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ENERGETIC CONVERSION OF ORGANIC FRACTION OF MUNICIPAL SOLID WASTE BY ANAEROBIC CODIGESTION WITH SEWAGE SLUDGE

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Introduction

To decrease the environmental pressure caused by landfill disposal, sustainable management practices for the organic fraction of municipal solid waste (OFMSW) consist nowadays in composting or wet and dry anaerobic digestion. Anaerobic digestion (AD) is a biological process that involves the degradation of organic matter and the production of biogas, a mix of methane and carbon dioxide in variable percentage. Biogas is a renewable energy source and a key factor for a future fossil fuels independent society. AD technology, combined with digestate composting, allows energy recovery and nutrient soil replacement.

Anaerobic codigestion (AcoD) is a challenging technology applied for both treatment of solid and liquid organic wastes (Alatriste-Mondragón et al., 2006) when the AD process of these mixtures is sustainable. AcoD of sewage sludge (SwS) with OFMSW may be one of the most viable solutions to optimize the oversized digesters efficiency in wastewater treatment plants (WWTPs): the typical free capacity of existing, traditionally designed, municipal SwS digesters can be well used adding the appropriate amount of OFMSW in AD process supply (Sosnowski et al., 2008). The substrate mixtures treated in AcoD process must be well balanced in all chemical-physical properties to allow positive interactions, to avoid inhibitions and to optimize methane production (Mata Alvarez et al., 2011).

The quality of organic wastes used in this process affects both the reactor operations and the subsequent use of the digestate as fertilizer on agricultural soils (Capela et al., 2008), likewise AD system management is strictly bound to the inlet waste mixture. An interesting study (Yoshida et al. 2012) reports greenhouse gas (GHG) emission analysis evaluation performed by different organic waste management practices in the City of Madison, Wisconsin (USA). Using Life Cycle Assessment (LCA) they found SwS and OFMSW AcoD process is a good practice not only for a general GHG emission reduction but also for the potential to save capital cost respect composting and mono-substrate digestion. The payback period of the investment for the up-grade to SwS-

OFMSW AcoD process is usually short (Mata Alvarez et al., 2011): existing AD reactors and WWTP operational facilities can be utilize, saving most part of initial and operational costs (Yoshida et al., 2012).
Various studies are reported on AcoD process operating with SwS and OFMSW or fruit and vegetables solid wastes (FVW) on lab scale (Stroot et al., 2001; Kim et al., 2003; Murto et al. 2004; Gómez et al., 2006; Gomez-Lahoz et al., 2007; Scaglione et al., 2009), pilot scale (Sosnowski et al., 2003; Caffaz et al., 2008; Liu et al., 2012; Cavinato et al., 2013) and full-scale plants (Rintala and Järvinen et al.,1996; Edelmann et al., 2000; Bolzonella et al., 2006; Zupančic et al., 2008; Zitomer et al., 2008). The main results show that SwS characteristics play an important role in AcoD with OFMSW: the nitrogen content of secondary sludge can remedy a possible lack of nutrients in OFMSW co-substrate as well as primary sludge (rich in lipids) can increase methane production yield of the AcoD process (Mata Alvarez et al., 2011). Similarly, the rate and the extent of anaerobic degradation and solid stabilization are functions of the intrinsic properties of the wastes and the microorganism involved (Gunaseelan et al., 2007), where the composition of organic matter depends greatly on the source of the organic fraction (Chen et al., 2008). A way to understand accurately the properties of the substrate to be treated is to perform BMP assays (Raposo et al. 2011b), likewise macromolecular composition analysis in terms of carbohydrates, proteins, lipids and volatile fatty acids (VFA) allows a good characterization of the organic features of substrates involved in the AD process. All these studies lead to the statement that the nexus between wastewater treatment and organic waste management is strictly related to the need of reaching an environmental sustainable economic system able to provide treated water, bioenergy and biofertilizer: integrated solid waste and wastewater treatment management could play a fundamental role in this challenge.
Whereas approximately 120 to 140 million tonnes of biowaste are produced every year in the EU, this corresponds to approximately 300 kg of biowaste produced per EU citizen per year (Communication from the commission to the council and the European parliament on future steps in biowaste management in the European Union COM(2010)235). The management of biowaste is covered by several pieces of EU legislation: according to the EU Landfill Directive (1999/31/EC) Member States shall reduce the amount of

biodegradable municipal waste landfilled, the Waste Framework Directive (2008/98/EC) encourages Member States to collect separately and recycle biowaste and enables the setting of EU minimum requirements for biowaste management and quality criteria for biowaste compost and digestate (end-of-waste criteria). Moreover the Directive on Renewable Energy Sources (2009/28/EC) promotes the biowaste use to replace fossil fuels. The biowaste separate collection and biological treatment with energy and matter recovery, represents an optimal solution to fulfil the European waste management strategy.

The PhD project is focused on the creation of an applicative protocol to optimize the WWTP anaerobic digesters up-grade and the project of new ones, basing the design on biochemical process equations rather than on classical empirical methods. To reach this purpose, a complete analysis of the whole anaerobic digestion process is designed, scaling up from micro to macro parameters. The research work was divided in the following four steps:

- Organic substrates characterization (measuring classic chemical-physical parameters and AD key macromolecular compounds such as carbohydrates, proteins, lipids and VFA);
- Biochemical methane potential (BMP) tests (to measure organic substrates methane yields);
- Pilot plant test (to investigate in a CSTR regime, the interaction between the substrates with increasing organic loading rates);
- Anaerobic Digestion Model no°1 (ADM1, Batstone et al., 2006) implementation.

The applicative case study regards the up-grade, of an existing anaerobic digestion unit within WWTP of the city of Udine (Italy), to lead to sewage sludge codigestion with organic fraction of municipal solid wastes. Different OFMSW streams, coming from an appropriate waste collection basin, were characterized as a perspective of the AD unit up-grade to AcoD. The waste collection basin was set considering an essential OFMSW management, built on the most productive and clean material streams reaching anaerobic digester. Source selected OFMSW (SS-OFMSW) selection criterion was fixed to conciliate minor distance to WWTP and higher quality waste, to avoid AD unit maintenance problems and to obtain the maximum biogas production. The organic substrates characterization was accomplished basing on traditional

physicochemical parameters (commonly used in the past to design anaerobic digesters), elemental analysis and macromolecular compounds. In BMP tests SwS and the more representative substrates for AD unit process, within the waste collection basin, were analysed. Further BMP tests on different SwS and SS-OFMSW mixing ratio were carried out to compare codigestion methane yields. Pilot plant test were performed at 2.3m^3 reactor. After start-up procedure, experimental loading cycles were applied to understand biomass behaviour in codigestion regime.
The ADM no°1 model was used to simulate the process in both bench-top and pilot plant tests with the aim of create a calibrated and validated model to optimize the AD unit up-grade. A feasibility study complete the PhD project: basing on results obtained in the experimental phase, two upgrade scenarios were defined considering the local substrates availability.

1 Organic substrates characterization

1.1 INTRODUCTION

The organic substrate characterization plays a fundamental role in the treatment process evaluation and in the mathematical modelling implementation.
Classical chemical-physical analysis constituted, in the past, the basis for anaerobic reactor design. Elemental analysis on feeding substrates is an easy tool to control nutrient ratio in the supply and macromolecular compounds analysis such as carbohydrates, proteins, lipids and volatile fatty acids allows to rich the information about the quality of organic matter and to understand the possible degradation paths in the bacteria metabolism. The sum of all these analysis allows to perform the COD fractionation procedure that is the first step to mathematical model implementation. A complete substrate characterization has the potential to base the AD design on biochemical process equations rather than on classical empirical methods.

1.2 MATERIAL AND METHODS

1.2.1 ORGANIC WASTES AND INOCULA

OFMSW samples were obtained by source selected producers in a 30 liters bins. The SS-OFMSW sampling has regarded the organic residues collected from two canteens (Canteen 1, Canteen 2), two supermarkets (Supermarket 1, Supermarket 2), one restaurant, one household, two fruit and vegetable markets (FVW 1, FVW 2) and one bakery. Household wastes were withdrawn before truck collection to avoid sample squeeze.

The SwS was drawn from the sludge thickener of Udine WWTP, Italy. SwS was a mixture of primary sludge and waste activated sludge.

1.2.2 ANALYTICAL METHODS

Total Solids (TS), Volatile Solids (VS), Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN), ammonium nitrogen ($N\text{-}NH_4^+$), total phosphorus, sulfate SO_4^{2-}, pH and alkalinity were measured according to Standard Methods (APHA et al., 2005). Soluble fractions of samples were obtained passing slurries through 0.45 μm cellulose filter.
Volatile Fatty Acids (VFA) concentrations were determined by gas-chromatography with mass spectrometer (Agilent 6890Plus/5973N) equipped with capillary column (Agilent HP-5MS). Carbohydrates were analyzed using Dubois method (Dubois et al., 1956) with glucose as standard. Total proteins were estimated multiplying organic nitrogen (TKN - $N\text{-}NH_4^+$) by 6.25. Lipids were measured by gravimetric analysis after acetone-hexane extraction. Elemental analysis (C,H,N) was carried out by Flash EA 1112 Elemental Analyzer (Thermo Finnigan, Italy).

1.3 RESULTS&DISCUSSION

1.3.1 WASTES CHARACTERISTICS

SS-OFMSW samples showed different composition: canteens and restaurant residues were the most heterogeneous with vegetables peels, rice, pasta, bread, meet and other scraps types. Supermarkets wastes were exclusively constituted by fruit and vegetables because all other organic wastes produced took ways of reuse and recycling. Bakery residues were almost pastry refuses and sweet creams. Inert materials in all samples were negligible. TS in raw wastes, after grinding, ranged from 8 and 70% TS, the lowest concentration for vegetable samples and the highest for bakery residues. Canteens, restaurant and household wastes showed the typical values of 30%TS, similar values were obtained for domestic and commercial food waste by other authors (Banks et al.

2011). In table 1.1 substrates characterization data are reported. VS/TS ratio of SS-OFMSW highlights the high organic transformation potential of these substrates in AD process respect SwS one. Methane yield in AD process depends by the amount of biodegraded VS as well as by the nature of the solid (Buffiere et al. 2006), so it's fundamental to distinguish the biochemical compounds that form VS in the various substrates. No mapped VS could be in part related to fibre fractions that weren't analysed in the samples.

SS-OFMSW from fruit and vegetable markets, household, canteens, restaurant and bakery had elevate carbohydrate load. SwS samples showed higher protein concentration than OFMSW samples, this is also confirmed by elemental analysis and C/N calculated ratios. High lipid concentrations were measured in bakery, canteens and restaurants wastes. Lipids must be considered very important macromolecular components related to methane productive fraction in organic substrates, an increment in lipid concentration could enhance methane production in anaerobic digestion but, at the same time, lipid charge in the matrices can lead to inhibitory effects caused by long chain fatty acids arising from lipid hydrolysis (Chen et al., 2008). VFA concentration in fresh samples showed the advanced state of fermentation of SwS, probably due to presence of anaerobiosis zone in the thickener of the WWTP. In SS-OFMSW samples, VFA are mainly made by acetic acid fraction, which is directly available to methanogens populations.

Table 1.1 Characteristics of organic substrates analyzed in this study, average values (std)

		SwS	FVW 1	Canteen 1
TS	[% WW]	3.50 (0.07)	4.40 (0.12)	3.80 (0.14)
VS	[% WW]	2.29 (0.06)	3.93 (0.06)	3.60 (0.10)
VS/TS	[%]	65.50 (3.22)	89.30 (4.78)	94.70 (2.85)
CODs	[mg/l]	1624 (159)	21400 (2931)	34500 (4840)
TKN	[mgN/l]	1465 (236)	1026 (149)	897 (119)
NH_4^+	[mgN/l]	205.7 (17.5)	130.4 (11.9)	129.7 (11.8)
P tot	[% of TS]	1.35 (0.09)	0.43 (0.04)	0.15 (0.01)
SO_4^{2-}	[mg/l]	2.3 (0.13)	143.4 (11.75)	59.4 (4.15)
pH	[-]	5.26 (0.01)	4.57 (0.01)	4.13 (0.01)
C	[% of TS]	37.68 (0.30)	46.45 (0.35)	42.75 (0.05)
H	[% of TS]	5.64 (0.35)	7.30 (0.20)	6.60 (0.10)
N	[% of TS]	3.56 (0.05)	2.05 (0.15)	2.50 (0.05)
C/N	[%TS/%TS]	10.59 (0.03)	22.66 (1.49)	17.10 (0.02)
Carb tot	[%g/gVS]	10.62 (0.56)	15.51 (0.96)	27.90 (1.76)
Carb sol	[%g/gVS]	0.23 (0.04)	6.12 (0.38)	2.85 (0.13)
Prot	[%g/gVS]	33.78 (2.29)	14.02 (1.11)	13.11 (0.97)
Lip	[%g/gVS]	11.42 (0.83)	6.26 (0.51)	11.59 (0.79)
HAc	[mg/l]	323.32 (6.78)	1162.39 (23.01)	191,33 (4.69)
HPro	[mg/l]	222.16 (3.99)	1.97 (0.04)	1.17 (0.03)
HBut	[mg/l]	19.71 (0.08)	0.49 (0.02)	1.15 (0.03)
HIso-but	[mg/l]	5.19 (0.14)	0.21 (0.01)	0.35 (0.01)
HVal	[mg/l]	2.95 (0.04)	0.41 (0.02)	0.00
HIso-val	[mg/l]	3.57 (0.08)	0.17 (0.01)	0.00

CODs=measured in filtrate sample, Carb tot=Total carbohydrates, Carb sol=Carbohydrates in filtered sample, Prot=Proteins, Lip=Lipids, HAc=Acetic Acid, HPro=Propionic Acid, HBut=Butyric acid, HIso-but=Isobutyric acid, HVal=Valeric acid, HIso-val=Isovaleric acid

		FVW 2	Supermarket 1	Household
TS	[% WW]	4.50 (0.26)	4.50 (0.18)	3.60 (0.15)
VS	[% WW]	4.01 (0.23)	3.96 (0.12)	3.30 (0.07)
VS/TS	[%]	89.10 (4.03)	87.90 (2.97)	91.80 (4.96)
CODs	[mg/l]	35104 (3440)	33000 (3739)	21604 (2594)
TKN	[mgN/l]	1108 (165)	1159 (169)	863 (127)
NH_4^+	[mgN/l]	196.4 (16.7)	189.5 (14.9)	77.6 (6.8)
P tot	[% of TS]	0.41 (0.05)	0.45 (0.04)	0.21 (0.02)
SO_4^{2-}	[mg/l]	213.5 (20.01)	315.9 (29.76)	47.7 (4.34)
pH	[-]	3.68 (0.01)	3.86 (0.01)	3.54 (0.01)
C	[% of TS]	39.05 (0.55)	42.40 (0.30)	37.60 (0.60)
H	[% of TS]	5.80 (0.10)	6.50 (0.05)	5.60 (0.50)
N	[% of TS]	2.40 (0.10)	1.80 (0.30)	2.75 (0.35)
C/N	[%TS/%TS]	16.27 (0.91)	23.56 (3.87)	13.67 (1.55)
Carb tot	[%g/gVS]	34.00 (1.73)	10.72 (0.64)	35.04 (2.21)
Carb sol	[%g/gVS]	3.66 (0.21)	2.34 (0.16)	4.77 (0.32)
Prot	[%g/gVS]	13.98 (1.25)	15.07 (0.14)	14.61 (0.17)
Lip	[%g/gVS]	5.95 (0.54)	5.82 (0.43)	6.09 (0.36)
HAc	[mg/l]	311.38 (9.40)	2109.79 (57.81)	389.05 (8.95)
HPro	[mg/l]	9.73 (0.26)	19.21 (0.52)	10.73 (0.30)
HBut	[mg/l]	2.77 (0.07)	1.89 (0.05)	1.74 (0.05)
HIso-but	[mg/l]	0.21 (0.03)	0.17 (0.01)	0.20 (0.01)
HVal	[mg/l]	0.00	0.00	0.00
HIso-val	[mg/l]	0.39 (0.01)	1.39 (0.02)	0.15 (0.03)

		Supermarket 2	Bakery	Restaurant
TS	[% WW]	4.50 (0.12)	4.40 (0.16)	3.70 (0.21)
VS	[% WW]	3.78 (0.09)	4.31 (0.12)	3.45 (0.16)
VS/TS	[%]	84.10 (4.29)	98.00 (1.68)	93.30 (2.51)
CODs	[mg/l]	30032 (3072)	22784 (2802)	22936 (2264)
TKN	[mgN/l]	1319 (193)	760 (106)	1318 (92)
NH_4^+	[mgN/l]	183.2 (16.0)	78.4 (6.6)	169.3 (15.4)
P tot	[% of TS]	0.37 (0.03)	0.21 (0.02)	0.36 (0.02)
SO_4^{2-}	[mg/l]	288.9 (32.3)	25.4 (2.46)	52.9 (4.22)
pH	[-]	3.79 (0.01)	4.00 (0.01)	4.00 (0.01)
C	[% of TS]	40.72 (0.35)	53.30 (0.30)	49.20 (0.90)
H	[% of TS]	6.15 (0.05)	8.40 (0.20)	7.30 (0.05)
N	[% of TS]	2.10 (0.05)	1.70 (0.05)	3.25 (0.05)
C/N	[%TS/%TS]	19.39 (0.08)	31.35 (0.18)	15.14 (0.04)
Carb tot	[%g/gVS]	13.75 (0.74)	34.14 (2.08)	42.47 (2.54)
Carb sol	[%g/gVS]	4.87 (0.36)	6.91 (0.44)	3.47 (0.19)
Prot	[%g/gVS]	18.46 (1.69)	9.72 (0.81)	20.46 (1.60)
Lip	[%g/gVS]	5.95 (0.51)	25.03 (1.91)	18.67 (1.27)
HAc	[mg/l]	1218.96 (36.69)	156.08 (4.49)	434.86 (13.01)
HPro	[mg/l]	14.63 (0.43)	10.77 (0.30)	6.20 (0.18)
HBut	[mg/l]	6.06 (0.18)	1.47 (0.03)	0.70 (0.02)
HIso-but	[mg/l]	0.26 (0.03)	0.10 (0.01)	0.18 (0.02)
HVal	[mg/l]	0.00	0.00	0.00
HIso-val	[mg/l]	0.19 (0.01)	0.00	0.00

		Canteen 2
TS	[% WW]	3.00 (0.18)
VS	[% WW]	2.87 (0.16)
VS/TS	[%]	95.80 (4.32)
CODs	[mg/l]	10772 (1475)
TKN	[mgN/l]	903 (131)
NH_4^+	[mgN/l]	104.8 (9.7)
P tot	[% of TS]	0.32 (0.03)
SO_4^{2-}	[mg/l]	22.8 (2.03)
pH	[-]	4.10 (0.01)
C	[% of TS]	56.50 (0.60)
H	[% of TS]	8.80 (0.209
N	[% of TS]	2.80 (0.10)
C/N	[%TS/%TS]	20.18 (0.94)
Carb tot	[%g/gVS]	34.24 (2.32)
Carb sol	[%g/gVS]	8.73 (0.65)
Prot	[%g/gVS]	17.08 (1.64)
Lip	[%g/gVS]	21.45 (1.80)
HAc	[mg/l]	29.95 (0.89)
HPro	[mg/l]	12.51 (0.33)
HBut	[mg/l]	0.14 (0.01)
HIso-but	[mg/l]	0.02 (0.01)
HVal	[mg/l]	0.00
HIso-val	[mg/l]	0.00

VS fractionation comparison, related to macromolecular compounds analysed, is reported in figure 1.1 to visually highlight the different organic characteristics.

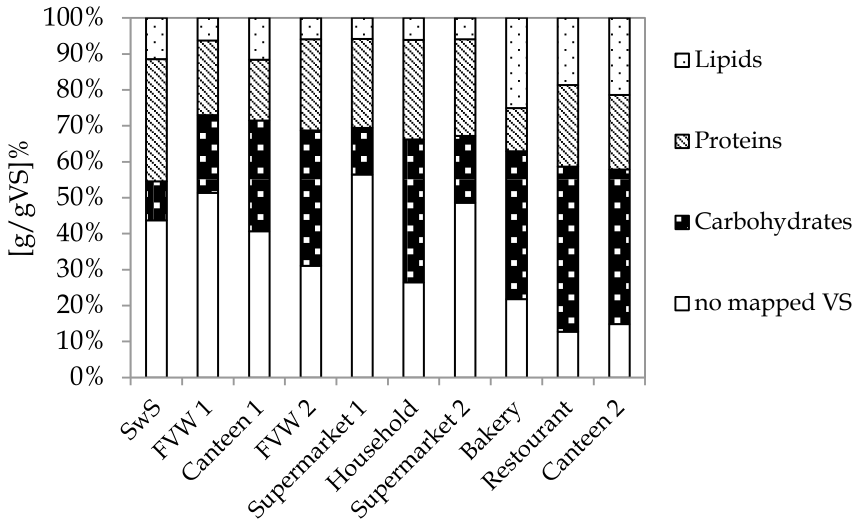


Figure 1.1 VS fractionation comparison of organic substrates analysed

1.4 CONCLUSIONS

The characterization phase had highlighted the difference between substrates both to an AD process perspective and to OFMSW management. For AD process, sewage sludge characterization underlined the necessity of a complementary substrate rich in carbohydrates and lipids to optimize AD feed. The collection basin analysis allowed to define which source selected producers can provide this kind of substrates.

The macromolecular compound analysis is a key step to characterize the substrates but a lack in literature guidelines, to perform this analysis, has emerged during the study. In particular, there isn't a defined protocol to perform substrates pre-treatments. The absence of standardized methodology implies a self-method adoption that causes a difficult data comparison between different studies.

2 Biochemical methane potential tests (BMP)

2.1 INTRODUCTION

The biochemical methane potential test (BMP) allows to determine the methane yield of an organic substrate by monitoring the biomass degradation activity in a lab reactor. BMP tests are influenced by several variables and the lack of international guidelines determines the absence of a clear procedure to apply. A wide literature is present and the last efforts done by the scientific community (Raposo et al., 2011a; Raposo et al., 2011b) enable to set reliable experimentation. The main factors affecting BMP test are linked to the inoculum characteristics (source, storage, activity), the gas measurement system (volumetric or manometric methods), the operational conditions (reactor volume, temperature, mixing system, trial duration), the chemical operational conditions (headspace gas, pH and alkalinity adjustment, mineral medium) and the inoculum to substrate ratio (ISR) choice (Raposo et al. 2011b).

2.2 MATERIAL AND METHODS

2.2.1 EXPERIMENTAL SET-UP AND PROCEDURE

BMP tests were carried out following guidelines proposed by two recent studies (Raposo et al., 2011b; Angelidaki et al., 2009). BMP tests were performed in two experimental phases: in the first one, tests were carried out on SwS and SS-OFMSW mono-substrates and in the second phase on SwS and SS-OFMSW mixture (OFMSW-MIX) in AcoD regime (these tests were named CO-DIG1 and CO-DIG2). In the first experimental session, glass bottles with a working volume of 400ml and headspace volume of 100ml were used. Bottles were maintained at mesophilic temperatures (37°C) in a thermostatic bath for 30 days and stirred by mechanical mixing at 40 rpm for 10 seconds every 1 minute. Before starting anaerobic digestion, each bottle headspace was flushed by N_2 gas. Methane measurements were performed by a volumetric device (AMPTS II, Bioprocess Control, Sweden) with alkaline solution for biogas washing (figure 2.1).

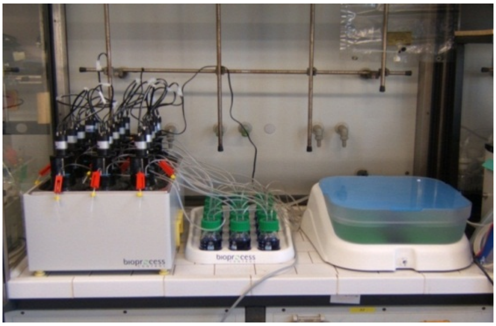


Figure 2.1 AMPTS II device, Bioprocess Control, Sweden.

No pH and alkalinity adjustments were performed due to high buffer capacity of sewage sludge seed and also to check process behaviour without any chemical interference (Sosnowsky et al. 2008). No any mineral medium was added to the mixture with the hypothesis that the lack in micronutrient and trace elements is offset by the inoculum. Blank controls were conducted to obtain the residual biogas production by inoculum alone. Particle size can affect process kinetics, due to the amount of available specific surface area for microorganism action (Lesteur et al. 2010). Accordingly, OFMSW samples were ground by a mincer, diluted with tap water and shredded by a kitchen mixer obtaining a common optimal ≤ 10mm particle size (Raposo et al., 2011b) in the mixture, in which Total Solids (TS) were maintained below 3÷4.5%TS. Inocula and substrates were stored for 3 days at 4°C before tests. BMP tests were carried out in triplicate. In the second experimental session, glass bottles working volume was increased to 1600 ml with an headspace volume of 400 ml, with the aim to supply significative amounts of substrates to AcoD. The same procedure previously described was followed. The net methane production of organic substrates in BMP test, was obtained detracting the inoculum contribution of the blank control. Methane and biogas yields were referred, together to specific methane production rates, to Standard Temperature and Pressure (STP) conditions. The results reported are expressed as average of three samples.

2.2.2 INOCULUM TO SUBSTRATE RATIO (ISR)

In literature experimental data demonstrated that the ultimate methane yield as well as the methane production rates are dependent on the specific substrates and inoculum (Eskicioglu et al., 2011). Large inoculations volumes ensure high microbial activity, low risk for overloading and low risk of inhibition (Angelidaki and Sanders, 2004).
Some researchers (Raposo et al., 2011a) considering that an ISR≥2, on VS basis, has never been reported as inhibitory, suggest this ratio as mandatory for standardized tests.
In this study, BMP tests were conducted at a safe ISR of 3 (on VS basis), which was chosen to prevent any inhibitory effect, bound to OFMSW anaerobic digestion. Only for BMP tests on SwS, different ISR (1, 1.5, 2 and 3) were adopted to verify the influence of this parameter on the biomass degradation activity. The inoculum was extracted by the primary mesophilic anaerobic digester by the Udine WWTP, Italy.

2.2.3 ANALYTICAL METHODS

The analytical methods used are the same described in the chapter 1.

2.3 RESULTS&DISCUSSION

2.3.1 INOCULA CHARACTERISTICS

Inoculum characterization was performed for each BMP trial. In table 2.1 the analyzed parameters results are reported as average values of all inocula used. Blank methane production was 84.52±12.98NmlCH_4/gVS add.

Table 2.1 Characteristics of inoculum.

		Inoculum
TS	[% WW]	2.22 (0.20)
VS	[% WW]	1.21 (0.13)
VS/TS	[%]	54.28 (1.53)
CODs	[mg/l]	1683.00 (525.49)
TKN	[mgN/l]	1292.20 (218.23)
NH_4^+	[mgN/l]	465.27 (45.17)
P tot	[% of TS]	1.36 (0.24)
SO_4^{2-}	[mg/l]	6.25 (2.92)
pH	[-]	7.15 (0.11)
Alkalinity	[mg$CaCO_3$/l]	2108.00 (250.96)
C	[% of TS]	27.77 (2.98)
H	[% of TS]	3.99 (0.70)
N	[% of TS]	3.10 (0.53)
C/N	[%TS/%TS]	9.07 (0.65)

2.3.2 BMP OF SwS AT DIFFERENT ISR

BMP tests on SwS at different ISR (1, 1.5, 2 and 3) highlighted that the increase of this parameter can influence both extent and rate of the biodegradation process. At ISR 3, the degradation process is rapidly developed. SMPR (specific methane production rate) curves had different production rate peaks, as showed in figure 2.2.

At ISR 3, the biomass to compete in substrate degradation was abundant and methane peak conversion occurred within the first 72 hours. At ISR 1, a large pick was registered bound to slow hydrolysis action by microorganism on particulate organic solids.

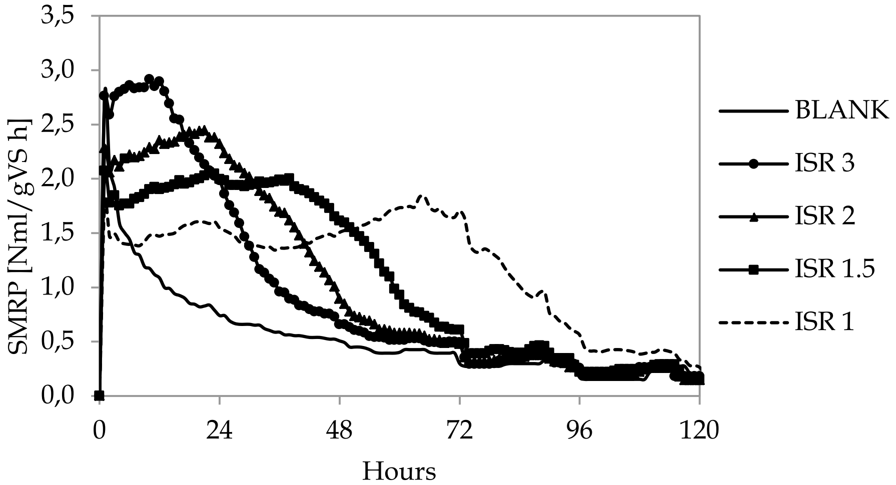


Figure 2.2 SMPR curves of SwS BMP tests at different ISR.

2.3.3 BMP OF MONO-SUBSTRATES

Cumulative methane yields trends are shown in figure 2.3. In table 2.2 results of mono-substrates testes are reported.

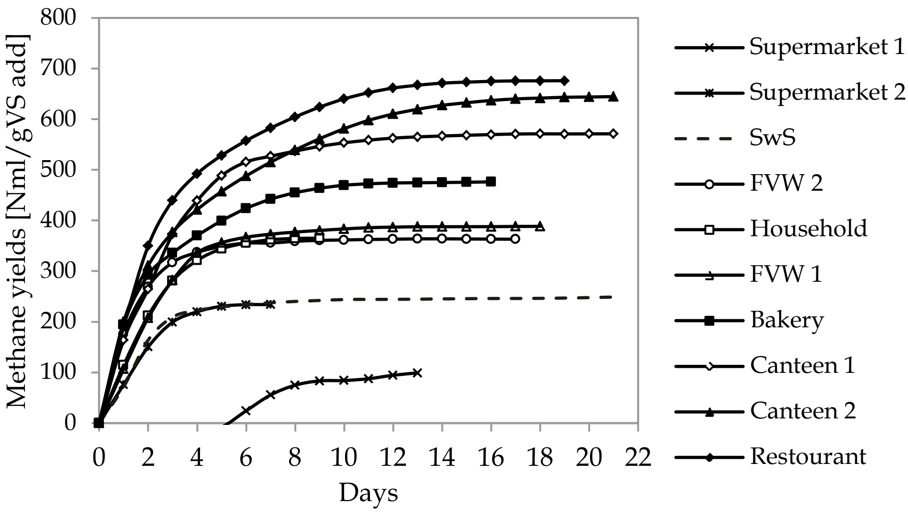


Figure 2.3 Cumulative methane yields curves of SS-OFMSW and SwS.

Table2.2 Results from BMP test on SwS and SS-OFMSW.

	Methane [NmlCH_4/gVS]
SwS	248.77 (4.13)
FVW1	338.37 (21.44)
Canteen1	571.16 (37.02)
FVW2	363.00 (20.86)
Supermarket1	99,08 (8.13)
Household	364,88 (7.28)
Supermarket2	233,85 (4.04)
Bakery	476,28 (22.15)
Restourant	675.22 (45.12)
Canteen2	644,64 (7.29)
OFMSW-MIX	491,00 (8.79)
CO-DIG1	293,03 (12.28)
CO-DIG2	365.49 (30.17)

Canteens, restaurant and bakery wastes highlighted good methane conversions degrees. The results obtained in this work revealed Supermarket1 and Supermarket2 haven't obtained BMP optimal trends probably due to initial high acid load of the matrices. Above all in the Supermarket1 test, the biomethanization process started after 6 days: one possible cause is related to very high organic acids concentration in the mixture (attested by VFA analysis) and the resulting inhibition of methanogen population.

Both FVW1 and FVW2 samples showed a methane yield somewhat greater than SwS substrate, while other SS-OFMSW have generally much higher methane production. Other similar researches (Jiang et al. 2012) reported a tendency of fruit and vegetable substrates to accumulate VFA which can lead to acidity, low pH and inhibition processes. In any case, it can be considered that supermarkets and FVW substrates are less adapt to be treated by mono-substrate AD process, while codigestion can be a solution to avoid VFA accumulation.

In table 2.3 data from literature about BMP tests on similar substrates are reported: between these authors only Zhang et al. (2012) and Ponsá et al. (2011) had performed tests with a high ISR, respectively of 4 and 2.

Table 2.3 BMP data from literature.

Organic substrates	BMP [$mlCH_4$/VS add]	References
Household waste	456	Zhang et al. 2012
	472	Cho et al., 1995
Restaurant waste	430	Liu et al., 2009
	390	Neves et al.2008
FVW	352	Jiang et al. 2012
OFMSW	382	Ponsa et al. 2011
	300-570	Davidsson et al. 2007
	353	El-Mashad and Zhang, 2010
	186-222	Owens and Chynowet., 1993
	360	Shanmugam and Horan, 2009
	525	Lissens et al., 2004

Values comparison confirmed the good methane production potential of some SS-OFMSW substrates considered in this study. This could be correlated both to organic quality of substrates and optimal ISR choice. As observed in other works (Labatut et al. 2011), substrates rich in lipids and easily biodegradable carbohydrates had commonly the highest methane yields, while more recalcitrant substrates with high lignocellulosic fraction had the lowest. Restaurant waste showed the highest methane yield. During sampling operations the presence of yeast residues (typically used as base for bread making process) were observed, the high extent and rate of restaurant waste biodegradation could be related to these yeast residues. Other authors (Zitomer et al., 2008) have observed the same phenomena, accounting high BMP values to promoted microbiological activity due to the presence of trace nutrients in yeast wastes. Further BMP tests were performed to deep understand the influence of yeast residues, results are reported in appendix.

2.3.4 BMP OF MIXED SUBSTRATES IN AcoD REGIME

In the second experimental session, tests were performed with selected OFMSW mixture to assay AcoD process with SwS. A mixture (OFMSW-MIX) of FVW2 and restaurant organic substrates was blended in ratio 1:1 (w/w) and used in AcoD tests.

The choice of OFMSW-MIX substrate components was based both on chemical-physical substrate characteristics and on waste management perspective, considering the substrates availability in sufficient quantities near the WWTP for an AcoD upgrade. The first test named CO-DIG1 had an OFMSW-MIX:SwS ratio of 0,23 gVS/gVS. The criteria to select the codigestion ratio CO-DIG1 followed suggestions given for a typical ratio reported in literature (Bolzonella et al., 2006) for AcoD in WWTP (10% of OFMSW in AD supply).

A second test (CO-DIG2) was carried out with a ratio of 2,09 gVS/gVS. CO-DIG2 ratio is linked to the maximum additional treatment capacity for the anaerobic digester considered in this study (50% of OFMSW added to supply feed). C/N ratio of CO-DIG1 and CO-DIG2 substrates increased, compared to SwS, respectively of 4.6% and 25.3%. The C/N ratio is a key parameter to understand the nutrient balance of AD supply, in this study the C/N ratio improvement was within the range 6÷15.4, a typical range as reported by other studies for OFMSW addition in SwS digestion (Iacovidou et al., 2012). In literature there are only few studies regarding batch AcoD in similar test conditions: Sosnowski et al. (2008) in AcoD regime with sewage sludge 75%vol. and OFMSW 25%vol. had registered a 38% methane yield increase respect sewage sludge only. Kim et al. (2011), had conducted test on OFMSW from kitchen residues and thickened sludge in a VS mixing ratio 40:60 obtaining a BMP of 240 mlCH_4/gVSadd. Li et al. (2011) observed that AcoD of waste activated sludge with synthetic kitchen waste enhanced methane production from 117±2.02 mL/gVS to 324±13.7 mL/gVS. BMP values for CO-DIG1 and CO-DIG2 are reported in table 2.2. CO-DIG1 and CO-DIG2 have highlighted an increase in methane production of 18% and 47% respectively, compared to SwS.

Methane yields curves were reported in figure 2.4. Only a minor synergistic effect can be observed in CO-DIG1 test on methane production, where a little increase (+6.9%) was registered respect absolute quantity calculated from BMP test results on single substrates.

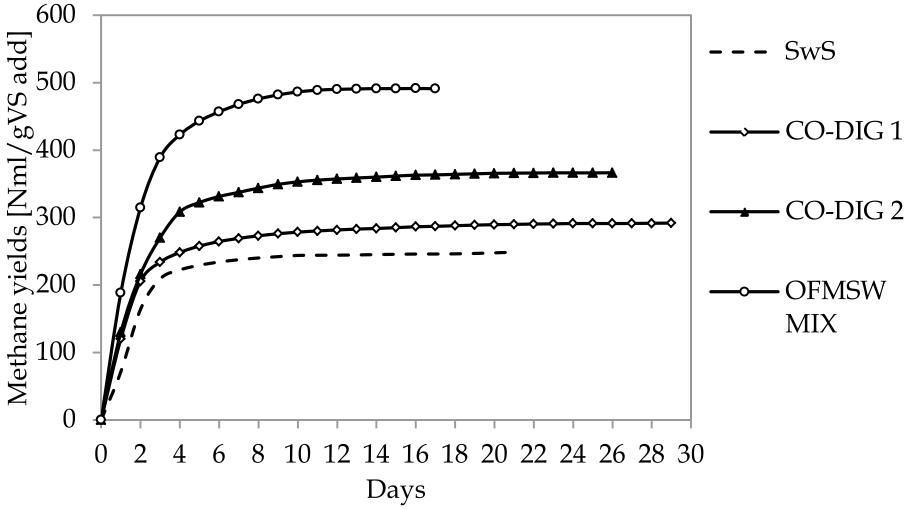


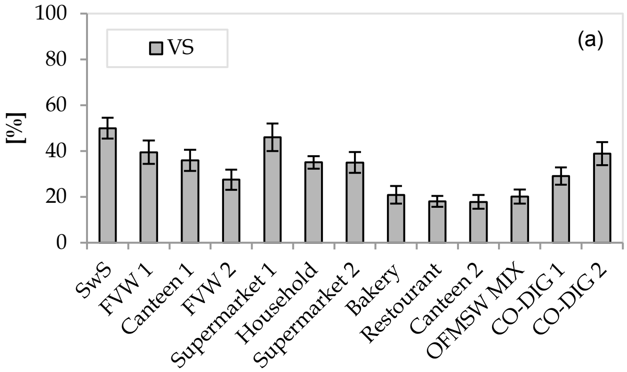
Figure 2.4 Cumulative methane yields curves of mixture: OFMSW-MIX, CO-DIG1 and CO-DIG2.

2.3.5 BMP ANALYTICAL PARAMETERS RESULTS

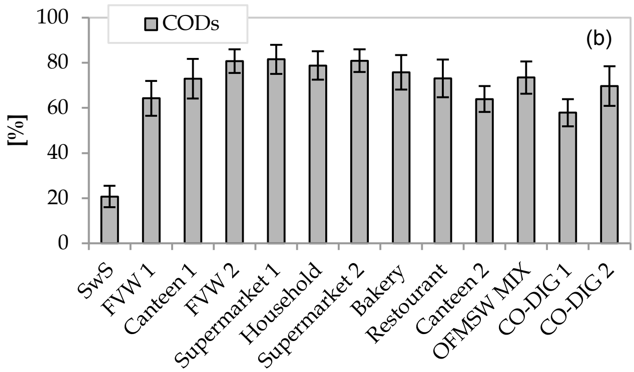
In the BMP samples analyzed, the final sludge concentration was between 2 and 2.4%TS. With an average VS removal efficiency of 33%, the figure 2.5a reports the VS decrease in each trial. A good abatement in soluble COD was registered (Fig.2.5b) with an average value of 69%.

Total and soluble carbohydrates (Fig.2.5c) were consumed in AD process with an average percentage respectively of 74% and 84%, while breakdown of total proteins concentration reach about of 40% on average (Fig.2.5d). Lipids percent removal was near 61% (Fig.2.5e).

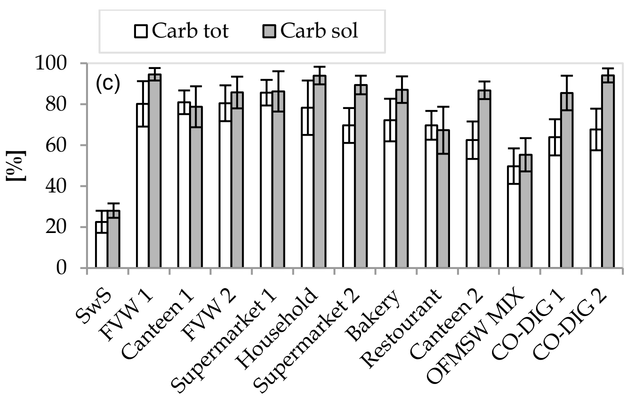
Final alkalinity in all samples ranged from 2047 to 2949 mg$CaCO_3$/l and pH from 7,27 to 7,96. Final SO_4^{2-} concentrations were included in the range 5÷21mg/l with an average abatement of 70%, due to sulfate reducing bacteria metabolism action.



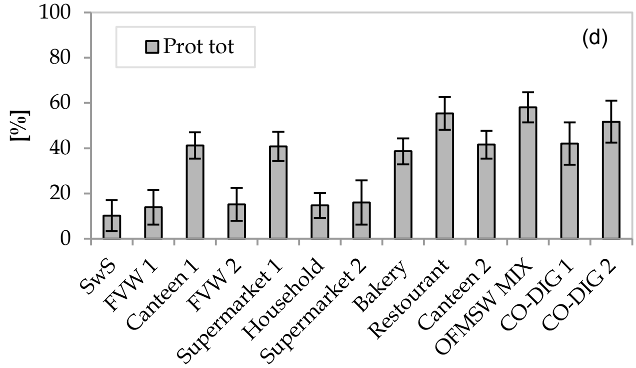
VS
(a)
[%]
100
80
60
40
20
0
SwS
FVW 1
Canteen 1
FVW 2
Supermarket 1
Household
Supermarket 2
Bakery
Restourant
Canteen 2
OFMSW MIX
CO-DIG 1
CO-DIG 2



CODs
(b)
[%]
100
80
60
40
20
0
SwS
FVW 1
Canteen 1
FVW 2
Supermarket 1
Household
Supermarket 2
Bakery
Restourant
Canteen 2
OFMSW MIX
CO-DIG 1
CO-DIG 2



Carb tot
Carb sol
(c)
[%]
100
80
60
40
20
0
SwS
FVW 1
Canteen 1
FVW 2
Supermarket 1
Household
Supermarket 2
Bakery
Restourant
Canteen 2
OFMSW MIX
CO-DIG 1
CO-DIG 2



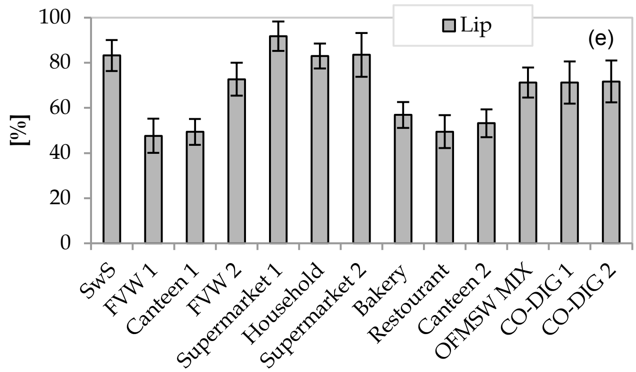


Figure 2.5 Abatement of VS (a), soluble COD (b), total and soluble carbohydrates (c), proteins (d) and lipids (e) in BMP test of SS-OFMSW and SwS.

2.4 CONCLUSIONS

The BMP test is a good tool to understand the availability of the substrate to the biomass metabolism and identify inhibition phenomena. The SMPR curves and methane yields curves analysis is useful to understand the kinetic mechanism of the biodegradation. A drawback in this kind of test is the lack of a standardized protocol recognised by international scientific community: in the last years some efforts were done, especially by interlaboratory tests but the device used and the boundary conditions of experiments still remain too different to determine always comparable results. In this research, the experimental conditions during trials were fixed in terms of ISR, measurement device, inoculum source, temperature, mixing, no mineral medium or trace elements additions. BMP values of different OFMSW substrates from the collection basin, had allowed to identify the best substrates to consider in the AcoD process.

3 Pilot plant test

3.1 INTRODUCTION

Pilot plant tests are performed to conduct processes in a comparable scale to real reactors. In this study, the aim was to reproduce in the pilot plant, the WWTP AD reactor behaviour and test the up-grade to codigestion by increasing the organic loading conditions. These types of trials in CSTR regime allows to stress biomass and verify the response, obtaining reliable result for the process application to full-scale reactors.

3.2 MATERIAL AND METHODS

3.2.1 PILOT PLANT CONFIGURATION

The pilot plant is designed to implement the AD process in a 1:1000 scale respect the AD existing unit in Udine WWTP. The pilot plant is formed by 3 sections:

- Substrates pre-treatment;
- AD unit;
- Biogas line.

3.2.1.1 Substrates pre-treatment

The substrates pre-treatment section has to guarantee the optimal size level of the incoming material. The shredding tank is designed with a volume able to contain the substrate load to fill the feeding tank. Inside the shredding tank a moving bulkhead allows to create the optimal free surface height for the shredding circuit. In the shredding circuit, a pump sends the substrates mixture to a perforated plate shredder: the substrate mixture is recirculated to achieve the optimal material size. From the shredding tank, a pipe allows to direct the mixture to the feeding tank. With the aim of define the correct substrates amounts required, the piping lines of the circuit volumes were considered and calculated as 48 liters. In table 3.1 technical data ara listed. In figure 3.1 a photo of the pre-treatment section is reported. Shredding times were defined in function of the material size: they ranged from 10 to 30 minutes. During experimentation a 5mm filtering mesh was inserted in the shredding circuit to intercept fibrous materials (abundant in sewage sludge) to protect the downstream pumps of the pilot plant.

Table 3.1 Pre-treatment section technical data.

Section unit		
Shredding tank	Total volume	540 Liters L 1,5m x W 0,6m x H 0,6m
	Partial volume with moving bulkhead inserted	150 Liters L 0,5m x W 0,5m x 0,6m
Shredder	n° holes	16 (ø 14mm)
	Power	2,2 kW

Figure 3.1 Substrates pre-tratment section.

3.2.1.2 AD unit

The AD unit is formed by:

- Feeding tank;
- Loading pump;
- Internal recirculation pump and heat exchanger;
- Anaerobic digester;
- External recirculation pump;
- Discharging pump.

3.2.1.2.1 Feeding tank

The feeding tank has a cylindrical shape and is equipped with a vertical mixing system in order to avoid material sedimentation. A pipe, connected to the tank bottom, allows the connection to the loading pump. In table 3.2 technical data are listed. In figure 3.2 a photo of the feeding tank is reported.

Table 3.2 Pre-treatment section technical data.

Section unit		
Feeding tank	Total volume	294 Liters ø 0,19m x H 2,4m
Mixer	Power	0,55 kW

Figure 3.2 Feeding tank.

3.2.1.2.2 Loading pump

The loading pump it's a monoscrew pump able to dose flow in the range 40÷70 ml/min of substrate necessary to perform the experimental phases. During the experimentation, the strong wear determined by sands and the obstruction due to the accumulation of fibrous materials present in the substrate, led to frequent rotor and stator replacements of the loading pump. This was partially solved by the adoption of the filtering mesh previously described. The incoming substrate is pumped into the load pipe of the internal recirculation pump, in order to convey the charge to the heat exchanger.

3.2.1.2.3 Internal recirculation pump and heat exchanger

The internal circulation pump sends to the heat exchanger an amount equal to 150 l/h of sludge from AD reactor together with the incoming substrate. This flow rate was chosen in order to maintain the correct process temperature of 37°C. The double-pipe heat exchanger receives hot water from a boiler with a maximum temperature of 45°C, controlled by the temperature regulation system. This choice has been made in order to avoid too high temperatures that can change the optimal range of activity and growth of the bacterial biomass. In figure 3.3 is shown, on the left, the double-pipe heat exchanger and, on the right, the temperature regulation system and the expansion vessel.

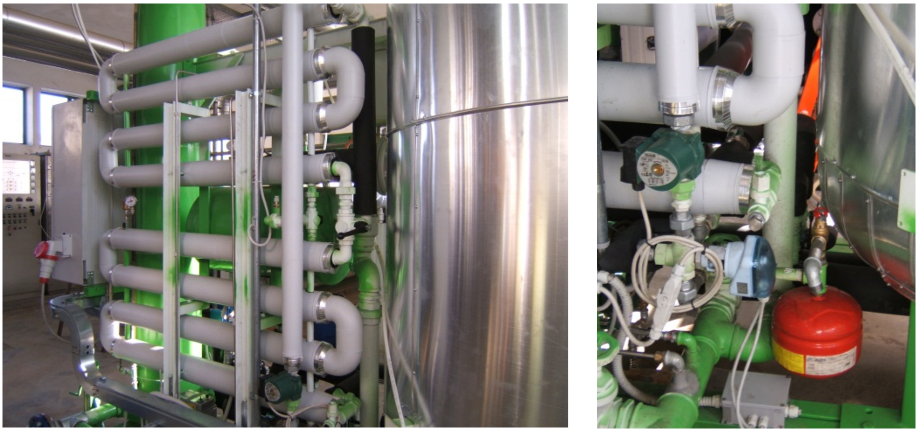


Figure 3.3 The double-pipe heat exchanger on the left and, on the right, the temperature regulation system and the expansion vessel.

3.2.1.2.4 Anaerobic Digester

The anaerobic digester pilot plant has a volume that reproduces the WWTP digester on a 1:1000 scale. It has been dimensioned for a 3.4 m^3 total volume with an effective volume ranging from 1.8 to 2.3 m^3. The remaining volume has a gasometer function. The mixture of fresh load and recirculated sludge, coming from the heat exchanger, are input in the digester by four vertical perforated pipes positioned to induce a mild mixing to the input stream, respect the vertical axis. The digester is provided, in the upper part, of a scraper set into motion by a hydraulic motor that allows to convey in special drains any foam or crusts. At 30 cm from the reactor bottom is placed a perforated plate, below which there are the inlet pipes of the internal recirculation and the external recirculation pumps.

On the bottom of the digester is placed the inlet pipe for the discharge pump. The digester is equipped with thermocouples that record the temperature at 6 different vertical points. The point below the free surface has been used for the temperature regulation probe housing, in order to optimize the control inside the digester. The reactor is also equipped with 6 lateral taps to withdraw samples and control biomass concentration.

In figure 3.4 the anaerobic digester is shown, on the right there are the scrapers internal detail and the piping extraction system.

Figure 3.4 On the left the anaerobic digester and, on the right, the scrapers internal detail and the piping extraction system.

3.2.1.2.5 External recirculation pump

The external recirculation pump, installed during the start-up phase, has allowed to increase the W/m^3 dedicated to digester mixing. The DVTT (Digester Volume Turnover Time) was decreased to 4 hours with a recirculation rate of 450 liters per hour.

This up-grade was performed to limit the internal temperature stratification phenomena and the develop of dead volumes.

3.2.1.2.6 Discharging pump

The discharging pump is, as the loading pump, a monoscrew pump. The digestate stream is direct in the discharging foams pipe. This pipe is U-bend pipe to avoid the biogas leakage.

3.2.1.3 Biogas line

The biogas flow is sent to the gas line, which is composed of:
- water condensation column;
- silica gel adsorption column;
- activated carbon adsorption column;
- flow meter and non-return valve.

3.2.1.3.1 Water condensation column

The water condensation column is a chamber surrounded by a cold water jacket. The contact between gas at 37°C and cold chamber walls allows to condense the water vapor, which is discharged manually through a bottom chamber valve.

3.2.1.3.2 Silica gel adsorption column

The silica gel eliminates the residual biogas humidity from the water condensate column downstream.
The adsorption column design was carried out assuming the silica gel renewal once a month with a 5 liters working volume.

3.2.1.3.3 Activated carbon adsorption column

The activated carbons adsorb acid gases such as H_2S in order to protect the downstream equipment.
The column volume was designed to contain 1 kg of active carbon to cover one year of biogas pilot plant work, under process conditions considered in the project.

3.2.1.3.4 Flow meter and non-return valve

The biogas production is monitored by a flow meter. A non-return valve is placed downstream of the flow meter to maintain the gas line at 20mbar pressure. In figure 3.5 are shown the pictures relative, on the left, to the biogas line columns and on the right of the flow meter.

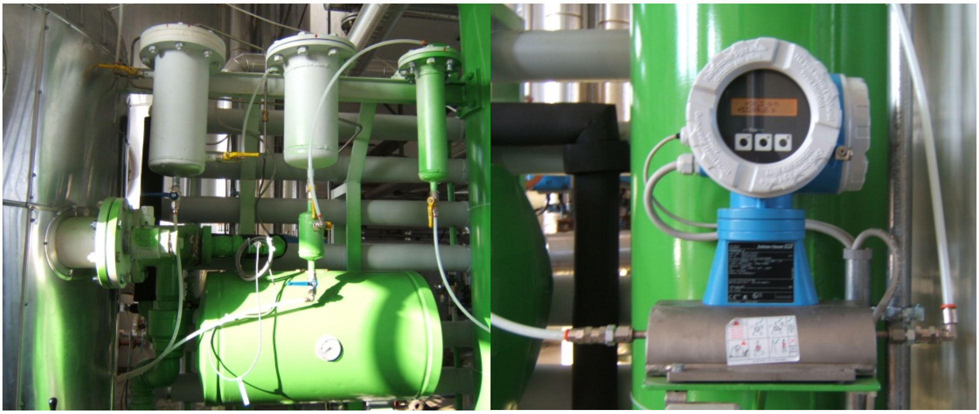


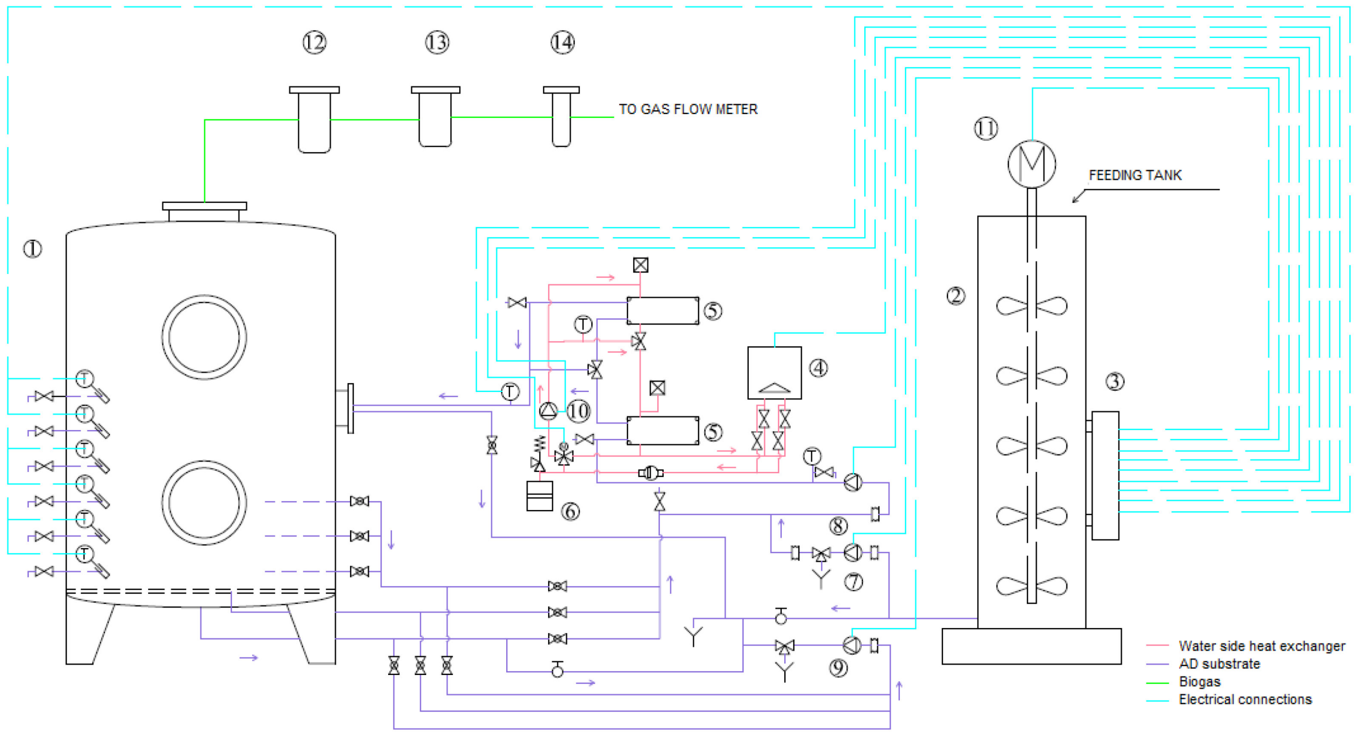
Figure 3.5 The biogas line columns and, on the right, the flow meter.

3.2.1.4 Pilot plant technical drownings

In figure 3.6 is reported the pilot plant process flow diagram without the substrate pre-tratment section and in figure 3.7 the axonometric view is depicted. In figure 3.8 and in figure 3.9 the pilot plant technical drowning of, respectively the front and the back view are shown.

3.2.2 ANALYTICAL METHODS

The analytical methods used are the same described in the chapter 1.
Methane, carbon dioxide and hydrogen sulfide content in the biogas were mesuered according to ISO 6974-6:2002/COR1:2003 method. Potassium, lead, cadmium, zinc, nickel and total chromium analysis were performed using EPA 2015A 2007 and EPA 6020A 2007. Mercury and its compounds were measured by CNR IRSA Q 64 1985 and CNR IRSA 3080 B1 Q 100:1994 methods.
FOS parameter, for volatile organic acids as mgHAc/l, and TAC parameter, for alkaline buffer capacity as mg $CaCO_3$/l, were determined following HachLange tritation procedure. The analysis were performed 3 times per week.



LEGEND: (1) AD reactor (2) feeding tank (3) electrical panel (4) boiler (5) heat exchanger (6) expansion vessel (7) feeding pump (8) recirculation pump (9) discharging pump (10) boiler pump (11) mixing motor (12) water condensation column (13) silica gel adsorption column (14) activated carbon adsorption column.

Figure 3.6 Pilot plant process flow diagram

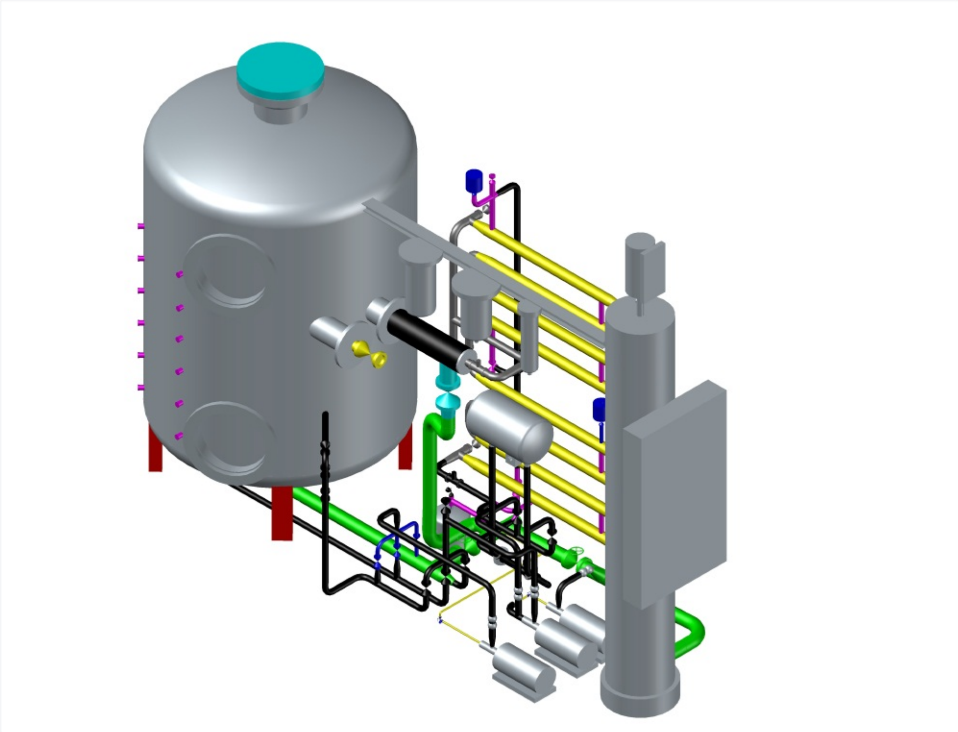


Figure 3.7 Pilot plant axonometric view (D'Orlandi, 2012).

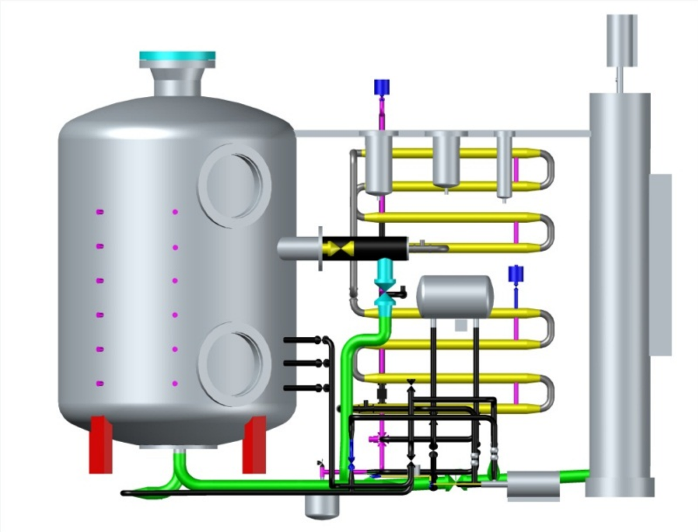


Figure 3.8 Pilot plant front view (D'Orlandi, 2012).

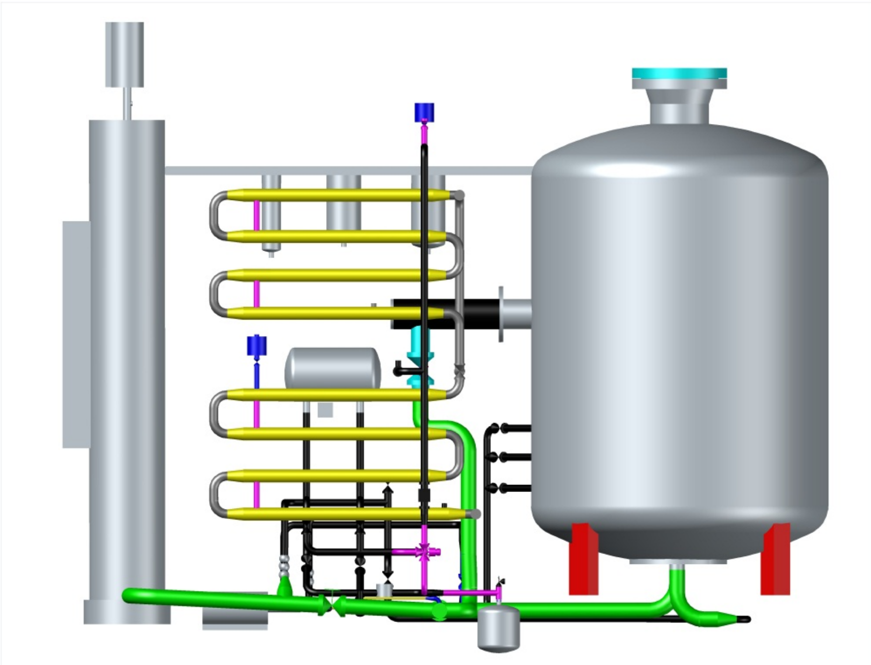


Figure 3.9 Pilot plant back view (D'Orlandi, 2012).

3.2.3 ORGANIC SUBSTRATES

SS-OFMSW substrates were collected from a canteen and in a friut and vegetable market, basing the choice on lab experimental results described in chapter 2. SwS was drown by the Udine WWTP thickener, as described in chapter 1. The inoculum, used for the start-up, was from the full-scale mesophilic AD unit digestate of Udine WWTP.

3.2.4 EXPERIMENTAL PROCEDURE

The experiment was conducted through six different stages with an increasing organic load to monitoring process efficiency and stability parameters. The OLR (Organic Loading Rate) ramp was based on cautionary feeding strategy increasing slowly OFMSW amounts in the supply, this is fundamental to avoid overload phenomena as reported by Cavinato et al. (2013). The AD reactor was operated under mesophilic conditions (37-38°C) and constantly mixed. The feeding and discharging operations were continuously carried out by pumps. The operation phase was 1 or 2 times the related HRT, phase 5 and 6 was conducted without achieve a complete HRT to test the biomass by a rapidly OLR increase. In the start-up phase pilot plant digester was inoculated with 1.8m^3 of biomass. After the start-up, stable conditions were reached by the sewage sludge digestion in phase 1 applying an OLR of 0.80 KgVS/m^{3}d with a HRT (Hydraulic Retention Time) of 24.3 days, to reproduce the full scale AD unit operational conditions. At the end of phase 1, the system was switched to AcoD increasing OLR and decreasing HRT to 20 days. The SS-OFMSW substrates were mixed, in equal proportions respect to the collection source, and the SS-OFMSW mixture amount was increased in the feeding mixture during the experimental phases: from 0.9 kg per day per m^3 of active reactor volume in the phase 2, to 17Kg/m^{3}d in phase 6.

Table 3.3 reports substrates percentages (weight based) in the feed during the experimental phases. In order to maintain the substrate in the fixed range in terms of the total solids concentration (to achieve the correct OLR increase and to not exceed the wet regime), treated wastewater was used to dilute and create the proper mixture. In Figure 3.10 the graph shows the OLR values applied: the bars indicate the minimum and maximum parameter value registered during each phase. In some phases, strong parameter variability was registered due to the sewage sludge daily variation, characterized by uncontrolled solids content, which has altered the final mixture properties of the pilot plant feed. Phase 3 has been particularly affected by this problem. OLR ranged from 0.80 KgVS/m^{3}d, in the first phase, up to 3.20 KgVS/m^{3}d in the last phase, in which the maximum loading conditions for the full scale AD unit were tested. (Figure 3.10).

Table 3.3 Substrates percentages (weight based) in the feed during the experimental phases.

Phase	1	2	3	4	5	6
SwS	100%	90,9%	90,9%	66,7%	66,7%	41,3%
SS-OFMSW	-	1,5%	3,0%	11,1%	16,7%	29,3%
Treated waste water	-	7,6%	6,1%	22,2%	16,6%	29,4%

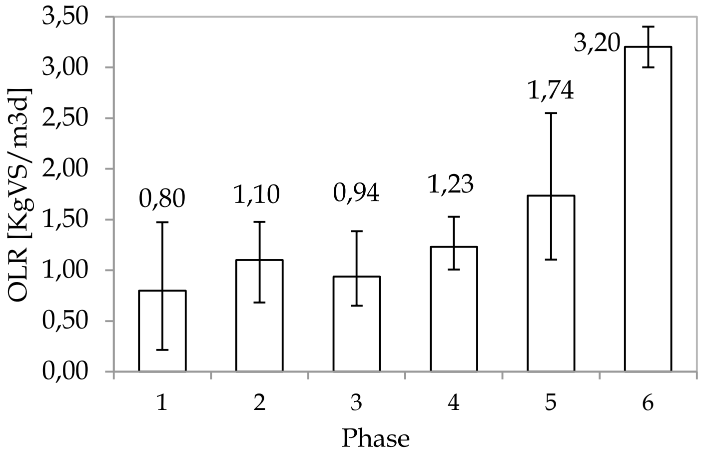


Figure 3.10 OLR values during the experimental phases, bars indicates parameter variability registerd in each phase.

3.3 RESULTS&DISCUSSION

The experimental pilot plant test was characterized by intensive parameters monitoring in order to control the process and establish its efficiency.
The physical-chemical parameters were measured both of input and output process substrates. A different set of analysis was performed in the substrate process withdrawn from the middle lateral digester taps (Table 3.4).

Table 3.4 Chemical-physical parameters analysed in each sample point.

Sample point	Feeding tank	AD reactor	Discharging pump
Parameters	pH	pH	pH
	TS,VS	Alkalinity	TS,VS
	Soluble COD	FOS/TAC	Soluble COD
	TKN	VFA	TKN
	Ammonia		Ammonia
	Sulphates		Sulphates
	Phosphorus		Phosphorus
	C,N		Heavy metals

In the following sections, monitoring results are illustrated. Graphs highlight average parameter value in each phase and the standard deviation.

3.3.1 TOTAL AND VOLATILE SOLIDS

The TS content was measured in each sample point. TS concentration ranged in the feeding mixture from 33mg/l to 75mg/l from phase 1 to phase 6 respectively (figure 3.11). Due to the high TS concentration variability of thickened sludge, as previously introduced, the TS feeding mixture concentration control was difficult in some phases: in particular phase 3 has been particularly affected by this problem.
In the digestate, total solids concentrations were measured in a variable range between 20 and 40mg/l, as shown in figure 3.11.
The SS-OFMSW biodegradability contribution is highlighted in figure 3.12 by VS data. The VS contraction has tripled compared from phase 1 to phase 6 in the extent of 20 to 64mg/l. The VS output values were registered in a range between 10 and 20mg/l during all phases, this underlines the good adaptability of the biomass to treat more concentrated loads, as tested in phase 5 and 6 where VS concentrations in substrate input were 35 and 65mg/l respectively.

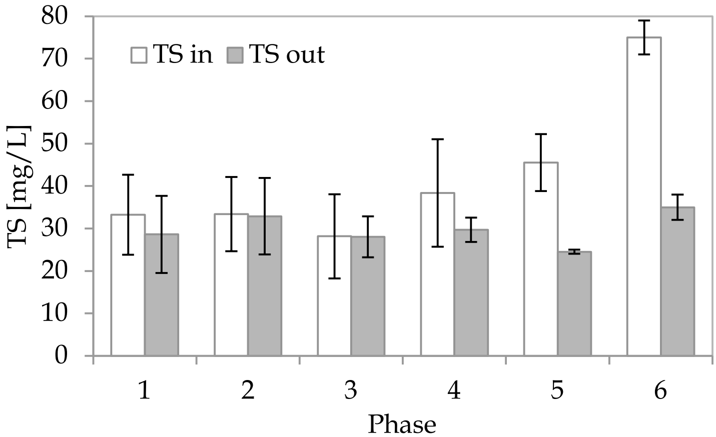


Figure 3.11 TS values during the experimental phases, in input substrate and digestate.

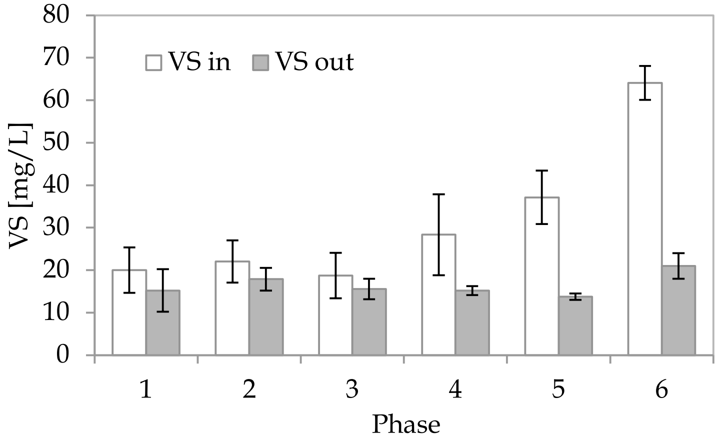


Figure 3.12 VS values during the experimental phases, in input substrate and digestate.

The VS/TS ratio increased from 61% of SwS digestion phase, up to 85% in phase 6 (figure 3.13). The linear interpolation on the average input shows the trend of increasing VS/TS ratio, highlighting the SS-OFMSW greater contribution to mixture biodegradability, whose typical TS/VS values is generally close to 90%, as reported in chapter 1.

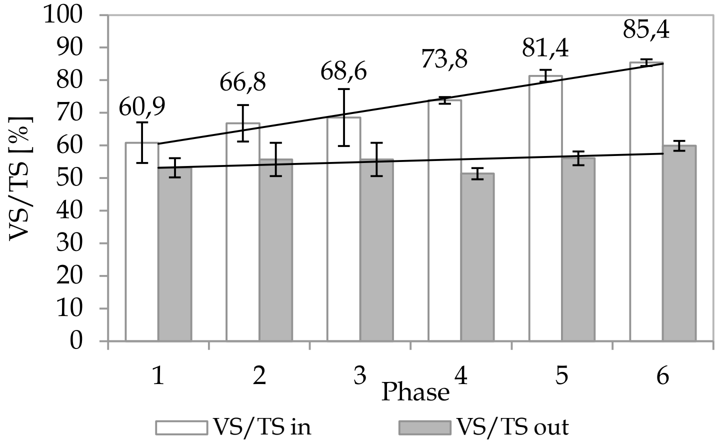


Figure 3.13 VS/TS ratio values in input substrate and digestate.

Data collected (table 3.5) from AD reactor sample point (tap n°3) analysis showed that TS were about 4mg/l reaching a minimum during the difficult management of phase 3.

These data underlined the substrate dilution in the central section of the active volume due to stratification phenomena. These data were confirmed by two samples extra campaigns performed, in which each lateral digester tap was sampled. Results are reported in figure 3.14: the stratification phenomena were limited to the 40 cm upper the reactor bottom and didn't influence negatively the process thanks to the high DDVT time imposed.

Table 3.5 TS, VS and TS/VS ratio values measured in each phase in relation to the sample point.

Sample point		**Phase**					
Feeding tank		**1**	**2**	**3**	**4**	**5**	**6**
TS	[mg/l]	33,2 (9,4)	33,4 (8,8)	28,1 (9,9)	38,3 (12,7)	45,5 (6,7)	75,0 (4,1)
VS	[mg/l]	20,0 (5,4)	22,1 (5,0)	18,7 (5,3)	28,3 (9,5)	37,1 (6,3)	64,1 (4,0)
VS/TS	[%]	60,9 (6,2)	66,8 (5,6)	68,6 (8,7)	73,8 (1,0)	81,4 (1,8)	85,4 (1,0)
Disharging pump							
TS	[mg/l]	28,6 (9,1)	32,9 (9,0)	28,0 (4,8)	29,7 (2,9)	24,5 (0,5)	35,0 (3,3)
VS	[mg/l]	15,2 (5,0)	17,9 (2,7)	15,6 (2,4)	15,2 (1,0)	13,7 (0,8)	21,0 (3,5)
VS/TS	[%]	53,2 (2,9)	55,7 (5,1)	55,7 (5,1)	51,4 (1,7)	56,1 (2,1)	59,9 (1,5)
AD reactor							
TS	[mg/l]	4,3 (1,8)	3,2 (0,8)	2,7 (0,5)	3,0 (0,3)	4,5 (0,5)	4,0 (0,5)
VS	[mg/l]	2,5 (1,0)	1,8 (0,5)	1,4 (0,3)	1,2 (0,1)	2,1 (0,3)	1,9 (0,3)
VS/TS	[%]	58,9 (2,3)	58,0 (1,9)	52,8 (4,3)	39,9 (2,7)	46,5 (3,1)	48,6 (2,3)

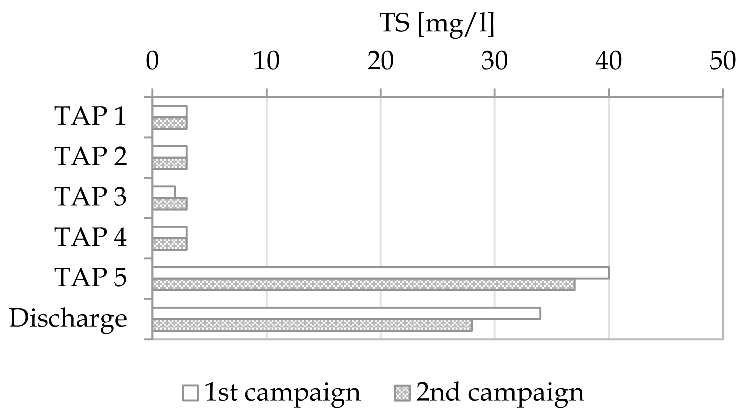


Figure 3.14 TS values registered in the extra sample campaigns in each lateral digester tap and in the discharge.

The VS reduction registered in phase 1 was 33%, similar to full-scale AD unit performance. In phase 2 a little decrease was registered, but in phase 3 the AcoD regime effect is visible: the VS breakdown value was 41,3% and increased in relation to OLR increase until reaching 67,3% in phase 6 (figure 3.15). This indicates that the biomass metabolism, in conditions of readily biodegradable substrate availability, is stimulated increasing the conversion efficiency.
Similar results are reported in literature (Caffaz et al., 2008; Capela et al., 2008), Liu et al. (2012b) shown a VS reduction rate above 60% (from 61.7÷69.9) increasing OLR from 1.2 to 8 KgVS/m^3d, using as feed substrate a mixture composed of 50% food waste, 25% FVW and 25 of WAS.

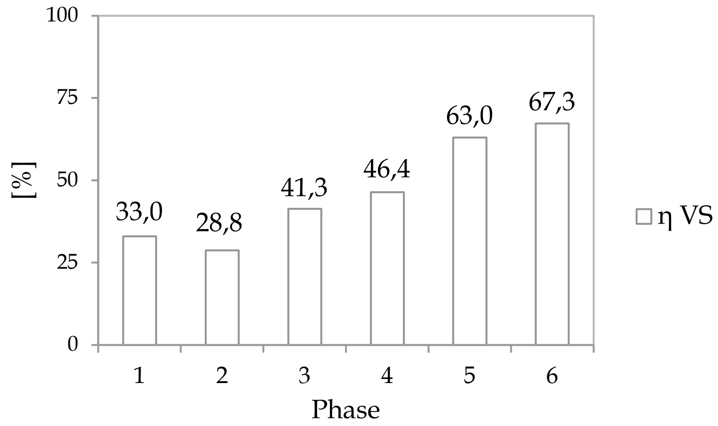


Figure 3.15 VS reduction values in each experimental phase.

3.3.2 TOTAL AND SOLUBLE COD

Total and soluble COD was measured in feeding substrate and in digestate (table 3.6). The total COD concentration increased of 53% from phase 1 to phase 6, with abtment percentages comprised between 18 and 48%. Soluble COD parameter was measured on 0.45μm filtered sample, it allows to identify the ready biodegradable substrate fraction.
Figure 3.16 shows the concentration trend of this parameter in each phase and reduction by the AD process. The values ranged from 2220mg/l in phase 1,

typical of sewage sludge, up to 28530mg/l in phase 6. The figure 3.16 highlights the remarkable increase of the biodegradable load directly available in the bacterial metabolism, thanks to OFMSW addition. In the AcoD regime, the CODs reduction percentage is comprised between 67 to 95%, confirming the biomass degradation capability at higher loadings.

Table 3.6 COD values measured in each phase in relation to the sample point.

Sample point		**Phase**					
Feeding tank		**1**	**2**	**3**	**4**	**5**	**6**
COD_{tot}	[mg/gTS]	936,7 (231,1)	1104 (205,6)	1168,6 (233,2)	1090,5 (156,0)	1217,0 (315,4)	1469,3 (298,6)
CODs	[mg/l]	2220 (1082)	2767 (1224)	3939 (1928)	7210 (1238)	10319 (2126)	28530 (1200)
Disharging pump							
COD_{tot}	[mg/gTS]	761,9 (97,8)	746,9 (200,2)	950,4 (205,9)	832,1 (190,5)	735,4 (131,9)	744,9 (150,5)
CODs	[mg/l]	912 (340)	918 (266)	1267 (584)	1223 (182)	1320 (206)	1435 (190)

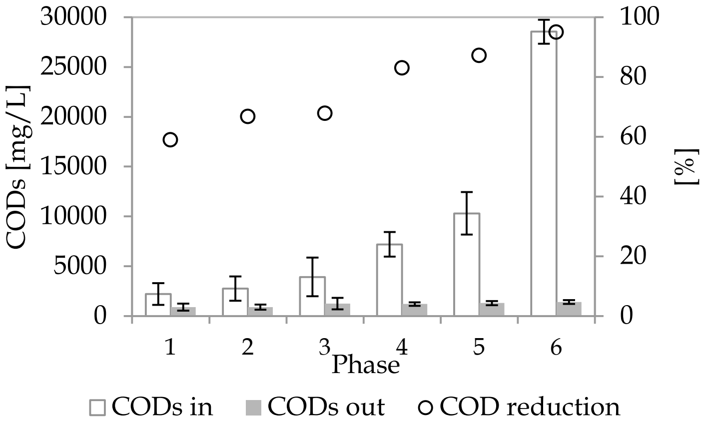


Figure 3.16 CODs values during the experimental phases, in input substrate and digestate.

3.3.3 TKN AND AMMONIA

Nitrogen rich organic substrates can induce high concentrations of ammonia in the AD process causing biomass inhibition phenomena. Moreover it's essential to know ammonia concentration in the outflow to properly size the post process treatments or to estimate the supernatant impact on the wastewater treatment line inside WWTP.
Ammonia inhibition usually cause methane production rate decrease and VFA intermediates increase: ammonia levels in the range 200÷1000mgNH_4-N have no antagonistic effect, while inhibition phenomena are reported from 1500 to 3000 mgNH_4-N/l (especially at higher pH values) and a complete inhibition, at any pH, above 3000 mgNH_4-N/l (Rajagopal et al., 2013).
During the experimentation, ammonia levels were measured in the soluble phase of input and output process substrates (Table 3.7). As it can be seen from Figure 3.17, in the input substrate the concentration varied between 120 and 300 mgNH_4^+/l.

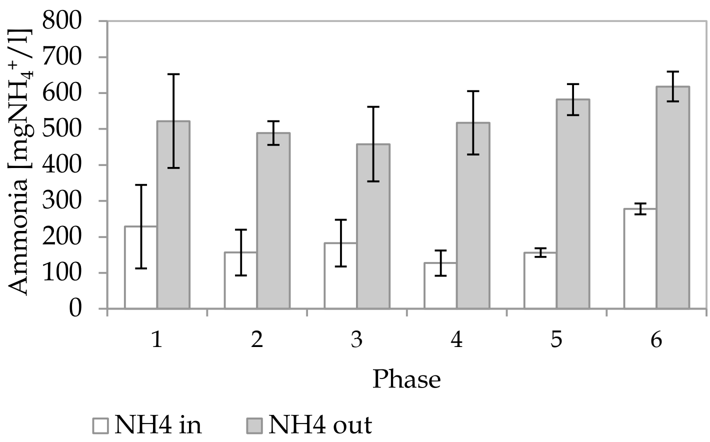


Figure 3.17 Ammonia values during the experimental phases, in input substrate and digestate.

Digestate concentration values were generally above 450 mgNH_4^+/l with an increasing trend along phases until the value of 618 mgNH_4^+/l in phase 6. It's possible to observe that the organic nitrogen of the feeding substrates was metabolized by biomass producing ammonia but the levels were maintained in a safe range for process stability. The average TKN in each phase is reported in table 3.7: in same phases, outflow higher values, respect incoming substrate, were measured probably due to lab technical problems. Consequently, TKN recovery percentages, taking in account precipitation losses, are difficult to estimate.

Table 3.7 Ammonia values measured in each phase in relation to the sample point.

Sample point		**Phase**					
Feeding tank		**1**	**2**	**3**	**4**	**5**	**6**
NH_4^+	[mg/l]	229(116)	157 (63)	183 (65)	127 (35)	156 (12)	278 (15)
TKN	[mg/l]	1254(434)	1205(260)	1147(361)	1460(191)	1939(139)	2947(180)
Disharging pump							
NH_4^+	[mg/l]	522(130)	488 (33)	458 (104)	517 (88)	582 (43)	618 (41)
TKN	[mg/l]	1420(379)	1597(347)	1590(160)	1455(67)	1431 (243)	1620 (135)

3.3.4 C,N

The elemental analysis was performed to identify carbon and nitrogen concentrations. The analysis allowed to calculate the C/N ratio, this ratio is a primary parameter in a proper AD process management. The C/N ratio feedstock control is one of the fundamental control strategies: the optimisation of the C/N ratio by AcoD is one of the cost-effective and easiest to implement technique to avoid ammonia toxicity (Rajagopal et al., 2013). In figure 3.18 it's possible to highlight the C/N ratio positive trend thanks to AcoD regime: from 10,11 in phase 1 (only sewage sludge digestion) to 13,57 in phase 6.

The higher N content in SwS is balanced by higher C content in SS-OFMSW, promoting AcoD methane yields (Sosnowsky et al., 2003). The typical range for OFMSW addition in SwS digestion is 6÷15.4 (Iacovidou et al., 2012), Sosnowski et al. (2003) reported a C/N ratio improvement from 9 to 14 by the addition of OFMSW (25% vol.) to sewage sludge (75% vol.).

In Table 3.8 C/N ratio of feeding substrates and C/N digestate percentages are reported.

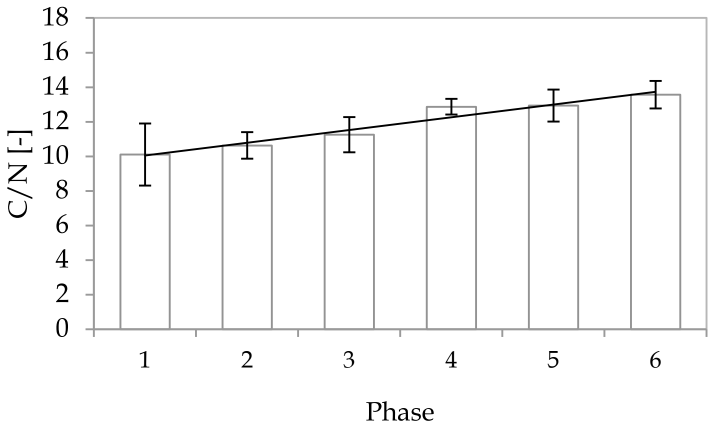


Figure 3.18 C/N values during the experimental phases in input process substrates.

Table 3.8 C/N ratio values measured in each phase in relation to the sample point.

Sample point		**Phase**					
Feeding tank		**1**	**2**	**3**	**4**	**5**	**6**
C/N	[-]	10,1(1,8)	10,6(0,7)	11,3(1,0)	12,8 (0,5)	12,9 (0,9)	13,6 (0,8)
Disharging pump							
C	[%]	30,4 (3,2)	30,4 (3,2)	32,0 (2,2)	31,1(3,5)	39,3 (1,2)	32,0 (1,4)
N	[%]	3,4(0,2)	3,2(0,5)	3,2 (0,1)	3,2(0,2)	3,9 (0,2)	4,2 (0,1)

3.3.5 SULPHATES, PHOSPHORUS AND POTASSIUM

Sulfates are metabolized by sulfate-reducing bacteria (SRB) that compete with the AD biomass for the organic substrate degradation. The byproduct of the metabolism of the SRB bacteria is hydrogen sulphide (H_2S), which accumulates in the biogas. This phenomenon involves the installation in the gas line of a H_2S treatment device, in order to protect downstream unit. Sulfates concentrations were measured in input and output substrate samples to understand the impact of AcoD to SRB bacteria. In figure 3.19 the sulfates concentration are shown. The OFMSW addition has determined sulfates increase up to about 38 mg/l in phase 6, against a value of 16 mg/l in SwS phase. The output values follow the input trend, indicating that SRB activity hasn't had increments along the experimentation. In table 3.9 sulfates data are listed.

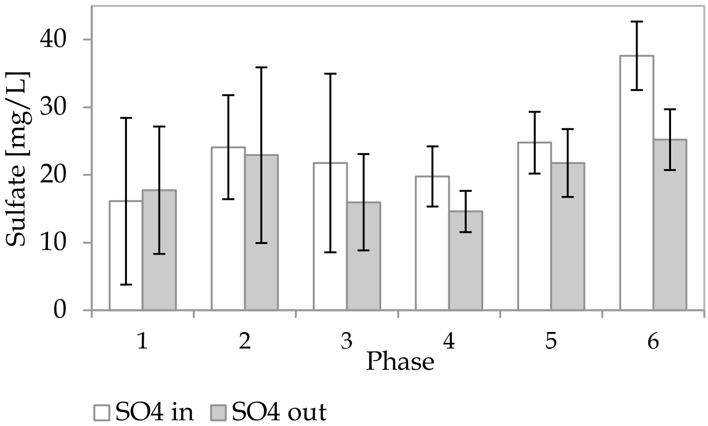


Figure 3.19 Sulfate values during the experimental phases in input substrate and digestate.

Table 3.9 Sulfate values measured in each phase in relation to the sample point.

Sample point		**Phase**					
Feeding tank		**1**	**2**	**3**	**4**	**5**	**6**
SO_4^{2-}	[mg/l]	16,1(12,3)	24,1 (7,7)	21,8(13,2)	19,8 (4,4)	24,8 (4,6)	37,6 (5,1)
Disharging pump							
SO_4^{2-}	[mg/l]	17,7(9,4)	22,9 (13,0)	16,0 (7,1)	14,6 (3,1)	21,8 (5,0)	25,2 (4,5)

Total phosphorus concentration is shown in figure 3.20. The OFMSW addition decreased the total phosphorus concentrations in substrates, since it had a lower content compared to SwS. The increase of phosphorus concentration in the output substrates, could be due to ferric phosphate precipitates release in anaerobic conditions in accord to Ge et al. (2013) hypothesis that iron salts added in the wastewater line (in the typical dose of 5-20 mgFe/l) can be utilized for sulfide control in anaerobic process. In the AD reactor ferric ions Fe^{3+} are released and utilized by sulfide precipitation, due to relatively low solubility of FeS respect ferric phosphate precipitates (Ge et al. ,2013) causing a phosphorus release. In Udine WWTP, $FeCl_3$ is add in activated sludge tank to phosphorus removal with a dose of 8,2 mg Fe^{3+}/l and this support, within H_2S data in subsequent paragraph 3.2.8, the Ge et al. (2013) hypothesis. In table 3.10 data related to phosphorus and potassium in digestate are reported, these value have a great importance to evaluate supernatant post treatment and solid fraction digestate characteristic as potential fertilizer.

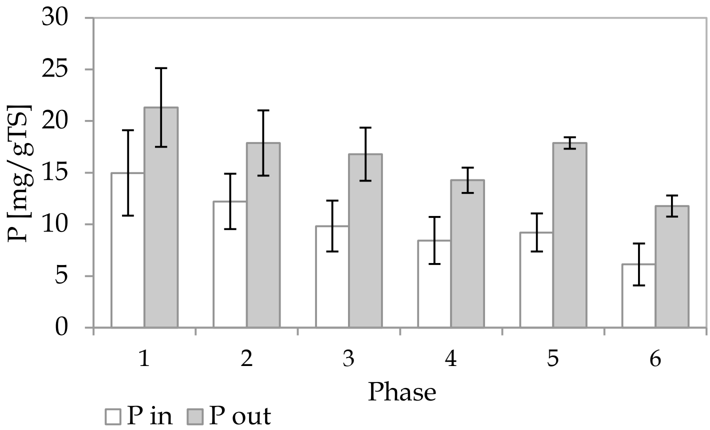


Figure 3.20 Phosphorus values during the experimental phases in input substrate and digestate.

Table 3.10 Phosphorus values measured in each phase in relation to the sample point.

Sample point		**Phase**					
Feeding tank		**1**	**2**	**3**	**4**	**5**	**6**
P_{tot}	[mg/gTS]	14,9(4,1)	12,2 (2,7)	9,8(2,3)	8,4 (2,3)	9,2 (1,8)	6,1 (2,0)
Disharging pump							
P_{tot}	[mg/gTS]	21,3(3,8)	17,9 (3,2)	16,8 (2,6)	14,3 (1,2)	17,9 (0,6)	11,8 (1,0)
K	[mg/gTS]	4,0 (0,3)	1,8 (1,0)	2,1 (1,1)	3,6 (0,9)	n.a.	8,9 (0,6)

3.3.6 HEAVY METALS

The average heavy metals concentrations of digestate are listed in table 3.11. The data are referred to no separate digestate in its solid and liquid fractions. Considering that the heavy metal concentrations in organic waste are negligible compared to SwS, as reported in literature (Banks et al., 2011b; Cavinato et al., 2013), a little dilution effect on heavy metals concentrations is visible. Moreover, the values fluctuations are linked to SwS characteristic variability, as showed by historical data (two years monitoring) reported in table 3.12 for the AD reactor digestate of the Udine WWTP.
The heavy metals concentrations data are important to perform mass balance in different scenarios and to evaluate the digestate use in the full scale reactor up-grade to an AcoD perspective (chapter 5).

Table 3.11 Heavy metals values measured in each phase.

Sample point		**Phase**					
Disharging pump		**1**	**2**	**3**	**4**	**5**	**6**
Pb	[mg/gTS]	85,2 (1,9)	93,9 (30,9)	82,3 (3,1)	84,6 (1,2)	n.a.	85,01 (4,6)
Cd	[mg/gTS]	1,6 (0,1)	1,16 (0,4)	0,6 (0,3)	1,9 (0,5)	n.a.	1,25 (0,2)
Ni	[mg/gTS]	55,6 (33,4)	79,3 (46,8)	42,1 (3,6)	34,6 (5,1)	n.a.	67,6 (10,4)
Zn	[mg/gTS]	1031,5 (169,4)	1057,8 (310,79	1058,5 (118,1)	935,8 (120,3)	n.a.	1425,6 (106,8)
Cu	[mg/gTS]	308,5 (94,6)	261,8 (63,5)	299,0 (30,1)	300,2 (34,7)	n.a.	386,4 (52,8)
Hg	[mg/gTS]	3,7 (2,2)	1,3 (0,6)	2,2 (0,5)	1,2 (0,7)	n.a.	2,1 (0,6)

Table 3.12 Heavy metals values measured in AD ful- scale unit digestate.

AD full scale unit digestate		Average	STD	min	max
Pb	[mg/gTS]	106,6	34,8	29,0	237,1
Cd	[mg/gTS]	1,5	0,6	1,2	3,0
Ni	[mg/gTS]	33,3	27,1	9,8	188,2
Zn	[mg/gTS]	1265,3	343,4	275,9	1942,2
Cu	[mg/gTS]	319,7	98,5	77,2	514,6
Hg	[mg/gTS]	n.a.	n.a.	n.a.	n.a.

3.3.7 CONTROL PARAMETERS

The fundamental process control parameters were monitored: pH was measured in the feeding substrate, inside the AD reactor and in the digestate. In figure 3.21, it's possible to note the input substrate acidification increase within the biowaste amounts in the mixture charge: from pH 5,9 of SwS to pH 4 in phase 6.

The figure also highlights the buffering capacity of the system: it's sufficient to compensate the input substrate acidity, in fact the pH inside the reactor was between 7.13 and 7.30 in all experimental phases, in the optimal range for the AD process.

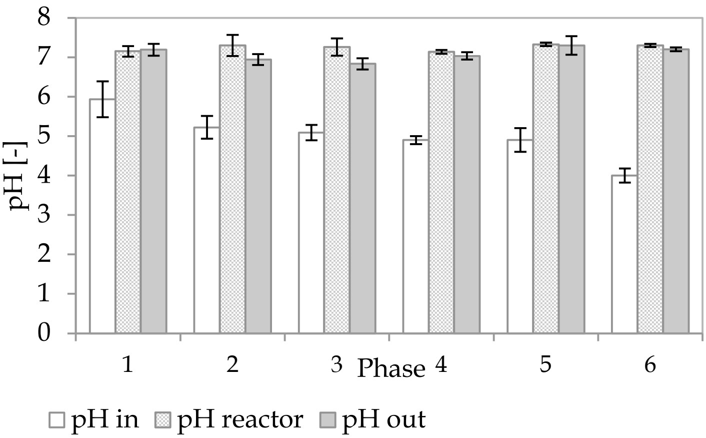


Figure 3.21 pH values during the experimental phases.

The alkalinity values are reported in table 3.13: along the experimental phases alkalinity increases from 1447,9 mgCaCO$_3$/l of SwS digestion to 2764,7 mgCaCO$_3$/l in phase 6, a similar trend was also reported in the study performed by Bolzanella et al. (2006) increasing OLR from 1.02 to 1.21 KgVS/m^{3}d in AcoD regime in Viareggio experiment. VFAs values are listed in table 3.13, VFA are considered a key parameter in AD control: they're intermediates metabolites between hydrolytic-acidogenic bacteria and methanogenic microorganism, a VFAs accumulation in AD reactor is considered a process inhibition signal. Measured VFAs had very low values, only a light pick could be reported passing from SwS digestion to AcoD.

Table 3.13 Alkalinity and VFA values measured in each phase in relation to the sample point.

Sample point		**Phase**					
AD reactor		**1**	**2**	**3**	**4**	**5**	**6**
ALK	[mgCaCO$_3$/l]	1447,9 (289,5)	1578,6 (145,9)	1453,4 (133,8)	1323,3 (253,3)	2088,5 (600,5)	2764,7 (161,3)
VFA	[mgCOD/l]	21,8 (8,2)	30,2 (16,7)	11,5 (5,1)	3,0 (2,8)	5,1 (4,8)	4,1 (2,7)

These values indicate no medium VFAs accumulation and they're similar to other results reported in literature (Bolzonella et al., 2006; Cavinato et al. 2013). It's important to consider the lack of standardized methods to perform VFAs analysis, this aspect was underlined by Raposo et al. (2013): the literature data are difficult to compare because different analytical procedures were used concerning instrumentation, sample preparation and calibration. In figure 3.22 is shown the value of FOS/TAC ratio measured by titration with sulfuric acid, which expresses the ratio between intermediate alkalinity caused by volatile organic acids and alkalinity caused by the bicarbonates, it's also called IA/PA ratio. This ratio indicates the acidification risk of the digester.

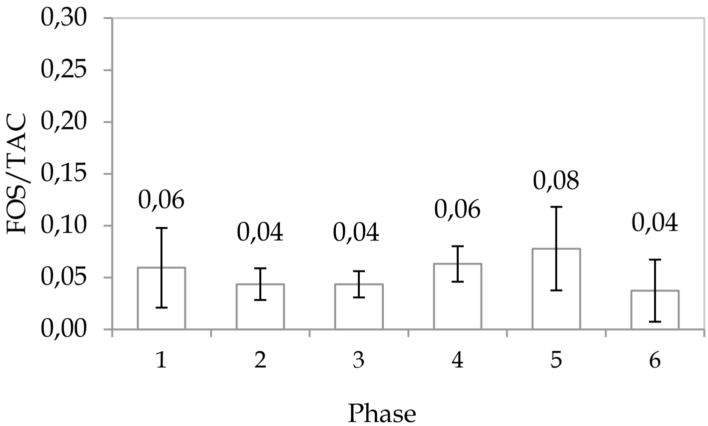


Figure 3.22 FOS/TAC ratio values during the experimental phases.

The value 0.3 for the FOS/TAC ratio represents the upper limit to obtain the optimal conditions for the biomass growth inside the digester. In the pilot plant digester FOS/TAC values were maintained in all the phases between 0.05 and 0.10, this shows that the biomass can also endure organic loads greater than the maximum value tested during experimentation (OLR 3.2 $KgVS/m^3d$). Liu et al. (2012) applying progressive OLRs from 1.2 to 6 $KgVS/m^3d$, reported stable process without inhibitions.

3.3.8 BIOGAS MONITORING

Biogas flow was constantly monitored, methane and carbon dioxide concentrations were measured one a week. The graph of figure 3.23 shows the biogas and methane flow average data in each phase, the error bars indicates the minimum and maximum values recorded during experimentation. On the secondary axis, the graph shows the flow increase percentages of the AcoD phase respect phase 1 of SwS mono digestion. In phase 6 an increment of 190% in biogas production, compared to phase 1, was registered. The methane and carbon dioxide content analysis has allowed to identify the biogas composition: methane percentage ranged between 64 and 71% during the AcoD, against a 63% value registered in phase 1. Due to technical problems methane percentages data aren't available for phase 5 and 6. Data are listed in table 3.14. Hydrogen sulphide values were under 100 ppm in all experimental phases. These results could confirm the hypothesis of Ge et al. (2013) that find, as previously introduced, that H_2S control in biogas can be achieved with the typical iron salt dosage rates applied in WWTP and, in this study, also in AcoD regime with S rich substrates like OFMSW in the AD supply.

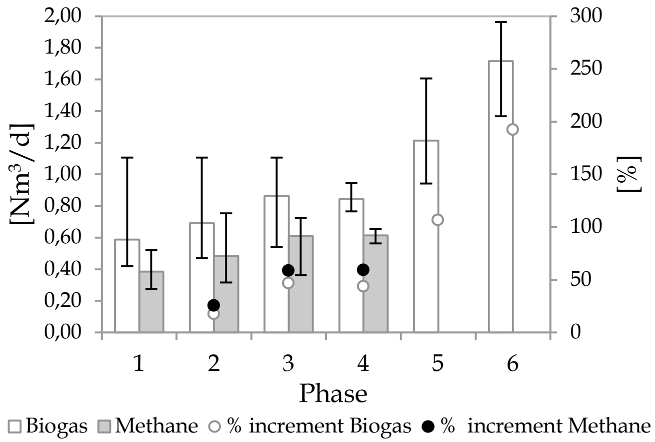


Figure 3.23 Biogas and methane flows during the experimental phases.

Table 3.14 Biogas and methane average flow and standard deviation, the increment is calculated respect phase 1.

Gas flows		Phase					
		1	**2**	**3**	**4**	**5**	**6**
Biogas	[Nm³/d]	0,59 (0,11)	0,69 (0,09)	0,86 (0,17)	0,84 (0,04)	1,21 (0,19)	1,72 (0,25)
Increment	[%]	-	17,6	46,81	43,6	106,5	192,2
Methane	[Nm³/d]	0,39 (0,07)	0,48 (0,08)	0,61 (0,12)	0,62 (0,03)	n.a.	n.a.
Increment	[%]	-	25,3	58,4	59,2		

3.3.9 EFFICIENCY PARAMETERS

The relationship between organic loading and gas production rate (GPR) is shown in figure 3.24: the error bars indicate the variation between minimum and maximum value for the OLR parameter. The GPR growth was proportional to OLR ramp: this indicates that overloading conditions weren't reached during the experimentation. At OLR 3.2KgVS/m^{3}d a 0,95m^3/m^{3}d GPR value was achieved.

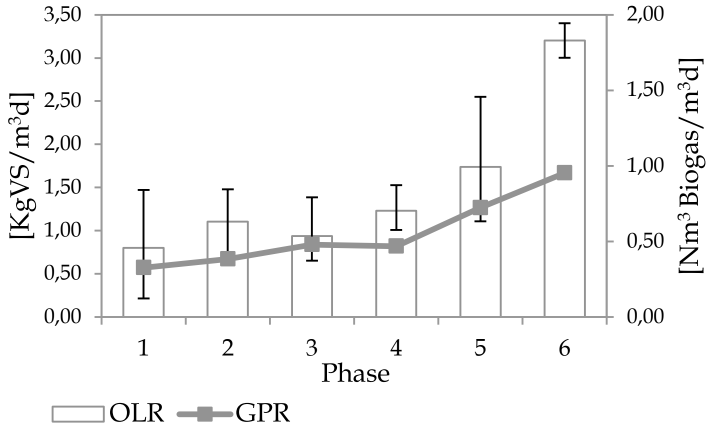


Figure 3.24 GPR and OLR trend in the experimental phases.

In figure 3.25 the SGP parameter trend for biogas is plotted. The bars indicate the range between minimum and maximum values recorded during each phase, by these values it can be seen there was a strong degree of fluctuation in biogas production.

By linear interpolation on the average, an increase of 0.10 m^3/KgVS in SGP is registered from phase 1 to maximum organic load tested. In table 3.24 GPR and SGP data are reported.

This efficiency parameter results are comparable with the study performed by Cavinato et al. (2013), where in mesophilic conditions with an OLR applied of 1.60 KgVS/m^{3}d, the yields observed in pilot- scale digester were: GPR and SGP equal to 0.53m^3/m^{3}d and 0.34m^3/KgVS, respectively.

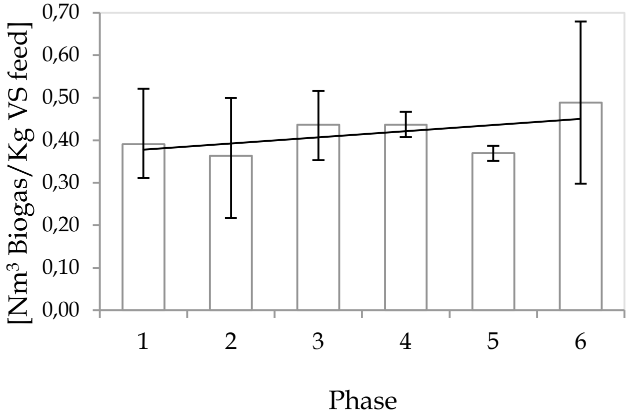


Figure 3.25 SGP trend in the experimental phases.

Table 3.24 GPR and SGP values in the experimental phases

EFFICIENCY PARAMETERS		**Phase**					
		1	**2**	**3**	**4**	**5**	**6**
OLR	[kgVS/m^{3}d]	0,80	1,10	0,94	1,23	1,74	3,20
GPR	[Nm^3 Biogas/m^{3}d]	0,33	0,38	0,48	0,47	0,72	0,95
	[Nm^3 Methane/m^{3}d]	0,21	0,27	0,34	0,34	n.a.	n.a.
SGP	[Nm^3 Biogas/KgVS feed]	0,39	0,36	0,44	0,44	0,37	0,49
	[Nm^3 Methane/KgVS feed]	0,25	0,26	0,32	0,32	n.a.	n.a.

In table 3.25 results of other studies related to AcoD experimentation, with similar type of organic substrate in CSTR mode, are listed: the comparison shows a good performance of the pilot plant reactor of this study, higher load could be implement as verify by Liu et al. (2012).

Table 3.25 GPR, SGP values in similar studies

	COMPOSITION	HRT	OLR	SGP
		[d]	[KgVSm^3/d]	
Gómez et al. (2006)	*Pilot scale* 22%d.w.PS; 78%d.w. FVW	37	-	0,4 [l/gVS]
Bolzonella et al. (2006)	*Viareggio WWTP* 15,7%olrOFMSW 84,3%olrWAS	19,8	1,21	0,26 [m3/KgVS]
	Treviso WWTP 41%olrOFMSW 59%olrWAS	22	0,78	0,43 [m3/KgVS]
Zupančic et al. (2008)	*Full scale* SwS OFMSW	20	1,1 (as VSS)	0,60 [m3/KgVSS]
Caffaz et al. (2008)	*Pilot scale* 23%olr FVW+KW 77%olr TAS	34	1.13	0,38 [Nm^{3}biogas/KgVS]
Liu et al. (2012)	*Pilot scale* 50%w.w.OFMSW 25%w.w.FVW 25%w.w.DSS	20	6,0	0,72 [m3/KgVS]
Cavinato et al. (2013)	*Pilot scale* OFMSW WAS	23,5	1,60	0,34 [m3/KgVS]
	Full scale OFMSW WAS		1,62	0,35 [m3/KgVS]
Huyard et al. (2013)	*Pilot scale* 39%olrFWP 61/olrWAS	20	1,8	0,25 [Nm3/KgVS]

PS=primary sludge; KW=kitchen waste;TAS=thickened activated sludge; DSS=dewatered SwS; FWP=food waste pulp

3.3.10 CONCLUSIONS

SS-OFMSW substrates confirmed their high biodegradable content and the low inert presence, but some efforts could be performed to prevent the conferment of bones, shells and little plastic pieces.

The switching in AcoD regime was conduct with a slow OLR increasing strategy. The AcoD process was stable in each phase, no inhibition phenomena were registered: the early indicators used (VFAs, FOS/TAC and biogas production) didn't revealed process imbalances. The process efficiency achieved was comparable with other experience reported in literature, as observed by Sosnowsky et al. (2003) the biogas production of the AcoD mixture increase with increasing proportions of OFMSW. It's possible to hypothesize, thanks to the results of recent studies (Facchin et al., 2013; De Vrieze et al., 2013), that AcoD process with SwS and OFMSW benefits of heavy metals presents in SwS that act like micronutrients in the AD process.
Feeding problems, due to SwS TS content variability, had determined management criticism in the first experimentation stages. These events caused an unstable feeding regime, especially in the early stages. In spite of this, the good process stability, that had characterize the experimentation, opens to the idea that unstable feeding regime, during low OLR steps, could have determined a microbial communities selection to more adaptive microorganism to increasing supply loads. This hypothesis has to be confirmed by deep experimental analysis.
Digestate management is very important issue, the analysis performed had allows to quantify nutrients contents (C, N, P, K) and polluting compounds like heavy metals. These data were used to perform mass balance and technical and economic evaluation in chapter 5 for the full-scale application study.
The sulphide and phosphorus importance in WWTP management arised in the experimentation, confirming the hypothesis of Ge et al. (2013) of ferric ion release by ferric phosphate precipitates and it recycle in AD sulfide precipitation. The phosphorus release in AD process implies the phosphorus return in wastewater line by the supernatant digestate: to avoid an overloading, special treatment units have to be insert before supernatant discharge. The dose of iron salt has to be managed and optimized by a WWTP integrate approach to perform the H_2S control.
In table 3.26 the summary data of pilot plant experimentation are reported.

Table 3.26 Summury data of pilot plant experimentation.

Parameters		Phase					
		1	**2**	**3**	**4**	**5**	**6**
TS in	[mg/l]	33,2	33,4	28,1	38,3	45,5	75,0
		(9,4)	(8,8)	(9,9)	(12,7)	(6,7)	(4,1)
VS/TS	[%]	60,9	66,8	68,6	73,8	81,4	85,4
		(6,2)	(5,6)	(8,7)	(1,0)	(1,8)	(1,0)
sCOD in	[mg/l]	2220	2767	3939	7210	10319	28530
		(1082)	(1224)	(1928)	(1238)	(2126)	(1200)
C/N	[-]	10,11	10,63	11,26	12,87	12,94	13,57
		(1,79)	(0,76)	(1,02)	(0,46)	(0,93)	(0,80)
OLR	[KgVS/m^{3}d]	0,80	1,10	0,94	1,23	1,74	3,20
		(0,27)	(0,25)	(0,27)	(0,22)	(0,52)	(0,20)
HRT	[d]	24,3	20	20	20	20	20
pH	[-]	7,15	7,30	7,26	7,13	7,33	7,30
VFAs	[mgCOD/l]	21,8	30,2	11,5	3,0	5,1	4,1
		(8,2)	(16,7)	(5,1)	(2,8)	(4,8)	(2,7)
ALK	[mg$CaCO_3$/l]	1447,9	1578,6	1453,4	1323,3	2088,5	2764,7
		(289,5)	(145,9)	(133,8)	(253,3)	(600,5)	(161,3)
NH_4^+	[mg/l]	522	488	458	517	582	618
		(130)	(33)	(104)	(88)	(43)	(41)
P tot out	[mg/kgTS]	21,3	17,9	16,8	14,3	17,9	11,8
		(3,8)	(3,16)	(2,6)	(1,2)	(0,6)	(1,0)
ηVS	[%]	33,0	28,7	41,3	46,4	62,9	67,3
GPR	[Nm^3/m^{3}d]	0,33	0,38	0,48	0,47	0,72	0,95
SGP	[Nm^3/KgVS feed]	0,39	0,36	0,44	0,44	0,37	0,49

4 Mathematical modeling of the anaerobic digestion process by ADMno°1

4.1 INTRODUCTION

Mathematical modelling, based on biochemical process equations, could be an useful instrument to optimize digesters design, the operating conditions and to better understand the biomass behaviour. Several mathematical models of AD have been proposed in the last three decades (Donoso-Bravo et al., 2011b), in 2002 the IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes has developed the Anaerobic Digestion Model no.1 (ADM1, Batstone et al., 2002), as a general start point for AD modelling.
The ADM1 components are expressed in terms of their COD ($kgCOD/m^3$). ADM1 has a five steps structure (figure 4.1) to represent disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis processes for a total of 32 dynamic state variables (or 26 depending on method chosen to implement equations), 6 acid-base kinetic processes, 19 biochemical processes and 3 gas-liquid transfer processes.
Extracellular steps are assumed to be of first order kinetic, Monod-type kinetics are used to describe substrate uptake and biomass growth. Inhibition phenomena are also included: pH for all microbial groups, hydrogen for acetogenic bacteria and free ammonia for acetoclastic methanogens. Thanks to the multi-step kinetic structure and the physico-chemical pathways described, ADM1 allows to assess HRT, basic biochemical overload and carbon dioxide concentration (Batstone et al., 2013).

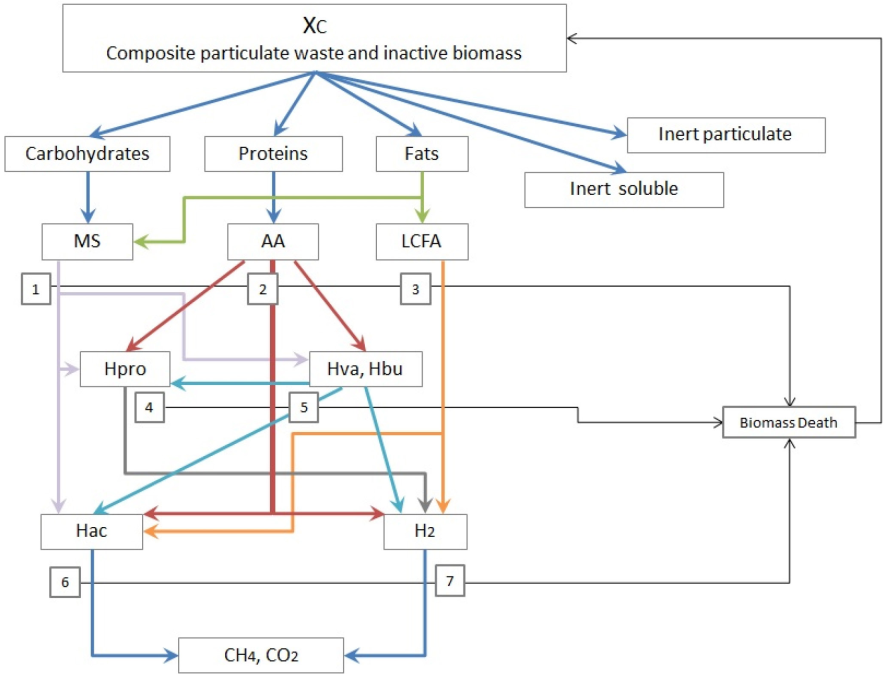


Figure 4.1 Biochemical processes implemented in ADM1 (adapted from Batstone et al., 2002) 1.Acidogenesis from sugars; 2. Acidogenesis from amminoacids; 3. Acetogenesis from LCFA; 4. Acetogenesis from propionate; 5. Acetogenesis from butyrate and valerate; 6. Acetoclastic methanogenesis; 7. Hydrogenotrophic methanogenesis. MS=monosaccarides; AA=amminoacids; LCFA=long chain fatty acids; Hva=valeric acid; Hbu=butyric acid

The large number of state variables and equations generate about more than one hundred parameters to be controlled by the ADM1 user: define correctly initial conditions, influent digester characterization, kinetic and stoichiometric parameters are the key challenges to obtain a reliable model.

The consequence is ADM1 needs a lot of experimental data to be used, accurate measurements of key variables of the process are very important (Donoso-Bravo et al., 2011b).

The modelling of AD reactor could be done as an unit part of the WWTP or by a stand-alone approach. ADM1, as stand-alone model, is based on the definition of only ADM1 state variables. A WWTP wide model implies the adoption of an interface to correlate ASM1 (Activated Sludge Model 1, Henze et al., 1987) and ADM1 state variables but allows to evaluate control strategies on both water and sludge lines.

The open challenges in ADM1 use are:

- the substrate characterization and translation in state variables;
- the calibration procedure to estimate the most sensitive parameter of the model (Giroult et al., 2012);
- the physicochemical modelling (to include P and S cycles in a plant wide domestic modelling);
- the application of multidimensional modelling (Batstone D.J., 2013).

The substrate characterization for ADM1 application is challenging (Lauwers et al., 2013). ADM1 requires a detailed characterization to identify the concentrations of soluble and particulate carbohydrates, proteins, lipids and VFAs that strongly influence the data quality of model output (Kleerebezem and Van Loosdrecht; 2006). Different approaches to modelling were developed at lab-scale to define substrate composition based on elemental analysis and biochemical fractionation (Huete et al., 2006; Kleerebezem and Van Loosdrecht, 2006; Yasui et al., 2006; Zaher et al., 2009; De Gracia et al., 2011; Giroult et al., 2012, Astals et al., 2013), but still a lack of standardized methodology remains.
The interface approach defines the mapping compounds between ASM1 and ADM1 models (figure 4.2), different interfaces were proposed in literature. In this study Copp interface (Copp et al., 2003) was considered and its up-grade performed by Nopens et al. (2009).

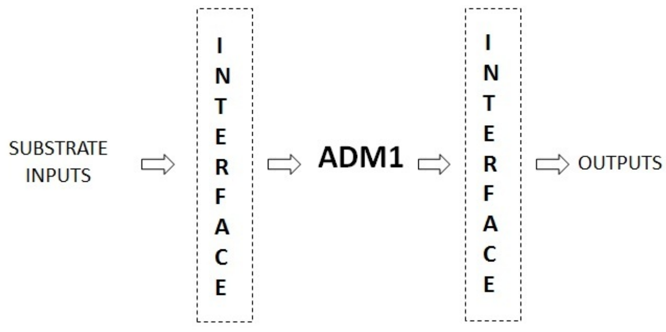


Figure 4.2 Interface approach scheme (adapted from Batstone et al., 2013)

Characterisation and interface models based on Xc state variable, used as main input variable to ADM1, have key limitations due to the applicability problems. In fact the ADM1 state variable Xc represents the pool of complexes substrates that have to be disgregate to primary substrate components like proteins, carbohydrates, lipids and inerts. Xc have a fixed COD:mass ratio and this can cause incorrect model predictions because, in this way, also the input COD type is fixed (Nopens et al., 2009). Another problem with the use of Xc state variable is the creation of correlation between influent particulate materials and biomass decay by-products with very different characteristics. This kind of approach doesn't account for changes in degradability or oxidation state with upstream plant operation (Batstone D.J., 2013). In WWTP application this problem is partially addressed using the Nopens interface (Nopens et al., 2013) but still remain the need to define a methodology for a systematic approach based on substrate type (Batstone D.J., 2013). The Nopens interface is based on Copp interface avoiding the use of Xc: the disintegration step is bypassed and the influent conversion is made directly into carbohydrates, proteins and lipids, avoiding secondary kinetics. The disintegration step remains active only for biomass decay products (Nopens et al., 2009).

Another fundamental point regards the kinetic and stoichiometric parameters calibration. Different approaches are reported in literature using anaerobic tests in batch, CSTR or by combination of these techniques (Batstone et al. 2009; Donoso-Bravo et al., 2011a; Giroult et al., 2011; Souza et al., 2013).

The use of BMP tests as source data for ADM1 hydrolysis parameter calibration for full-scale application is an open issue. To simulate complex substrate, the ADM1 limiting step is the disintegration/hydrolysis step. Souza et al. (2013) find BMP tests suitable data source for ADM1 calibration, providing adequate fit quality. Batstone et al. (2009) reported consistent differences between simulation using BMP testing and full-scale parameters: the evidence from this work was that BMP test are useful data source for project feasibility analysis but the values obtained should not be used for dynamic modelling.

A solution to solve the key issues of substrate characterization and model calibration could be the defining of a procedure that uses a combination of BMP test, macromolecular analysis and numerical optimization by ADM1. A method based on these assumptions was developed by Giroult et al. (2012) using the technique of anaerobic respirometry.

In this study, the feasibility of using BMP test, macromolecular substrate composition data and numerical optimization to calibrate ADM1 was analysed to simulate the pilot and full-scale reactor AD process in two regimes: sewage sludge digestion and AcoD process with SS-OFMSW.

4.2 MATERIAL AND METHODS

4.2.1 FULL-SCALE AD UNIT

The AD unit is located in Udine's WWTP, Italy. WWTP has a treatment capacity of 100000 P.E., sewage sludge is formed by a mixture of primary and secondary sludge. The AD unit is a two-step process with an anaerobic mesophilic digester (2800 m^3 total volume) used for sewage sludge stabilization and biogas production and a secondary anaerobic digester for sewage sludge thickening. In this study, only the primary digester has been considered for the sampling and the ADM1 modelling.

4.2.2 ANALYTICAL METHODS

To obtain substrates characterization, the classic chemical-physical parameters and key macromolecular compounds for anaerobic biodegradability were measured in each sample by the methods identified in the previous chapters. Flow in, biogas flow and temperature were monitored daily at digester unit. To refer data analysis in terms of COD, the following data were chosen: COD content of carbohydrates is 1,19 gCOD/g carbohydrate based on $(C_6H_{10}O_5)_n$, COD content of proteins is 1,42 gCOD/g protein based on $(C_5H_7NO_2)$, COD content of lipids is 2,90 gCOD/g lipid based on $(C_{57}H_{104}O_6)$, COD content of acetic acid is 1,07 gCOD/g acetic acid, COD content of propionic acid is 1,51 gCOD/g propionic acid, COD content of butyric acid is 1,82 gCOD/g butyric acid, COD content of valeric acid is 2,04 gCOD/g valeric acid.

4.2.3 EXPERIMENTAL PROCEDURE

In the first step, the simulation by ADM1 of the full-scale AD unit, in Udine WWTP, operating only with sewage sludge was performed. Two months monitoring period was carried out: two samples of thickened sewage sludge and digestate were collected weekly and analysed to implement the model.

COD fractions in input substrates were defined basing on macromolecular compounds analysis. Moreover, data coming from one year of AD unit running were examined to check the model.
The simulation was performed using two different approaches: a plant-wide model with an ASM1/ADM1 interface (Copp interface) and a stand-alone model with a modified ADM1 version (as described in Batstone et al., 2009) based on Nopens approach to Xc state variable.
BMP tests and macromolecular analysis on sewage sludge and digestate were used to optimize COD fractionation and estimate kinetic and stoichiometric parameters to use the Copp interface. Macromolecular analysis were also used to define biodegradable COD fractions to apply modified ADM1.
In the second step, ADM1 was used to simulate the AcoD process in pilot plant and to predict AcoD process applied to full-scale WWTP unit.

4.2.4 MODEL IMPLEMENTATION

ADM1 plant-wide model was implemented in GPS-X® 6.1 (Hydromantis Inc., Canada) according to the ADM1 COST benchmark (Rosen, 2006) using an ASM1/ADM1 interface (Copp's interface, Copp et al., 2003). In the COST version, to overcome the inorganic C and N imbalance of STR-13 version, stoichiometric coefficients, biomass degradation equations and composition parameters were adjust (Lauwers et al., 2013). ADM1 stand-alone model was implement in Aquasim 2.1 (Reichert P., 1994) using a modified form of the Nopens interface that translates total influent COD to proteins, carbohydrates, lipids and inerts through the key parameters: f_d degradability parameter and a single k_{hyd} parameter.
This modification overcame the Xc problem definition and isolates the disintegration process only to the biomass decay products. The key difference between Nopens and COPP interfaces is the way of X_I definition: in Nopens interface X_I is mapped in relation of f_d degradability parameter (Batstone et al., 2009).

4.3 RESULTS&DISCUSSION

4.3.1 SwS AD PROCESS SIMULATION

Due to the complexity of ADM1, an accurate application of the model requires a detailed characterization of the sludge composition: the feed stream should be well characterized with respect to its COD content and the biodegradable fraction of its material (Parker W.J., 2005).

Macromolecular analysis is a fundamental step to understand the sludge properties in AD process and to estimate biodegradable COD. Moreover ammonia and TKN concentrations present in the feed need to be well characterized because of their impact on pH buffering and inhibition functions (Parker W.J., 2005).

4.3.1.1 Bmp tests modelling with COPP Interface adoption

In table 4.1 the sewage sludge input in BMP tests and initial inoculum characteristics are reported, these values were used to define state variables and initial values of ADM1.

The use of ASM1/ADM1 interface allows an easy insertion of the ADM1 model in a general WWTP model for a valuation of global WWTP performances and, as consequence, shifts the state variables definition problem on ASM1 fractions.

Yasui et al. (2008b) found that in general ASM state variables were well correlated to the state variables of ADM1, the composite variable Xc could be considered as sum of state variables X_S and X_H, while X_I in both the models showed direct correspondence.

Creating the input data based on ASM1 state variables, the subsequent hypothesis were made: input oxygen is zero, only $X_{B,H}$ is considered in secondary sludge, X_P is set to zero because all inerts are included in X_I.

Table 4.1. Sewage sludge and inoculum characteristics.

Parameters	Units	Sewage Sludge	Inoculum
COD_{TOT}	[mgCOD/l]	36444	20640
COD_S	[mgCOD/l]	1624	1304
TS	[g/l]	35	20
VS	[g/l]	22,9	10,4
TKN	[mgN/l]	1465	1341
NH_4^+	[mgN/l]	206	478
pH	[-]	5,26	7,01
ALK	[$mgCaCO_3$/l]	1295	2506
Carbohydrates $_{TOT}$	[mgCOD/l]	2900,80	1249,07
Carbohydrates $_S$	[mgCOD/l]	63,80	107,40
Proteins $_{TOT}$	[mgCOD/l]	11144,01	7641,51
Proteins $_S$	[mgCOD/l]	77,09	181,21
Lipids	[mgCOD/l]	7593,65	4785,29
Acetic acid	[mgCOD/l]	344,87	2,78
Propionic acid	[mgCOD/l]	336,24	2,89
Butyric Acid	[mgCOD/l]	35,84	0,53
Valeric Acid	[mgCOD/l]	6,02	0,03

In this study, in order to implement ADM1 model by an ASM1 state variables characterization, an applicative procedure to characterize sewage sludge was proposed: as a first step particulate fraction in terms of COD was quantified, basing on the measurement on total and soluble phase of substrates (eq.4.1).

$$COD_X = COD_{TOT} - COD_S \qquad (4.1)$$

Soluble fraction COD_S is the sum of S_I and S_S as (eq.4.2), where the latter parameter could be considered as the sum of biodegradable soluble ADM1 state variables, as in eq.4.3.

$$COD_S = S_I + S_S \qquad (4.2)$$

$$S_S = S_{SU} + S_{VFA} + S_{FA} + S_{AA} \qquad (4.3)$$

S_{SU} and S_{VFA} are known by macromolecular analysis: S_{SU} is equal to carbohydrates measured in soluble phase, S_{VFA} is the sum of acetic, propionic, butyric, valeric acids concentrations in samples. S_{AA} can be estimated from proteins measured on soluble phase and converted in COD by ADM1 stoichiometric parameter N_{AA}=0,098gN/gCOD (Batstone et al., 2002). The unknown variable S_{FA}, can be obtained assuming an initial zero value, the maximum value of S_I can be approximate by difference (by equations 4.2 and 4.3).

The optimal value of S_{FA} (and as a result S_I), can be estimated fitting the model by data coming from BMP test on sewage sludge.
The same method based on macromolecular compounds analysis can be applied in the fractionation of particulate COD: eq.4.4 and eq.4.5 lead by difference to estimation of the maximum possible value of X_I. The optimal value can be identified by model fitting with experimental data. Concentrations of carbohydrates, proteins and lipids in eq.4.5 are referred only to particulate phase of samples.

$$COD_X = X_I + X_S + X_B \tag{4.4}$$

$$X_S + X_B = Carbohydrates + Proteins + Lipids \tag{4.5}$$

Nitrogen parameters can be quantified in the soluble phase: S_{NH} as the ammonium concentration and S_{ND} represents the soluble biodegradable organic nitrogen that is identifiable with S_{AA}.
The particulate organic biodegradable nitrogen X_{ND} represents the nitrogen associated to X_S, it has to be calculated in order to obtain a consistent input influent. Eq.4.6 shows how to perform this calculation, where $N_{I,Xi}$= 0,06 gN/gCOD and $N_{I,Xb}$= 0,086 gN/gCOD are the stoichiometric ASM1 parameters for inert fraction in X_B and X_I.

$$X_{ND} = TKN - S_{NH} - S_{ND} - X_I \cdot N_{I,Xi} - X_B \cdot N_{I,Xb} \tag{4.6}$$

Alkalinity, pH, ammonia and VFA measured data help to resolve charge balance (as the procedure reported by Nopens et al., 2009) for the definition of initial concentrations of ADM1 state variables S_{CAT}, S_{AN}, S_{IN}, S_{IC}.
COD/VS ratio was optimized basing on experimental results.

BMP tests were realized both on inoculum (as blank) and sewage sludge at ISR 3 to determine the methane production (Chapter 2). Blank BMP test allowed to assess the residual methane production of inoculum: methane production rate (MPR) curve obtained in BMP test was used to fit the model and find correct initial values of ADM1 state variables to be used for modeling BMP test on sewage sludge. In this case no ASM1/ADM1 was adopted because there wasn't an additional substrate to be degraded by biomass. The analysis performed has permitted to define ADM1 state variables. Default ADM1 values (Batstone et al., 2002) for kinetic parameters were adopted. Figure 4.3 shows the performance of the model. The model had a relative error on cumulate experimental methane production of 11,5%.

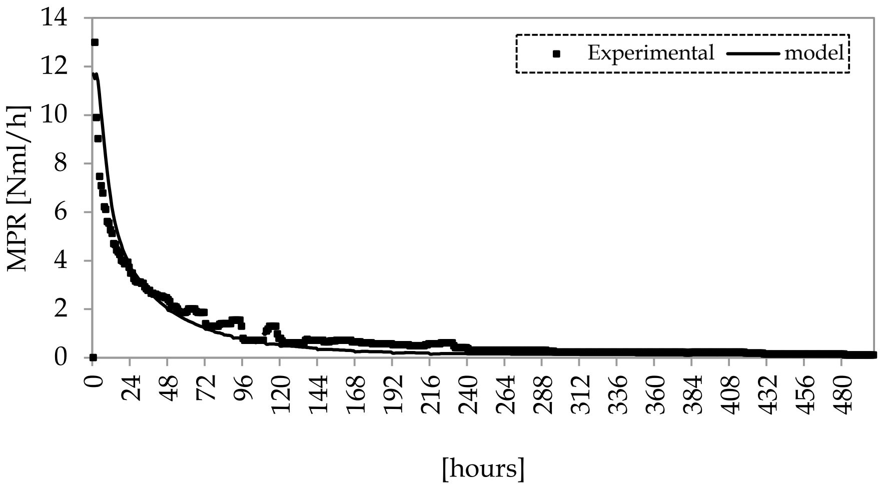


Figure 4.3 Comparison of real and simulated MPR curve for inoculum.

Characterization of ADM1 state variables for seed sludge has allowed the definition of initial concentration of state variables to be used in the simulation of sewage sludge BMP test.

COD fractionations S_I and X_I were optimized decreasing the values obtained by influent characterization. Using a computational optimization tool of the process simulator GPS-X® (Hydromantis Inc., Canada), calibration of the most sensitive kinetic parameters was performed until best fits were achieved between the simulated and experimental MPR curves. Yield stoichiometric parameters on X_C: $f_{ch,xc}$, $f_{pr,xc}$, $f_{li,xc}$, $f_{si,xc}$, $f_{xi,xc}$ were optimized (Table 4.2). These data are similar to ones obtained by the experimental study of Astals et al. (2013) on seven different sewage sludges. Further gCOD/gVS ratio was changed to improve the model accuracy, this ratio is important when VS measurement is used for digester performance monitoring (Ozkan-Yucel, 2010).

Table 4.2 Yield stoichiometric parameters on X_C used in the model and suggested values (Batstone et al., 2002) .

Parameters	Units	BMP on sewage sludge	Suggested values
$f_{ch,xc}$	[gCOD/gCOD]	0,13	0,20
$f_{pr,xc}$	[gCOD/gCOD]	0,25	0,20
$f_{li,xc}$	[gCOD/gCOD]	0,21	0,25
$f_{si,xc}$	[gCOD/gCOD]	0,10	0,10
$f_{xi,xc}$	[gCOD/gCOD]	0,31	0,25

Figure 4.4 shows experimental MPR curve and simulated ones for BMP test on sewage sludge. Relative errors between experimental data and simulated values by the model at the end of BMP test. Cumulative methane production, total COD, volatile solids and ammonia were simulated successfully by the model with a relative error respectively of 2,3%, 4,5%, 11,8% and 12,8%.

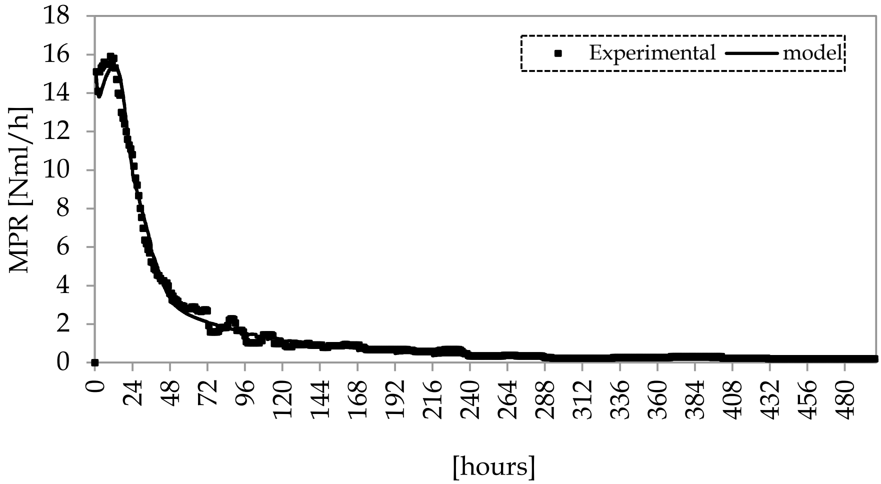


Figure 4.4 Comparison of real and simulated MPR curve for sewage sludge.

4.3.1.2 Full-scale AD reactor

The model was tested by monitoring period performed on full-scale anaerobic digester using dynamic influent data arranged by the on-line registered flow and the sludge characterization performed on sewage sludge samples.

The monitoring period has highlighted a strong daily variability of sewage sludge characteristics: average TS content of the influent sludge was 32,5±5,7g/l and VS 22,1±4,5g/l, COD_{TOT} and TKN were respectively 32537±8185mgCOD/l and 1385±189mgN/l.

The macromolecular analysis carried out on samples in monitoring period allowed to define the average sewage sludge composition. Organic Loading Rate (OLR) was 0,92±0,16 kgVS/m^3day in monitoring time with an hydraulic retention time (HRT) of 24,4±1,54 days.

4.3.1.2.1 Full-scale AD reactor simulation with COPP Interface adoption

The model calibrated on BMP test, was used to simulate the two months monitoring period of full-scale AD reactor. Figure 4.5 shows the comparison of measured and simulation biogas production: the day average relative error is 17,8% between real data and simulated ones, with minimum and maximum values respectively of 0,3% and 40,2%.

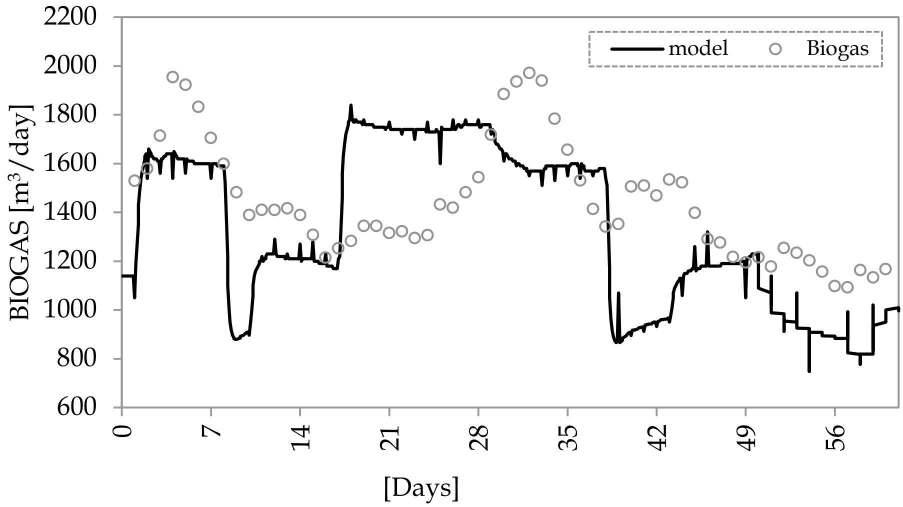


Figure 4.5 Comparison between model simulation and average daily data of biogas production.

In the figure 4.6 the VS simulated and measured data are reported. Simulated VS have an error of 0,3% respect average parameter value measured in monitoring period and simulated pH of 4,3%. Finally, the calibrated and validated model was applied in a simulation of a one-year biogas production, comparing data obtained with one-year historical monitoring record available for the full-scale digester. Influent ASM1 state variables were obtained from mean values of parameters assessed in two months monitoring period. The data set was comprised of daily sludge flow and digester temperature, so a dynamic organic loading conditions simulation was performed. OLR during the analysed year has an average value of 0,94±0,30 kgVS/m^3day. The biogas production trend in the year of simulation is reported in figure 4.7, the average relative annual error is 35,5% with a minimum and maximum value respectively of 0,2% and 227,9%.

Calibrate model has a good fit on methane percentage in biogas, some standard measures of biogas samples in full-scale digester resulted in 63% of CH_4, simulation data indicated an average value of 63,4%.

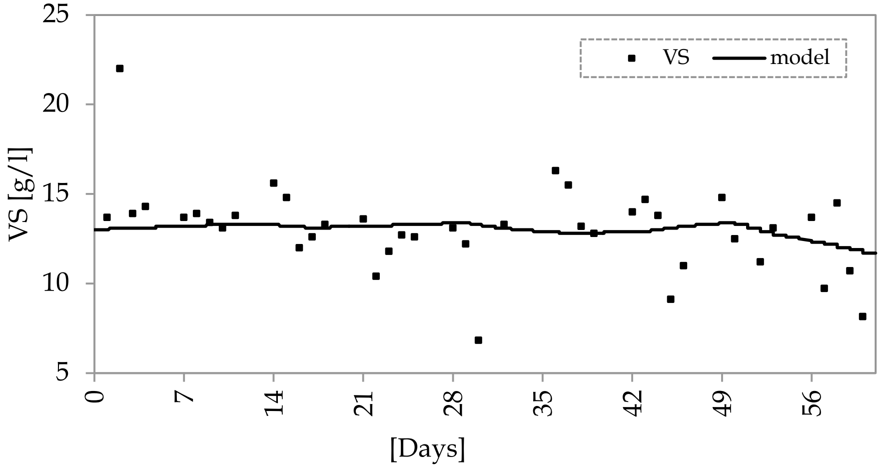


Figure 4.6 Comparison between measured and simulated data of VS for monitored period.

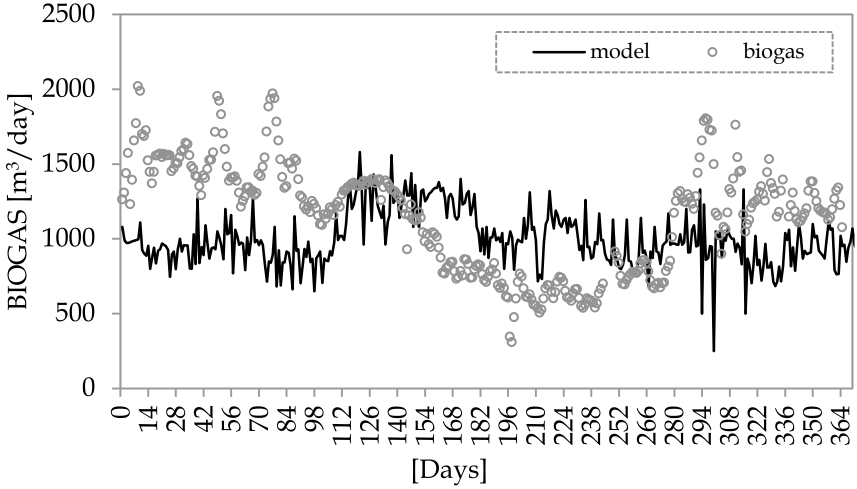


Figure 4.7 Measured and simulated biogas flows for one-year period of full-scale digester.

4.3.1.2.2 Full-scale AD reactor simulation with modified ADM1

The modified ADM1 model was calibrated on the two months monitoring period and validated on the one year data. Dynamic organic load simulation was implemented as previously described. The f_d variable was defined basing on macromolecular compounds expressed in terms of COD: the sum of all biodegradable compounds was related to the total input substrate COD to define the initial f_d value. K_{hyd} and f_d were optimized by a computational tool using the gas flow and VS data. The f_d parameter average value was 0,62 with a minimum at 0,48 end a maximum value at 0,74.

The two month simulation result, with calibrated parameters, is reported in figures 4.8 and 4.9 for biogas flow and VS, respectively. The average error in biogas flow prediction was 5,0% (minimum value of 0,1% and maximum value of 12,5%). The VS were estimated with an average error of 3,9%.

The calibrate model was tested for the one year data set. Simulation results for biogas flow are reported in figure 4.10. The average error on one year data was 13,0% with a minimum value at 0,4 and a maximum value at 71,8. The f_d parameter was adjusted during the one year simulation to account the changes in sewage sludge degradability over the year caused by ambient temperature. This phenomenon is exacerbated during summer season and implies a value of f_d near to 0,3.

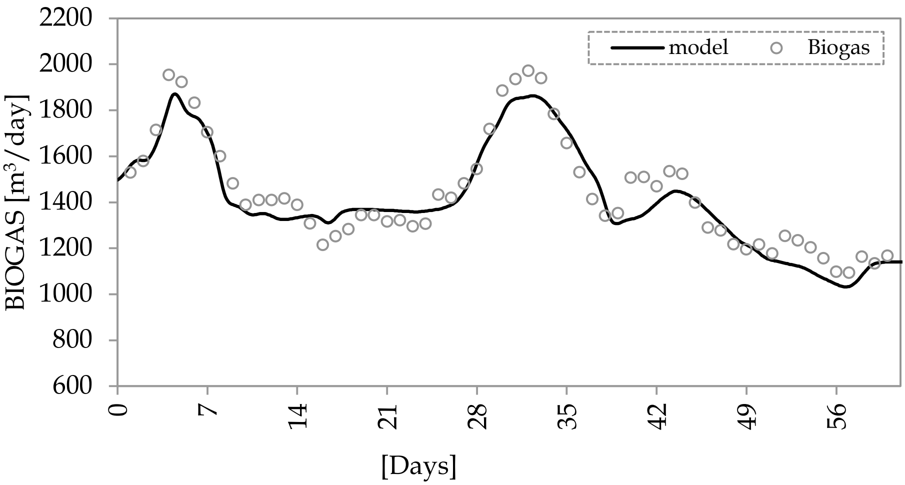


Figure 4.8 Comparison between model simulation and average daily data of biogas production.

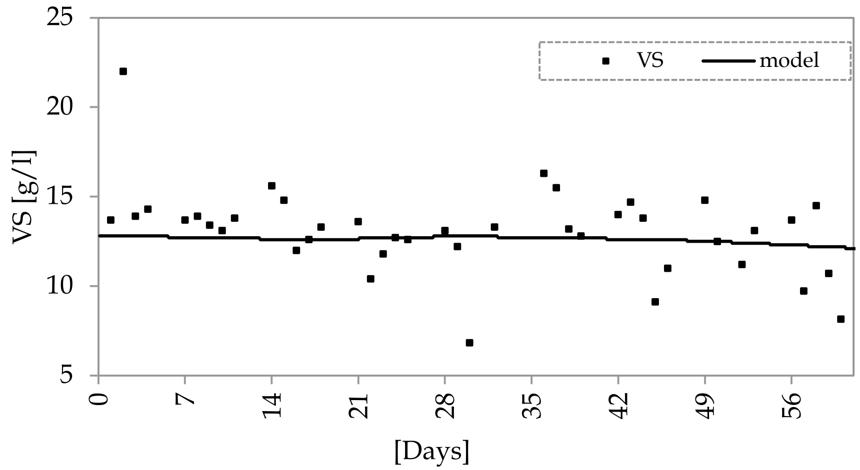


Figure 4.9 Comparison between measured and simulated data of VS for monitored period.

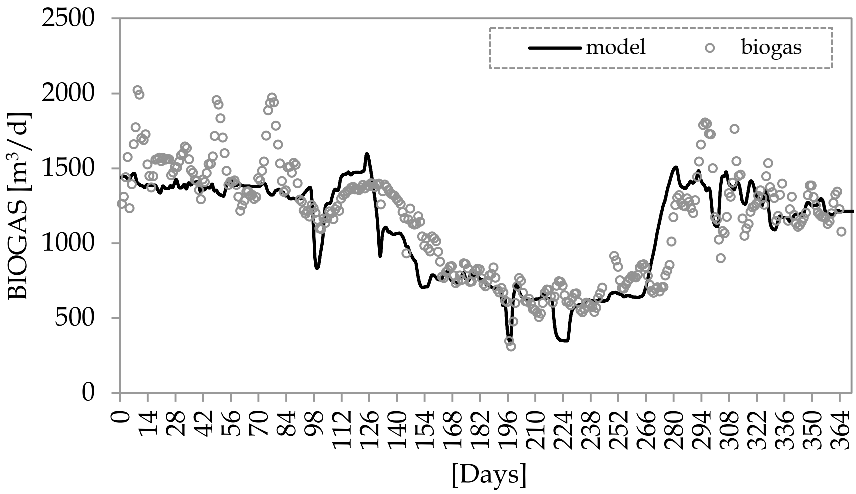


Figure 4.10 Measured and simulated biogas flows for one-year period of full-scale digester.

4.3.2 AcoD SIMULATION

4.3.2.1 Pilot plant

The experimental pilot plant phases were simulated basing the substrate characterization on experimental data collected (chapter 3). The modified

ADM1 was used to better performance obtained. A dynamic organic load simulation was performed. During phase 1 only sewage sludge was treated: the model parameters previously used to calibrate the model, were adopted. From phase 2 to phase 6 the AcoD regime was simulated changing the input substrate characterization parameters, to follow the macromolecular compounds trends in the feeding mix. The parameters X_{pro}, X_{lip}, X_{ch} were set basing on macromolecular experimental results and the f_d parameter was optimized. The simulation results are depicted in figure 4.11.

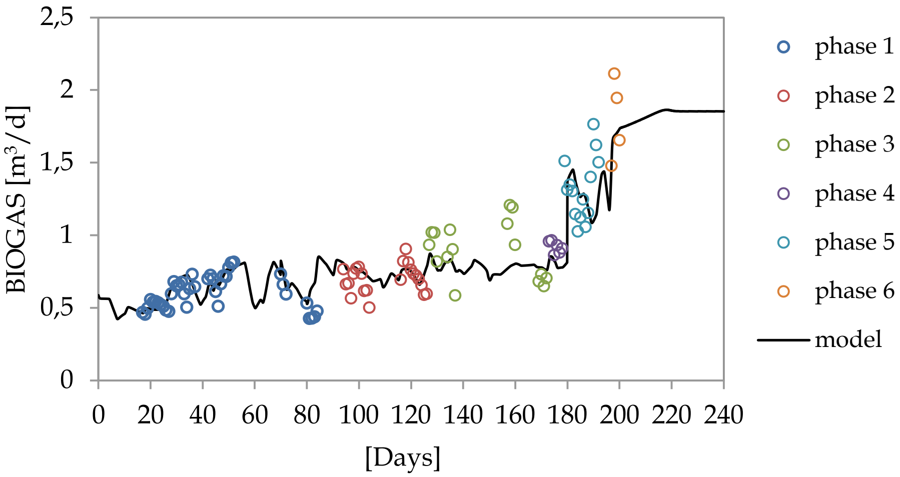


Figure 4.11 Measured and simulated biogas flows in pilot plant experimentation.

4.3.2.2 *Full-scale AD reactor*

Basing on the model implementation realized for the pilot plant, a forecast scenario was developed to simulate AcoD process in the full scale AD reactor of Udine WWTP. AD reactor experimental data were collected for the same period of pilot plant experimentation: the SwS feeded at the two plants was the same. Two dynamic organic loading simulations were performed: the first to describe the AD reactor working only with SwS and the second to test the switch to AcoD regime in the full-scale reactor following the experimental conditions applied to pilot plant. The results are reported in figure 4.12. The model estimates the biogas production increase from 1980m^3/d for phase 2, growing up to 4682m^3/d for phase 6 with an increase of 136%.

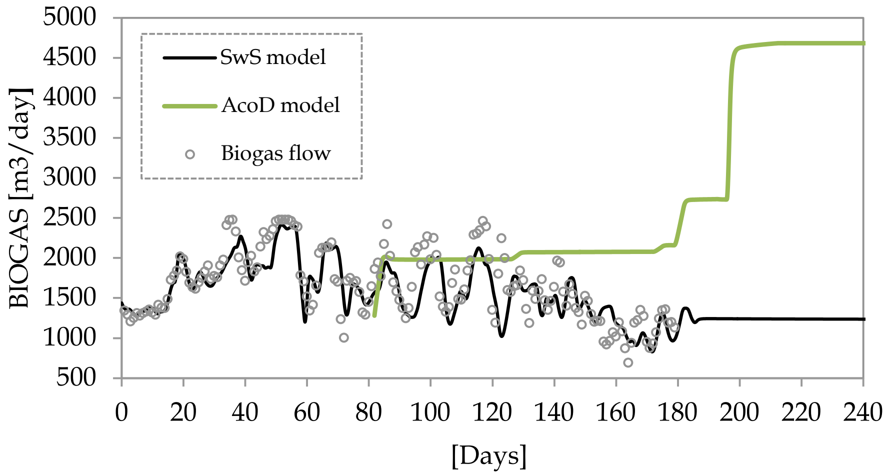


Figure 4.12 Measured and simulated biogas flows in full-scale reactor and AcoD model simulation results.

4.4 CONCLUSIONS

Define a proper modelling process, including model calibration, is a key issue for successful model application in practice (Makinia J., 2010). In general, the literature shows a lack of systematic and clear procedure for modeling AD process (Donoso-Bravo et al., 2011b). The modelling scale-up from batch test to full-scale CSTR involves naturally an error, as also highlighted by Batstone et al. (2009) and Donoso-Bravo al. (2011a) and confirmed by this study for dynamic modelling.

This work aims to give a contribution in this area by a full-scale digester modeling study. A limiting aspect about anaerobic digestion modeling application in ADM1, it's the use of a single composite variable Xc to describe sewage sludge and, in general, complex substrates. It's a simplification considering that the nature of primary sludge and secondary sludge is inherently different (Yasui et al., 2008) and introduce artificial kinetics. This could be overcome basing the modelization on the Nopens interface approach: as tested in this study the model performances were higher in relation to biogas and VS calculations. Convert directly the substrate in carbohydrates, proteins, lipids and inerts allow to separate the disintegration of substrate and the disintegration of biomass by-products.

The input characterization and translation in ADM1 state variables isn't an easy task and the lack of standardised methodology for complex substrate it's the major barrier to ADM1 application (Batstone D.J., 2013). The use of an ASM1/ADM1 interface allows a simplified approach to the model implementation in relation to an easier fractionation of feed influent but the parameter identificability problem is an open issue. Macromolecular analysis for COD fractionation helps to reduce the inconsistencies in ADM1 simulations due to poor influent characterization and to contain errors in acceptable range for full-scale reactor simulation, respect literature ranges of approximately 5-15% simulated data difference from measured data (Rieger et al. 2013).

5 Feasibility study of AcoD plant up-grade

5.1 INTRODUCTION

Basing on results obtained by pilot plant experimentation, different scenarios for full-scale AD unit up-grade to AcoD were defined developing feasibility studies.
Two scenarios were hypothesized:

- Scenario 1: AcoD of SwS and SS-OFMSW in AD WWTP reactor to deplete the spare treatment capacity;
- Scenario 2: AcoD of SwS and OFMSW in AD WWTP unit in existing reactor and in a new one, to treat the amount of OFMSW received by the Udine waste treatment plant.

Wet and semi-dry regimes are considered, achieved with the use of purified water by WWTP. The substrates dilution allows to obtain the correct OLR and the proper TS concentration to avoid mixing problems, clogging pumps phenomena and usury inside the reactor. Energy balance and economic evaluations were performed to define the sustainability of each scenario.
The scenario n°2 was considered in relation to an evident constrain condition: Udine WWTP and Udine waste treatment plant are geographically adjacent (as possible to see in figure 5.1) and this opens to the hypothesis of a synergy between the two plants to integrate aerobic and anaerobic treatments of OFMSW.
The common assumptions of both scenarios were:

- Cogeneration of all biogas produced;
- Solid and liquid digestate fractions separation;
- Liquid digestate pre-treatment before the discharge in WWTP water line;
- Composting of the solid digestate fraction.

The investments were evaluated for a 20 years, in relation to the actual duration of Italian government feed-in tariffs.

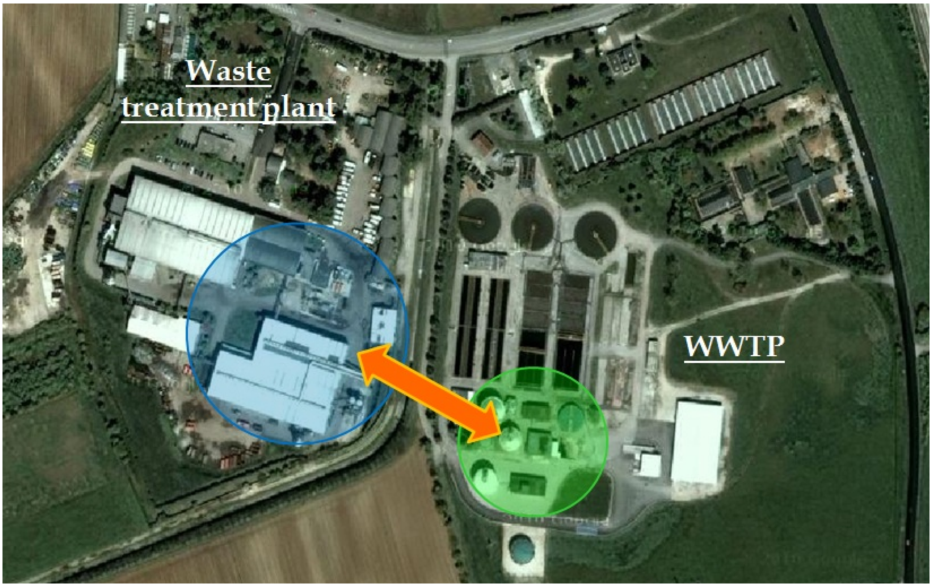


Figure 5.1 WWTP and waste treatment plant aerial photo with in blue circle the OFMSW collection building and the composting plant, in the green circle the AD unit inside WWTP.

The following conditions were fixed to define the economic model. The waste contribution tariffs were defined analysing the market price: due to the uncertainty link to future price variations, a range was selected and minimum and maximum values tested. The range chosen is 75-85 €/ton for OFMSW and 35-50 €/ton for green waste. No extra transport costs were considered due to the plants proximity. The waste disposal (rejected materials from pre-treatment section) cost was evaluated in 100 €/ton for inert material from waste pre-treatment and 40 €/ton for chemical sewage sludge.

The management costs comprise:

- CHP maintenance (25€/MWh year);
- General maintenance (3,5% of initial investment cost per year);
- Reagents for biogas purification (2,18 €/m^3 biogas);
- Lab analysis (12000€/year);
- Employees (35000€/year person);
- Insurance (10000€/year).

Post-treatments of digestate, in its solid and liquid fractions, were considered. Extra management costs in chemicals were accounted for liquid digestate treatment. The composting cost of solid digestate fraction was considered only in scenario n°1, because in scenario n°2 the two plant synergy allows to adsorb this cost. A 10% of extra cost was added for every year on total expenses, to consider administrative and extra technical costs.
The revenues from biogas use to produce electric energy (EE) and thermal energy (TE) were evaluated basing on "D.M. 6 luglio 2012"of the Italian government. The feed in tariffs are:

- Power 600÷1000 kW: 216€/MWh;
- Power 1000÷5000 kW: 109€/MWh.

Moreover it's possible to consider 10€/MWh as bonus for high-performance cogeneration. The savings on the energy bill were defined considering the tariff of 150 €/MWh as average grid cost. The calculations on energy production were made considering that from 1 m^3 of biogas is possible to generate 1,8KWhEE and 2,8KWhTE. The saving of sewage sludge disposal are fixed at 300 000€/year. The common cost item to both scenario regards the up-grade of the existing AD reactor to AcoD, it's estimated in 400 000€. The working days per year were fixed at 250.

5.2 SCENARIO 1

In this scenario the overcapacity of the existing AD reactor is exploited. Basing on pilot plant results the calibrated ADM1 allowed to define the AD operative conditions and basing on model results the feasibility study was completed. The total amount of SS-OFMSW to be used is 16,7 ton/d, these quantities could be collected in selected source to avoid intensive pre-treatments: 10% of inerts are hypothesized. The clean SS-OFMSW amount after pre-treatments is 15,0 ton/d at 30%TS. The SwS amount is 115 m^3/d at 3%TS. No water dilution is planned to perform the process at the limit of the wet regime, pushing the OLR to maximum possible value. The operative conditions and the biogas production are listed in table 5.1.
The evaluation of the biogas production over the year is obtained considering a low biogas production during weekends due to only SwS feeding.

Table 5.1 Scenario 1: operative conditions and biogas production

Scenario 1		
HRT	20	[d]
Volume	2800	[m^3]
Qin	140	[m^3/d]
Qin_SwS	115	[m^3/d]
Qin_OFMSW	25	[m^3/d]
TS_in	7,8	[%]
OLR	3,3	[KgVS/m^3d]
Q Biogas	3640	[m^3/d]

5.2.1 Energy balance

The energy balance was performed considering the whole WWTP. The average annual EE consumption is equal to 2200MWhe. The extra-EE consumption due to AcoD up-grade is linked to pre-treatment section and composting, it is evaluate in 80KWhe/ton for incoming waste and in 90KWhe/ton for compost (data from Righi et al., 2013). The actual TE consumption for AD reactor is 4965KWht/d, with a new insolation a consumption of 3200KWht/d can be achieved. The energy balance flows are depicted in figure 5.1.

5.2.2 Digestate

After dewatering process, a production of 51,9m^3/d of solid digestate at 20%TS and 81,3 m^3/d of liquid digestate is estimated. The solid digestate could be treated with green waste in a composting process to produce organic fertilizer. By the Italian law (D.Lgs 75/2010 and subsequent amendments), SwS has to be present in the starting substrate mix under the limit of 35% w/w and heavy metals has to respect limit concentrations. Basing on heavy metals analysis performed on green waste (Rizzardini et al., 2013) final heavy metal concentrations in compost were calculated (Table 5.2). To achieve a proper starting mixture for composting process the amount of green waste was evaluated in relation to C/N ratio and humidity. From experimental pilot plant data, digestate has a C/N ratio of 9. Green waste is composed by a mixture of grass cuttings and pruning wastes. A total amount of 52 ton/d of green waste was considered necessary to respect constrain conditions. The compost production was estimated in 11948 ton/year.

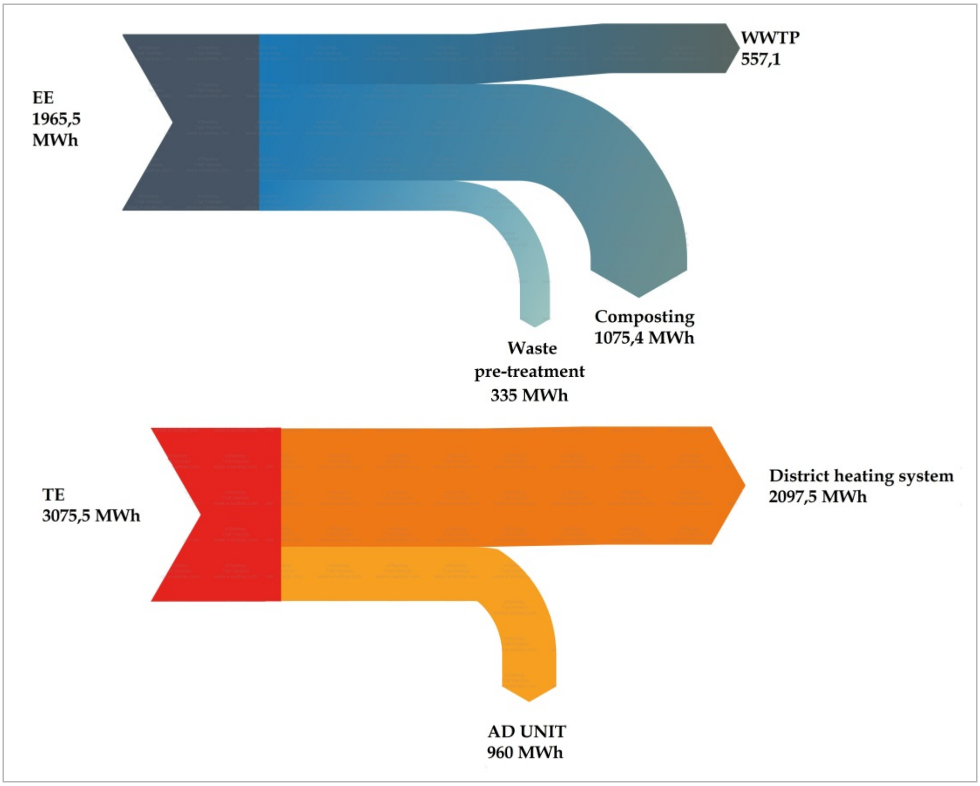


Figure 5.1 Energy balance flows for scenario n°1.

Table 5.2 Heavy metals in digestate, green waste and in compost.

Heavy metals [mg/gTS]	Solid digestate	Green waste	Compost	D.Lgs. 75/2010
Pb	93,9	10	35,1	140
Cd	1,25	1	1,1	1,5
Ni	79,3	11	31,4	100
Zn	1425	64	471,1	500
Cu	386,4	34	139,4	230
Hg	2,2	0,2	0,8	1,5

5.2.3 Economic evaluation

5.2.3.1 Investment

In table 5.3 the items that compose the total investmet for scenario n°1 are listed.

Table 5.3 Total investment of scenario n°1

Item		[K€]
Civil works - Pre-treatment shed; - Piping.		400
OFMSW pre-treatment line - Conveyor belts; - Bags opener; - Sieve disc; - Deferizzation unit; - Eddy current separator; - Hydropulper; - Water tank.		800
Up-grade of existing AD reactor - Mixing; - Isolation.		400
Solid digestate fraction treatment: - Centrifuge and Composting plant.		1500
Liquid digestate fraction treatment: - Chemical physical treatment unit.		170
Biogas treatment - Desolforation unit up-grade;		50
Automation and control		30
CHP		250
Technical costs		+10%
	TOT	3960

5.2.3.2 *Economic feasibility*

The investment was evaluated calculating the EBITDA (Earnings Before Interest, Taxes, Depreciation and Amortization) and EBIT (Earnings before Interest and Taxes) to define the net income and cash flows over the 20 years. The NPV (net present value), the PB (pay back) and the IRR (internal rate of return) were calculated to evaluate the investment efficiency. The results are listed in table 5.4: the definition of a value ranges is due to the variability accounted for waste treatment contribution tariffs.

Table 5.4 Investment parameters for scenario n°1

Investment	3960,00	[K€]
Expenses	436,42	[K€/year]
Revenues	1537,01÷1773,89	[K€/year]
NPV	4735,47÷6477,98	[K€]
PB	7÷5	[years]
IRR	20÷25	[%]

5.3 SCENARIO 2

Scenario n°2 is based on the synergy of WWTP and waste treatment plant, the feasibility study was build assuming the creation of an integrated waste and wastewater treatment hub.
The amount OFMSW treated in this scenario is 22000 ton/year equal to the organic waste collected in all the Udine district in 2012 reported in "Rapporto Rifiuti Urbani 2012" of "Ispra- Istituto Superiore per la Protezione e la Ricerca Ambientale".
It is assumed to realize:

- in the WWTP area: the AD feeding mixture preparation, the AD process and the liquid digestate treatment;
- in the waste treatment plant: the substrate selection and pre-treatment and, after AD process, the solid fraction digestate composting.

Economic and energetic assessment was performed considering the whole hub.
It's necessary to build a new digester to treat the whole amount of OFMSW. To define the optimum reactor volume and operative conditions, mathematical

simulations were performed. ADM1 model was implemented in sub-scenarios to test different HRT and OLR conditions.

Different dilution levels were considering for OFMSW, respectively 5, 10, 15 and 20%TS. The HRT was varied from 18 to 20 and 22 days. COD in the supply flow was calculated basing on COD/VS ratio measured during pilot plant experimentation. The ADM1 parameters X_{pro}, X_{lip}, X_{ch} were calculated and customized for each simulation. Each supply mix has determined different operative conditions for the existing digester (DIG 1) and the new reactor (DIG 2): for each scenario one simulation for each digester was performed. The SwS inflow was split to both digesters in a variable ratio in relation to assure the best operative conditions to each scenario. The OLR conditions tested in each scenario for each digester are reported in the graphs of figure 5.2: for digester 1 the absence of data indicates not feasible condition in that point.

The volumes tested for the new reactor (DIG 2) are summarized in figure 5.3 respect HRT and the TS content in the OFMSW substrate.

The results obtained for biogas production, implementing the modified ADM1 model, are reported in figure 5.4 for the whole AD unit, constituted by digester 1 and digester 2.

To identify the best operative conditions to maximize the biogas production, limiting the digester failure risk, a feasibility index (FI) was defined accounting digester volume, simulated biogas production and organic load applied. The coefficients for feasibility index calculation are listed in table 5.5. The equation to calculate FI is:

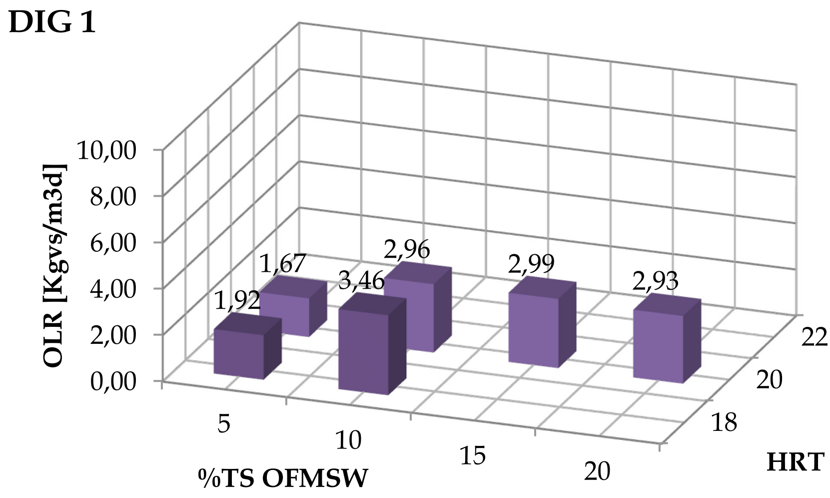
$$FI = (V_{DIG2}\alpha + Q_{BIOGAS}\beta) * (OLR_{DIG1}\gamma_1 + OLR_{DIG2}\gamma_2)/1000 \quad \text{(eq. 5.1)}$$

Table 5.5 FI parameters value and ranges

FI parameters	[-]	
α	-0,1	
β	0,4	
		OLR [KgVS/m^{3}d]
γ	1	0-2
	0,8	2-4
	0,6	4-5.5
	0,4	5.5-6.5
	0,2	6.5

Higher the FI value, more economic valuable the scenario is. The calculation results for the FI are reported in figure 5.5. The best results were obtained at

[HRT 18, 10% TS of OFMSW] and at [HRT 20, 15 %TS of OFMSW]. Considering the lower amount of water to use, the option [HRT 20, 15%TS] was chosen.



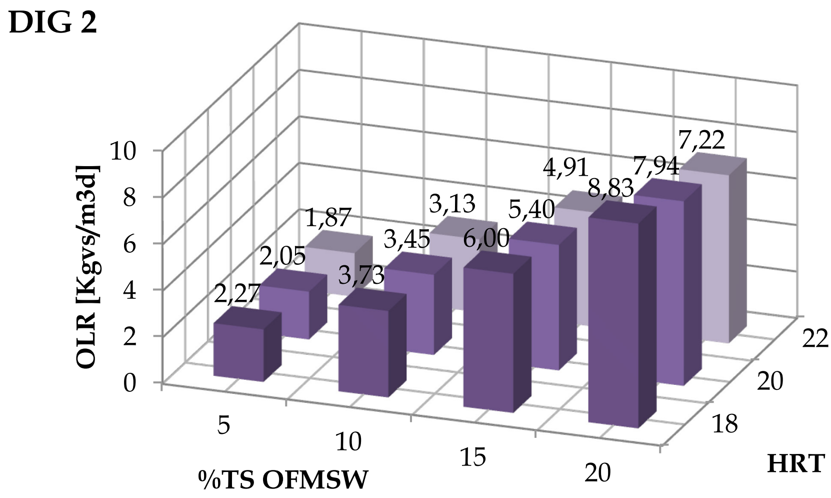


Figure 5.2 OLR conditins tested in simulation for digester 1 and digester 2.

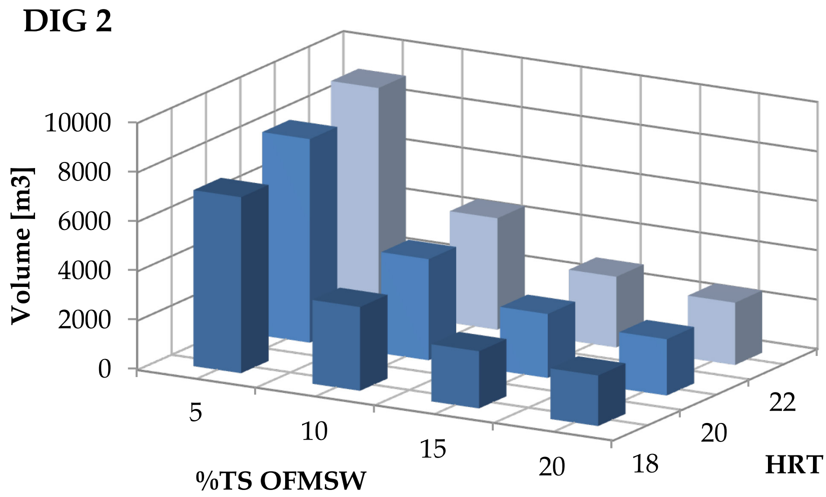


Figure 5.3 Volumes of digester 2 tested in simulations.

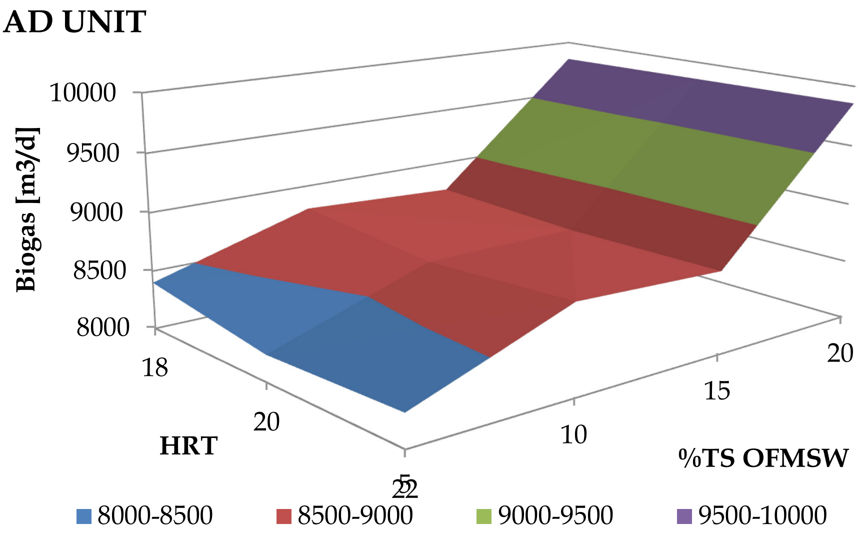


Figure 5.4 Simulated biogas production for the whole AD unit.

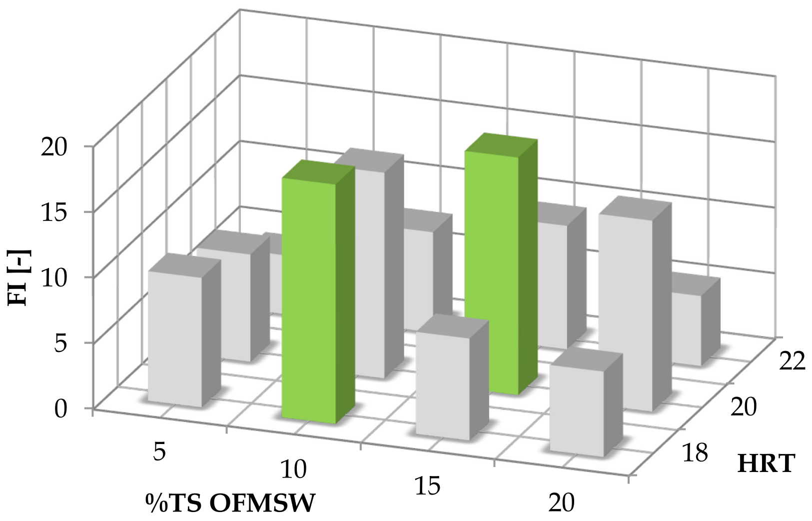


Figure 5.5 FI values for the AD unit.

In table 5.6 the operative conditions and the biogas production for each digester in the selected scenario are listed. A daily flow of 72m^3 of purified water from WWTP is needed to dilute the OFMSW to 15% of TS content.

Table 5.6 Scenario n°2: operative conditions and biogas production

Scenario 2	DIG 1	DIG 2	
HRT	20	20	[d]
Volume	2800	2600	[m^3]
Qin	140	130	[m^3/d]
Qin_SwS	90	30	[m^3/d]
Qin_OFMSW	50	100	[m^3/d]
TS_in	7,2	12,2	[%]
OLR	3,3	5,4	[KgVS/m^{3}d]
Q Biogas	3420	5265	[m^3/d]

5.3.1 Energy balance

Basing on total biogas production of 8685m^3/d, the energy flows were evaluated. To exploit the total amount of biogas for energy production, a new

CHP unit is necessary. The total energy demand for the integrated hub is 4000MWhe/year. In figure 5.6 the energy flows are represented. Composting and pre-treatment energy consumptions aren't considered because they are already operative in waste treatment plant.

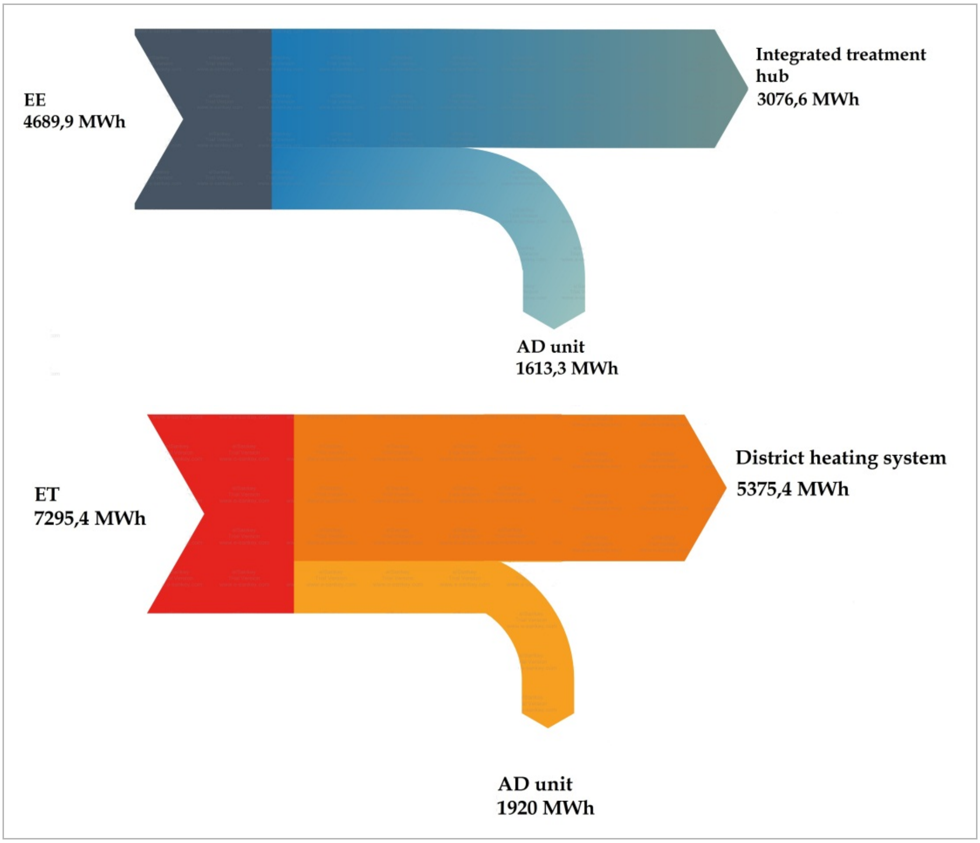


Figure 5.6 Energy balance flows for scenario n°2.

5.3.2 Digestate

A production of 103,4m^3/d of solid digestate at 20%TS and 162,0 m^3/d of liquid digestate is estimated. As explained in paragraph 5.2.2 the final heavy metal concentrations in compost were calculated (Table 5.7). A total amount of 100 ton/d of green waste was considered necessary to respect constrain conditions. The compost production was estimated in 23400 ton/year.

Table 5.7 Heavy metals in digestate, green waste and in compost

Heavy metals [mg/gTS]	Solid digestate	Green waste	Compost	D.Lgs. 75/2010
Pb	93,9	10	35,0	140
Cd	1,25	1	1,1	1,5
Ni	79,3	11	31,4	100
Zn	1425	64	470,3	500
Cu	386,4	34	139,2	230
Hg	2,2	0,2	0,8	1,5

5.3.3 Economic evaluation

5.3.3.1 Investment

In table 5.8 the items that compose the total investment for scenario n°2 are listed. The revamping cost of waste treatment unit for composting process was considered.

Table 5.8 Total investment of scenario n°2

Item	[K€]
Civil works - Pre-treatment shed; - Piping.	400
OFMSW pre-treatment line - Conveyor belts; - Bags opener; - Sieve disc; - Deferizzation unit; - Eddy current separator; - Hydropulper; - Water tank.	2000
Up-grade of existing AD reactor - Mixing; - Isolation.	400
New AD unit - Buffer tank; - AD reactor.	1200

Solid digestate fraction treatment: - Centrifuge and Composting plant up-grade.		520
Liquid digestate fraction treatment: - Chemical physical treatment unit.		250
Biogas treatment - Desolforation unit up-grade; - Chiller.		170
Automation and control		60
CHP		1400
Technical costs		+10%
	TOT	7040

5.3.3.2 *Economic feasibility*

The results of the economic evaluation are listed in table 5.9, following the same pattern of scenario n°1 but considering the two treatment plant as an integrated hub.

Table 5.9 Investment parameters for scenario n°2

Investment	7040	[K€]
Expenses	1283,71	[K€/year]
Revenues	3598,82÷4198,82	[K€/year]
NPV	11039,14÷15425,06	[K€]
PB	6÷4	[years]
IRR	24÷30	[%]

5.4 SCENARIOS COMPARISON AND CONCLUSIONS

Scenario n°1 could be a profitable solution considering the substrates amount treated and the PB of the investment. A synergy between the waste treatment plant and WWTP could make this scenario more economically attractive. Scenario n°2 allows to recover the energy need of the WWTP and, partially, of the waste treatment plant. However it requires huge amounts of green waste to make a compost according to law. Both scenarios reveal the availability of extra thermal energy that could be used by a district heating system, the advantages of this solution weren't counted in the economic evaluation of scenarios. The investment size of scenario n°2 is heavier than scenario n°1 but allows a faster PB with a maximum NPV of 15425,06K€. The IRR index is higher for scenario n°2 but good levels were achieved also by scenario n°1. The scenario parameters comparison is highlighted in table 5.9 and, in graph of figure 5.7, the investment trends in the different scenarios are depicted. It's important to underline that this two scenarios represent the solutions at the limit of the constrain conditions: more feasible scenario could be identify by the treatment plant collaboration on available key data. ADM1 model was a fundamental instrument to test different operative conditions, as highlighted by the results obtained.

In relation to digestate fate, a wide number of treatment solutions are present on the market. Solid fraction can be treated by composting process to achieve the nutrient recovery, reminding that the agricultural direct utilization of fermentation residues depends on the legal prescriptions on fertilizers. Aside a chemical-physical treatment of liquid digestate was hypothesized, but as reported by Rodriguez-Garcia et al. (2013) the supernatant digestate has the characteristics (high N and P concentrations, low COD and solids, temperature approximately 37°C) to apply particular biological treatments instead of charging the WWTP water line. An interesting solution developed is the biological N and P removal option by the short-cut nitrification-denitrification (SCND) and denitrifying phosphorus removal via nitrite (DPNR) in scSBR using short chain carbon sources obtained from OFMSW fermentation liquid (Frison et al., 2013).

Table 5.10 Investment parameters comparison

	Scenario n°1	Scenario n°2	
Investment	3960,00	7040	[K€]
Expenses	436,42	1283,71	[K€/year]
Revenues	1537,01÷1773,89	3598,82÷4198,82	[K€/year]
NPV	4735,47÷6477,98	11039,14÷15425,06	[K€]
PB	7÷5	6÷4	[years]
IRR	20÷25	24÷30	[%]

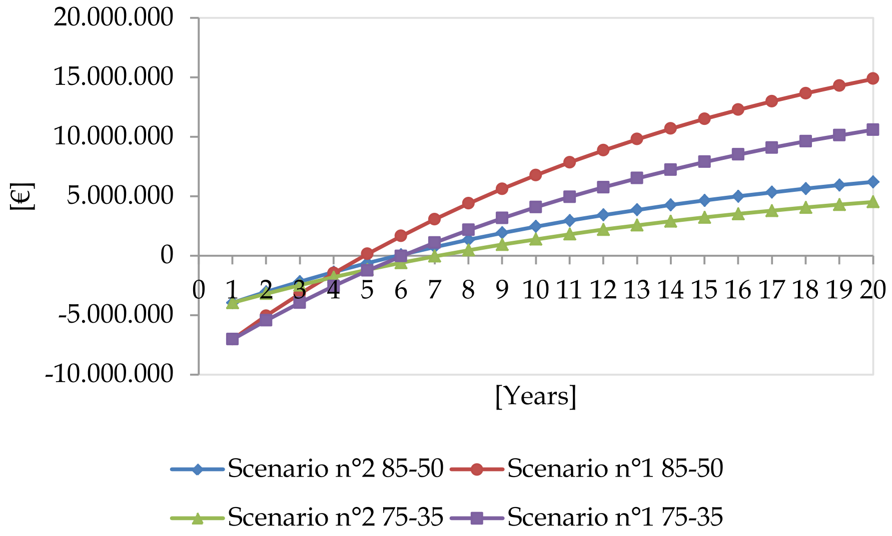


Figure 5.7 Investment trends in scenario tested.

6 Conclusions

In this study the analysis of the AD process to optimize an existing plant and design a new one was performed. A multi-level engineering approach was implemented from micro to macro parameters analysis. Every step has highlighted strengths and weaknesses and allowed to define a practical protocol to how define the best process conditions to optimize reactor performances.

This protocol can be defined as follow:

- Deep substrate characterization has to be focalized on macromolecular compounds analysis (carbohydrates, proteins, lipids and VFA) and chemical-physical parameters analysis: total COD, soluble COD, TS, VS, TKN, NH_4^+, pH and alkalinity measurements are mandatory to evaluate the substrate for AD process and to perform COD and nitrogen fractionation. This step implies high lab efforts and a standardized methodology for complex substrate is necessary, nevertheless is essential to obtain reliable data for AD process design.
- BMP tests allow to understand the biomass performance in substrates degradation and to highlight potential inhibition phenomena. The operative conditions of BMP trials, such as mineral medium, trace elements addiction and also the value of ISR, are still under discussion in the scientific community. However complying with the most recent guidelines, comparable results can be obtained. From the results of this study, BMP test can't be used to calibrate ADM1 model for dynamic simulation but from MPR curves it's possible to optimize the substrate characterization by mathematical model implementation, as the novel technique of anaerobic respirometry (Giroult et al., 2012).
- Pilot plant experimentation is fundamental to understand the AD process performance under dynamic organic loading conditions: the limits of acceptable operative conditions can be identified. Basing on pilot plant experimental data, ADM1 model can be calibrate to achieve dynamic organic loading simulations. In case of non-conventional

substrates or non-conventional operative conditions pilot plant test is mandatory.

- ADM1 modeling allows to test different HRT and OLR scenarios and to define the best operative conditions. ADM1 requires a lot of experimental data and the quality results is strictly linked to substrate characterization. When the ADM1 is calibrated, it can be used in a very wide field of operations: numerous operative scenarios can be tested. It's fundamental to underline the robustness of this model: due to inhibition pathways described, the AD process failure is hardly forecast by ADM1, engineering control by the user on the results obtained it's essential for the proper use of the modeling tool.

In relation of obtained results by the applicative case of Udine WWTP, different operative solutions were identified. The SS-OFMSW substrates analysed had highlighted their different characteristics in relation to the source. The OFMSW characterization is highly variable in terms of macromolecular compound, the OFMSW composition can vary widely in relation to the source (Iacovidou et al. 2012). In the entire collection basin several potential sources of SS-OFMSW were identified. To avoid elevate amounts of inerts in the digester feeding mix and high pretreatment costs, an innovative waste management strategy based on SS-OFMSW could be apply. Nevertheless OFMSW delivery and treatment regulations are now a barrier to wastewater management companies to up-grade its facilities: a synergy with waste treatment plant can facilitate legislative procedures.

The impact of the different compositions of SS-OFMSW macromolecular compounds was highlighted by BMP tests (Cabbai et al., 2013). As experimental data had confirmed, the mono digestion of SS-OFMSW can be limited by lack of nutrients (N, P and metals) and by VFAs inhibition phenomena (Iacovidou et al., 2012). Moreover, light metal ions are present in many type of food waste and, at high concentrations, can cause toxicity in AD process due to osmosis effect.

The AcoD process of sewage sludge and OFMSW can benefit of trace elements carried by sewage sludge, smoothing the inhibition risk. AcoD performances were tested in batch trials and verified in CSTR regime by pilot plant experimentation: after the pilot plant start-up the different phases tested allowed to understand the biomass behaviour switching to AcoD and the response to an increasing OLR. Process monitoring was fundamental to achieve a good pilot plant start-up and process experimentation management: early indicators like VFAs concentrations, FOS/TAC ratio were constantly controlled: no inhibition or instability phenomena were detected. The feeding strategy adopted was affected by large fluctuation in SwS TS content that led to variable OLR application: in relation to process stability achieve, this may have determined a positive effect on microbial community selection. Digestate quality was monitored and experimental data were crucial for develop feasibility scenario of full-scale AD reactor up-grade.

ADM1 model application has allowed to investigate a large set of AcoD implementation scenarios for the full-scale AD unit as a part of WWTP or a part of an integrated waste and waste water treatment hub. ADM1 can be used to determine both optimal reactor design and process control but, as a very robust model, a heavy OLR has to be applied to predict the AD reactor collapse (Jeppsson U., 2007). Different problematic technical aspects are still to be solved: from the definition of a clear applicative procedure to the limited use of the single composite state variable Xc.

The feasibility study conducted, based on experimental results, has allowed to evaluate the two scenarios for AD full-scale up-grade. The investment size and management solutions are very different but both respect the conditions for an attractive investment from economical and environmental point of view. Final compost quality was checked by calculations according to Italian law. The liquid digestate fate is an open point and different treatment and use can be further evaluated.

AcoD of OFMSW and sewage sludge could become a strategic and cross-sectorial solution based on water industry and waste management synergy where the necessary infrastructures and human resources could be provided (Iacovidiu et al., 2012). A holistic approach to waste and waste water treatment can drag the waste management to more sustainable solutions.

Collaboration of all stakeholders can have a direct impact on the application of this technology to overcome the entry barriers. The OFMSW quality in terms of low levels of impurities (<10%) is mandatory for the AD reactors operations. The digestate management must involve the entire supply chain until the farmer use of the final product. Biogas can be used for energy production directly in CHP units or by injection in methane grid or as transport fuel.

The solutions, evaluated in this study, are based on CHP adoption and allow to increase the local renewable energy production with benefit for the local community by the potential construction of a district heating system and the application of low public service taxes, thanks to economic benefits guaranteed by the new AD unit.

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APPENDIX

Basing on experimental results obtained by BMP tests (chapter 2) for substrate from restaurant waste, where yeast residues were observed and higher methane production was registered, BMP tests to evaluate a possible pre-hydrolysis action of yeast on OFMSW substrate were performed.

BMP tests were conducted following the same experimental procedure described in chapter 2. An ISR of 3 was used.

A sourdough sample from the bread production and OFMSW from a canteen were collected.

Pre-treatment were performed on 500gr of grinded OFMSW adding fixed amounts of yeast (25gr and 50gr) at 32°C storage temperature, achieved by an incubator. The pre-treatment duration was of 24 hours. Blank references samples were considered. Samples were defined as follow:

- OFMSW storage, without yeast, at 4°C (OFMSW_4);
- OFMSW storage, without yeast, at 32°C (OFMSW_32);
- OFMSW storage at 32°C with 25gr of yeast (OFMSW_32_25);
- OFMSW storage at 32°C with 50gr of yeast (OFMSW_32_50).

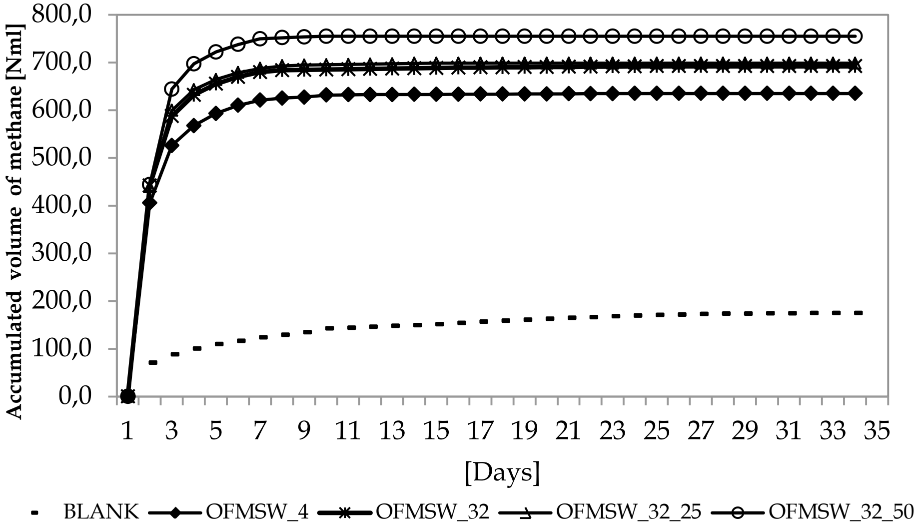
After pre-treatment, OFMSW samples were diluted to 5%TS and shredded by kitchen mixer to obtain a substrate size <10mm.

Soluble COD was measure in each pre-treated sample, with the results reported in the following table:

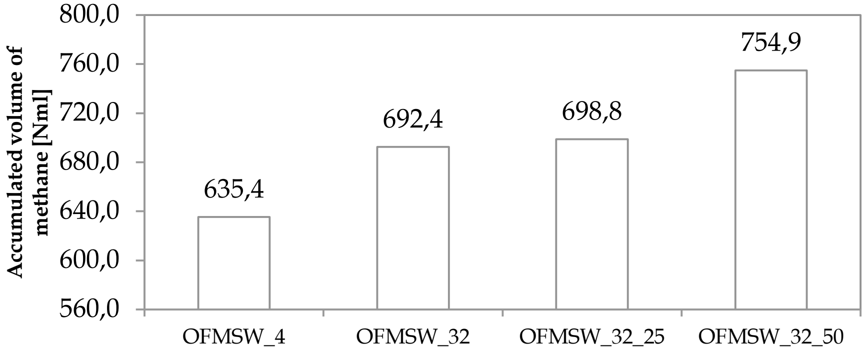
Sample	OFMSW_4	OFMSW_32	OFMSW_32_25	OFMSW_32_50
CODs [mg/l]	15520	16520	17740	19940
Increment respect OFMSW_4		+6,44	+14,30	+28,48

It's possible to observe the slight increment of the sample maintained at 32°C without yeast, due to hydrolysis action performed by bacteria already present in substrates. In sample treated with yeast, after 24 hours, a visible rising effect was registered. The soluble COD increase was near the 30% for OFMSW_32_50.

Blank and the 4 trials BMP tests were performed in triplicate. The results are depicted in the following figure.



The final accumulated volume of each trial is reported in the following graph.



Data were used to make a comparison to understand the effectiveness of biological pre-treatment with yeast. From OFMSW_32 to OFMSW_4 an increase of 9% on methane production was registered. OFMSW_32_50 has highlighted a growth of 18,8% respect OFMSW_4, but only of 9% respect OFMSW_32. The increase of OFMSW_32_25 respect OFMSW_32 wasn't appreciable (0,9%). Data from this trial could encourage a possible pre-treatment base on yeast action, but several conditions have to be tested (for example with larger amounts of yeast) before drawing conclusions.