1. Tables 4 and 5 shown the main characteristics of the inoculum and feedstock. Figure 1 illustrates the accumulated Nml CH_4/g VS (a) and the Flow rate (Nml/day) of the three SIR ratios. Table 4 summarizes the composition of the SIR feedstock and inoculum used in the batch test. Finally, table 5 depicts the main characteristics of each bench scale bioreactor during the start-up phase and after the end of the batch experiment.

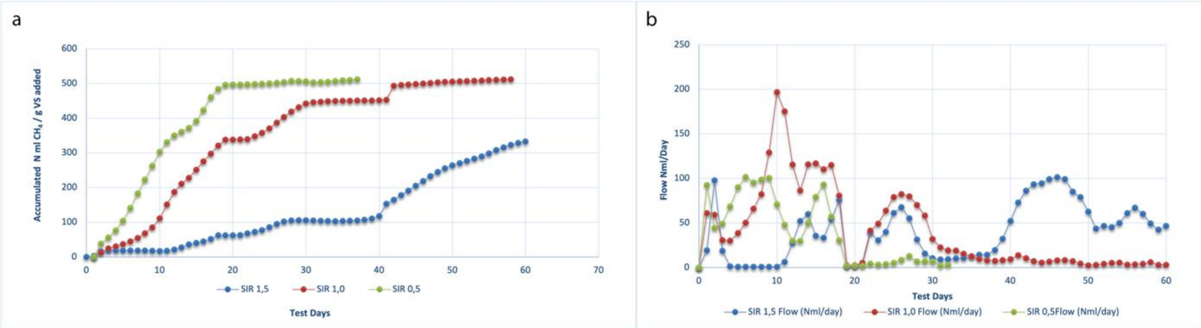

Figure 1. (a)Accumulated Nml CH4/g VS added of SIR 0,5, 1,0 and 1,5. (b) Flow (Nml/day) of SIR 0,5, 1,0 and 1,5.

Table 2. Complete characterization of compost leachate. VFAs represent the cumulated concentration of acetate, propionic and butyric acid.

Parameter	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
pH	4,29	4,65	4,52	3,84	4,02	4,82	4,35	4,91	4,48	4,05
TS (g/l)	118	24	69	114	36	18	33	26	41	60
VS (g/l)	98	14	45	100	28	14	25	17	31	48
COD (mg/l)	47202	49500	51800	38850	53924	16620	40154	25102	25601	31794
NH_4^+ (mg/l)	470	956	985	212	134	138	104	303	484	117
TOC (mg/l)	15580	14150	14140	34430	13930	7368	9990	19885	16660	3692
TN (mg/l)	2558	3435	3588	3973	579	267	314	511	771	273
VFAs (g/l)	30508	18349	16041	37046	41780	8847	12768	14874	21613	24946
C/N ratio	6,1	4,1	3,9	8,7	24,1	27,6	31,8	38,9	21,6	13,5

Table 3. Major and minor trace elements of compost leachate.

Parameter (mg/l)	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Na	6208	7210	7506	7005	3980	2075	233	577	552	1251
K	874	869	891	1329	145	280	1011	1320	1905	2779
Mg	337	227	226	532	370	166	90	316	168	895
Zn	1,4	2,1	2,1	4,3	4,0	1,4	12	27	18	16
Fe	203	335	340	164	281	357	1,4	0,5	31	32
Cu	0,3	0,3	0,5	0,6	0,6	0,2	0,6	0,3	1,1	1,6
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Ni	nd	nd	nd	nd	nd	nd	1,5	1,0	1,2	2,5
Cr	nd	nd	nd	nd	nd	nd	1,2	3,4	3,3	2,6
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Mn	nd	nd	nd	nd	nd	nd	1,2	1,2	3,8	3,4

Table 4. Composition of the SIR feedstocks and inoculum used in the batch experiments in bench scale bioreactors.

Parameter	Inoculum	FW (0,5)	FW (1,0)	FW (1,5)
Alkalinity (mg/l CaCO3)	15000	3225	4150	5075
VS (mg/l)	24000	2400	4800	7200
COD (mg/l)	22820	8173	16047	23921
NH_4^+ (mg/l)	972	67	83	103
TOC (mg/l)	6623	952	1940	2930

Table 5. Main characteristics of each bench scale bioreactor during the start-up phase and after the end of the batch experiment. VFAs rep-resent the cumulated concentration of acetate, propionic and butyric acid.

Parameter	**FW (0,5)**		**FW (1,0)**		**FW (1,5)**	
	Initial Concentration	Final Concentration	Initial Concentration	Final Concentration	Initial Concentration	Final Concentration
pH	6,41	7,95	6,03	7,79	5,80	7,88
VS (g/L)	19,54	2,65	31,6	4,24	47,38	4,71
VFAs (mg/L HACeq)	4371	1678	5175	1076	9366	948
NmL CH_4/g VS	512,00		511,76		333,02	
COD (mg/L)	7138	1204	12451	3349	26880	3983
NH_4^+(mg/L)	552	1053	818	1553	669	1355
Test Days	32		60		60	

4. Discussion

The pH values of samples ranged between 3,84 to 4,91. According to literature [10], at the process of degradation of organic material, carbon dioxide and a low amount of ammonia are produced and these two products have further resulted in the formation of ammonium ions and carbonic acid. The carbonic acid dissociates to produce hydrogen and bicarbonate ions, which influence the level of pH.

Solids (TS, VS) are influenced by the total amount of dissolved organic and inorganic material. According to the literature a typical leachate ranged from 0,589-196 g/L[8]. The present values in this study remain within this range, and the range of volatile solids is between 13,5 g/L to 98 g/L.

The range of TOC values is between 3.500 mg/L to 35.000 mg/L. The TOC content decreases during composting due to the microorganisms activity [11] and the further degradation of organic substances necessary for their metabolism.

Nitrogen is oxidized mainly to ammonium and to nitrite and subsequently, to nitrates when nitrification is achieved [10]. The values of ammonium range between 985 mg/L to 134 mg/L and Total Nitrogen between 3.973 mg/L to 267 mg/L.

The COD values include the oxygen demand created by biodegradable as well as non-biodegradable substances. COD is highly variable and this is due to the food waste composition and the climate characteristics [8], with reported values are varying between 16.620 and 53.924 mg/L.

Finally, the values of VFAs were present in high concentrations, that means the composting process is in an initial stage or it is a raw compost material and characterized as immature [12].

The batch experiments lasted 32 days for the SIR 0,5 and for 60 days SIR 1,0 and 1,5 respectively, until minimum or no biogas production was observed. Almost 2400 Nml and 2456 Nml methane were produced from SIR 1,5 and 1,0 respectively, and 1326 Nml methane from SIR 0,5. According to Figure 1a, the values of Nml methane correspond to methane yields 333,02 Nml CH_4/g VS added, 511,76 Nml CH_4/g VS added and 512 Nml CH_4/g VS added for SIR 1,5, 1,0 and 0,5 respectively. SIR 0,5 led to higher methane yield in 32 days instead of the other two SIR in 60 days. The degradation of VS, VFAs and COD for each SIR are shown in Table 5.

As illustrated in figure 1b, a high biogas flow rate was observed from the 1st day of the three SIR batch experiments and continued until the 19st day. Furthermore, the flow reduction for SIR 0,5 ceased at the 32nd day. SIR 1,0 displays a high flow rate until the 30th day. After the 30th day a continuous reduction of biogas flow rate was observed until it stops at 60th day. Finally, SIR 1,5, after the 30th day displays a continuous increase of biogas flow rate until the cease of the batch experiments test at the 60th day.

5. Conclusions

In this study the changes of food waste compost leachate were monitored with regard to the seasonality, the composting time and the biomethane yield in three different SIR. The compost leachate showed a high organic load that means an ideal substrate for composting or anaerobic digestion, but simultaneously showed high values of Volatile Fatty Acids, that means the compost is in the initial stages of the composting process and considered as immatured. Regarding the values of COD and total nitrogen, in this stage of the process, they are in high concentrations thus recommended to use the leachate in low application rates or after dilution.

Finally, food waste compost leachates could be characterized as an ideal substrate for anaerobic digestion. The three different food waste SIR ratios in the bench scale experiment, produced in sufficient quantity (expressed as Nml CH_4 /g VS added) biomethane, however the SIR 0,5 produced higher biomethane yield at the half days of the procedure. The degradation of the COD rates of the SIR 0,5, 1,0 and 1,5 were 83,13%, 73,11% and 85,18% respectively.

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