Investigation on anaerobic co-digestion of vegetable tannery sludge and fleshing in laboratory scale experiments.

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Abstract

In this work, the efficiency and the technical feasibility of the anaerobic digestion of vegetable tannery industry primary sludge (VTPS) was investigated. Tests were conducted under mesophilic conditions in three laboratory scale (150 L) reactors. The investigation included two different solids retention time (15 and 25 d) and the co-digestion of VTPS plus fleshing.

Results showed that an increase of SRT, from 15 to 25 days, not many increases the specific biogas production of 0.06 NL biogas g^{-1} VSS removed, but the addition of 1:4 (in mass) of fleshing in the feeding increases the VSS reduction of 10% at the end of the period.

Keywords

Anaerobic Digestion, Anaerobic Co-digestion, Anaerobic Digestion of Vegetable Tannery sludge.

INTRODUCTION

Tannery industry generates a large amount of both solid and liquid wastes: more than 594.000 tons per year of solid wastes and 15-30 m^3 of water per ton of finished product are produced in the Italian context (UNIC 2013). Tannery wastewaters are characterized by high COD concentration (12-23 gCOD L^{-1}), Suspended Solids (6-31 gSS L^{-1}), Ammonium (0.12-0.25 $gN\text{-}NH_4$- L^{-1}), Chlorides (0.3 to 8 g L^{-1}) and Sulphate (1.7-2.7 gSO_4^{2-} L^{-1}), (Mannucci et al., 2010). The Tuscan tannery district is the second largest in Europe and is divided into two different sectors were chrome and vegetable tanning processes are separately operated. In this context, the Cuoiodepur WWTP (San Miniato, Pisa-Italy) treats almost exclusively vegetable tannery wastewater; tannery primary sludge, after thermal drying and mixing with by-product of industrial tannery process is used to produce fertilizers. Since European regulation on land application is becoming increasingly stringent, it is important to evaluate alternative options such as anaerobic digestion of primary sludge.

The potential benefit of the anaerobic treatment of tannery wastewater is confirmed by the increasing attention dedicated to the investigation of the anaerobic process as a technological solution to treat this particular industrial wastewater (Daryapurkar et al. 2001, Lefebvre et al. 2004, Rajesh Banu and Kaliappan, 2007). However, the presence of inhibiting compounds such as polyphenols, metals and sulphide (Roy et al., 2013), limited the application of anaerobic processes to tannery wastewater at full-scale.

Moreover, tannins are commonly recognized as biorefractory compounds and their presence potentially affect anaerobic processes (Munz et al., 2009).

In this context, sulphate reduction remains a major issue due to higher kinetics of sulphate reducing bacteria (SRB) respect to methanogens; sulphide produced by SRB is, moreover, toxic to both SRB and methanogens.

Only few works on anaerobic digestion of tannery sludge have been published (Dhayalan et al. 2007; Thangamani et al., 2010; Zupancic et al., 2010; Sri Bala Kameswari et al., 2012) and no information about the application of anaerobic processes on the sole vegetable tannery primary sludge are present in literature.

Dhayalan et al. 2007 confirms the possibility to treat, in batch conditions, untanned solids leather wastes, chrome and vegetable tanned samples obtaining higher performance from the digestion of chrome tanning wastes than vegetable tanning ones.

Zupancic et al., 2010 investigated the potential of the anaerobic digestion of different types of tannery waste: chrome tannery sludge, waste fleshing and waste skin trimmings. Used tannery sludge is a mixture of primary chrome tannery sludge and biological sludge from an industrial WWTP treating tannery wastewaters.

The aim of this work is to evaluate the efficiency of the anaerobic digestion process of vegetable tannery industry primary sludge (VTPS). The technical feasibility of the process was investigated through semi-batch tests in laboratory scale reactors. The tests were carried out to evaluate the potential effect of co-digestion of VTPS and fleshing and the evaluation of two different solid retention time (SRT) 15 and 25 days.

MATERIALS AND METHODS

Anaerobic test were conducted using three semi-batch CSTR (Continuous Stirred Tank Reactor), 150 L each. R1 and R2 were fed with VTPS, R3 was fed with VTPS and fleshing (1:4 mass ratio). Temperature was continuously measured trough a probe and the control was obtained by a thermal blanket. Sludge mixing was ensured by shovels installed on a vertical shaft (Figure1).

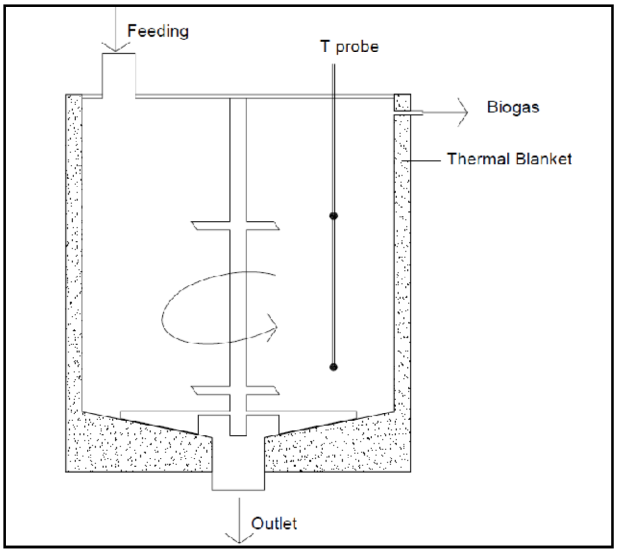

Figure 1. Experimental set-up.

The process was operated at 36±0.5°C, pH value was measured in the outlet and maintained around 7±0.1. Solids retention time (SRT) was controlled at 15 days for R1, 25 days for R2 and R3. Feeding and outlet were change three times a week and were analyzed once a week. The following parameters were monitored according to IRSA-CNR (Italian Institute of Water Research-National Research Council) methods: COD, TSS and VSS. Sulphates were evaluated through ionic chromatography (ICS1000, Dionex, U.S.A) while Sulphides and ammonium was measured through colorimetric analysis using cuvette test (Hach-Lange, Germany). Volatile fatty acids (VFAs) were evaluated. The Gas was measured continuously by an electrovalve system and methane fraction in the produced biogas was evaluated through gas chromatography.
As inoculums, for all reactors, a mixture of anaerobic sludge from an industrial chrome tannery anaerobic digester (75 %) (Santa Croce, Pisa – Italy), and primary tannery sludge from Cuoiodepur WWTP (VTPS, 25%) have been used.
Reactors were feeding with only VTPS and were maintained at the same SRT (15 d) during the start-up phase that lasted 100 days. Once verified that all three reactors where operating in a same manner, the SRT and the feeding where adjusted to the conditions to be tested.
Cumulative biogas production, COD and VSS removal efficiency, biogas production and CH_4 percentage in the produced biogas were used as key parameters for the estimation of the anaerobic process efficiency.
To solve the carbon mass balance Eq. 1 and Eq. 2 have been used:

$$\mathrm{CH_{4_{COD}}} = (\mathrm{COD_{in}} - \mathrm{COD_{out}} - \mathrm{COD_{SO_4}}) * 0.35\,\frac{\mathrm{NLCH_4}}{\mathrm{gCOD}} \qquad \text{(Eq. 1)}$$

$$\mathrm{CH_{4_{VSS}}} = (\mathrm{VSS_{in}} - \mathrm{VSS_{out}}) * 1.42 * 0.35\,\frac{\mathrm{NLCH_4}}{\mathrm{gCOD}} \qquad \text{(Eq. 2)}$$

Where:

- COD_{in} is the influent COD;
- COD_{out} is the effluent COD;
- COD_{SO_4} is the COD used in the sulphate reduction process ($COD_{SO_4} = \Delta SO_4 * 0.67\ gCOD\ g^{-1}SO_4$)
- 1.42 gCOD g^{-1}VSS is the conversion between COD and SSV.

RESULTS AND DISCUSSIONS

Figure 2 shows the VSS reductions after the start-up phase. Reactor 1 (feeding VTPS, 15 d SRT) had an average VSS reductions of 19±4%, while R2 (feeding VTPS, SRT 25 d) 28±9 % and R3 (feeding VTPS + fleshing, 25 d SRT) 41±12 %.

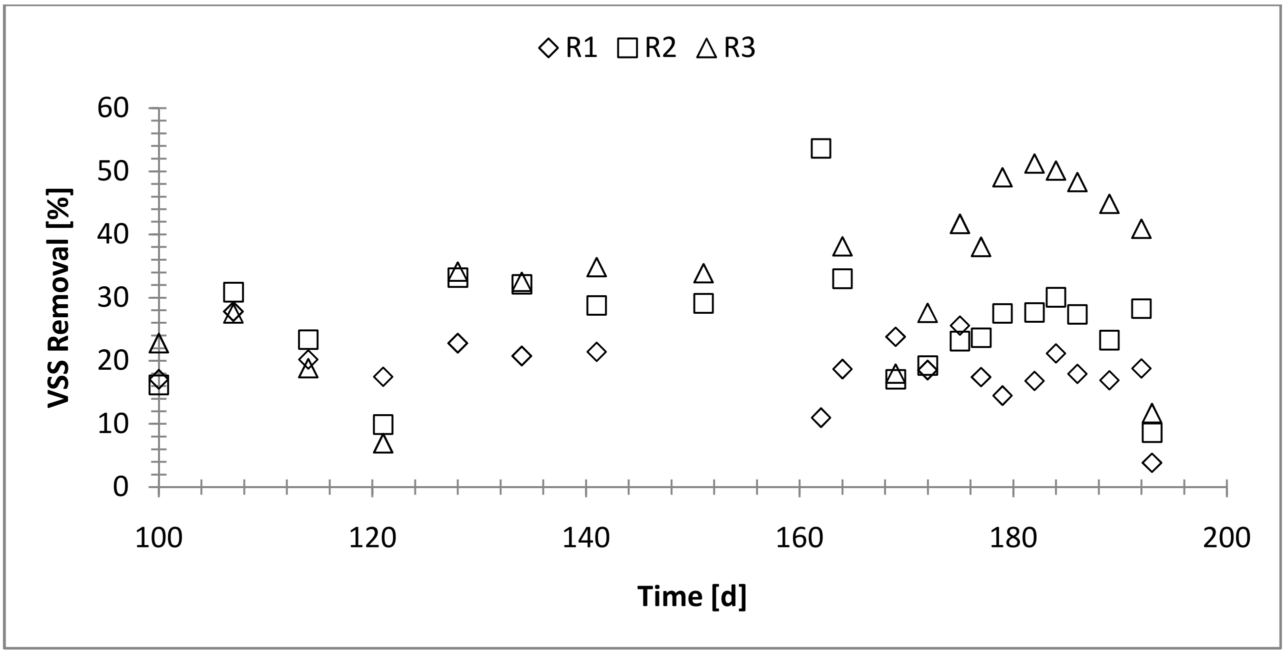

Figure 2. VSS reductions in the reactors after start-up phase.

The VSS reductions increase in R2 and R3 with the increase of the SRT, furthermore R3 had the highest VSS reductions at the end of the period.

On the contrary sulphate removal efficiency was more influenced by the feeding changes than the conditions maintained in the reactor (such as the SRT). As shown in Figure 3, the sulphate removal were for all reactors in the average more than 90% and its decrease or increase was correlated with the concentration of sulphate in the feeding.

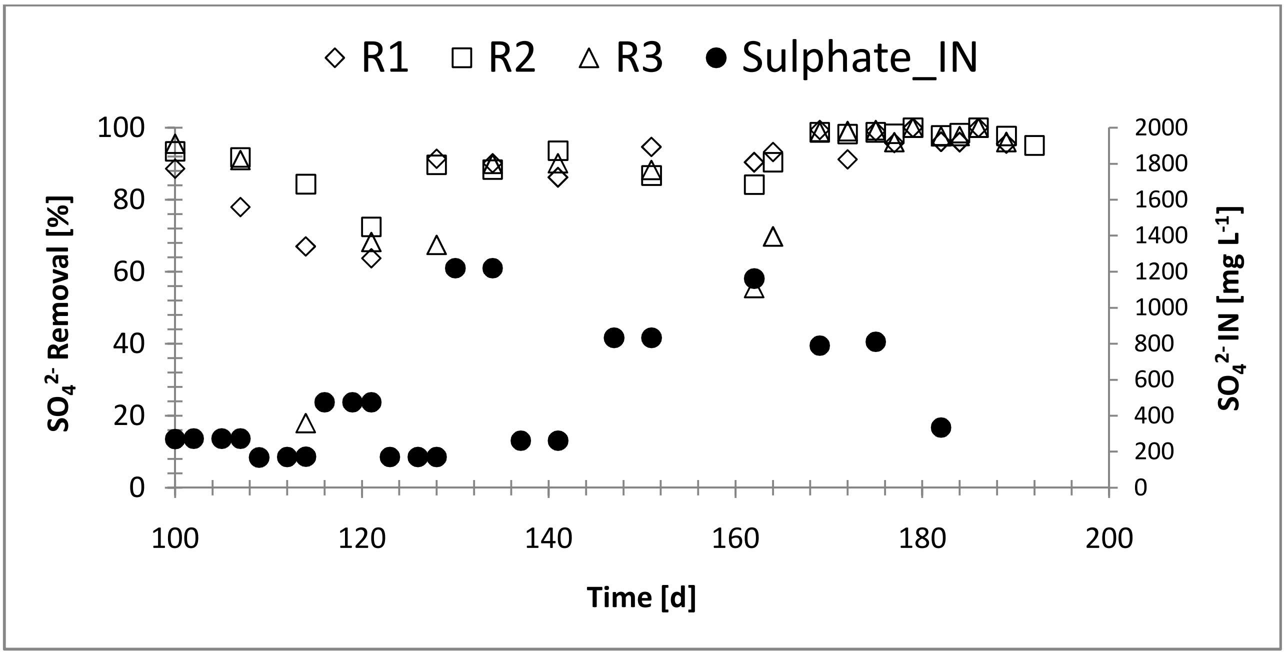

Figure 3. Sulphate reductions in the reactors after start-up phase.

According to the mass balance, eq 1 and 2, the methane productions in the reactors were 19±5 NL methane d^{-1}, 19±4 NL methane d^{-1}, 40±10 NL methane d^{-1} for R1, R2 and R3, respectively.
Through gaschromatographic analysis the CH_4 percentage in the gas was around 60-70 % (R1=68%, R2=66% and R3=66%).
The sulphates reductions was always above 50 % in all reactors, the average was around 90%.
Throughout the mass balance and the GC analysis was estimated the Specific Biogas Production (SBP) and the Specific Methane Production (SMP), Table 1.

Table 1. Specific Biogas and Methane Production in the reactors.

	Unit	R1	R2	R3
SBP	**NL biogas g^{-1} ΔVSS**	0.81±0.19	0.87±0.09	0.92±0.09
SMP	**NL CH_4 g^{-1} ΔVSS**	0.54	0.47	0.53

As table 1 shows, Reactors 2 and 3 had the highest SBP and SMP, moreover R3 had the highest VSS reductions.

CONCLUSIONS

The study was carried out in laboratory scale reactors with the aim of evaluate the efficiency of the anaerobic digestion process of vegetable tannery industry primary sludge (VTPS). Semi-continuous fed CSTR experiments shown that with an appropriate inoculum the anaerobic digestion of vegetable tannery sludge is feasible, even though with low reductions yield. The process could be enhanced with an increase of SRT up to 25 days and with the addition of fleshing. This upgrade allow the improvement in terms of biogas productions and VSS removal. An increase of ten days of SRT, increases the specific biogas production of 0.06 NL biogas g^{-1} VSS removed and the addition of 1:4 (in mass) of fleshing in the feeding increases the VSS reduction of 10% at the end of the period.

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