Mesophilic and Thermophilic anaerobic co-digestion of winery wastewater sludge and wine lees: an integrated approach for wine production.

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Abstract

Winery wastes generation of a cellar producing about 300,000 of wine per year was monitored for one year. On average, 196 liter of wastewater, 0,1 kg of sludge (dry matter), and 1.6 kg of wine lees were produced per hl of wine processed. Anaerobic digestion may reduce management costs of waste disposal and produces biogas, a renewable source of energy usable inside the same production process and wastewater treatment plant. In order to assess the feasibility of the anaerobic co-digestion of winery wastewater treatment and winery wastes, a pilot scale study was carried out. Pilot-scale reactors were employed to test anaerobic process treating sludge and wine lees both at mesophilic and thermophilic temperature ranges. Process at 37°C was steady for a long period with pH ranged between 7.22 and 7.80 and average biogas production of 0.386 $m^3/kg\ COD_{fed}$. On the other hand, in the thermophilic reactor volatile fatty acids accumulated and the process failed after one hydraulic retention time at stationary conditions. In order to recover the biological process, trace metals were added; metals augmentation improved the process stability and yields at 55°C: pH ranged between 7.8 and 8, specific gas production was 0.450 m^3/kg COD corresponding to solid and COD removal of 34% and 88%, respectively. Although the better performance, the thermophilic process showed constrains related to both the necessity of metal addition and worse dewatering. The mesophilic digestates reached good dewatering quality by adding 6.5 g of conditioner for kg of dry matter, while the needed dosage for thermophilic one was greater than 10 g/kg.

Keywords: Anaerobic digestion; dewatering; mesophilic; thermophilic; trace elements; winery wastes

1. Introduction

Wine making process produces large volumes of waste streams, including solid organic waste, wastewater, greenhouse gases and packaging waste [1]. Winery wastewater, is a major waste stream resulting from a number of activities that includes tanks cleaning, floors and equipment washing, barrel cleaning, wine and product losses, bottling facilities, filtration units and rainwater captured in the wastewater management system [2]. The wastewater quantification is not easy, it depends on dimension of cellar and technologies applied. In general, wastewater production ranges from 0.7 to 14 l per liter of wine produced [3] but specific studies carried out in South Africa [4], Chile [5], Portugal [6], Italy [7], and Greece [8], all demonstrated that typical values are around 2-6 liter per liter of wine produced.

This effluent generally presents a considerable level of COD, the major part of which is soluble [9] and with high biodegradability [10] because of the presence of ethanol, sugars, and organic acids [8, 11-13].

Because of their characteristics, these streams are generally treated by means of both aerobic and anaerobic processes [2]. Among biological processes, activated sludge technology is the most diffused because of its high efficiency and ease to use. It can remove 98% of COD and withstands large variation in hydraulic and pollution load [9, 11, 14].

The removal of organic material generates considerable quantities of waste sludge, normally in the range 0.21 - 0.28 kg MLVSS/kg $COD_{removed}$ [15-16]. Ruggieri et al. [17] reported that 12% of organic solid waste produced by wineries, is composed by dewatered wastewater sludge and that the management via external companies is expensive and sometime difficult. An alternative to valorize this waste stream could be anaerobic digestion process. Anaerobic digestion (AD) is a mature technology and it is applied to treat different type of organic wastes (municipal solid wastes, sewage sludge, agro-industrial residues, livestock effluents, etc). Combination of conventional activated sludge process (CAS) and AD may reduces external management costs and produces biogas, a renewable source of energy usable inside the same production process and wastewater treatment plant. Moreover, effluent from anaerobic process should be an interesting amendment to be spread on vineyards: because it is enriched in nutrients content, and makes nitrogen and phosphorus more available thank to organic matter degradation. AD removes pathogens and polyphenolic compounds with different efficiencies based on the operational conditions applied. Pathogens cut-off is affected by temperature, retention time and fed substrates [18 – 19], while polyphenols removal mainly by operational temperature [20 - 21].

Once AD of winery wastewater sludge is implemented, co-digestion with other wine-making process residues (such as lees) should make the anaerobic process economically more advantageous.

Wine lees (WL) are produced throughout the year. Like wastewater, also WL show high organic content and their disposal is an environmental problem that requires appropriate treatment. The composition of WL depends on the winemaking technology although, according to Bustamante and Temiño [22], the main characteristics are an acidic pH, between 3 and 6, a COD greater than 30,000 mg/L, potassium in concentrations greater than 2,500 mg/L, and phenolic components in quantities up to 1,000 mg/L.

This paper reports the results obtained from a pilot scale study where winery wastewater sludge and lees where co-digested both in mesophilic and thermophilic conditions, assessing the process feasibility and evaluating the effluent quality in terms of pollutant removal and dewatering capacity.

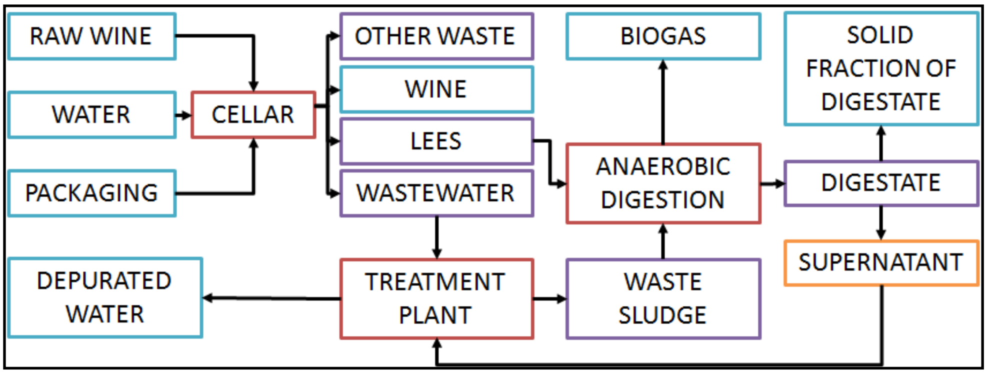


Fig. 1 Integration of anaerobic digestion in the wine-making process

2. Materials and methods

2.1. Experimental set-up

2.1.1. Winery wastewater treatment plant

The substrates used in this experimental trial were collected in a winery wastewater treatment plant, located inside a cellar situated in north-east of Italy, that produces about 300,000 hectoliters of wine per year. The cellar processes and bottles both produced and bought wines, hence the working period is not concentrated during the grape harvesting period but it is rather distributed along the year. The production picks are therefore connected with market requests rather grape harvesting, therefore there is not a real seasonal variation. Fig. 1 shows a schematic of the WWTP. After pre-treatment (screening and primary sedimentation) the wastewater is sent to the 1,400 m^3 aerobic bioreactor. Operational conditions of the activated sludge process are reported in Table 1. Treated water and sludge are separated in a secondary sedimentation tank. Treated water is (eventually) disinfected and filtrated on quartz sand. The sludge treatment process consists of a thickening section followed by a filter press, stabilization is not present.

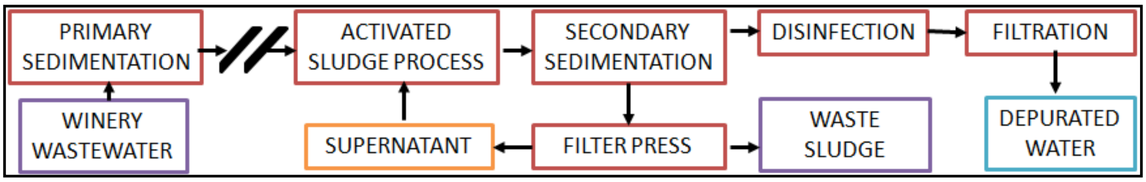


Fig. 2 Flow chart of winery wastewater treatment plant

Table 1 Operational conditions of activated sludge process (Q: flow rate; HRT: hydraulic retention time; SRT: sludge retention time; OLR: organic loading rate; MLSS: mixed liquor suspended solid; MLVSS: mixed liquor volatile suspended solid; F/M: food to microorganisms ratio; Y_{obs}: observed biomass yields)

Q	**HRT**	**SRT**	**OLR**	**MLSS**	**MLVSS**	**F/M**	**Y_{obs}**
m^3/d	d	d	$kgCOD/m^3d$	mg/l	mg/l	kgCOD/kgMLVSS	$kgMLVSS/kgCOD_{rem}$
170	6.7	35	0.60	3,552	3,010	0.26	0.21

Influent and effluent of wastewater treatment plant were monitored for one year in order to determine their characteristics, also dewatered sludge after filter press was collected and analyzed.

2.1.2. Pilot scale anaerobic reactors

Two parallel continuous stirred tank reactors (CSTR), of 230 liters working volume, were employed for anaerobic co-digestion tests. Mesophilic (37°C) and thermophilic (55°C) conditions, were maintained by hot water recirculation system in the external jackets of the reactors. PT100 probes monitored process temperatures and managed water recirculation pump. Biogas productions was continuously monitored by drum-type gas flow meters (Ritter, Germany).

The experimental design contemplated a start-up period while the organic loading rate and wine lees content in the feed mixture increased step by step; during this period the anaerobic microorganisms acclimated to substrates and to different readily biodegradable compounds present in winery by-product. Once the operational conditions were reached, the tests were carried out for several HRTs in order to obtain steady state in terms of biogas production, stability parameters and digestates characteristics.

2.2. Analytical methods

The substrates and the digesters effluents were collected and monitored once a week in terms of total and volatile solids content (TS and VS), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN) and total phosphorus (P_{tot}) [23]. The process stability parameters, pH, volatile fatty acids (VFAs) content and composition, total and partial alkalinity, and ammonia concentration, were checked two or three times per week. VFAs content was monitored using a gas chromatograph as reported by Cavinato et al. [21]. At steady state conditions, total phenols were analyzed spectrophotometrically by the Folin–Ciocalteu assay [24] and concentration was reported in terms of Gallic acid equivalent per liter (mg HGal/l). Biogas composition (CO_2, CH_4, H_2 and O_2) was determined by a gas chromatograph (GC Agilent Technology 6890 N) equipped with the column HP-PLOT MOLESIEVE, 30 × 0.53 mm ID ×25 μm film, using a thermal conductivity detector and argon as gas carrier.

The anaerobic process leads to changes of the structural matrix of sludge flocs and particles, affecting consequently particle size distribution and dewaterability [25]. Filterability characteristics of the raw and conditioned effluents were determined by capillary suction time (CST) test using a CST instrument (Triton, A304M model), according with Standard Methods [23] and by specific resistance to filtration (SRF) according with IRSA-CNR [26].

3. Results and discussion

3.1. Winery wastewater treatment plant monitoring

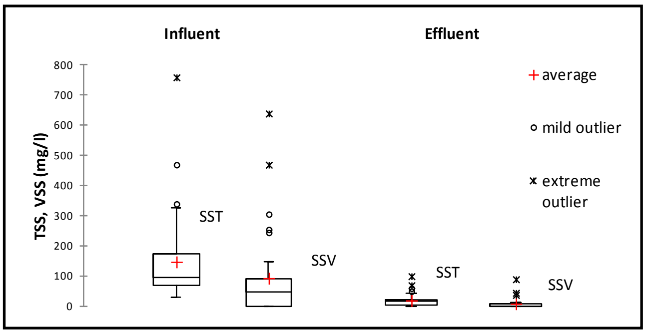
The winery wastewater treatment plant was monitored for one year in terms of influents, effluents (Table 2) and dewatered sludge characteristics. Considering the treated water and wine production in 2012, the wine-making process generated 1.96 liter of wastewater per liter of wine produced.

Table 2 Influent and effluent characteristics

Parameter	Unit	Influent			Effluent		
		Average	St.Dev	Range	Average	St.Dev	Range
TSS	mg/l	148	144	30 - 760	19	21	0 - 100
VSS	mg/l	94	141	0 - 640	9	20	0 - 90
COD	mgCOD/l	3,747	2,478	518-12,731	33	27	1 - 148
TKN	mgN-NH_4^+/l	25	13	9 - 57	11	4	3 - 19
N-NH_4^+	mgN-NH_4^+/l	1.9	1.7	0.6 -10.1	0.5	0.4	0.0-1.3
Ptot	mgP-PO_4^{3-}/l	7.5	4.0	2.0 - 19.3	3.3	2.3	0.3 - 9.6
P-PO_4	mgP-PO_4^{3-}/l	2.5	2.0	0.2 - 7.4	0.2	0.4	0.0 - 1.3

Concentration of solids in the influent depended by winery activities: total solids ranged from 30 to 328 mg/l (Fig.3), with 63% of volatile solids. They were completely removed during depuration process and treated water had solid concentration usually lower than 50 mg/l with 66% due to inert material.

(a)



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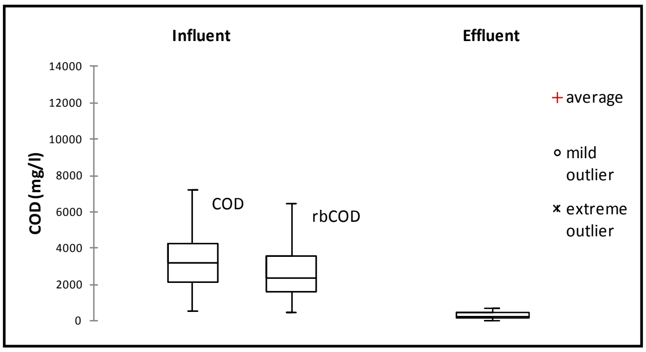


Fig. 3 Distribution of total suspended and volatile solid (a), COD and rbCOD (b) in the influent and effluent of winery wastewater treatment plant

COD concentration ranged between 518 and 12,731 mg/l (Fig. 3) but average value was 3,747 mg/l . About 71% of COD was due to readily biodegradable COD (rbCOD): sugars, ethanol, and other products of fermentation, dominated by the presence of acetate, were the main components. The rbCOD fraction was consistent with value reported by Andreottola et al. [10]. The remaining fraction was readily hydrolysable fraction, while the not biodegradable COD was negligible. Thanks to organic matter high biodegradability, COD removal was generally higher than 97% with one exception during the monitoring period (95%). Concentrations of 25 mg N-NH_4^+/l and 7.5 mg P-PO_4^{3-}/l were relatively low if compared with COD content and determined unbalanced COD:N:P ratio (500:3:1).. For this reason urea and ammonium phosphate were added in biological reactor to improve activated sludge activity..

Wastewater treatment plant well worked and effluents nutrients contents met the law threshold limits (Table 2).

Waste activated sludge was separated in the secondary sedimentation tank and was dewatered twice a week by addition of a chemical conditioner. In average 3,858 kg of wet sludge, with dry mass content between 15 and 20% , were produced per week corresponding to some 613 kg dry matter per week, that means 0.1 kg of dried sludge per hectoliter of wine. Dewatered sludge is usually managed via external companies by composting and the cellar pays 110€/ton for this purpose.

3.2. Seed biomass and substrates

The pilot-scale reactors were filled with mesophilic and thermophilic digestates deriving from previous experimentations. The inocula were well stabilized, solids content was lower than 10 gTS/kg and stability parameters were in the optimum ranges for AD (Table 3). Good biological stability was evident looking at nutrients concentrations (41.6 and 33.1 mg $N\text{-}NH_4^+$/gTS, 27.7 and 26.8 mg $P\text{-}PO_4^{3-}$/g TS at 37° C and 55°C respectively).

Table 3. Inocula characteristics

Parameter	Unit	37°C inoculum	55°C inoculum
TS	g TS/kg_{ww}	8.84	9.37
VS	g VS/kg_{ww}	5.92	4.69
VS/TS	%	67%	50%
COD	mg/g TS	552	751
sCOD	g/l	911	1,073
pH	-	7.53	8.33
TKN	mg $N\text{-}NH_4^+$/g TS	41.63	33.09
NH_4^+	mg $N\text{-}NH_4^+$/l	193.4	539.4
P_{tot}	mg $P\text{-}PO_4^{3-}$/g TS	27.7	26.8
Polyphenols	mg HGal/l	83.75	58.35

Substrates fed to reactors were waste activated sludge from winery wastewater treatment and wine lees originated from the same cellar.

Solids in dewatered sludge ranged from 129.0 to 193.7 g TS/kg but a wide concentration variability was observed because of technical reasons (conditioner doses, filter press setting) (Table 4). Volatile to total solid ratio in winery sludge was higher (88%) than typical value of sludge from municipal wastewater, probably due to high biodegradability of raw wastewater. Also COD concentration (868 mg/g TS) was indicative of low biological stability of the sludge. Instead nutrients ratio is well balanced for biological stabilisation (Table 4) with COD:N:P ratio of 124:7:1. Chemical analysis of sludge showed limited contamination of metals (Cd <0.5 mg/kg TS, Cr^{6+} <0.5 mg/kg TS, Cr 46 mg/kg TS, Hg <0.1 mg/kg TS, Ni 18 mg/kg TS, Pb 7 mg/kg TS, Cu 280 mg/kg TS, Zn 97 mg/kg TS), so it is possible to apply sludge on land as amendment.

Wine lees were formed during wine decanting step, adding bentonite; about 10 tonnes of lees were produced per week, corresponding to 1.6 kg/hl of wine produced. In this cellar, the typical wine lees production was lower than average production in Italian winery (6 kg/hl, [27]), this is because the wine is partially produced within the cellar, and the remaining is usually bought. Both wine lees from red and white wine processing were used during the experimentation to evaluate substrate variability and how it affects the process. About the 90% of wine lees samples had solid concentrations between 37.9 and 77.2 g TS/kg, but extreme values were also detected (Table 4). Generally this winery residues were characterized by low content of volatile solids (57% of total solids) due to presence of bentonite. COD was concentrated in the soluble form (sCOD was the 83% of total COD) while particulate fraction was typically between 417 and 627 mg COD/g TS. Nitrogen and phosphorus levels were limiting for bacterial growth if compared with COD concentration, in fact the COD:N:P ratio was 502:5:1.

Table 4 Waste activated sludge and wine lees characteristics

Parameter	Unit	Waste Activated Sludge			Wine Lees		
		average	**St.dev**	**range**	**average**	**St.dev**	**range**
TS	**gTS/kg_{ww}**	158.9	49.3	22.7-267.8	62.0	27.9	12.3 -120.0
VS	**gVS/kg_{ww}**	143.5	41.6	20.7 – 237.3	33.6	15.1	10.3 -73.0
VS/TS	**%**	88%	3	79- 93%	57%	13%	29 - 86%
COD	**mg/g TS**	868	69.4	749-1008	559	151	312 – 919
sCOD	**g/l**	nd	nd	nd	167	45	111 -204
TKN	**mg $N\text{-}NH_4^+$/g TS**	52.7	16.3	14.5 -80.3	30.3	12.7	9.7 -68.7
NH_4^+	**mg N NH_4^+/l**	nd	nd	nd	33.9	22.7	6.7 – 95.3
P_{tot}	**mg $P\text{-}PO_4^{3-}$/g TS**	7.3	2.0	2.5 -10.7	6.2	2.9	2.6 - 14.3
Polyphenols	**Mg HGal/l**	nd	nd	nd	1537	1189	260-3980

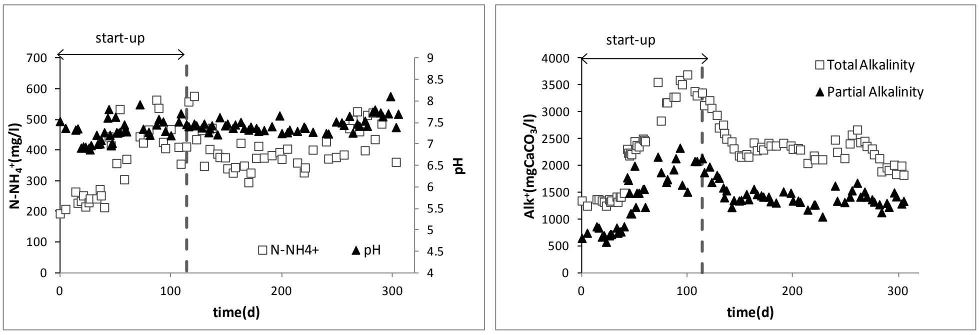
nd: not determined

Waste activated sludge is often associated with poor methane yields because of low biodegradability of microorganisms cells, on the other hand wine lees had unbalanced COD:N:P ratio; anaerobic co-digestion of these two wastes together should improve biogas conversion efficiency and consequently economically sustainable. Hence this process configuration was tested at pilot-scale, working in semi-continuous mode.

3.3. Performances of the mesophilic anaerobic co-digestion process

The organic load was gradually increased during the start-up phase, from day 1 to day 114. In particular, a constant quantity of sludge was used (0.6 kg COD/m^3d), and the amount of wine lees fed to the reactor was increased gradually from 0 to 2.6 kg COD/m^3d. Long start-up phase and little variation on operational condition favored biomass adaptation. Although the organic load increasing, the stability parameters improved, ammonium concentration went up to 555 mg $N\text{-}NH_4^+$/l, total alkalinity reached 3,690 mg $CaCO_3$/l while pH remained at 7.5. During the start-up the gas production rate rose from less than 0.1 $m^3/m^3_{reactor}$d up to 0.3 $m^3/m^3_{reactor}$d.
Total OLR at the end of transient period was 3.2 kg COD/m^3d and HRT of 23 d.

After day 114, alkalinity reduced until stable values of 2,248 mg$CaCO_3$/l. The pH value didn’t change significantly and ranged between 7.22 and 7.80. The ammonium concentration was the most changing parameter (Fig. 4) because of high variability of substrates characteristics; anyway the process stability was not affected by this fluctuation.

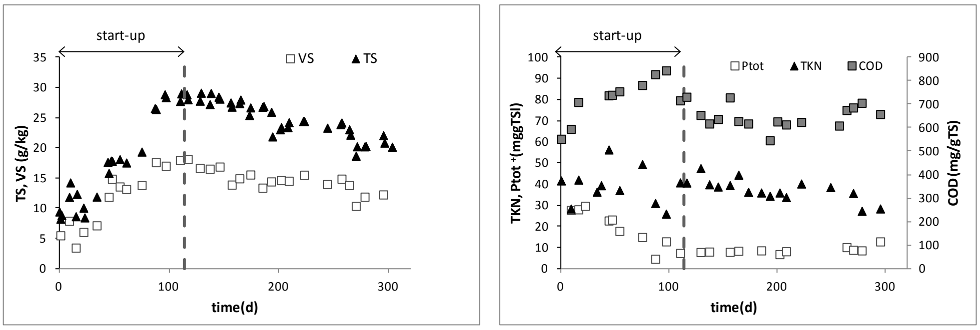


(a) (b)

Fig. 4 Trend of pH and ammonium concentration (a), partial and total alkalinity (b)

On the basis of the stability parameters the process didn't show particular difficulties, moreover in the long period the performances improved. Total solids and COD concentrations reduced with time down to average values of 24 gTS/kg, 58% volatile, and 640 mg COD/g TS, respectively (Fig. 5). Particulate COD removal was coupled with slightly increase of soluble COD, that anyway was lower than 1000 mg COD/l,. 40-50% of which was due to volatile fatty acids. Acetic acid was the dominant volatile fatty acid (52% of total VFAs) while propionic acid was the second most abundant with 12% of VFAs.

Nutrients concentrations generally reduced until steady values were reached (37 mgN/gTS and 9 mg $P\text{-}PO_4^{3-}$/gTS). The effluent COD:N:P ratio was 70:4:1 and can be considered like potential biofertilizer.

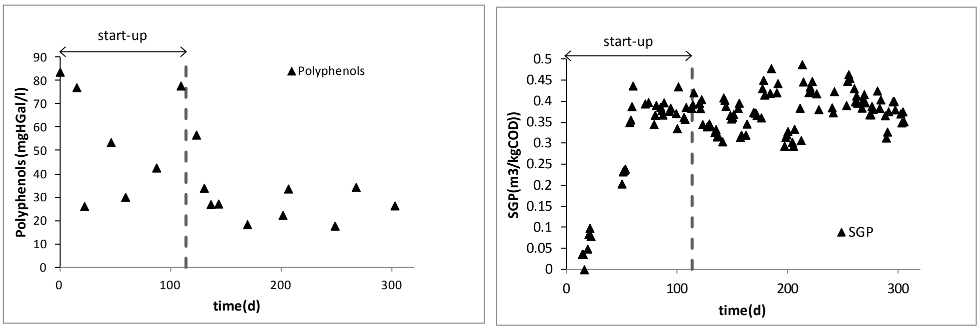


(a) (b)

Fig. 5 Trend of total and volatile solids (a), COD, TKN e Ptot (b)

Polyphenolic compounds were in the range 20 - 80 mg HGal/l during the start-up and at steady state their concentration was lower than 40 mg HGal/l: the anaerobic microorganisms adapted to these substrates and were eventually able to degrade them until the 94% of influent polyphenols.

Biogas production scattered a lot, depending on the type of wine lees in the influent: average biogas production was 0.386 m^3/kg COD_{fed} with 64-73% of methane but values as low as 0.30 m^3/kg COD_{fed} were also observed (Fig. 6).



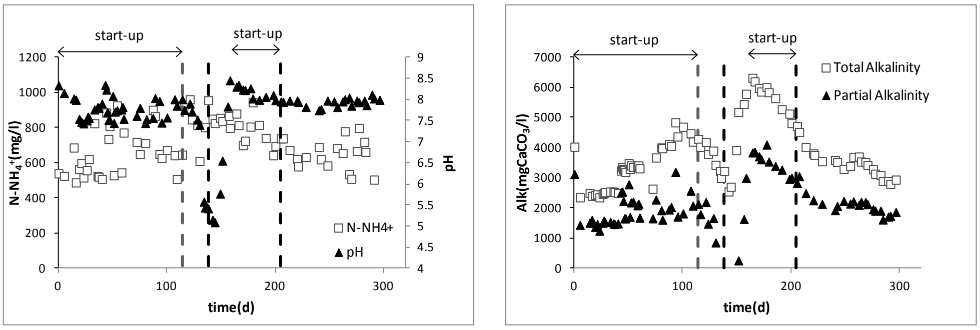
(a) (b)

Fig. 6 Trend of polyphenols concentration (a) and specific gas production (b)

Mass balances showed removal of 28% of total solids, 40% of volatile solids and 79 % of COD. Most of biogas derived from degradation of soluble COD (92%) that was less than 1 g/l in the effluent, while particulate substances were only partially degraded. Hydrolysis of organic matter appeared the limiting step of the process. In the same way nitrogen was fed to reactor mainly in organic form (less than 1% is due to ammonium ion) and during the digestion was transformed into soluble form for about 32%, consequently it could be recovered by supernatant treatment.

1.1. Performances of the thermophilic anaerobic codigestion process

Also in the case of the thermophilic process the start-up phase took a long time: it lasted 114 days while OLR was increased stepwise in order to obtain OLR of 3.2 kgCOD/m^3d and HRT of 23 d. Although during transient period pH was stable above 7.5 due to high buffer capacity in the inoculum (defined by total alkalinity), at the end of this period VFAs started to accumulate. At stationary conditions VFAs reached 6 gCOD/l, pH fell down to 5 after one HRT (Fig. 7) and the specific biogas production reduced accordingly. Comparing mesophilic and thermophilic processes it's clear that temperature affected the stability probably due to different behavior of thermophilic microbial community [21, 28]. Thermophilic bacteria could be more susceptible to toxic compounds like polyphenols, that accumulated in the reactor and reached 160 mg HGal/l. It is well documented the different capability of degrading polyphenols by mesophilic and thermophilic bacteria [20].

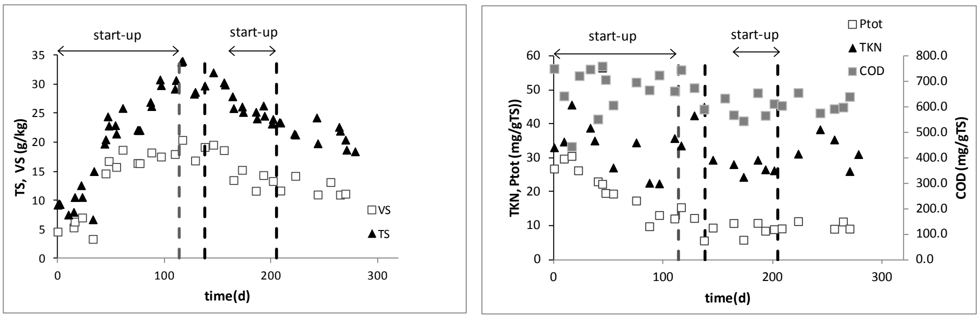


(a) (b)

Fig. 7 Trend of pH and ammonium concentration (a), partial and total alkalinity (b)

VFAs in the bulk were composed mainly by acetic and propionic acids (78% and 10% respectively), while longer fatty acid represented less than 15%. This distribution indicated that activity of the acetate consuming microorganisms (aceticlasic methanogenisis or syntrophic acetate oxidizing microorganisms) was the rate limiting step [29 - 31]. The process was recovered increasing pH with lime addition and, from day 170, a new start-up was carried out with addition of a metals solution [32-33]. This approach aimed to evaluate the beneficial effect determined by the supplementation of metals (Fe, Co and Ni). Trace elements addition affects sulfides concentration: they promote precipitation of insoluble metal sulfides and reduce H_2S toxicity. At high doses trace elements could be more available for microorganisms and support the activity of fundamental enzymes [34-35]. Several authors [29, 32] demonstrated positive effect of combined supplementation of Fe, Co and Ni into anaerobic digester and suggested different doses. Takashima et al. [36] evaluated the best concentrations of these metals and the values they reported were used also in this research: metals were added to the feed in order to obtain concentrations of 4.3 mg Fe-$FeCl_3$/l, 0.46mg Ni- $NiCl_2$ $6H_2O$/l and 0.51 mg Co- $CoCl_2$ $6H_2O$/l in the medium.

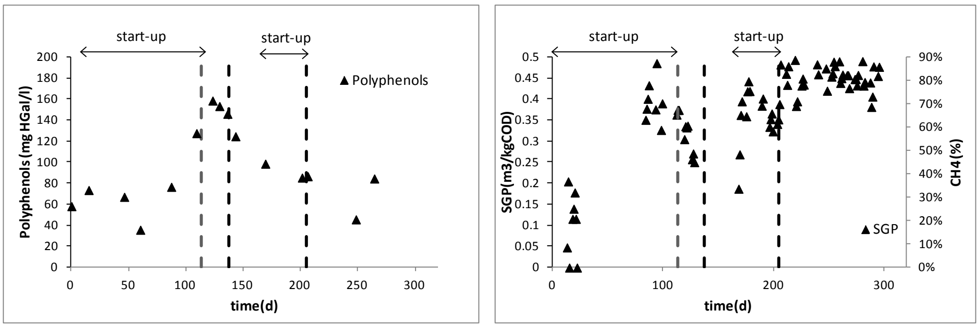
The addition of metals better stabilized the biological process: ammonium concentration stabilized around 630 mgN-NH_4^+/l and alkalinity reduced to 3,360 mg$CaCO_3$/l, as a consequence pH ranged between 7.8 and 8 (Fig. 7). In this operational condition removal efficiencies increased (29% of TS and 88% of COD) and effluent had 20.6 g TS/kg (Fig. 8a) at steady state. High hydrolysis rate in thermophilic range caused better solid reduction and organic matter stabilization. Accordingly with solid reduction, biogas production increased to 0.450 m^3/kg COD (Fig. 9) with 69% of methane.



(a) (b)

Fig. 8 Trend of total and volatile solids (a), COD, TKN e Ptot (b)

Average polyphenols contents reduced from 153 to 66 mg HGal/l (Fig. 9a) because of removal efficiency increased from 67 % to 78 %. Comparing removals observed in this study with that reported by Cavinato et al. [21], it seemed that higher influent polyphenols concentration stimulated degradative enzymes and supported growth of competent organisms also at 55°C.



(a) (b)

Fig. 9 Trend of polyphenols concentration (a) and specific gas production (b)

1.2. Comparison of the performances of the mesophilic and thermophilic processes

One of the main advantages of thermophilic condition was higher waste stream reduction (34% of solids reduction) because of improvement of hydrolysis rate, but biological stabilization of substrates appeared similar in the two reactors, with VS/TS ratio of 57-58% and particulate COD concentration of 613-640 mg/g TS (Table 5). Agree with solid and COD removal, biogas production at 55°C improved by the 18% compared with mesophilic process.

Hydrolysis affected also ammonification that caused higher ammonium concentration at 55°C (630 mg N-NH_4^+/l) than at 37°C (400 mg N-NH_4^+/l). In both reactors free ammonia content was far lower than inhibiting level because of low nitrogen concentration in the wine lees.

In order to evaluate process feasibility, the treatment of supernatant obtained by dewatering of digestates, had to be considered. Often management of digestate liquid fraction is considered a cost because it needs specific reactor for nitrogen removal/recovery or it leads to an increased nitrogen load of wastewater treatment plant. In winery contest, recirculation of supernatant in wastewater line may represent a way to reduce management cost because it limits urea and orthophosphate addition during biological process.

In term of stability thermophilic process with metals augmentation had higher buffer capacity defined by total alkalinity (3,560 mg$CaCO_3$/l) and, although volatile fatty acids concentration in the bulk was higher, the pH stayed between 7.8 – 8. VFAs and polyphenols likely determined higher soluble COD in thermophilic digestate In fact mesophilic reactor was characterized by polyphenols concentration of 26 mg HGal/l while the reactor with metals addition had 66 mg HGal/l. Lower polyphenols degradation rate at 55°C was due to temperature denaturation of enzymes involved in polyphenolic compounds degradation pathway.

Table 5 Characteristics of mesophilic and thermophilic digestates, average values and standard deviations

Parameter	Unit	37°C		55°C (with metals)	
		Average	St.dev.	Average	St.dev.
pH	-	7.46	0.19	7.91	0.09
PA	mg $CaCO_3$/l	1,375	126	2,043	134
TA	mg $CaCO_3$/l	2,248	200	3,390	193
$N\text{-}NH_4^+$	mg $N\text{-}NH_4^+$/l	400	56	630	73
TS	gTS/kg_{ww}	24.3	2.9	21.3	1.7
VS	gVS/kg_{ww}	14.2	1.7	12.1	1.5
VS/TS	%	58	4	57	7
COD	mg COD/gTS	640	46	613	34
sCOD	mg COD/l	360	152	852	223
TKN	mg $N\text{-}NH_4^+$/gTS	36.3	4.5	32.8	5.4
P_{tot}	mg $P\text{-}PO_4^{3-}$/gTS	8.8	1.6	10.2	1.3
Polyphenols	mg HGal/l	26	7	66	28
SGP	m^3/kgCOD	0.386	0.049	0.454	0.030
COD removal	%	76%		88%	

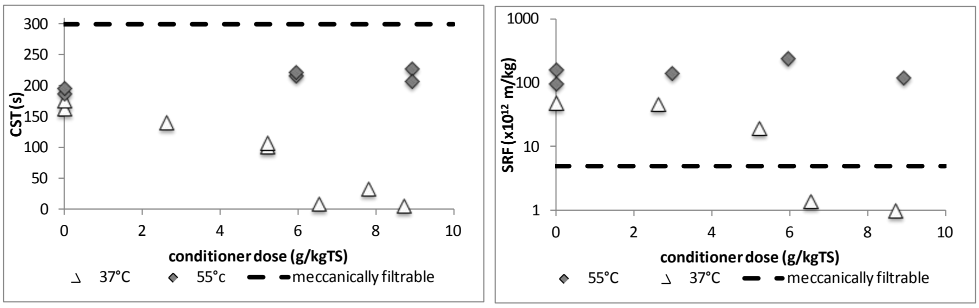
Although the metals augmentation improved the process efficiency, metals costs and energy needed to operate at 55°C should keep in mind. In fact quoted prizes for metal salts range from 0.27 to 6.61 €/kg for $FeCl_3$ [37], 137 €/kg for $NiCl_2$ $6H_2O$ and 1,340 €/kg for $CoCl_2$ $6H_2O$ [38]. Moreover energy consumption to heat feeding mixture from 15°C to 37°C or 55°C should icrease of 81%, while the biogas production should improve of lower than 20%.

1.3. Dewatering proprieties

Dewatering operation allows to separate liquor and solid fraction of the digestate for storage, transportation, post-treatment and other purposes. Effective dewatering can significantly reduce the volume of digestate and the cost of further processing [39]. The dewatering capability of digestate was determined by means of two indicators: the capillary suction time (CST) and the specific resistance to filtration (SRF). Tests were carried out with mesophilic and thermophilic digestates in order to evaluate the dewaterability properties of substrates and the optimal doses of chemical conditioner (Tillflock 6480 –Tillmanns).

Raw digestates had CST values of 171 and 193 s while SRF were 5.1 x 10^{13} and 1.3 x 10^{14}, at 37°C and 55°C. CST values were significant lower than those reported by Da Ros et al. [40] probably due to presence of bentonite in the winery wastes. In fact bentonite is a mineral conditioner that reacts with suspended organic matter for its surface charges and tends to weaken the water retention of the polymer [41] As reported by Jin et al. [42] CST was strongly influenced by the free water since it constitutes a large portion of the water and can be easily released on the filter paper. On the other hand the SRF values were consistent with literature data [40], with slightly worse dewaterability at 55°C.

Tests with use of chemical conditioner showed different dewaterability values trends for mesophilic and thermophilic digestates (Fig. 9). Digestates at 37°C showed improve of its quality reducing the SRF value until 1.5 x 10^{12} with addition of 6.5 g/kgTS of chemical conditioner, while thermophilic effluent needed higher dosage. In the same way CST of mesophilic digestate reduced to less than 10 s while thermophilic one had CST value higher than 200 s.



(a) (b)

Fig. 10 Trend of CST (a) and SRF (b) increasing chemical conditioner dose

As reported by Alvarenga et al. [41] application of physical conditioner (bentonite) can reduce the use of chemical conditioner and hence the cost of the treatment process, while still achieving the same level of dewatering performances. In fact the dosage used for mesophilic digestates was similar to typical dosage for waste activated sludge dewatering.

2. Conclusions

The monitored cellar, producing about 300,000 hectoliter of wine per year, generated 196 liter of wastewater, 0,1 kg of dry matter of sludge and 1.6 kg per hl of wine produced. Anaerobic co-digestion of wastewater sludge and lees was feasible, both in mesophilic and thermophilic conditions, operating with OLR of 3.2 kgCOD/m^3d and HRT of 23 d. Mesophilic process was stable in the long period in terms of stability parameters (pH 7.46, 400 mg N-NH_4^+/l and 2.248

mg $CaCO_3$/l) and of biogas production (0.386 m^3/kgCOD). Thermophilic digestion process accumulated VFAs and after one HRT the process failed. Metals augmentation (Fe, Co and Ni) at 55°C improved stability and biogas yields (0.450 m^3/kgCOD). Solid removal increased of about 20% comparing with mesophilic process and ammonification determined higher ammonium concentration in thermophilic digestate (630 mg $N\text{-}NH_4^+$/l). In terms of dewaterability properties the mesophilic process appeared more advantageous: 6.5 g conditioner/kgTS were sufficient for mechanical dewatering of digestate, while thermophilic digestate dewaterability didn't change within the dosage range of 0-10 g polymer/kg TS.

Acknowledgments

The authors of this work are thankful with Vinicola Serena srl. for its collaboration and with ATS scarl and Treviso City Council for the hospitality.

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