



# ANAEROBIC DIGESTION OF OFMSW (ORGANIC FRACTION OF MUNICIPAL SOLID WASTE) AND BNR (BIOLOGICAL NUTRIENT REMOVAL) PROCESSES: A POSSIBLE INTEGRATION – PRELIMINARY RESULTS

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## ABSTRACT

The paper presents preliminary experimental results which aim to demonstrate the possibility of producing easily biodegradable carbon from a two phase anaerobic digestion process for a biological nutrient removal process. Crystallization of phosphorus into struvite from the liquor of the digested flow is the second goal of the process studied. With this integrated process approach it is possible to double the amount of readily biodegradable COD entering the wastewater works by sewers and to recover up to 70% of phosphorus from the digested flow as struvite without using little amount of chemicals. Struvite granules are useful for agricultural purposes.

## KEYWORDS

Biological nutrient removal, Anaerobic digestion, Municipal solid waste, Struvite, Crystallization-Nucleation

## INTRODUCTION

The CEC Directive 271/91 requires more stringent nitrogen and phosphorus standards in the wastewater discharged from treatment works. Considering the low environmental impact technologies, the choice of biological treatments appears obvious. In this field amongst the problems to be deeply studied are those connected with the availability of an external easily biodegradable carbon source (Lotter and Pitman, 1992) and the removal of orthophosphates through precipitation or crystallization (Pitman et al., 1991). In fact, recycling of phosphorus-rich sludge processing liquors to the head works of the plant determines a loss of efficiency of enhanced biological phosphorus removal (Murakami et al., 1987).

High concentrations of volatile fatty acids (VFAs) and other easily degradable compounds are obtainable by anaerobic fermentation (AF) of the organic fraction of municipal solid waste (OFMSW) (Antonopoulos & Wene, 1988, D'Addario et al., 1993, Virtutia et al., 1992).

The high concentrations of Ca, Mg, and  $\text{NH}_4$  in digested effluents, in relation to the phosphorus content, which sometimes causes severe fouling production by nucleation inside the anaerobic fermentation system (Loewenthal et al., 1994), satisfy the stoichiometric requirements related to the phosphorus content either for hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) or for struvite ( $\text{Mg NH}_4 \text{PO}_4$ ) formation (De Wall, 1990; Shao, 1992, Fujimoto et al., 1991;). The lower pH requested for struvite formation (Momborg, 1992) and the absence of chemical sludge production by nucleation, suggests the choice of a struvite crystallization process (SCP).

According to this scenario, it seems possible to propose an integrated AF-BNR-SCP system.

The twofold aim of this paper is to present preliminary experimental results in: VFAs production by anaerobic fermentation of source sorted OFMSW (SS-OFMSW) before codigestion with sewage sludge and struvite nucleation in digested flows using different reactors.

## MATERIALS AND METHODS

A two phase anaerobic digestion is the means for producing easily biodegradable COD (see Fig.1). In the experiments the fermenter had a working volume = 0.8 m<sup>3</sup>. It was mechanically stirred at 30 rpm and the temperature inside was kept within a range of  $\pm 1^\circ\text{C}$  from the operative temperature (23 or 35°C).

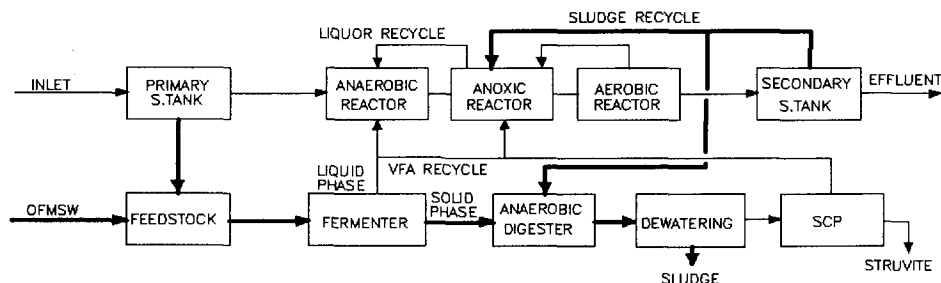


Fig. 1. Flow-sheet of the integrated AF-BNR-SCP process.

The substrate used for the experiments was Source Collected OFMSW obtained daily from supermarkets and canteens of the city of Treviso. Main characteristics of SC-OFMSW are reported in Table 1.

TABLE 1. Main characteristics of the waste used for the study.

	Average	Min.	Max	Std. Dev.	n.of samples
TS, g/Kg	81.8	54.4	132.7	15.7	90
TVS, g/Kg	67.0	46.8	105.6	11.3	90
TCOD, KgO <sub>2</sub> /KgTS	1.0	0.7	1.5	18.1	55
TKN, %TS	2.1	1.4	3.3	0.5	30
P, %TS	2.8	1.3	3.3	0.5	30

TS, TVS= Total and volatile solids, TCOD=Total COD, TKN=Total Kjeldahl Nitrogen, P=Total Phosphorus

Refuse was shredded by a hammer mill and then fed once a day to the fermenter by a membrane pump. The plant was monitored according to the plan in Table 2 using the Standard Methods (APHA, 1993). VFA determination was performed using a gas-chromatographic method (Column: Nukol 15m, 0.53 ID; Temp: 85-125°C, 30°C/min.; Carrier: N<sub>2</sub>, 5 ml/min). Lactic acid was analysed by ionic chromatography (Column: Dionex Ionpac AS 11, 4 mm ID; Eluent: NaOH 0.2 mM, 1 ml/min).

TABLE 2. Plan of the digester monitoring.

Parameter:	n. analyses/week
TS, TVS, STS, SVS, TA, Lactic acid	3
TCOD, SCOD, TC	1
VFA, pH	5
Temperatures (Fermenter and Environmental)	every 10 minutes (on-line)

STS, SVS=total and volatile soluble solids, TA= total alkalinity, SCOD=soluble COD, TC=total carbon, VFA=volatile fatty acids

Struvite crystallization was studied at laboratory level using batch, packed bed and fluidized bed reactors (PBR, FBR). Sand (carbonatic sand, 30% quartz) and quartz were the nucleation media used (size 0.21-0.35mm). The PBR column was 200 mm high and 1.5 mm i.d.. FBR, 90 mm i.d., had 310 and 150 mm high of expanded and

unexpanded bed. Critical supersaturation curves were obtained measuring the transmittance of phosphate solutions. The minimum transmittance value individuates the supersaturation point. Physical-Chemical characteristics of wastewaters were measured according to Standard Methods (APHA, 1993).

## RESULTS AND DISCUSSION

The AF-BNR-SCP process proposed (Fig. 1) requires explanation of the following aspects: why has SC-OFMSW been chosen as feed for the fermenter? Is co-digestion possible? Is struvite formation possible without any chemical addition? Which plant configuration can be used for the struvite formation?

### Anaerobic fermentation.

Antonopoulos & Wene (1988) experimented the fermentation of a simulated MSW in a laboratory scale reactor in mesophilic range. With an hydraulic retention time of 8 days, they reached a concentration of 10-15 gVFA/l, without any pH control.

**TABLE 3 Operative Conditions and Effluent Characteristics of the Fermentation Process Studied.**

	RUN I	RUN II
Operative conditions:		
T, °C	23.3	35.6
HRT, d	6.0	4.1
OLR, KgTVS/m <sup>3</sup> d	4.1	16.4
Feed characteristics:		
TS, g/Kg	98.3	80.3
TVS, g/Kg	74.8	67.6
TCOD, g/Kg	106.2	107.9
SCOD	45.8	42.8
TC, %TS	38.3	32.3
C2, gAcH/l	6.1	3.5
Other VFA, gAcH/l	0.4	0.1
Total VFA, g AcH/l	6.5	3.6
Lactic acid, g/l	11.7	5.2
Effluent characteristics:		
TS, g/Kg	96.7	73.1
TVS, g/Kg	72.0	59.1
TCOD, g/Kg	110.2	99.0
SCOD	51.6	48.6
TC, %TS	40.0	32.3
pH	4.74	4.74
TA, gCaCO <sub>3</sub> /l	7.87	5.74
C2, gAcH/l	8.9	8.8
Other VFA, gAcH/l	0.6	0.6
VFA, gAcH/l	9.5	9.4
Lactic acid, g/l	12.1	6.1

HRT=hydraulic retention time; OLR= organic loading rate; C2=Acetic acid, C3=propionic acid, iC4=isobutyric acid, C4=butyric acid, i-C5=isovaleric acid, C5=valeric acid.

In a two-stage A.D. process of sewage sludge (SS), Ghosh obtained both at laboratory and pilot scale 5-10 gVFA/l in the fermentation step (Ghosh, 1977, 1991). Zoetmeyer (1982) studied the fermentation of a 1% glucose solution

at pH of 5.7-6.4, obtaining a conversion yield of 13.4%. Higher concentration (10-24 gVFA/l) was obtained by D'Addario *et al.* (1993), in a study focused on the production of VFA by biodegradation of OFMSW mechanically sorted in a full-scale plant. Without any chemical control, the process worked at an average pH of 5.5, with a retention time of 21 days.

All these studies do not consider separate collection of OFMSW which has recently been suggested as the future approach in solid waste management in different countries (Rec.'93). With this substrate, some preliminary anaerobic fermentation experiments have been carried out in this work (see Tab.3). Two set of operative conditions were studied. In the first condition, the fermenter was controlled at a temperature of 23°C, HRT=6 days and OLR=4.1 KgTVSf/m<sup>3</sup>d. No pH correction was necessary to maintain this parameter over the value of 4, which is considered critical for this process (Hanaki *et al.*, 1987) and VFA concentration in the effluent was very high, mainly due to the acetic acid and lactic acid concentrations. In the second run, performed at the mesophilic range of temperature (35°C), HRT=4.1 days and OLR=16.4 KgTVSf/m<sup>3</sup>d (four times larger than run I), a lower concentration of VFA in the effluent was achieved, even if the operative pH was the same. Data clearly suggests the necessity to study the influence of operating parameters on VFA production. In fact, considering the process performance, the second run performed better than run I (increase of VFA concentration with respect to the feed was 158% in run II against 46% in run I, about 3 times larger; the same behaviour can be observed in terms of lactic acid content, which increased in run II by 18% against 5% in run I). However, according to the aim of the paper, some considerations can be drawn because in both cases the amount of readily biodegradable compounds produced is very large.

Thus the mass balance of this step of the process, considering from 200 to 400 g SC-OFMSW w.w./p.c.d., their characteristics (12%TS, 0.85 TVS/TS) and the best performance of the fermentation process obtained (see Tab.3), gives from 1.8 to 3.6 g of acetic acid, from 2.4 to 4.8 g of other VFAs and from 10.3 to 20.6 g of SCOD (this includes all VFAs) per inhabitants per day. These figures, compared with averaged characteristics of readily biodegradable COD (RBCOD) of wastewater with 400 mgCOD/l estimated by Henze (1992), allow the evaluation of the contribution to RBCOD obtainable through this approach for the BNR process (see Tab.4).

**TABLE 4 Contribution of RBCOD to the BNR Process from Raw Wastewater, Fermentation of SC-OFMSW and Recycled Flow After A.D. and Struvite Formation Steps(\*)**

	Wastewater		Fermentation		A.D.(**)	
	(Henze, 1992)	%(***)	(this study)	%(***)		%(***)
Acetic acid	25	74.9-60.4	7.7-15.4 (*)	23.6-38.1	0.65	1.5
Other VFA(+Lactic acid)	10	47.5-30.9	10.3-20.6 (*)	50.7-67.3	0.65	1.8
Alcohols	5	-	-	-	-	-
Lower Aminoacids	10	-	-	-	-	-
Simple carbohydrates	10	-	-	-	-	-
SCOD	-	-	41.2-82.4	-	-	-
Total:	60	76.9-62.5	41.2-82.4(°)	23.1-37.5	1.3	-

(\*) Data are calculated considering 250 l/d per inhabitant. All concentrations are expressed in terms of COD, mgO<sub>2</sub>/l.

(\*\*) Considering 1.5 l primary and secondary sludge produced per capita per day.

(\*\*\*) Contribution of each fraction to the RBCOD.

(°) The total contribution is equal to the SCOD contribution because it includes all the VFA.

A further contribution to RBCOD comes from the overflow of the digester after struvite formation (see Table 4). In this case, although the flowrate is relatively high with respect to the fermentation step, the VFAs concentration is limited (100-200 mg VFA/l; 50% acetate); thus, the increments to the RBCOD are more or less negligible. The SCOD from this flow can not reasonably be considered readily biodegradable because of the A.D. step. As can be seen from Tab. 4 the acetic acid and the other VFAs from fermentation allow to double the already existing fraction of RBCOD in the raw wastewater. Furthermore, considering that the SCOD in the fermenter is mainly composed of free sugars (hydrolysis of vegetables, fruits etc.), it seems reasonable to consider it from 50 to 100 RBCOD. Consequently, the overall contribution of fermentation to RBCOD can be estimated as 100-150% of the existing RBCOD in raw wastewater. This relevant amount of RBCOD possibly allows the overcoming of the threshold indicated by Wentzel *et al.* (1987) for operating at the highest rate of phosphorus release in the anaerobic reactor of BNR process.

The answer to this question together with optimization of co-digestion of sewage sludge with the solid stream from

fermentation of SC-OFMSW will be the aims of future experimental work. This part of the work was not included in the preliminary study because the authors and other researchers have been investigating the co-digestion approach with positive results for many years (Ahring, 1992, Cecchi *et al.*, 1988) with no problems of process stability.

Struvite formation.

In order to choose real conditions in crystallization experiments, effluents from conventional civil wastewater plants (without enhanced biological phosphorus removal) characterized by mesophilic digestion sludges (A,B Tab. 5) or from Phostrip process (C,D) were examined. The orthophosphate concentrations observed, 28-81 mg PO<sub>4</sub>/L are much lower than those reported in literature for BNR plants (180 mgPO<sub>4</sub>/L Momberg, 1992; 180-400 mgPO<sub>4</sub>/L. Pitman *et al.*, 1991). This can be ascribed to the limited phosphorus content in the sludges; however, considering the stoichiometric ratio of struvite components, amounts of magnesium and ammonia are enough for struvite formation even when the phosphorus content is higher than that in the conditions examined. This reason allows the use of the effluent from the Falconara plant (the closest to the University) (A, Tab.5), adjusting the phosphorus content to the desired level by means of phosphate additions.

TABLE 5. Chemical characteristics of A.D. effluents after sludge dewatering

WASTEWATER WORK	Ca mg/l	NH <sub>4</sub> mg/l	Mg mg/l	PO <sub>4</sub> mg/l	NH <sub>4</sub> :Mg:PO <sub>4</sub> (*)
A FALCONARA	150-220	376	44	28.5	60 :6 : 1
B SAV.RUBICONE	180	640	66	45	75.5:5.9:1
C CERVIA	86	720	29	64	59:1.8:1
D REGGIO EMILIA	-	-	-	80.9	-

A e B conventional plants, C e D Phostrip process, overflow after phosphorus stripper.  
(\*) stoichiometric ratio.

Phosphorus precipitation due to aging of the real effluents was preliminarily tested. The tests were conducted, with and without phosphate addition, leaving the effluent aside in a thermostatic room (25 °C).

Fig2 Phosphorus precipitation in dewatering effluents  
Initial CO<sub>3</sub>=0.5 meq/l, HCO<sub>3</sub>= 18 meq/l. Final CO<sub>3</sub> 1 meq/l, HCO<sub>3</sub> 16.5 meq/l

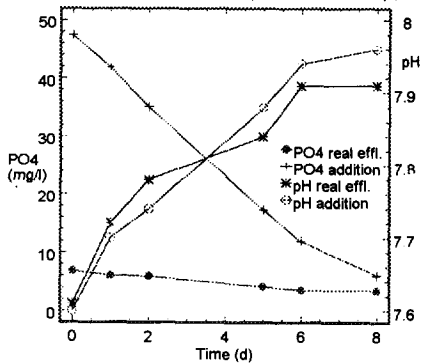
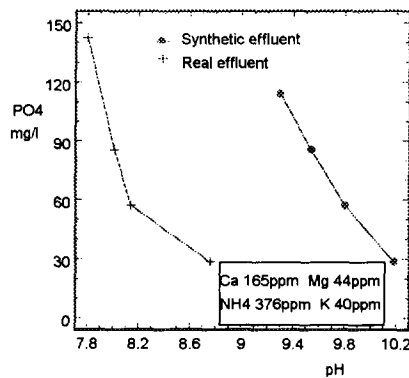


Fig.3 Struvite supersaturation curves



Results (Fig.2) show that the precipitation process is completed within 6-8 days and that phosphorus gradually precipitates along with the pH of the solution increase. Loss of bicarbonate alkalinity and the partial gain of the carbonate species cause the increment of 0.3 units of pH. The percentages of phosphorus removal were from 52 to 87% respectively for the low (7.5 mg PO<sub>4</sub>/l) and high (47 mg PO<sub>4</sub>/l) initial concentrations.

Although the natural behaviour of the process points to interesting results, the long time required does not allow an industrial application and a different approach is required. For this reason, in order to understand and to optimise a nucleation process, supersaturation curves characterizing the struvite formation in real or synthetic systems, were studied (Fig.3). With real effluents, supersaturation is reached at pH values substantially lower than those necessary for the synthetic ones when magnesium and ammonia are at the same concentrations, but without the calcium and alkalinity characteristic of the real effluent. This allowed us to speculate that nucleation could be achieved through addition of only minimal quantities of chemicals.

TABLE 6 Phosphorus crystallization tests

TEST	Seed material	HRT	pHi	PO <sub>4</sub> i	E%	V.A.		RT
						CO <sub>3</sub>	HCO <sub>3</sub>	
		min		mg/l		meq/l	meq/l	h
BATCH	sand	-	8.3	22	71	-	-	-
BATCH	quartz	-	8.3	22	68-70*	-	-	-
PBR	quartz	2	8	35.7	53	+1.4	-9.2	0.6
PBR	quartz	5.7	8	23.7	45	+2.7	-9.3	0.6
PBR	quartz	0.5	8.3	27.2	60	+0.5	-3.4	0.3
PBR	quartz	2.2	8.3	18.4	62	+1.1	-6.9	0.6
PBR	quartz	0.25	8.3	27.2	58	+0.7	-3.7	0.1
PBR	quartz	3	8.3	23.8	74	-	-	0.5
PBR	quartz	1.8	8.3	28.5	78	-	-	0.6
PBR	quartz	4.4	8.3	27.2	70	+0.5	-3.4	0.6
PBR	sand	0.25	8.3	38.9	61	+0.7	-3.7	0.1
PBR	sand	2	8.3	18.2	50	-	-	0.4
PBR	sand	1	8.3	18.2	65	-	-	0.2
PBR	sand	0.5	8.3	38.9	58	+0.7	-3.6	0.3
PBR	sand	3.1	8.3	27.2	63	+0.5	-3.6	0.6
PBR	sand	4.4	8.3	28.5	56	+0.4	-3.5	0.6
FBR	quartz	0.8	8	23.1	12.5	+1.2	-5.3	0.6
FBR	quartz	0.8	8.3	18.2	43	+0.7	-2.5	0.6
FBR	quartz	0.8	8.3	27.4	53	+0.7	-2.5	1.5

V.A. alkalinity variation (meq/l), PO<sub>4</sub>i initial content \*results obtained using quartz (1 to 10% of sample)  
pHi starting value

The region between the supersaturation and the solubility curves, the metastable zone, was considered for obtaining the crystallization of struvite on the surfaces of seed crystals. The influence of some parameters (i.e. initial pH, hydraulic retention time (HRT) and initial phosphate concentration) was studied. Sand and quartz were selected as seed crystal in batch, PBR and FBR reactors. Results obtained are summarized at Tab.6. The percentage of the added quartz (1 to 10%), does not notably affect the struvite nucleation (Fig.4) and neither does the sand to quartz substitution.

Data can be better understood using reaction time (RT) as the normalizing parameter (Eq.1). the role of HRT in the phosphorus removal, for PBR reactors, shown in eq.1, may be represented by plotting HRT versus RT. Considering from Tab.6 all runs with pHi=8.3 and efficiency over 60%, RT vs. HRT trend in Fig.5 shows the superiority of quartz as seed material.

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Fig.4 Struvite nucleation in batch reactors

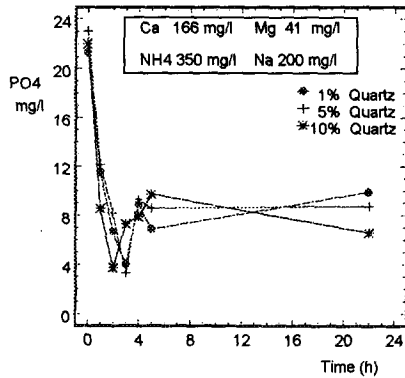
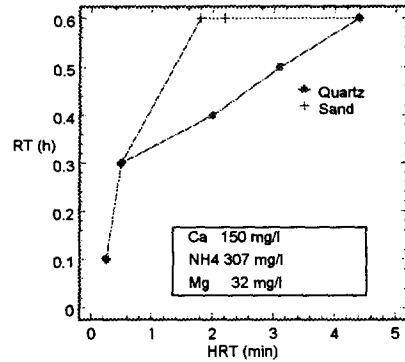


Fig.5 Struvite nucleation inPBR reactors ( pH=8.3 )



$$RT = HRT * n = t * V/V_s \quad (1)$$

RT=reaction time; HRT=hydraulic retention time ; V=PBR or FBR volume; n=number of runs in column; V<sub>s</sub>=starting sample volume

The starting pH<sub>i</sub>, obtained adding alkali (0.4 meq/l for pH 8; 0.7 meq/l for pH 8.3), fulfils an important part in circumstances of low phosphorus content (<40 mg PO<sub>4</sub>/l); in fact, only at a pH<sub>i</sub> greater than 8.3 can a removal greater than 50% be obtained. Practically, a pH lower than 0.1-0.2 unities respect to that at supersaturation represents the best operative condition for nucleation. In all the experiments, after nucleation, a total alkalinity loss of 2-5 meq/l was noticed. Specifically a gain of the carbonate versus a loss of the bicarbonate fraction was observed.

FBR reactors are best qualified for applications since the fluid bed does not hold head losses and flow variations, but, on the other hand, they necessitate longer reaction times for ensuring phosphorus removal equal or greater than 50%.

## CONCLUSIONS

The results obtained, even if they have a preliminary role, underline the advantages of the integrated approach suggested. They are:

- 1) exploitation of a carbon source for the BNR process requirements that is always available;
- 2) energy recovery and landfill volume saving through co-digestion option;
- 3) fitting of the new laws of MSW management;
- 4) phosphorus removal equal or greater than 60% by struvite nucleation in the digester overflows is possible;
- 5) comparing FBR and PBR, FBR seems easier to use;
- 6) quartz and carbonate sands may be used indifferently as nucleation seed;
- 7) a crucial role in the phosphorus removal process is played by pH, thus it is essential to research the process conditions capable to minimize the alkali requirements;
- 8) loss of alkalinity is observed during the nucleation.

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