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Acidogenic fermentation of source separated mixtures of vegetables and fruits wasted from supermarkets

P. Traverso[1], P. Pavan[1,*], D. Bolzonella[2], L. Innocenti[1], F. Cecchi[2] & J. Mata-Alvarez[3]
[1]*Department of Environmental Sciences, University of Venice, Calle Larga S. Marta 2137, 30123 Venice, Italy;* [2]*Department of Science and Technology, University of Verona, Strada Le Grazie, 37134 Verona, Italy;* [3]*Department of Chemical Engineering, University of Barcelona, P.ta Marti y Franquez, Barcelona, Spain (* author for correspondence; e-mail: pavan@unive.it)*

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Abstract

A pilot scale mesophilic anaerobic acidogenic fermenter was fed with mixtures of vegetables and fruits shredded by a hammer mill and mixed in a stock tank, in order to produce a liquid phase suitable as RBCOD source in denitrification and EBPR processes. Different operative conditions were studied working with a HRT in the range 1–12 days. The effluent coming from the fermenter was screw pressed, and the solid phase was recycled adopting different ratios to the fermenter, in order to define its effect on the final liquid phase composition. The variations of the VFA, lactate, methyl and ethyl alcohol concentrations, TCOD, SCOD and pH during more than one year were analysed and discussed both with reference to the fresh feed, and to the content of the fermenter. It was found that almost all the organic matter in the liquid phase inside the fermenter was represented by VFA (mainly acetate), lactate (in particular) and methyl and ethyl alcohols when HRT was longer than 6 days.

Introduction

Large quantities of vegetables and fruits residues are wasted by markets, supermarkets and fast-food factories. This organic matter is normally free of contaminants and can be easily collected and transferred to a treatment plant without any particular cost increase. Taking these aspects into account, SS-OFMSW can be considered as an optimal substrate for acidogenic fermentation processes. The liquid phase obtained from the fermenter proved to be an excellent substitute for acetate and methanol in nutrients removal processes both in a sequencing batch reactor (SBR pilot plant, V = 1 m^3) fed with mixed (civil and industrial) wastewater, and in a continuous process fed with municipal wastewater (Cecchi et al. 1994; Pavan et al. 1994, 1998). In fact, the need for a readily biodegradable carbon source (RBCOD) in BNR processes (Wenzel et al. 1987; Carlsson et al. 1996; Mino et al. 1998) can possibly be satisfied if the fermentation treatment of OFMSW is connected to the wastewater treatment. In Italy, in particular, the municipalities are now pressured to adopt separate collection of the putrescible fraction of MSW and to adopt planning and upgrading of WWTPs to meet the 271/91 EC Directive in terms of N and P standards. Thus, this means that the OFMSW fermentation process can be the connection ring between wastewater and OFMSW treatments. The need for RBCOD, indeed, can widely be better satisfied than the classic fermentation of primary sludge (Rabinowitz et al. 1987; Lotter & Pitman 1992; Kristensen et al. 1992; Aesoy & Odegaard 1994; Isaacs & Henze 1995), because of the low yields that can be obtained. Using OFMSW acidogenic fermentation, the yields obtainable considering the mass balance between the wastewater and the organic waste pro capita productions (300 g/d OFMSW-250 l/d wastewater), in terms of VFA and light alcohols, are up to the 40% of the influent TCOD; this is a promising result.

Considering the state of the art of the fermentation process applied to putrescible substrates such as OFMSW, it is generally accepted today that in anaerobic mesophilic conditions, based on a number of investigations (see e.g. Zoetemeyer 1982; Wuelfert 1985; Verrier 1987; Albin 1989; Hanaki et al. 1987; Zhang & Noike 1991; Dinopoulou et al. 1988; Gosh 1991):

(a) hydrolysis is the rate determining step of the acidogenic fermentation process of vegetable wastes,
(b) hydrolysis can be fastened by shredding the raw matter before feeding the fermenter,
(c) acidogenic fermentation naturally occurs without the necessity of any inoculum,
(d) the hydrolytic process proceeds rapidly at first (a few hours after feeding,) and much slowly later on,
(e) the value of pH inside the fermenter influences the product pattern of acidogenesis,
(f) the hydraulic retention time (HRT) and the organic loading rate (OLR) influence the fermentation yields and the ratios among the major products,
(g) the pH that naturally occurs in the fermenter was found to depend on the nature of the vegetables.

Furthermore, the seasonal variations on the types of vegetables and fruits offered to the European people (in the cities, in particular) are now much smaller than only a few tenth of years ago, but they are still large enough to deduce that the liquid phase produced by a full-scale fermenter of wasted vegetables and fruits may be not constant in its quality. This fact can be a problem when dealing with the destination of the fermentation products, because the sale of the liquid phase can give an important money saving for waste disposal.

On the basis of these statements, this research was carried out. In particular, in this paper the main characteristics of the shredded mixtures of vegetables and fruits, coming from supermarket wastes (Treviso city, Italy), are assessed, and their variations during more than 400 days are analysed. Then the fermentation products and their dependence on operational parameters in mesophilic conditions are discussed.

Materials and methods

The experiments were carried out using a completely mechanically stirred fermenter (1 m^3 working volume) in the mesophilic range (37 ± 1 °C). The reactor (Figure 1) was fed discontinuously twice a day, from a 1 m mixed feed stock tank. A screw-press (1mm mesh) was used to separate the liquid from the solid phase, and the latter was recycled, in different ratio (RR) to the fermenter. Substrates were acquired and daily used from supermarkets of the city of Treviso (SS-OFMSW). They were hands-sorted in order to eliminate bulky and packaging wastes and then shredded and mixed before feeding using a hammer mill. Both the sludge fed in and that inside the digester were analysed every two days according to Standard Methods (1992). The Volatile Fatty Acids (VFA) and alcohols determinations were performed using a gas-chromatographic method, Lactic acid was analysed by ionic chromatography; more details are reported elsewhere (Sans et al. 1995).

Results and discussion

The characteristics of the feed

From the data in the left side of Table 1 it is possible to deduce that the qualitative variations of the collected organic matter gave to a feed to the fermenter characterised by small variations in the ratios TVS/TS (in particular) and SVS/STS, but by noticeable variations in the ratios STS/TS and SVS/TVS. The pH was always acidic and its variations did not depend on temperature (R^2 = 0.055) but mainly on the quality of the substrates. The liquid phase suffered from noticeable variations both with reference to SCOD and, in particular, to the volatile fatty acids, lactate and methyl and ethyl alcohol concentrations (see the data in the right side of Table 1). No seasonal variations were found, hence it can be deduced that the consequences of the variations in the proportions among the various types of vegetables and fruits were large enough to hide those coming from the seasonal variations.

Fermenter performances

The tested experimental conditions are in Table 2; the main characteristics of the feed to the fermenter and of the matter inside the fermenter are shown in Table 3, where only the data referred to the time ranges of pseudo steady-state conditions are collected. The pH was always in the range pH = 4 ± 0.2 without any necessity of addition of any chemicals addition, and the total alkalinity (TA) was in the range 2 ± 0.5 $gCaCO_3/l$. A comparison among the data in Table 1 and the related ones in Table 3 (left side) shows that the differences between the related terms are generally as small as to be inside their approximation ranges.

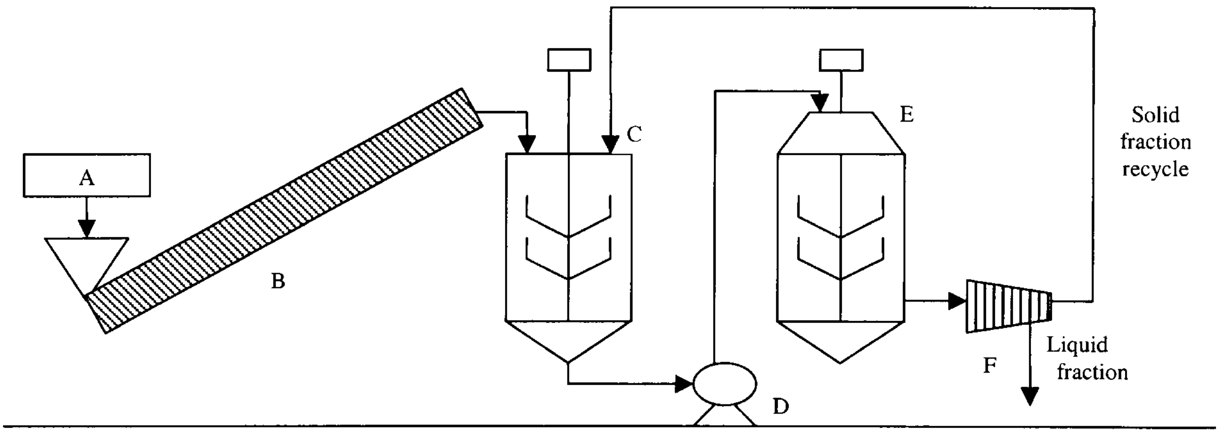

Figure 1. Scheme of the pilot plant. A = shredder; B = screw feeder; C = feedstock tank; D = feed membrane pump; E = fermenter; F = screw press.

Table 1. The characteristics of the shredded matter fed to the fermenter

Constituent	Average	Std. dev.	No. of samples	VFA, lactate Alcohol, SCOD	Average	Std. Dev.	No. of samples
TVS (g/Kg)	87.9	8.0	241	C2 (mgCOD/dm^3)	2252	772	198
TVS/TS, %	91.1	1.8	241	C3 (mgCOD/dm^3)	322	236	198
STS (g/dm^3)	44.8	5.9	184	i-C4 (mgCOD/dm^3)	484	261	198
STS/TS, %	43.2	6.5	187	C4 (mgCOD/dm^3)	429	210	198
SVS (g/dm^3)	40.1	5.3	185	iC5 (mgCOD/dm^3)	181	92	198
SVS/TVS, %	41.8	7.1	184	C5 (mgCOD/dm^3)	313	177	198
SVS/STS,%	88.5	4.0	185	C6 (mgCOD/dm^3)	104	68	172
TCOD (g/Kg)	101.7	11.6	48	C7 (mgCOD/dm^3)	784	816	172
pH	4.6	0.4	235	Lact. (mgCOD/dm^3)	1873	806	162
T (°C)	15.1	5.3	252	Met. (mgCOD/dm^3)	209	64	19
TKN (g/Kg)	23.1	4.6	95	Et. (mgCOD/dm^3)	1434	955	19
P (g/Kg)	3.7	0.6	90	SCOD (gO_2/dm^3)	46.3	5.7	67

The data in Table 3 allow to deduce that the terms SCOD (g/dm^3), TCOD (g/Kg) and TCOD/SCOD in the feed are strictly similar to those in the fermenter, while the term SVS is clearly lower in the fermenter than in the feed. This fact, that promotes some consequences up to some other parameters (SVS/TVS and SVS/STS, for instance) can be due to the fermentation process that gives to large fractions of products (i.e., VFA, methyl and ethyl alcohol etc.) that can be easily lost from the samples during the treatments suggested by the Standard Methods for STS and SVS measurements.

These considerations do prevent the terms SVS and TVS from part of their significance and, in particular, from the possibility of a careful determination of the fraction of the particulate organic matter in the feed that undergoes solubilisation inside the fermenter: the average values of the terms SVS/TVS cannot be used to this aim. However, references to TS, TVS, STS and SVS terms were and are still a custom for the researchers, since they are very common technical terms, cheap and easy to obtain by analysis. The only parameter that might be used to obtain information on the development of the solubilisation of the particulate organic matter fed to the fermenter is possibly TCOD/SCOD; unfortunately, however, in this paper the measures of the terms TCOD required pre-treatments of the samples at 105 °C (the measures are too expensive and affected by very large approximations if the pre-treatments are avoided), hence the terms TCOD/SCOD in the table are underestimated, and such an underestimate grows when the volatile compounds concentrations grow. As a consequence, the fact that the data in Table 3 show no noticeable

Table 2. The tested experimental conditions

Run	Month	Fermenter HRT(d)	OLR* (Kg TVS/m^3.d)	RR** (%)
1	Dec.–Jan	3.4–4.4	16–30	16–26
2	March	6.0	11–13	0
3	May	1.5–1.8	91–102	40–60
4	June	1.4–1.5	80–90	0
5	July	6.0	75–97	0
6	August	7.4–8.1	16–20	50–60
7	Sept.–Oct	8.2–11	17–22	Tot.***
8	Nov.–Dec.	6.4–8.4	30–34	Tot.***
9	January	1.0	85–97	0

* Reference to the fresh feed; ** RR (%) = (KgTVS recycled/KgTVS fresh feed) × 100; *** tests performed recycling all the effluent solid phase to the fermenter.

Table 3. Main characteristics of the matter in the feed stock tank and inside the fermenter during the experimental runs. (Referred to pseudo steady-state conditions)

Feedstock tank				Fermenter			
Constituent	Average	Std. dev.	No. of samples	Constituent	Average	Std. dev.	No. of samples
TVS (g/Kg)	93	8.4	45	TVS (g/Kg)	84	12.7	46
TVS/TS, %	91	1.5	45	TVS/TS, %	88	2.3	46
STS (g/dm^3)	45	6.2	34	STS (g/dm^3)	42	14.3	46
STS/TS, %	42	5.8	34	STS/TS, %	33	7.1	46
SVS (g/dm^3)	37	5.0	34	SVS (g/dm^3)	30	6.7	46
SVS/TVS, %	41	6.1	34	SVS/TVS, %	31	8.2	46
SVS/STS,%	89	3.4	34	SVS/STS,%	70	17.4	46
SCOD (g/dm^3)	45	5.7	24	SCOD (g/ dm^3)	44	3.8	46
SCOD (g/kg)	40	3.0	24	SCOD (g/kg)	40	3.5	46
TCOD/SCOD (g/g)	2.3	0.18	24	TCOD/SCOD (g/g)	2.3	0.24	46

difference between the terms TCOD/SCOD in the feed and in the fermenter does not prevent from concluding that a fraction of the particulate matter in the feed undergoes hydrolysis inside the fermenter. This possibly suggests that the solubilisation that occurs in the fermenter is almost complete. Anyway, the TCOD/SCOD ratios are so large that it seems reasonable to deduce that a large fraction of the mixtures of vegetables and fruits were resistant to hydrolysis and fermentation in the tested conditions.

The ultimate organic products of anaerobic fermentation of organic matter are mainly VFA, lactate and methyl and ethyl alcohol; the contributions of each of them to the global SCOD inside the fermenter is shown in Table 4, with reference to each experimental run (see Table 1). No important biogas production was observed during the experiments, thus this stream was neglected, also considering the approximations on the characteristics determinations on the other main streams.

The data in Table 4 clearly show that the term ⟨SCODr⟩ suffered from rather large variations run by run, but this happened also during the time ranges of pseudo steady-state conditions for each run (data not shown). This is an unavoidable consequence of the variations of the feed to the fermenter (see Table 1). Anyway, some comments are possible: (a) acetate and lactate are the main products of the fermentation process at HRT in the range 1 d–10.5 d, hence, the homolactic and the heterolactic transformations of pyruvate seem to be both well developed, notwithstanding the quite low values of pH (according to Pipyn et al. 1980); (b) propionate and methyl + ethyl alcohol (ethyl alcohol, in particular, as methyl alcohol concentration was always a little fraction of the sum, data not shown) concentrations are generally rather high, hence, the alcoholic and propionic transforma-

Table 4. Main fermentation products (VFA, Lactic acid and alcohols) in the fermenter liquid effluent

Run	SCOD (g/dm^3)	C2, range ($gCOD/dm^3$)	C3, range ($gCOD/dm^3$)	iC4, range ($gCOD/dm^3$)	C4, range ($gCOD/dm^3$)	iC5, range ($gCOD/dm^3$)	C5, range ($gCOD/dm^3$)	iC6, range ($gCOD/dm^3$)	C6, range ($gCOD/dm^3$)	C7, range ($gCOD/dm^3$)	Lact., range ($gCOD/dm^3$)	(Met.+Et) ($gCOD/dm^3$)
1	39–50	5.8–18.6	0.6–3.8	0.5–0.6	1.6–4.0	0.0–0.2	0.3–0.5	0.0–0.1	0.4–0.6	0.0–0.1	11.0–20.0	2.0–4.0
2	36–41	11.0–15.7	1.8–2.8	0.4–0.5	0.6–1.7	0.0–0.3	0.1–0.5	0.1–0.2	0.0–0.2	0.2–0.5	8.3–14.3	2.0–4.0
3	35–39	7.2–11.0	0.5–1.1	0.2–0.4	1.2–1.4	0.1–0.1	0.1–0.2	0.5–0.6	0.0–0.2	0.1–0.2	9.8–13.0	2.0–3.0
4	37–45	8.5–8.5	0.7–1.1	0.2–0.5	1.5–2.2	0.1–0.3	0.2–0.4	0.1–0.4	0.0–0.0	0.0–0.0	15.0–16.0	2.5–3.0
5	35–56	11.1–11.9	1.9–3.0	0.3–0.4	1.3–4.4	0.0–0.2	0.2–0.8	0.0–0.4	0.1–1.7	0.1–0.2	14.0–16.1	4.0–5.0
6	41–46	12.4–13.9	2.8–3.4	0.2–0.3	4.8–6.0	0.1–0.2	0.8–0.9	0.0–0.4	0.0–0.6	0.0–0.4	14.9–18.0	3.9–4.9
7	41–45	12.1–15.8	2.9–3.9	0.2–0.3	2.4–5.2	0.1–0.2	0.5–1.0	0.0–0.1	0.3–0.5	0.0–0.3	14.7–17.3	1.1–2.9
8	43–47	14.5–19.2	2.3–3.4	0.2–0.3	1.2–2.0	0.1–0.1	0.3–0.4	0.0–0.4	0.1–0.2	0.1–0.4	19.0–23.5	1.3–1.6
9	49–51	6.6–7.7	0.1–0.2	0.4–0.7	0.1–0.4	0.1–0.5	0.0–0.1	0.0–0.1	0.1–0.1	0.2–0.3	8.1–9.8	2.2–5.7

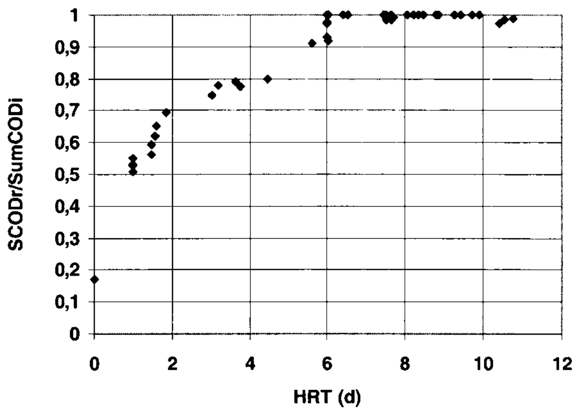

Figure 2. The dependence on HRT* of the contributions of the sum of the volatile fatty acids, lactate and methyl and ethyl alcohol to the COD of the liquid phase inside the fermenter ($SCOD_r$). * The value at HRT = 0 is the mean value in the feed.

tions of pyruvate seem to play an important role; in particular, the propionic transformation seems to take a longer time than those for alcohol formation (compare the related data in Table 1 and in Table 4); (c) the concentrations of C4 are rather high and affected by large variations; (d) the concentrations of i-C4, C5, i-C5 and C6 are small enough to be comparable with those in the fresh feed; (e) the concentrations of C7 are generally much lower in the fermenter than in the feed.

The data shown in Table 4 do suggest the hypothesis that the sum of the concentrations (COD basis) of the volatile fatty acids, lactate and light alcohols, can be much near to the values of the related $SCOD_r$ terms, at least when HRT is large. Such an analysis asks comparisons between each $SCOD_r$ term with the related $\Sigma_i COD_i$ term (the suffix i individuates the substrates shown in Table 4). This comparison must be performed day by day during the steady state conditions of each run. The results of such an analysis are plotted in Figure 2. The plot in Figure 2 states that, at least in the operational conditions shown in Table 1, the fermentation process in mesophilic conditions asks for not more than 6 days retention time to transform the soluble complex organic matter into VFA, lactate and methyl + ethyl alcohol. No consequence of sludge recycling (at least in the range HRT = 6.0–8.4 d) can be deduced from the plot in Figure 2, possibly because the variations are small enough to be hidden by the experimental approximations.

The qualitative variations of the feed gave to negligible consequences on the dependence of the term $\Sigma_i SCOD_r/SCOD_i$ on the hydraulic retention time in-

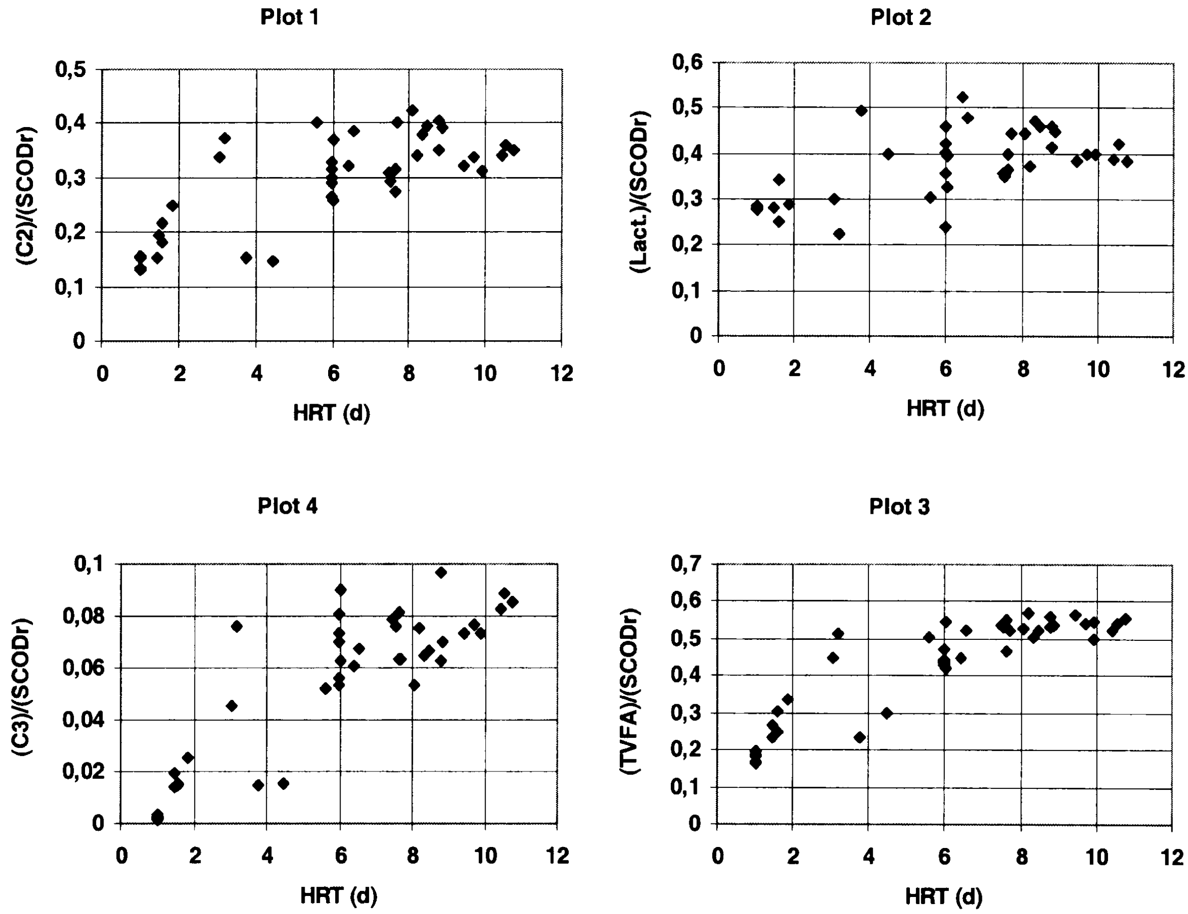

Figure 3. The dependence on HRT of the contributions of the COD equivalents of propionate (C3), lactate (Lact.), acetate (C2) and of the sum of the VFA (TVFA) to the SCOD inside the fermenter ($SCOD_r$).

side the fermenter. This is not the case, however, with respect to each main product of the fermentation process, as the plots in Figure 3 clearly show.

Plot 1 shows as that the contribution of acetate to SCOD inside the fermenter suffers from large variations both when HRT is lower and when it is larger than 6 days and plot 2 shows that the same holds for the contribution of lactate to SCOD. Acetate and lactate are the main end-products of the fermentation, whichever is the value of the term HRT, as shown in Table 4 and in the plots in Figure 3, which are to be compared with the plot in Figure 2.

Plots 2 and 3 in Figure 3, in particular, show that the competition between the homolactic and the heterolactic transformations of pyruvate continues all along the tested HRT ranges.

Plot 4 in Figure 3 shows that the qualitative variations of the feed do not hide the dependence of the term $C_3/SCOD_r$ on HRT: the propionate concentration grows with HRT, as was observed by Ghosh (1991) for anaerobic fermentation of activated sludge. The results obtained from a matricial correlation analysis revealed no dependence ($-0.6 < R < 0.6$) between HRT and the methyl and ethyl alcohol or the VFA heavier than propionate. Methyl alcohol is an end-product of fermentation, then its production seems to reach its end in the feed stock tank; ethyl alcohol could be transformed into acetate in a fermenter, but only when the pH value is in the range that allows acetate methanation, hence not at pH < 5 as in the tested conditions. It seems that the production of ethyl alcohol comes near to its end in the feed stock tank.

Table 5. Average values and standard deviations of the contributions to SCOD coming from the fermentation products when HRT ≥ 6 days

Product	Lact	C2	C3	i-C4	C4	i-C5	C5	i-C6	C6	C7	Et.
Average (%)*	41	33	7	0.7	8	0.3	1	0.4	0.7	0.5	7
Std. Dev. (%)	4	3	0.8	0.2	3.3	0.1	0.5	0.3	0.3	0.4	3

* average values of the terms $(SCOD_i/SCOD_r) \times 100$.

Conclusions

The main results that arise from the data and from the considerations in this paper can be summarised as follows:

(a) the treatment of a mixture of vegetables and fruits in the system of Figure 1 allows to obtain the transformation into SCOD of about 43% (average value, see Table 3) of the TCOD of the raw matter;

(b) when HRT > 6 days in the fermenter, the organic matter in the liquid phase is (almost) completely due to VFA, lactate and ethyl alcohol, even if the average contributions of each of them to $SCOD_r$ suffer from rather high variations with time, as is shown in Table 5: an equalisation tank seems to be necessary to cut the quality variations of the fermented liquid phase. However, using these operational conditions (HRT > 6 days), the fermentation products obtained seem to be an excellent substitute for the RBCOD sources for the BNR processes more widely used.

(c) When high percentages of VFA and light alcohols are present in the liquid phase, it is possibly problematic to continue to acritically adopt the typical parameters of anaerobic digestion processes description, like VS, SVS, TVS, and TCOD, due to the analitycal problems described above.

List of abbreviations

BNR: biological nutrients removal
C2: acetic acid (g/dm^3)
C3: propionic acid (g/dm^3)
i-C4: isobutyrric acid (g/dm^3)
C4: butyric acid (g/dm^3)
i-C5: isopentanoic acid (g/dm^3)
C5: pentanoic acid (g/dm^3)
C6: exanoic acid (g/dm^3)
C7: eptanoic acid (g/dm^3)
EBPR: enhanced biological phosphorous removal
HRT: hydraulic retention time (d)
MS-OFMSW: mechanically sorted organic fraction of municipal solid waste
OLR: organic loading rate ($kgTVS/m^3/d$)
P: total phosphorous (g/Kg)
RR: recycle ratio
SCOD: soluble chemical oxygen demand (g/dm^3)
SS-OFMSW: source sorted organic fraction of municipal solid waste
STS: soluble total solids (g/m^3 ,%TS, VS)
SVS: soluble volatile solids (g/dm^3
TCOD: total chemical oxygen demand (g/Kg)
TKN: Total Kijeldhal Nitrogen (g/Kg)
TS: total solids (g/kg)
TVS: total volatile solids (g/kg FOP; %TS)
VFA, TVFA: volatile fatty acids ($gAcH/ m^3$)

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