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Batch and continuous mesophilic anaerobic digestion of food waste: effect of trace elements supplementation

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Trace metals are essential for the enzyme cofactors involved in the biochemistry of methane formation and are needed in a balanced anaerobic digestion process. Food and kitchen waste generally contains low concentrations of trace elements, especially metals. As a consequence the anaerobic digestion process may result instable. The aim of this study is to evaluate the effect of metals addition on mesophilic anaerobic digestion of food waste, both in batch tests and in laboratory scale CSTR reactors.
Batch anaerobic trials using source-separated food waste as substrate with inoculums of different origins were carried out under mesophilic conditions. Reactions were operated both with and without trace elements (Co, Mo, Ni, Se, W) supplementation. Supplementation with trace metals had either neutral or slightly negative effects with inoculums originating from reactors with a high background level of metals, such as those for the co-digestion of biowaste and waste activated sludge. For inoculums from reactors treating food waste only, which inherently contain low levels of trace metals, supplementation with these metals increased methane production. In particular, Mo concentrations in the range of 3-12 mg/kgTSfed and Se concentrations of 10 mg/kgTSfed increased methane production to as high as 30-40 %. Supplementation with a metal mixture (Co, Mo, Ni, Se, W) increased the methane production to the range 45-65 % for inoculums with low background concentrations of trace metals. These findings demonstrate the importance of Co, Mo, Ni, Se, W for high-performance anaerobic digestion process.
Trace metals additions that showed the best batch results (100mgNi/kgTSfed, 100mgCo/kgTSfed, 6mgMo/kgTSfed, 10mgSe/kgTSfed, 10mgW/kgTSfed) were selected for CSTR experimentation. Performances of a continuous anaerobic digester fed with trace elements were compared to a “control reactor” fed with the same substrate but without metals addition. Preliminary CSTR results showed that metals addition allowed for a stable anaerobic digestion process at Organic Loading Rate greater than 3 $kgVS_{fed}$ m^3•d but were not essential.

1. Introduction

The introduction of separated collection for different fractions of municipal solid waste (MSW), in addition to subsidies for renewable energy production, have been the main drivers for the implementation of the anaerobic digestion (AD) of biowaste in recent years (De Baere, 2006). Food/kitchen waste originating from door-to-door collections contains low levels of inert materials and is a suitable substrate for AD, enabling biogas productions as high as 180 m^3/tonne of waste treated (Bolzonella, 2006). On the basis of this figure, complete anaerobic digestion of the biowaste collected in the EU-27 area could generate approximately 35,500 MWh/d of electric power, assuming an organic material collection rate of 0.2 kg/person/day. On the other hand, biogas can be converted into methane for a total energy recovery.
In recent years, several studies have pointed out how food and kitchen waste can present low concentrations of trace elements, especially metals, and thus determine the anaerobic digestion process failure (Banks et al., 2012). Specific trace metals such as Co, Ni, W, Se or Mo typically serve as cofactors in enzymes which are involved in the biochemistry of methane formation and are therefore essential for the

correct and balanced anaerobic digestion process (Schonheit and Thauer, 1979). In fact, if any required enzyme is limited, the total process may be disturbed (Kastner and Schnitzhofer, 2011) . For example, with specific reference to the role of the metals mentioned above, it has been reported in literature that Co is present in specific enzymes and corrinoids. A corrinoid, such as vitamin B12, containing cobalt ion, is known to bind to coenzyme methylase which catalyses methane formation in both acetoclastic methanogens and hydrogenotrophic bacteria (Schonheit and Thauer, 1979).
The aim of this study is to investigate about the effect of trace metal supplementation on the mesophilic anaerobic digestion of foodwaste, both in batch tests and in laboratory scale CSTR reactors.

2. Materials and Methods

Batch and CSTR tests were performed under mesophilic (37 °C) conditions. Chemical analysis were performed according to the Standard Methods for the Examination of Water and Wastewater. Microbiological analysis were conduced according to APAT guidelines for compost analysis.
Both for batch and CSTR test, the substrate used was food waste (FW) collected in the Treviso municipality in north-eastern Italy. This material originated from a door-to-door collection scheme and was composed primarily of kitchen waste (Cavinato et al., 2011).

2.1 Batch tests

Preliminary batch tests were performed according to the guidelines given in Angelidaki et al. (Angelidaki et al., 2009). Batch anaerobic trials using a source-separated food waste as a substrate were performed with inoculums of different origins: one originated from an anaerobic reactor treating food waste and waste-activated sludge (called “Inoculum A”, high metal content) and the other originated from an anaerobic reactor treating food waste only (called “Inoculum B”, low metal content). Reactions were operated both with and without trace element (Co, Mo, Ni, Se, W) supplementation. The amounts of the trace metals to be added were determined by the quantities of each metal typically found in food waste, taking into consideration the typical requirements reported in literature (e.g., Banks et al., 2010 and Facchin et al., 2013). Four concentration levels were used to characterize the process and determine whether there are possible threshold effects or an inhibition level. The supplementation concentrations were calculated on a dry mass basis.

2.2 CSTR tests

Trace metals addition that showed the best batch results were selected for CSTR experimentation (Facchin et al., 2013). Trace elements addition in CSTR tests were: 100 mgNi/kgTS, 100 mgCo/kgTS, 6 mgMo/kgTS, 10 mgSe/kgTS, 10 mgW/kgTS.
Performances of a continuous anaerobic digester fed with trace elements and food waste (called R1) were compared to a “control reactor” fed with the same substrate but without metals addition (celled R2). The following Figure shows the experimental apparatus which comprised: thermostatic bath, reactors, hydraulic guards, Mariotte flasks for the measure of biogas production with “water displacement method” (Figure 1).

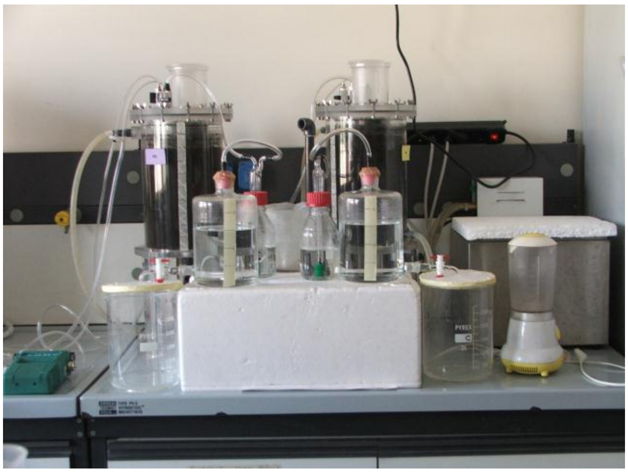

Figure 1: CSTR experimental apparatus.

3. Results and Discussion

3.1 Inoculums and substrate characterization

The food waste and the two inoculums used in this experimentation were characterized for both macro parameters and trace metal concentrations. Table 1 shows the characteristics of Treviso municipality, included microbiological analysis and Table 2 shows the representative characteristics of the inoculums.
The characterization of Organic Fraction of Municipal Solid Waste (Table1) was comparable with those reported in DEFRA (Banks et al., 2010). About characterization of inoculums, the measurements for both macro-parameters and trace metal were representative of this type of waste (Bolzonella D et al., 2006; Banks et al., 2010).
The characteristics of Inoculum A and B differed appreciably. Inoculum A showed greater levels of total and volatile solids, a very low level of volatile fatty acids, and a relatively high concentration of trace metals. Compared with the representative values found in Inoculum B, these concentrations were typically two to four times higher for most trace metals and up to 10 times for selenium (Table 2).

Table 1. Characterization of Organic Fraction of Municipal Solid Waste (OFMSW)

OFMSW	Units	Min value	Max value	Average
Total Solid	g/kg	223	237	226
Total Volatile Solids	g/kg	178	192	181
TVS %TS	%	79	81	80
COD	g/Kg TS	793	1075	970
Total Phosphorus	g/Kg TS	4.0	7.6	5.3
Total Kjeldhal Nitrogen	g/Kg TS	15.6	38.0	27.0
Nickel	mg/Kg TS	5.27	8.30	6.61
Cobalt	mg/Kg TS	0.78	1.25	1.01
Molybdenum	mg/Kg TS	< 0.02	2.09	1.62
Selenium	mg/Kg TS	< 0.02	0.37	0.17
Tungsten	mg/Kg TS	< 0.02	0.64	0.42
Total colony number at 36°C	CFU/g	1.4 • 10^7	8.8 • 10^8	4.47 • 10^8
Total Coliform	CFU/g	1.1 • 10^3	1.0 • 10^4	5.5 • 10^3
E.coli	CFU/g	2.0 • 10^3	1.0 • 10^4	6.0 • 10^3
Salmonella spp.	CFU/g	n.d	n.d	n.d.

Table 2. Characterization of Inoculum A originated from an anaerobic reactor treating food waste and waste-activated sludge and Inoculum B originated from an anaerobic reactor treating food waste only

Parameter	Units	INOCULUM A	INOCULUM B
Total Solid	g/Kg	41.2 ± 1.2	12.5 ± 0.5
Total Volatile Solid	g/Kg	23.4 ± 1.5	7.0 ± 0.3
TVS %TS	%	56.7± 2.3	55.0 ± 1.0
COD	g/KgTS	629.7 ± 8.4	571.5 ± 8.0
Total Phosphorus	g/KgTS	14.40 ± 2.35	9.20 ± 0.28
Total Kjeldhal Nitrogen	g/KgTS	41.90 ± 2.99	42.80 ± 1.84
N-NH3	mg/l	640 ± 49	884 ± 44
pH		7.6 ± 0.1	8.3 ± 0.1
Partial Alkalinity	mg$CaCO_3$/l	5339 ± 24	5040 ± 24
Total Alkalinity	mg$CaCO_3$/l	7343 ± 35	7767 ± 24
Volatile Fatty Acids	mgCOD/l	144 ±100	2500 ± 100
Nickel	mg/Kg TS	47 ± 2.0	24.2± 2
Cobalt	mg/Kg TS	7.4 ± 2	2.9 ± 2
Molybdenum	mg/Kg TS	15.9 ± 2	4.0 ± 2
Selenium	mg/Kg TS	9.1 ± 1	< 1
Tungsten	mg/Kg TS	5.2 ± 1	2.7 ± 1

3.2 Batch tests

The specific methane production values (as m^3/kgVS fed) at 37 °C measured during the BMP trials using inoculums A and B are reported in Figure 2 and Figure 3, respectively.

Using inoculum A, the digestion of food waste as the sole substrate generated approximately 0.76 m^3 of biogas per kg of VS added (57% CH4). The supplementation of Co, Mo, Ni, and W gave no or negative responses. On the other hand, the addition of Se, up to 2 mg/kg of dry matter, improved methane production (Figure 2). The observed increase was approximately 10 %, a value that is insufficient to justify the addition of this metal at large scale. These results are consistent with those reported by Ishaq et al. (Ishaq et al., 2005) indicating that the supplementation of unneeded metals may have negative effects on metabolic pathways of anaerobic digestion process.

For the batch trials using inoculum B, the addition of any metal or mix of metals was beneficial, with high variability. In particular, Mo in the range 3–12 mg/kgTS, Se at 10 mg/kgTS and the metals mix supplementation, consistently improved methane production, with the metals mix reaching improvement levels in the range of 60–70% (Figure 3).

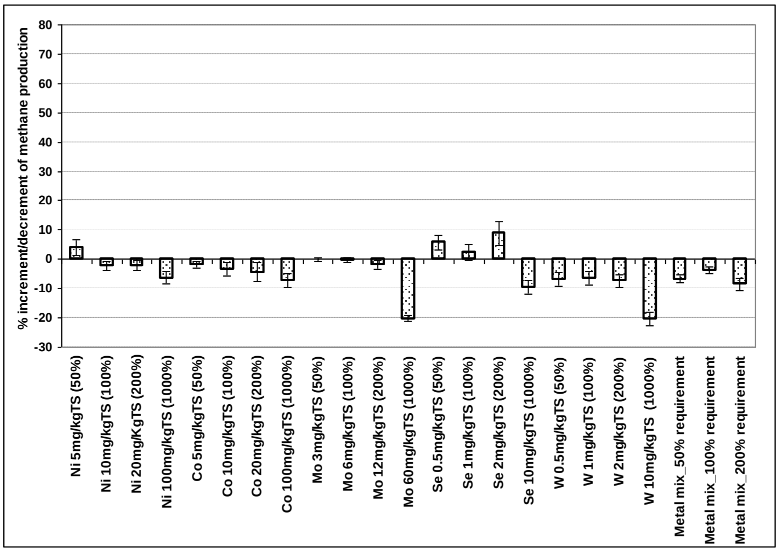

Figure 2: Histogram of increment or decrement on methane production of different condition tested compared to control test, expressed as a percentage. Results referred to Inoculum A

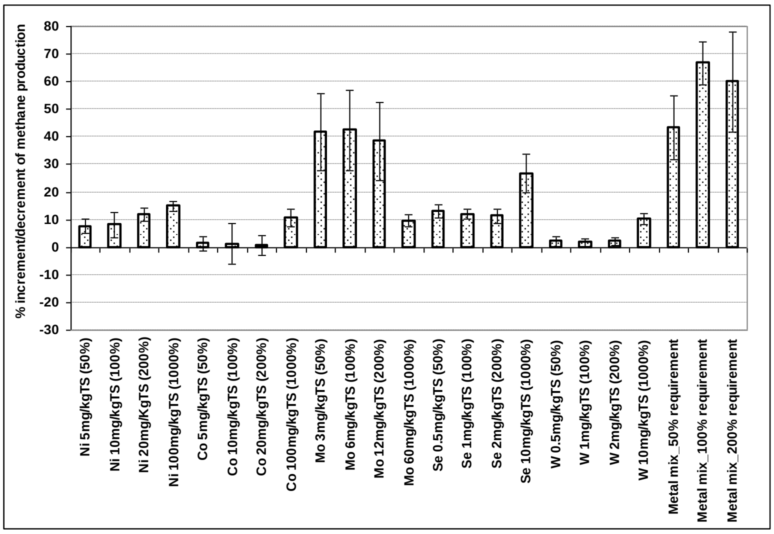

Figure 3. Histogram of increment or decrement on methane production of different condition tested compared to control test, expressed as a percentage. Results referred to Inoculum B

In these experiments, a threshold effect and a synergistic effect from the addition of all the trace metals could be observed (Facchin et al., 2013; Lindorfer et al., 2011).

Different Inoculum origin, and as consequence different background of trace metals, slightly influenced the effect of trace elements addition. These findings may have an important impact in the commercial production of methane from food waste.

3.3 CSTR tests

Trace metals additions that showed the best batch results (100 mgNi/KgTS$_{fed}$, 100 mgCo/KgTS$_{fed}$, 6 mgMo/KgTS$_{fed}$, 10 mgSe/KgTS$_{fed}$, 10 mgW/KgTS$_{fed}$) were selected for CSTR experimentation (Facchin et al. 2012). Performances of reactor R1 (with trace metals addition) and R2 (without trace metals addition) were compared in Figure 4 and in Table 3.

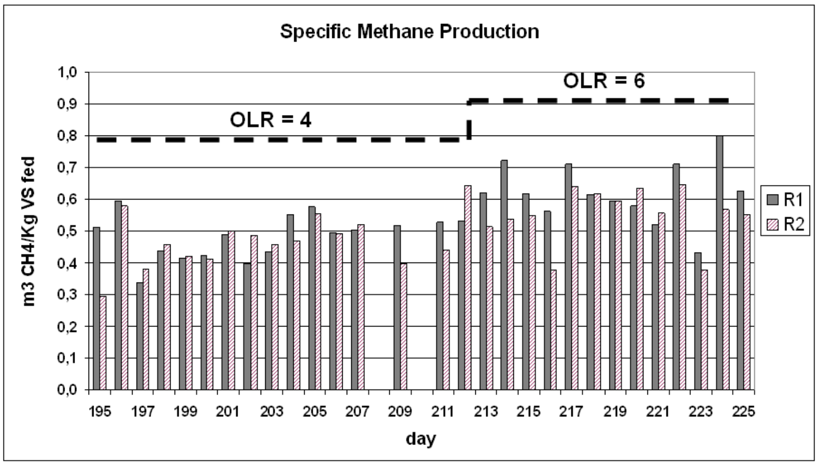

Figure 4. Comparison between Specific Methane Production of Reactor 1 and Reactor 2 during changing of OLR from 4 to 6.

Table 3: Results of reactors R1 and R2. For both reactors, the Oragnic Loading Rate (OLR) varied from 1,5 to 6 kgVSfed/ m3/d and the average Hydraulic Retention Time (HRT)of the entire period was 30 days. Trace metal addition started at the middle of OLR = 2,5 kgVSfed/ m3/d. n.d means "not detected"

		Reactor **R1** with trace metal addition					Reactor **R2** without trace metal addition				
Parameter	**Unit**	**OLR=1,5**	**OLR=2,5**	**OLR= 3**	**OLR= 4**	**OLR=6**	**OLR=1,5**	**OLR=2,5**	**OLR= 3**	**OLR= 4**	**OLR=6**
TS	**g/kg**	8.4	16.6	35.3	55.8	71.2	9.0	17.4	38.5	52.9	71.3
TVS	**g/kg**	5.6	10.8	23.6	35.7	43.1	5.7	11.6	25.6	33.5	41.8
TVS	**%TS**	61.1	64.5	66.6	63.9	60.6	63.5	66.2	66.3	63.2	58.7
TCOD	**g/Kg TS**	696	768	716	567	650	715	810	688	560.3	598.4
SCOD	**mg/l**	1,110	1,460	1,780	3,190	6,860	1,120	1,660	1,833	3,450	7,140
TKN	**g/Kg TS**	45.9	53.7	48.4	55.1	51.5	46.7	55.7	54.2	47.7	53.8
N-NH3	**mg/l**	325	402	696	1030	1044	325	403	681	1080	1138
TP	**g/Kg TS**	9.57	9.30	8.44	6.66	6.48	9.32	9.00	8.82	6.55	6.22
T.Alcalinity	**mgCaCO3/l**	4254	4086	6911	8678	9814	4285	4201	7052	8858	10007
P.Alcalinity	**mgCaCO3/l**	2565	2466	4242	5494	5919	2619	2516	4423	5579	6044
VFA	**mgCOD/l**	190	301	57	38	72	101	412	65	276	176
Formate	**mg/l**	4	7	7	6	0	5	12	14	12	7
Ni	**mg/Kg TS**	42.7	72.58	115.05	200.00	n.d.	42.4	26.5	27.3	18.3	n.d.
Co	**mg/Kg TS**	2.7	48.48	95.64	190.00	n.d.	1.5	1.74	1.79	2.21	n.d.
Mo	**mg/Kg TS**	4.62	6.75	9.50	15.00	n.d.	5.32	5.13	7.13	3.12	n.d.
Se	**mg/Kg TS**	0.50	2.68	5.00	4.80	n.d.	0.46	0.65	1.34	<0.05	n.d.
W	**mg/Kg TS**	0.70	6.22	11.21	21.20	n.d.	1.53	1.22	2.39	<0.03	n.d.
% CH_4	**%**	53	50	61	63	63	53	50	60	60	63
SGP	**m3/KgVS**	0.61	0.67	0.82	0.93	0.80	0.58	0.69	0.80	0.87	0.75
SCH_4P	**m3/KgVS**	0.32	0.27	0.50	0.59	0.51	0.31	0.28	0.48	0.53	0.47

Results demonstrate that R1 showed a more stable anaerobic digestion process during the Organic Loading Rate increase and an higher Specific Methane Production than R2, especially at high OLR (Figure 4). In particular, at high OLR, R1 showed an amount of volatile fatty acids and formate significantly lower

than R2. Formate is an intermediate of methanogenic pathways and its concentration is always higher in R2 than R1.
This results are comparable with those of Banks (Banks et al. 2012) who demonstrated that the addition of Se and Co are indispensable for a stable anaerobic digestion in digesters treating food waste and operating at high ammonia concentrations.

4. Conclusions

Batch and CSTR tests showed conflicting results. Batch experiment showed that trace metal addition is indispensable for an high-performance anaerobic digestion process with and increase of specific methane production up to 60-70 %.
According to Banks, CSTR experiment showed that an adequate amount of trace metal addition is indispensable for a stable anaerobic digestion at high Organic Loading Rate. Contrarily to Banks, this work demonstrates that trace metal addition promotes the stability of the process, but this marginal improvement on specific methane production does not justify the addition of metals in full scale.

Acknowledgements

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