An integrated approach in a municipal WWTP: anaerobic codigestion of sludge with organic waste and nutrient removal from supernatant

S. Caffaz, E. Bettazzi, D. Scaglione and C. Lubello

ABSTRACT

Co-digestion appears to be an interesting solution to increase the biogas production of poorly performing under-loaded digesters of waste activated sludge. In the Florence WWTP anaerobic codigestion could increase nitrogen and phosphorus loading rates and thus lower the nutrient removal efficiency. In order to develop an integrated solution to upgrade the Florence WWTP, the different process units were tested in experimental plants. Anaerobic codigestion with source-collected organic solid waste in a pilot-scale bioreactor showed an increase of GPR from 0.15 to 0.45 Nl biogas/l/d with 23% of organic waste loaded. Autotrophic nitrogen removal was carried out in two lab-scale pilot plants which were fed with a real anaerobic supernatant after phosphate removal via struvite formation. The nitritation MBBR has been working for one year at steady-state conditions with a perfect nitrite/ammonium ratio equal to 1:1. Anammox biomass enrichment was performed in a suspended biomass SBR and the specific nitrogen removal rate increased from 1.7 to 58 gN/kgVSS/d in 375 days.

Key words | anaerobic codigestion, Anammox, partial nitrification, MBBR, OFMSW

INTRODUCTION

Florence municipal Wastewater Treatment Plant (WWTP) treats about 600,000 p.e. and discharges the effluent into the Arno river, which is a sensitive area according to European Directive Dir CEE 91/271. Nitrogen removal is operated by a conventional denitrification/nitrification process, while phosphorus is, eventually, removed by a chemical coagulation-flocculation process. The influent organic load is very low (160 mgCOD/l on the average) with a low content of RBCOD (25% of total COD) and COD/N ratio is about 6. Nitrogen removal efficiency achieves an average value of 50% and the limit on total nitrogen (10 mg/l) was breached in 30–40% of final effluent samples. The sludge production is much lower than the designed value. Consequently, the existing anaerobic sludge digesters (six mesophilic reactors, 4,800 m³ each) present more than 50% of spare capacity, making it possible to co-digest other organic wastes. Anaerobic digesters for sludge stabilisation are often under-loaded (Organic Loading Rate, OLR = 0.5 kgTVS/m³/d on the average) and their performance in term of biogas production is poor (biogas yield, \( Y_b = 0.22 \text{N}m^3/\text{gVSfed} \) on the average).

In the Florence municipal area, available candidate co-substrates are the organic fraction of municipal solid waste (OFMSW), olive mill wastewaters (OMW) and septage (Caffaz et al. 2005). The OFMSW collected in Florence (about 40–50,000 t/y) is currently stabilised by the composting process; however, high treatment costs as well as the limited marketability of compost lead to investigating alternative solutions.

From an environmental point of view, the anaerobic codigestion problem is the nutrient transfer from a solid matrix to liquid phase (supernatant). This fact unbalances the COD/nutrient ratio in the inlet wastewater of municipal WWTP. Side-streams are responsible for 10–20% of total
nutrient load in WWTPs, but anaerobic codigestion could increase that percentage due to the nitrogen and phosphorous content in the treated organic waste. OFMSW is composed of 10–25% of TS, and the dry mass is characterized by 85–90% of TVS. Nutrient content over dry-mass is about 2–3% of nitrogen and 0.4–0.9% of phosphorus (Bolzonella et al. 2006a, b).

An integrated approach (Bolzonella et al. 2006a, b) has to combine the anaerobic codigestion (for energy recovery, organic waste treatment) with a BNR process (for legal limit respect, Dir CEE 91/271). With a grant of the Tuscany Region, Publiaqua SpA and the Civil and Environmental Engineering Department of the University of Florence have carried out a research project named CONAN in order to develop an integrated approach for the Florence WWTP. The main project issues were: a) to exploit spare capacity of anaerobic digesters (Bolzonella et al. 2006a, b) b) to remove/recover phosphorus through struvite (MAP) precipitation (Battistoni et al. 2001) c) to remove nitrogen through a completely autotrophic process, based on the Anammox process (van Dongen et al. 2001; van Loosdrecht & Salem 2006). Figure 1 shows a possible upgrading of the Florence WWTP investigated in this experimental study.

METHODS

The anaerobic pilot-scale plant consists of a single CSTR (polypropylene), mechanically mixed, provided with an external jacket connected to a thermostat to keep a temperature of 35–37°C. The operating volume is 200 L and it has been operated in a fed-batch mode. The measurement of the biogas flow is performed by means of liquid displacement. Influent and effluent samples were taken before the feeding for analytical determinations. Off-line measurements of pH, temperature and ORP were periodically performed. Biogas samples were periodically collected and analyzed by the micro-gas-chromatograph (Agilent 3000). The mixed liquor fed was composed of waste activated sludge and OFMSW. The pilot-plant was inoculated with 200 L of anaerobic sludge taken from the Florence WWTP anaerobic digester and operated in a fed-batch mode; digested sludge discharge and feeding were performed from 1 to 3 times per week. GPR, biogas and methane yields and the ΔCOD/ΔVS ratio were assessed for each load. Two different kinds of source-sorted OFMSW were used as feedstock: fruit and vegetable wastes (FVW), coming from a Florence wholesale market (2,500 t waste/y) and household kitchen wastes (KW). Before testing, the organic waste samples were shredded and homogenized by an electric mixer.

The partial nitrification process (Gut et al. 2005; Rosenwinkel et al. 2005) was tested in a lab-scale Moving Bed Bio-Reactor (MBBR), with an operating reactor volume of 7.4 L. The start-up was performed by adding: a) 3 litres of biofilm carriers (Kaldnes, K1), in order to guarantee a volumetric filling of 40% and a specific surface of 200 m²/m³, b) 6.4 litres of anaerobic supernatant and
c) 300 ml of nitrifying activated sludge as inoculum taken from the Florence WWTP. Oxygen, temperature, pH control and monitoring of the lab-scale reactor were performed by a biocontroller (ADI 1010 Applikon).

The Anammox enrichment reactor was fed with the effluent from the nitritation MBBR and consisted of a 30 L bioreactor with an external jacket for temperature control (35°C), fed by a peristaltic pump. The pilot plant was operated as a 24 h cycle SBR with Anammox suspended biomass. The supernatant was extracted once-a-day and the volume of reactor was variable between 28 and 38 litres. Redox, temperature and pH control were performed by handheld probes. The pH control was performed with non-automated N2-CO2 sparging.

In the inlet and outlet samples from the three reactors, N-NH$_4^+$, N-NO$_2^-$, N-NO$_3^-$, P–PO$_4^{3-}$ were monitored daily through ionic chromatography (Dionex) or Kit Lange, as well as the total COD, soluble COD, total alkalinity, TSS (or TS) and VSS (or TVS) through Standard Methods (2005).

Anaerobic batch tests for stBMP (short term Bio-Methane Potential) evaluation of different organic waste and Anammox batch tests for activity assessment were performed using the OxiTop technique. The OxiTop® Control system (WTW) is a manometric device consisting of 6 vessels (1,140 ml) placed in an incubator at 35°C, mixed by a magnetic stirrer and provided with measuring heads. Two lateral holes, one sealed by a rubber septum and the other by a teflon airtight valve, are used respectively for substrate injections and for biogas discharge. During anaerobic or anoxic tests, the overpressure (hPa) due to biogas accumulation in the vessel headspace is automatically registered by the measuring heads and the cumulative biogas volume can be calculated.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Phase I</th>
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<th>Phase III</th>
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<td>34</td>
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<td>33</td>
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<td>$Y_b$</td>
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<td>%</td>
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<td>62</td>
<td>58</td>
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</table>

Table 1 | Digester operational conditions and yields observed during the experimental period

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**Figure 2** | TVS removal efficiency (left) and GPR (right) of the pilot plant.
RESULTS AND DISCUSSION

Anaerobic codigestion of OFMSW in a pilot plant

During the start-up period (36 days), the pilot-plant was fed with thickened activated sludge (TAS). The pilot-plant reactor ran for 281 days and showed an evident efficiency increase, in particular due to the organic waste feeding (started at day 37), as proven by the increasing TVS removal efficiency which increased from 24%, during the start-up period (phase I), to about 32% during the co-digestion period (phase II and phase III). According to OLR both from TAS (0.9 gVSfed/lreac/d) and the organic waste (0.23 gVSfed/lreac/d), and according to stBMP data reported in Table 1, a VS removal efficiency of 33% during the last codigestion experimental phase (from day 175 onward) was expected. This matched with the biogas production increase observed in the pilot-plant.

Figure 2 (right) shows the comparison between the measured biogas production rates of the pilot reactor and the maximum GPR values measured in the control lab-scale tests, which were inoculated with the digested pilot-plant sludge, sampled before feeding. The peaks of the pilot-scale reactor data relate to the biogas production measured the day after each loading. As indicated in table1 the reactor biogas yield (Nbiogas/gVSfed), measured in phase III was about 5 times higher than the phase I value. However during the start-up period, the biogas production data measured in OxiTop batch tests were found to be much higher than those measured by the pilot plant volumetric gas counter, suggesting a biogas loss in the this latter system. Between day 115 and 160 the system was removed, the three way solenoid valve was cleaned up and the measuring liquid displacement water column was recalibrated. Later the GPR values measured before each feeding in the pilot plant were closer to the lab-scale control tests. The average CH₄ content was within the range of 60–65% during the start-up, and of 55–63% during the codigestion phase.

The manometric net biogas productions measured for all experimented feedstocks is depicted in Figure 3 and Table 2. Compared to the TAS, KW and FVW are characterized by a high anaerobic degradability. These results, although measured during short-term tests, agreed with the previously reported literature data for similar feedstocks, confirming the feasibility to obtain a rough indication of substrate anaerobic biodegradability under these more convenient test conditions.

By preliminary analyses it is estimated that, by using only three of the six anaerobic digesters in Florence WWTP,
it could be possible to treat all the source sorted OFMSW now collected in Florence with the waste TAS. If compared to the present condition, the codigestion process would lead to a high increase in the biogas yield from 0.22 to 0.59 Nl biogas/gVS fed and to a biogas production ten times higher than the actual value.

**Partial nitrification in a lab-scale MBBR**

The anaerobic supernatant used in the experimental research was taken from Florence WWTP; it was characterized by a concentration of N-NH$_4^+$ and P-PO$_4$ of about 651.3 $\pm$ 100.4 mg/l and 75.3 $\pm$ 24.8 mg/l respectively.

The inlet wastewater was pretreated in order to reduce solids with a 0.8 mm sieve. Phosphate content was reduced by chemical precipitation operated in a 50 l completely mixed reactor adding MgCl or MgCO$_3$. In this chemical reactor P–PO$_4$ decreased to 18.3 $\pm$ 7.9 mg/l, with molar ratio P:Mg equal to 1:1.3 and a 24 h reaction time. According to struvite formation and partial NH$_3$ stripping, N-NH$_4^+$ concentration in the supernatant decrease of 4.5%.

At the start-up the MBBR was fed with a HRT = 2 days in order to stabilize the AOB (ammonia oxidising bacteria) growth. No pH control was fixed, while temperature was set to 30°C. The oxygen concentration was maintained in the range of 2–3 mg/l at no limiting concentrations. Nitrifying biomass activity was observed at $t = 22$ d. The pH decreased to 6.2 and the nitrite/ammonium ratio achieved an expected value equal to 1:1.

Main results of the MBBR pilot plant can be summarized as follows: 1) the minimum HRT achieved was about 0.5 d that is less than the SRT$_{min}$ of both autotrophic microorganisms, AOB and NOB (Nitrite Oxidising Bacteria). In this condition only attached biomass can grow. Respirometric and titrimetric tests confirmed a negligible presence of nitrifying suspended biomass in the bulk liquid of MBBR. 2) The achieved maximum nitrogen loading rate was equal to 1.2 kgN/d/m$^3$. This rate is higher than the value found for a chemostat reactor with the same anaerobic supernatant (0.75 kgN/d/m$^3$, Caffaz et al. 2006) 3) The process was very stable up to $t = 330$ days and no NOB activity occurred. Figure 4 shows time series of the inorganic nitrogen fractions in the MBBR effluent. The average concentrations of nitrogen forms were N-NH$_4^+$ = 319.3 $\pm$ 51.4, N-NO$_2$ = 310.8 $\pm$ 58.5 and N-NO$_3^-$ = 1.6 $\pm$ 0.6.
The limiting growth factor for NOB was the low pH (6.1–6.3). In this case N-HNO₂ concentration (free nitrous acid) was in the range of 0.3–0.8 mg/l and has a substrate inhibition effect on NOB (Anthonissen et al. 1976, Tan et. al. 2007).

Anammox enrichment in a lab-scale suspended biomass reactor

The inoculum Anammox sludge (30 litres) was enriched for 360 days in a previous study (Caffaz et al. 2005) and then it was maintained at 4°C for two years. At the start up a negligible Anammox activity was observed and the enrichment was performed with an imposed doubling time of 25–30 days and under nitrite limiting-conditions. At the beginning, the feeding solution was composed of pure water, anaerobic supernatant and KNO₂. After the first 200 days, the bioreactor was fed directly with MBBR effluent at increasing flow rates.

The increase of nitrogen removal rate is shown in Figure 5. Table 3 summarizes main results.

Compared to the stoichiometric values, a very low nitrate production was observed and it corresponds to a low nitrite/ammonium removal rate ratio and to high total nitrogen removal efficiency (≥90%). This result was due to residual heterotrophic activity in the sludge (anoxic digestion). The MLVSS increased very little from 1.3 (start up) to 2 g/l during the whole experimentation.

Anammox activity was monitored with OxiTop batch tests which measure the overpressure due to produced nitrogen gas (Depena-Mora et al. 2007). After 7 months from the reactor start-up, the batch tests investigation began and samples of 1 L of biomass were periodically taken and used in the trials. For each test the maximum NO₂⁻ removal rate (V_max, mg N-NO₂⁻ /l/d) and the specific Anammox activity SAA (mgN₂_produced/gVSS/d) were calculated.

Figure 6 shows the net N₂ production due to Anammox activity after the 10 mgN-NO₂⁻ addition in eight batch tests, with no-limiting ammonium concentrations (>10 mg/l N-NH₄⁺), pH = 7.6–7.8, and T = 35°C. Figure 7 shows SAA measurements during Anammox enrichment. The biomass concentration in the OxiTop bottles in every test was the same as that of the bioreactor. Thus it was possible
to compare $V_{\text{max}}$ data with the nitrite removal rate of the pilot plant and to calculate the reactor over-capacity ($V_{\text{max}}/V_{\text{reactor}} - 1$, van Dongen et al. 2001).

The sudden and rapid loss of activity of Anammox biomass observed at $t = 376$ (~45%) was probably due to phosphate concentration increasing from 30 mg/l to 55 mg/l in 7 days, as the pilot plant was fed with MBBR effluent without previous phosphate removal in order to verify a specific inhibition for Anammox microorganisms (Van de Graaf et al. 1996). OxiTop batch tests (data not shown in this work) highlight a severe but reversible activity reduction of Anammox biomass (~50%) when phosphate concentration increased from 30 to 100 mg/l. In the pilot plant nitrite concentration dropped to 22 mg/l in one day because of $V_{\text{max}} < V_{\text{reactor}}$ (Figure 7). The process started again in batch conditions with an addition of 2 mg/l N-NH$_2$OH (hydroxylamine). Intermediate compounds were used to increase the nitrogen removal rate and to reduce long term inhibition effects due to high nitrite exposition (Strous et al. 1999). After the pilot plant was fed with nitritation effluent at low level of phosphate (<20 mg/l) and Anammox activity restarted to increase. At $t = 396$ the pilot plant showed a second sudden reduction of activity with a nitrite concentration increase up to 28 mg/l and, at the same time, a pH decrease from 7.6 to 7. Bicarbonate addition into the reactor (300 mg/l) allowed for the complete recovery of nitrogen removal efficiency. The net increase of SAA from 48 to 70 mgN$_2$/gVSS/d after bicarbonate addition, during two tests conducted at the same initial pH, suggests a possible IC limitation for Anammox biomass. According to Anammox stoichiometry about 90–120 mg HCO$_3^-$/l were necessary as a carbon source if maximum yield is considered. The possible IC limitation problem on the Anammox process would need further investigation.

CONCLUSIONS

Results of short term batch tests (performed with low F/M value to shorten the digestion time) on several organic substrates (thickened activated sludge, kitchen wastes, fruit and vegetable wastes) and fed-batch pilot-plant performances showed the efficiency and feasibility to implement a full-scale co-digestion process in Florence WWTP which has a 50% spare capacity.

Treating 50,000 tons of OFMSW with anaerobic codigestion, biogas production could increase 10 times, but nutrient loads which enter the Florence WWTP would increase about 16% and 18% for nitrogen and phosphorus respectively. In order to enhance nutrient removal efficiency autotrophic nitrogen removal, after precipitation of phosphate to MAP, was tested in two lab-scale reactors.

During about one year stable nitritation was performed in a MBBR pilot plant with Kaldnes biofilm carriers. NOB activity was been always negligible and ammonium conversion efficiency was 50% with a mean nitrogen loading rate of 1 kgN/m$^3$/d.

Anammox enrichment in a suspended biomass reactor showed a fragility after rapid changes of inlet wastewater characteristics such as phosphate concentration or
bicarbonate alkalinity. A simple method to evaluate Anammox activity by means of short-term batch tests was set up using the OxiTop® Control device. This method can be used to control maximum Anammox activity and to perform specific inhibition and kinetic tests. A frequent SAA determination could be helpful to avoid sudden losses of Anammox activity. However recent reports on full scale application of the Anammox process show that a stable high nitrogen removal rate can be achieved by using granular biomass (van der Star et al. 2007) or Kaldnes biofilm (Sztatkowska et al. 2007) technologies. The pilot-scale CONAN experimental study showed the feasibility and the efficiency of the suggested integrated system which is able to enhance the WWTP energy savings (biogas production increase) without nutrient overloads.

REFERENCES


