**Olive Mill Wastewater treatment by a continuous-flow**

**anaerobic co-digestion process with municipal sewage sludge**

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**1.Introduction**

The disposal of olive mill wastewater (OMW) represents a significant environmental problem due to the high organic load, the presence of phenolic compounds (PCs), which are harmful for plants, soil and water microbial population, and the very unpleasant smell [1, 2]. The treatment of OMW represents a significant cost for olive mills and an issue for waste management treatment plant in Mediterranean countries. Numerous processes for OMW treatment have been proposed which have high cost and of difficult application due to the seasonality of OMW production and the small scale of several olive mills [3]. OMW anaerobic digestion (AD) is of high interest, but a challenging process because of the high concentration of inhibitory and recalcitrant compounds such as PCs. On the other hand, polyphenols recovery has become interesting as PCs found several applications in many industrial fields as they are used as antioxidants and antimicrobials in animal feeding, cosmetics and health care products. Adsorption proved to be a feasible and interesting possibility [2-5]. The co-digestion of OMW with the sewage sludge (SwS) represents a potential solution for OMW disposal thanks to the widespread presence of digesters used for the stabilization of the sludge produced by wastewater treatment plants (WWTP) [6]. Thus, combining OMW co-AD with a preliminary recover the OMW PCs by adsorption represents an interesting possibility to decrease potential inhibition effects on the AD process and to recover high-added value products [7]. In this work [8], the co-AD of OMW with SwS was investigated in continuous bioreactors, under different conditions. The targets of the research were: (i) to compare the performances obtained with untreated and dephenolised OMW; (ii) to assess operational conditions for a stable co-AD of OMW and SwS, with a high OMW content; (iii) to develop strategies for the integration of the OMW/SwS co-AD process in the network of existing SwS digesters; and (iv) to perform a cost-benefit analysis (CBA) relative to process both with and without a dephenolisation pre-treatment.

**2. Methods**

The OMW used in the present study was provided by a 3-phase olive mill located in Sant’Arcangelo di Romagna (Rimini, Italy). The partially dephenolised OMW (def\_OMW ) was produced by PCs adsorption on the neutral adsorbent resin Amberlite XAD16N (DOW Chemicals Europe GmbH, Horgen, Switzerland). The PCs concentration was reduced from 1010 ± 40 mg/L to 65 ± 5 mg/L (6.4 % of the untreated OMW concentration). However, the dephenolisation caused a loss of 32% of the COD, 35% of the BOD5 as a significant amount of organic matter was removed together with the PCs. All continuous tests were made in laboratory-scale PVC bioreactors with a capacity of 1.7 L operated under at 34 ± 1°C and 12 different mixtures OMW/SwS ratios: from 5:95 to 40:60. The main parameters analysed to follow the process were: total solids (TS), VS, COD, volatile fatty acids (VFAs) and PCs. The CBA of the process was performed based on the full-scale scenario of a 500000 people equivalent (PE) WWTP, in which it was assumed to co-digest OMW in the existing digester during a 4-month period, with an OMW / (OMW + SwS) volumetric ratio equal to 0.25. Two distinct CBA approaches were applied: i) untreated OMW co-AD and ii) OMW dephenolisation followed by co-AD. More details on materials, methods and apparatuses are in [5] and [8].

**3. Results and discussion**

Different volumetric OMW:SwS ratios up to 100% OMW were fed in continuous 1.7-L bioreactors. In the scenario to perform a OMW co-digestion process in an operating real SwS digester, the inlet volumetric flow rate increases and, if the liquid volume is kept constant, the HRT decreases. Thus, to simulate the co-AD process performances with a decreased HRT, the first part of this study was focused on OMW/SwS co-AD with an HRT equal to 23 days, close to the lower HRT limit of WWTP digesters operating range (20-40 days HRT). The reactor fed with 100% SwS was used as the internal benchmark of the AD process. The biogas and methane yield trends over time achieved a stable steady state after less than 7 days as the inoculum of the bioreactors were made with a digestate taken from an SwS industrial anaerobic digester. The average yields were 194 ± 13 NL/kgVS fed and 110 ± 11 NL/kgVS fed, for biogas (Ybiogas) and CH4 (YCH4) respectively. The mean production rates were 0.20 ± 0.02 NLbiogas L-1 day-1 and 0.12 ± 0.01 NLCH4 L-1 day-1. The mean volatile solid (VS) conversion was 37% and the VS concentration was 16 ± 2 g/L. pH was stable at 7.2. In the AD tests with 100% of treated OMW, the OMW fraction in the feed was gradually increased from day 1 to day 35 in order to help the biomass adaptation to the new feed. Both biogas and methane yields increased during the first 35 days, with maximum values at the end of the OMW fraction increase (790 NLbiogas/kgVS fed and 470 NLCH4/kgVS fed) largely higher than those attained in the 100% SwS benchmark. However, starting from day 35, when the untreated OMW was the only feed, both the yields rapidly decreased and in 30 days the methanogenic activity the complete halted. These results suggest that, as expected, the untreated OMW is a strong inhibitor on the methanogenic activity. VFAs, initially low, increased steadily up to a maximum value of 5.5 g/L and the pH gradually decreased, reaching 6.1 on day 63. These results confirmed the inhibition on the methanogenesis, with a consequent VFAs accumulation. Analogous results were obtained in the AD of dephenolised OMW: both the biogas and methane yield initially increased to maximum values on day 42 (1100 NLbiogas/kgVS fed and 750 NLCH4/kgVS fed), then, they yields decreased, though with a slower trend than in the case of the untreated OMW and after 100 day the methanogenic activity completely stopped. The trends of VFAs and pH were similar to that of untreated OMW. The results obtained with untreated OMW and dephenolised OMW showed that the OMW volatile solids have a large biomethane potential, higher than that of the SwS. The time evolution of methane yields for the co-AD bioreactors are shown in Figure 1. For both untreated OMW and dephenolised OMW fed bioreactors, the replacement of SwS with OMW caused the biogas and methane production yields and rates to increase with time and almost stabilized in about 60 days, showing that, contrary to the case of pure OMW AD, steady-state conditions can be successfully achieved. For both untreated and dephenolised OMWs the best performances were obtained with the higher OMW fraction (25%): methane yields of 226 NLCH4/kgVS fed for untreated OMW and 179 NLCH4/kgVS fed for dephenolised OMW, values much higher than that obtained with the sole SwS (110 NLCH4/kgVS). The untreated OMW showed higher performances than the corresponding dephenolised OMW, indicating that dephenolisation did not lead to a beneficial effect in terms of methane production whereas the higher VS content of untreated OMW seems to the reason of the higher methane yield. The results obtained so far showed that: i) the co-AD of OMW and SwS leads to a significant enhancement of the biomethanation performance, ii) the OMW dephenolisation is not economically justified, unless the produced PC mixture can be sold at a price high enough to repay the investment in the adsorption/desorption plant.

**Figure 1** - Comparison between the CH4 yields obtained in the bioreactors operated with different OMW/SwS ratios with a 23-day HRT. A) untreated OMW; B) dephenolised OMW.

At day 100, a second part of the work was started aimed at maximizing the OMW/SwS ratio and, in turn, the biogas productivity with a stable performance without a long adaptation time, hardly compatible with the typical seasonality of OMW production. The HRT of the bioreactors fed with 25% OMW contained a methanogenic microbial consortium acclimatized to a PCs concentration of 260 mg/L and 23 mg/L, respectively for untreated and dephenolised OMW, was raised from 23 to 40 days and the OMW fraction was increased to 40%. In both the bioreactors a rapid increase of the CH4 yields, that reached 268 ± 3 NLCH4/kg VS fed for untreated OMW and 235 ± 13 NLCH4/kg VS fed for dephenolised OMW, corresponding to increases of 19% and 31% in methane yield respectively. The 40% untreated OMW bioreactor achieved a stable PCs concentration with a mean value of about 125 mg/L with a 70% PCs conversion. These results showed that the OMW PCs can be effectively degraded by a co-AD process and that the residual PCs does not significantly inhibit the methanogenesis.

Finally, the last part of the work was meant to assess the large-scale applicability of the OMW/SwS co-AD process and a cost-benefit analysis (CBA) on two possible scenarios. In particular, two Italian regions, Apulia and Tuscany, with a very high production of olives for oil were considered. For both the regions, the volumetric production of SwS was estimated and a mean volumetric OMW fraction in the feed of the OMW/SwS co-AD was estimated under the following simplifying assumptions: i) the OMW produced in a given region is treated in a fraction of the total AD capacity of that region (for example 1/4 to 1/3 of the total capacity), ii) the OMW co-AD process is distributed over a 4-month period. The estimated OMW fractions required to dispose all the regional OMW was 25-35% for Apulia and 6.8-9.1% for Tuscany, values below those successfully applied in this work. The CBA was based on the following scenario: i) a 500,000 PE WWTP, that receives 0.2 m3 d-1 PE-1, and therefore treats 100,000 m3/d of municipal wastewater (MWW), ii) the digester was assumed to treat 600 m3/d of SwS, iii) a OMW/SwS volumetric ratio equal to 0.25 is applied for a 4-month period with an untreated OMW (no dephenolisation) flowrate equal to 200 m3/d, iv) a 10% spare capacity is present in the digester, that lead to an HRT reduction from 30 to 25 days. The benchmark scenario was the treatment of only SwS AD, assuming the characteristics and performance used in this work. The scenario to be compared was untreated OMW/SwS co-AD, assuming the characteristics and performance used in this work. The CBA estimated a total additional revenue associated to OMW co-AD in the existing digester varying in the 1,440,000-2,640,000 € range. Assuming a mean total cost of MWW treatment declared by several WWTP managers in Northern Italy of 0.65 €/m3 (average value), the additional revenues correspond to an 18-34% reduction of the cost of MWW treatment, during the 4-month OMW season. In a second scenario with dephenolisation of the OMW and OMW/SwS co-AD, the market price at which the PC-rich antioxidant product obtained from OMW dephenolisation should be sold in order to attain a 6% FRR was estimated. This price resulted equal to 8.17 €/kgPC. Considering that the market price of PC-rich antioxidants varies between 250 and 2500 €/kgPC, even if the antioxidant product obtained from the above-described plant needs a further refining before being placed in the market, the resulting price for the generation of an attractive business case is considered a realistic one. In this scenario, a lower but significant 16-32% reduction of the cost of MWW treatment during the 4-month OMW season was calculated. The comparison between the two scenarios allows some conclusions: i) the benefit is substantial in both cases, ii) the largest fraction of the additional revenue is associated to the OMW disposal tariff, iii) the difference between the two scenarios is low, considering the uncertainties that affect this analysis, iv) the scenario of OMW dephenolisation requires additional investments in plants and personnel formation, and v) it has an economic uncertainty associated to the actual feasibility of selling at a reasonable price the entire PC-rich antioxidant mixture produced in each season, vi) a significant degradation of the OMW PCs is obtained also without the additional dephenolisation step. For these reasons, the scenario of untreated OMW co-AD is considered the best choice.

**4. Conclusions**

This work showed that it is technically possible and economically profitable to co-digest the entire OMW production in regions characterized by intense olive oil production by taking advantage the existing network of SwS anaerobic digesters. A substantial increase in methane production yield (144% increase in comparison to 100% SwS) was achieved. The increase of the revenues of the OMW treatment, mainly associated to the OMW disposal tariff, can potentially lead to a substantial decrease in the cost of MWW treatment during the 4-month of the OMW season.

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