Co-digestion of tanning residues and sludge

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Abstract Codigestion experiments on sludge from tanneries' industrial wastewater treatment plant (WWTP) mixed with chromium free ("green") tanneries solid wastes were carried-out in a 15 m^3 pilot plant reactor, operating at 20 days hydraulic retention time (HRT) and at mesophilic temperature (35 ºC). The goal was to evaluate the feasibility of a full-scale unit.

Addition of "green" solid wastes improved biodegradability of the sludge and biogas production. The removal efficiencies of organic matter varied, according to the feedstock mixture. Averaged results are: COD and VS more than 55 %; TOC = 69 %. Hydrolysis of suspended volatile solids was initially moderate (36 %), but increased up to about 50 %, when the feedstock contained proteolytic enzymes. Fat removal was quite high (77 %).

Biogas production was highly dependent from the fleshing content in the feedstock. Addition of 30 % by weight of fleshing to the sludge increased 4 times the average biogas production (from 3,85 m^3/day to 14,62 m^3/day). The maximum Biogas production rate was 38 liter/kg of feedstock. Fleshing biogas yield was found to be 630 l/kg Volatile Solids loaded, higher than the value recorded for the sludge (288 l/kg Volatile Solids loaded). Methane content in biogas was about 75 % CH_4. The average biogas productivity of the reactor was 1.49 l/l/day.

Sulphate removal carried-out by the biologic community ($SO_4^{=} \geq 35\%$) increased Hydrogen sulphide concentration in the biogas up to 1800 ppm (average), a value higher than the limits allowed for use in internal combustion engines.

Grinding and maceration of fleshing was hard, due to smell, repugnant look and high strength of its components. This feedstock must be pre-treated in order to avoid excess hydrogen sulphide and lime.

Codigestion of "green" tannery wastes with sludge and others residues revealed technically feasible and a low cost solution for the environmental problem of these residues from small/average tanning factories. The potential biogas production for full scale plant is about 11 000 m^3/day, making this solution refundable within 5 years. Codigestion allows substantial reduction in bio solids volume, pathogens, and odor, increasing landfill life. This is an important evolution on current solution and gives time to plan and implement new sustainable projects.

Keywords: Anaerobic co-digestion; biogas; leather industry; tanneries; sludge; fleshing;

1. Introduction

Tanning processing is by nature a huge waste producer, mainly solid wastes, which have no profitable use as end product. Only about 25-30 % by weight of the primary matter is transformed into leather (Sengül, F. and Gürel, O. 1993). Reuse of lime fleshing, rawhide and pelt trimmings in the production of animal glue or other valuable products, is frequently not feasible. Most of the green and chrome leather solid wastes in Portugal are currently landfilled, resulting in air and water pollution, as well as emission of greenhouse gases like methane and carbon dioxide.

In the Alcanena Region, sited in the centre of the country, are under activity about 100 tanning industries, responsible for about 75 % of Portuguese industrial production and, also, for a large wastewater volume (70 000 m^3/day). The environmental degradation observed in the seventies decade has been attenuated by the implementation of a large collective wastewater treatment plant, by a centralized chromium recovery unit, which processes the separately collected spent chrome solutions, and by an industrial solid waste controlled landfill.

Tanneries wastewater treatment plant (WWTP) includes physicochemical separation and biological processes, which generates more solid wastes: the chemical sludge removed from precipitation and the biologic sludge settled in the secondary settling tank. These wastes are currently dewatered in a filter press (40 % T.S.) mixed with a clay based stabilizing agent and disposed in a controlled industrial landfill, but this practice is being restricted by recent environmental laws. The existing facilities are being filled and new uses or disposal solutions for the solid wastes and sludge had to be sought.

Anaerobic digestion is a favorable technologic solution which degrades a substantial part of the organic matter contained in the sludge and tannery solid wastes, generating valuable biogas, contributing to alleviate the environmental problem, giving time to set-up more sustainable treatment and disposal routes. Digested solid waste is biologically stabilized and can be reused in agriculture.

When the locally available industrial WWTP is not provided by anaerobic digester, a large scale digestion can be planned in regions accommodating a big cluster of tanneries, if there is enough waste to make the facility economically attractive. In this circumstance, an anaerobic codigestion plant based on sludge and tanneries may be a recommendable option, which reduces the quantity of landfilled waste and recovers its energetic potential. It can also incorporate any other domestic, industrial or agricultural wastes. Chrome free digested tannery sludge has a definite value as a fertilizer based on its nutrient content.

With this purpose, degradation of mixtures of “green” tannery solid wastes and sludge from the industrial WWTP, under anaerobic conditions has been addressed, with the goal to evaluate the degradation extent, define the acceptable organic load, estimate the biogas yield, watch the occurrence of inhibition or operational problems and assess the technical feasibility of a full-scale facility. The studies were carried both at laboratory and pilot scale.

In next stage, when further investigations on detanning chrome solid waste (Dhayalan et al., 2006) will be ready, this organic matter can also be added to the system, increasing biogas production and avoiding any tanning solid waste landfill disposal.

2. Description of the treatment facility

The co-digestion pilot plant was prepared to work in mesophilic and, also, in thermophilic temperature regimes. As the organic wastes contain different moistures and can be mixed in different proportions, the facility was equipped with three storage 2 m^3 volume polypropylene tanks and pre-treatment facilities, ensuring maximum flexibility, continue operation and different feedstock mixtures. Figure 1 shows a block scheme of the process.

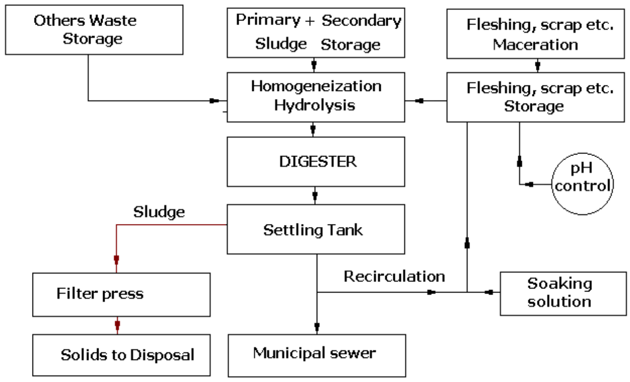

Figure 1: Process scheme of co-digestion pilot plant

The tanks were equipped with hermetic covertures, mixer and recirculation system. The chromium free tannery wastes were previously macerated, and then joined to the other liquid residues. Maceration required adjustment of the viscosity and moisture of the fleshing solution. On this purpose, some treated effluent was recycled, obtaining a proper pumpable mixture. In later stage the recirculation was substituted by addition of spent solution from soaking operation, containing proteolytic enzymes.

The storage tank of the macerated solution was equipped with a mixer, a pH control system and a ventilation arrangement, to strip hydrogen sulphide.

Each substrate was joined in adequate proportion in the homogenization tank, which was equipped with a variable speed stirrer, to assure homogeneity. During the retention some moderate hydrolysis and acidification of the feedstock spontaneously occurred. Afterward the solution was pumped to the anaerobic digester.

Based in INETI’s previously experience and patent, the hydrodynamic regime of the methanogenic reactor was up-flow. The waste feed entered tangentially in the bottom of the reactor and left it on the top. The combined up-flow and mixing regime assured a spiral flow of the materials inside the digester, high solid retention time (SRT), good conditions for dissolution and efficient contact between food and organisms. With the proposed configuration, the non degradable floatable solids (hairs, fats etc.) did not accumulate inside the reactor and clog it. After reaching the upper part of the reactor, they left with the effluent.

The heating system was constituted by a double pipe external exchanger receiving heat from a cogeneration system, provided with a 20 kW electrical generator and fueled by the biogas and natural gas. The digester effluent was settled and discharged into the local sewer line and treated by the Industrial Wastewater treatment plant. The settled sludge was dewatered by a filter press. A part of the settled effluent was recycled to the homogenization tank, as process water.

3. Methodology

3.1. Analytical and operational determinations

The pilot plant was prepared and operated according to a pre-established plan. The facility worked at HRT of 20 days and 35 ºC temperature. The co-digestion of the substrates was assessed by comparison of performance data during periods with different waste input, controlling several parameters of the input and out-put line.

Mass flow, volumetric streams, biogas production, reactor and environmental temperatures, natural gas consumption and electricity consumption and production, were recorded daily. Liquid effluents were characterized in order to assess the efficiency of removal in terms of soluble and suspended organic matter, nitrogen, fats, sulphate, to prevent inhibition (hydrogen sulphide) and to control toxicity (chromium (Cr^{+3} and Cr^{+6}). The digester stability was controlled by routine measurements of Volatile Fatty Acids (VFA), alkalinity, pH and REDOX potential. The biogas composition was controlled periodically by mean of gas chromatography. Analytical determinations were according to (APHA) standard methods.

3.2. Start-up procedure

Previous experiments with a laboratorial reactor showed that hydrogen sulphide and other compounds contained in the biologic sludge and in the “green” tanneries solid waste caused frequent inhibitions of the bacterial communities, making the digester incapable to work with efficiency and stability. For this reason were carried-out preliminary activity tests, in order to find adequate available seeding sludge for the pilot plant facility. A municipal digester accommodating a sulphate rich waste industrial effluents, having a wider bacterial community, revealed to be the more suitable option. Its Methanogenic acetoclastic activity was: ACmax=0,105 gCQO-CH_4/gSSV.d. The methanogenic reactor was completely filled with this sludge, in order to accelerate the start-up and adaptation.

4. Result and Discussion

4.1. Composition of feedstock:

Table 1 refers the quantities of sludge, industrial solid wastes and also some manure, locally available as feedstock for the codigestion facility.

Table 1: Sludge and Waste availability

Type of waste	Waste availability (ton/day)
Fleshing and trimming	34
Splitting	7,3
Shaving	1,4
Unhairing and Liming	2,3
Total tanneries “green” waste (TW)	45
Primary sludge (PM)	320
Secondary sludge (SS)	60
Total Sludge (TS=PM+SS)	380
Swine manure (SM)	10
Total Waste	435

The sludge was collected after gravity thickening. Its average concentration was quite variable [3-6,1 % Total Solids (T.S.)] This sludge was dewatered to 39,6 5 ± 2,3 % T.S. by a very efficient filter press, in the local WWTP.

Unless the regional wastewater management system is provided with a trivalent chromium collecting and recovery system, involving all the tanneries, a fraction of this compound is discharged in the sewer, probably from washing baths and finishing operations, were it is not economic to proceed to its recovery, or from uncontrolled discharges in some of the industrial plants. During the wastewater treatment system this compound precipitates with the sludge in the chemical pre-treatment and is bio absorbed in the biologic sludge, in the secondary treatment.

According to the values presented in table 2, the activated sludge is more efficient than chemical precipitation to remove chromium Cr^{+3}.

Table 2: Chromium concentrations (mg/l)

Substrate	Cr^{+3}
Biologic Sludge	303±193
Mixed Sludge	177±95
Sludge+Tanning Waste	120±117

Its concentration is much higher than value detected in the industrial wastewater but is lower than the limit for toxicity in anaerobic process (1500 mg/l) (Alkan *et al*, 1996). However, this compound reduces the applicability of sludge in agriculture. The hexavalent chromium in the mixed sludge was lower than 0,6 mg/l, the detection limit of the used method. The pH value of this sludge (pH=7,9) and the negative Redox potential (-0,172 mV), were unfavorable to the existence of Cr^{+6} compound in the fresh sludge, which was assumed as negligible.

The received fleshing showed variable organic matter concentrations, due to the procedure used to remove this waste from the factories, based on water flushing (T.S.=36-120 g/l). Some samples were quite diluted. Water control measures and improved sampling of this feedstock should be implemented in order to obtain a more favorable composition. About 65 % of the organic matter was as suspended solids, and hydrolysis played an important role in the degradation process. The fat content was about 8.4 g/kg, corresponding to more than 35% of the TVS, which promised high methane yield of the waste. The pH average value was 7.18, but was often very high, more than 9, due to presence of lime-rich shavings, capable to create a scale problem in the anaerobic reactor.

Total organic (Kjeldahl) nitrogen (TKN) was present in relatively high quantities (2000 mg/l) but insufficient to establish ammonia inhibition. The Phosphorous content, on the contrary, was low (70 mg $PO_4^{=}$/l), a situation of potential deficiency of this element.

Intense acidification of the mixed feedstock occurred in the storage and in the homogenization tank, before the feeding (Redox potential -300 mV; AGV =1500-2000 mg/l), particularly in Summer time.

4.2. Solid waste pre-treatment

The received fleshing and the other green tannery waste showed to be a complex and hard substrate, not only due to its offensive smell and repugnant look, but also to its mechanical resistance to maceration and pumping.

The high strength materials contained in this waste made its grinding and maceration difficult, obliging to repeated operations. They also caused frequent blockages of the machinery and required a power increase of the motor. The macerated slurry, having a 0.8 mm diameter, looked like a viscous fluid. It was pumped to the homogenization tank by a volumetric progressive engine, which also displayed operational problems during all the period of experiments. This operation must be carefully evaluated at full scale plant.

This “green residue” was then aerated, to avoid excess hydrogen sulphide concentration in the feed. The existing aeration facility reduced H_2S concentration from 22-77 mg/l range to 0-3 mg/l.

4.3. Efficiency of removal

The Tannery “green waste” as well as the sludge from the industrial wastewater treatment plant contained some moderately AD inhibitory compounds, which complicated the digester start-up. Overcoming this problem required bacterial adaptation, by preparing appropriate substrate mixture during the start-up period.

During the normal operation, the addition of the “green” tannery wastes to the secondary and primary sludge of the WWTP exerted a favorable effect on degradation efficiency , improving gas production and methane content (viz. Table 3 and 4).

The outputs corresponding to the higher organic loads (VS, COD) of the input just slightly increased during the corresponding feeding experimental period. The effluent from the reactor still contained high organic concentration (VS =8,5 g/l; COD 12 g/l) and suspended solids (TSS=15,9 g/l; VSS=10,4g/l), and low concentration of soluble organics (TOCs=710 mg/l, CODs =1,8 g/l)), VFA (VFA=647 mg/l), and fats (Fats=1,6 g/l). The majority of the remaining not easily degradable organic compounds were the volatile suspended solids.

The decrease of TSS and VSS in the reactor effluent is moderate. Unless the value was influenced by the change of feedstock composition, they confirm the existence of low hydrolytic activity. On the other hand, fat degradation is apparently very efficient, resulting in quite lower values in the treated effluent.

Addition of the “green” tannery wastes considerably increased the alkalinity of the digesting media, reaching a quite high value (16000 mg/l $CaCO_3$), making possible calcium carbonate precipitation.

Sulphate compounds contained in the feedstock, ($SO_4^{=}$=300-1200 mg/l) stimulated significant sulphate reduction activity inside the reactor, decreasing the biogas quality. Hydrogen Sulphide concentrations (HS^{-}=0-57 mg/l) in digesting liquid, were always inside the limits of toxicity for anaerobic digestion (150 mg/l) (Speece, 1983).

Table 3: Efficiency of removal (%) (Average)

Parameter	Removal Efficiency (%)
ST	47,5
SV	55,0
SST	36,1
SSV	36,3
COD	55,0
Fats	77,5
TOC	69,1
$SO_4^{=}$	35,1

Efficiency increased during the experimental period as a result of bacterial adaptation and improvement. Table 3 sums up the obtained average efficiency value of removal of several parameters, during the entire period. In the last two month of operation, when proteolytic enzyme containing solution, from washing tanning operations, were used to prepare the feedstock, the efficiency of removal of SSV increased from 36,3 % to about 50,3 %, which is in agreement with Vasudevan N. and Ravindran A. D. (2007).

4.4. Biogas production

Biogas production was variable and dependent from the fleshing content in the feedstock. Addition of 30 % by weight of fleshing to the sludge increased 4 times the average biogas production (from 3.85 m^3/day to 14,62 m^3/day). The maximum Biogas production rate was 28 liter/kg of feedstock. Fleshing biogas yield was found to be 630 l/kg Volatile Solids loaded, higher than the value recorded for the mixed sludge (280 l/kg Volatile Solids loaded). Methane content in biogas varied in the range 68 -77 % CH_4 (average value = 75 % CH_4). The average biogas productivity of the reactor was 1.49 l/l/day.

Biogas production varied according to the organic load of the feed and the type of mixture, as can be seen in table 4.

Table 4: Biogas production and organic load

feedstock	Biogas Production (m^3/day).	Organic Load (Kg VS/day)
SM(40%)+TW(20%)+SS(40%)	6.24	10.0
SM(10%)+TW(25)+SS(65%)	7.12	37.6
25 % TW + 75 % SS	8.90	28.0
100 % TS	3.85	8.0
TW (30 %) + TS (70%)	14.62	31.4

The gas productions also indicated the increase of about 10 m^3 was caused by the 30% of Tannery wastes to the mixed sludge

Tannery wastes showed a very high biogas production and a gas-Yield of around 630 lit/kg VS added. It is rather probable that by the addition of fresh wastes (contain ing nutrients and positive additives), the sludge had undergone a better degradation than without wastes.

The “green” tanneries wastes provided the major contribution for gas production, increasing significantly the volume of biogas obtainable from the sludge. In the last period average production was 14.62m^3/day, corresponding to a productivity of about 1.49 liter/liter of reactor, a good value for a mesophilic completely mixed digester. The maximum measured production was 19,6 m^3/day.

Sulphate reduction activity generated Hydrogen sulphide concentration in biogas was, on average, 1829 ppm, considerably greater than the allowed limit for use in Internal Combustion engines (500 ppm). Its value varied between 831 e 3843 ppm.

5. Environmental and technical benefits

Biogas production is a valuable renewable energy which contributes to fossil fuel and emission reduction. In this case the average expected biogas production from the available feedstock is relevant, corresponding to about 11 500 m^3/day and an electric production of about 20 000 kWh/day.

The anaerobic digester allows degradation and conversion in biogas of about 55% of the Volatile Solids contained in the initial substrate, reducing the volume and the organic load of sludge and solid waste to discharge in the industrial landfill. Its implementation will increase more than two times the foreseen useful life.

The reduction of sludge solids (VS) will be about 50% while the expected reduction of fleshing solids is about 70%, involving a significant decrease of energy and chemical consumption for dewatering and transportation.

The digestate contains chromium compounds that will difficult agricultural reuse of digested material. However, as the European directive on organic matter landfilling (1999/31/EU) defines progressive reduction organic waste to be landfilled, anaerobic digestion contributes to fulfillment of the directive, giving more time to study and implement more sustainable solutions. In a long term perspective, anaerobic digestion should allow products adequate for agricultural purposes or adequate to its incineration. This implies a better control of the waste sources, more efficient chromium separation in industrial facilities or changes in tanning technology.

Anaerobic digestion provides additional environmental benefits. The digestate is biologically stabilized and, providing the facility with a hygienisation, this residue will be also safer, in pathogenic terms. It will release less unpleasant and dangerous odors, which currently are spread into the surrounding area and cause discomfort in the local population.

The dewatered landfilled sludge is mixed and chemically conditioned with a clay based compound to stabilize it and avoid chromium diffusion in the landfill. Anaerobic digestion keeps chromium (Cr^{+3}) compounds in reductive conditions, reducing the possibility of oxidation to Cr^{+6}, and can avoid any chemical conditioning.

6. Economic outcome

Economic study to compare and show the advantages of codigestion vs. the current solution were based on the more relevant costs factors, summarized in table 5. Construction works for the infrastructure and equipment for dewatering digested slurry were not included, considering adequate the filterpress existing in the actual WWTP. Operational cost does not include the waste collection, which is assumed to be already present, and chemical products for dewatering, considered, for safety, as equivalent to the actual consume.

Table 5: Cost and incomes evaluation

	Value	
Capital Cost	4.800.000	€
Energy +O & M costs	279.500	€/year
Electricity Sales	846.000	€/year
Reduction sludge disposal	98.500	€/year
Reduction fleshing disposal	345.000	€/year
Net annual income	1.010.000	€/year

The economic outcome of this project revealed interesting benefits. Recent incentives on electric energy produced from renewable sources (0.116 €/kWh), improved significantly the economic revenue from electric energy sale, making the anaerobic digestion plant competitive without significantly increasing the operation and maintenance costs of the WWTP, excluding the motor-generator maintenance.

Digestion reduced the volume of output to be landfilled. The saved landfill disposal costs were evaluated about 30 €/ton.

The capital cost for the digestion facility construction is high, about 4 800 000 €. It includes the execution of the fleshing pretreatment tank, the digester, the gas recovery and treatment and the cogeneration units (2 x 500 kW motor generators). This amount can be recovered in less than five years.

7. Conclusions

Codigestion of “green” tannery wastes with sludge from the industrial WWTP and others residues revealed technically feasible and a low cost solution for the environmental problem of these residues from small/average tanning factories.

The sludge contains some compounds which are moderately inhibitory, requiring bacterial adaptation and appropriate mixtures of substrate during the start-up period.

The experiment demonstrated good compatibility between the waste and sludge. The addition of the “green” tannery wastes exerted a favorable effect on biodegradation and gas production, overcoming any inhibition phenomena.

Sulphide rich “green” tannery wastes must be pretreated in order to avoid smell, corrosion and inhibition. Calcium hydroxide in these wastes must be watched, in order to prevent calcium carbonate precipitation inside the reactor.

The equipment for maceration and transfer of solid wastes must be carefully selected, to facilitate waste reduction and transportation.

The degradation of suspended organic solids is moderate, and penalized the global performance of the system. Addition of proteolytic enzyme containing tanning wastewater can improve degradation and gas production. Its use can increase the performance. Otherwise the insertion of a hydrolisation-acidification step or the thermophilic anaerobic digestion process can be recommendable. These options are under evaluation. Protein and fat degradation proceeded better than suspended solids.

In any case the studied system premised favorable incomes by electric energy sell. Codigestion achieved also substantial reduction in bio solids volume, pathogens, and odor. This is an important evolution on current solution. Important savings are also obtained by transport reduction and increase of landfill useful life. This alleviates the current situation and gives some time to plan and implement new sustainable projects, recovery of valuable compounds contained in the waste and fertilizer capacity of degraded biomass.

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