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Citation	Trzcinski, A. P., & Stuckey, D. C. (2009). Continuous treatment of the organic fraction of municipal solid waste in an anaerobic two-stage membrane process with liquid recycle. Water Research, 43(9), 2449-2462.
Date	2009
URL	http://hdl.handle.net/10220/42520
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Continuous treatment of the Organic Fraction of Municipal Solid Waste in an anaerobic two-stage membrane process with liquid recycle.

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ABSTRACT

The stability of a two-stage anaerobic membrane process was investigated at different organic loading rates (OLR) and Hydraulic Retention Times (HRT) over 200 days. The Hydrolytic Reactor (HR) was fed semi-continuously with the Organic Fraction of Municipal Solid Waste (OFMSW), while the leachate from the HR was fed continuously to two Submerged Anaerobic Membrane Bioreactors (SAMBR1 and 2). The Total COD (TCOD) of the leachate varied over a wide range, typically between 4000 and 26,000 mg/L while the Soluble COD (SCOD) in the permeate was in the range 400-600 mg/L, achieving a COD removal greater than 90% at a HRT of 1.6-2.3 days in SAMBR1. The operation was not sustainable below this HRT due to a membrane flux limitation at 0.54-0.78 L/m².h (LMH), which was linked to the increasing MLTSS. SCOD in the recycled permeate did not build up indicating a slow degradation of recalcitrants over time. SAMBR2 was run in parallel with SAMBR1 but its permeate was treated aerobically in an Aerobic Membrane Bioreactor (AMBR). The AMBR acted as a COD-polishing and ammonia removal step. About 26% of the recalcitrant SCOD from SAMBR2 could be aerobically degraded in the AMBR. In addition, 97.7 % of the ammonia-nitrogen was converted to nitrate in the AMBR at a maximum nitrogen loading rate of 0.18 kg NH_4^+-N/m³.day. GC-MS analysis was performed on the reactor effluents to determine their composition and what compounds were recalcitrant.

Keywords: membrane bioreactor, nitrification, Municipal Solid Waste, two-stage process, recalcitrants.

INTRODUCTION

A major issue in the UK is the shortage of landfills in which to dispose of MSW. In addition, rainwater percolating through landfills leads to the generation of a highly contaminated wastewater (leachate) which is characterized by a high COD and ammonia. Unlike aerobic composting, anaerobic digestion (AD) is an energy producing process that is becoming very attractive due to more restrictive legislation and concerns about carbon footprint. AD of the OFMSW can take place either in dry or wet systems depending on the Total Solids (TS) content of the reactor. For wet fermentation, the dry matter content is adjusted to 8-16% by addition of process water, whereas for dry systems little or no process water is added to moisten the feedstock. An example of a full scale wet two-stage system is the Schwarting-Uhde process which can sustain an OLR of up to 6 kg VS/m³.day, whereas a full scale dry 2-stage process such as the BRV plant can achieve up to 8 kg VS/m³.day (Trösch and Niemann, 1999). When a biomass retention scheme is added, as in the BTA and Biopercolat designs, an OLR up to 15 kg VS/m³.day can be applied successfully (Wellinger *et al.*, 1999; Gallert *et al.*, 2003). The biofilm growth in the second stage of the Biopercolat process allows the system to run at an overall retention time of 7 days. In the BTA process the HRT could be reduced to 5.7 days.

For laboratory and pilot scale anaerobic leachate treatment experiments, OLRs from 3 to 22 kg COD/m³.day with COD removal efficiencies of 68 – 97% and HRTs between 1.5 and 2.6 days have been reported previously (Kennedy *et al.*, 1988; Henry *et al.*, 1987; Chang, 1989). In contrast, aerobic leachate treatment in the literature have been applied to leachates with CODs between 3000 and 48,000 mg/L. Aerobic COD removal efficiencies reported are higher than 70%, with HRTs ranging from 2.5 to 20 days (Boyle and Ham, 1974; Cook and Foree, 1974; Uloth and Mavinic, 1977; Robinson and Maris, 1985; Maris *et al.*, 1984). However, less sludge is generated and less energy is required if an anaerobic step is followed by an aerobic one. In this process sequence the

final aerobic stage serves as post-treatment to improve the final effluent quality (Agdag and Sponza, 2005; Hoilijoki *et al.*, 2000). For instance, Borzacconi *et al.* (1999) loaded a UASB at an OLR of 20 kg COD/m³.day at an HRT of 2 days and achieved a COD removal greater than 80%; the subsequent aerobic rotating biological contactor achieved 72% COD removal. Another process advantage is the possibility of removing ammonia from the leachate in the aerobic step, but it is known that high influent COD promotes heterotrophic growth and inhibits ammonium oxidation (Cheng and Chen, 1994; Hanaki *et al.*, 1990). Different process configurations have been reported for the simultaneous removal of COD and ammonia from landfill leachate. Im *et al.* (2001) used an up-flow anaerobic biofilm reactor (36°C), an activated sludge reactor (23°C) and a clarifier achieving an organic removal rate of 15.2 kg COD/m³.d in the anaerobic reactor and an ammonium removal rate of 0.84 kg N/m³.day in the aerobic reactor operating at 4 days HRT. Agdag and Sponza (2005) obtained 98% COD removal of food waste at an OLR of 16 kg COD/m³.d in two UASBs (HRT=1.25 day) and an aerobic CSTR in sequence. 99% of NH_4^+ was removed at 4.5 days HRT in the aerobic CSTR. Chen *et al.* (2008) used an anaerobic-aerobic moving-bed biofilm system and achieved a COD removal of 92% at an OLR of 15.7 kg COD/m³.d, while 97% of NH_4-N was removed when the HRT of the aerobic step was more than 1.25 days. Jokela *et al.* (2002) obtained over 90% nitrification at 0.13 kg N/m³.day at 25°C and 1.4 day HRT in an upflow filter with crushed bricks.

Another pertinent question related to continuous wet anaerobic fermentation process when effluent recycle is used is whether recalcitrants such as humic and fulvic acids build up over time, or are slowly degraded. Light metals ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, PO_4^{3-}, SO_4^{2-}) and ammonia may also accumulate to inhibitory levels (Gallert et al., 2003). Leachate recirculation over a tank filled with MSW is relatively well documented (Hao *et al.*, 2008, Bilgili *et al.*, 2007), but recirculation of stabilized leachate in membrane bioreactors is not. Recycling the stabilized leachate to the head of a

continuous wet process treating OFMSW could significantly reduce the use of fresh water, and reduce the environmental impact of MSW disposal.

The objectives of this present paper were numerous: the effect of the inoculum on the behaviour of the SAMBR was investigated; the stability of the SAMBR was tested at different HRTs and OLRs; and an AMBR operating at ambient temperature was set up to determine whether the recalcitrants from the SAMBR could be biodegraded aerobically. After 200 days of operation, another objective was to see if there was a build up of recalcitrants with time due to the permeate recycle, or if there was slow degradation, and GC-MS analysis was performed to determine what if any these recalcitrants were. Finally, the different forms of nitrogen were analyzed to determine if nitrification/denitrification was occurring in the system.

MATERIALS AND METHODS

Feedstock

The simulated OFMSW mixture used in this study consisted of 41.3% Kitchen Wastes, 10.8% Garden Wastes and 47.9% Paper Wastes on a wet basis. Kitchen wastes came from a canteen in Southampton University, UK, and were passed through a kitchen grinder and mixed in a large tank with a drill mixer and then frozen until required. Garden waste was collected from the Downend Quarry centralised composting site near Fareham (Hampshire, UK) and kept at 4°C until the experiment. The composition of the simulated paper waste used for the study is listed in Table 1. The organic content was in the range 84-86% of dry matter, and the COD/VS ratio was found to be 1.2-1.6 g COD per gram of volatile solids. The ultimate biodegradability of the feedstock or Biochemical Methane Potential (BMP) was analyzed by Owen *et al.'s* bioassay method (1979), and it was observed that the method was highly dependent upon the inoculum to substrate ratio. Several

tests were performed in triplicate and after 120 days ultimate methane yields of 242 (±12.2), 233.1(±15.4), 312.1 (one test performed), 389 (±65.3), 508.5 (±54.3) ml CH_4 STP/g VS fed were obtained for I/S ratios of 0.7, 1.2, 1.35, 6 and 10.8, respectively.

Reactors

The HR (10L working volume) was an acrylic cylinder with a stainless steel mesh which followed a concentric arrangement inside the cylinder, and had a grid of 1mm holes. A stirrer moved inside the mesh allowing two pieces of rubber to rub against the perforated mesh: the speed of the stirrer (Heidolph)was 40 rpm and was operated intermittently (15 min ON-15 min OFF). The HR was fitted with a 51 micron stainless steel macrofilter (Spectrum Laboratories Inc.) on the inside of the stainless steel mesh in order to retain the large partially hydrolyzed particles, and thereby separate the coarse solids from the leachate being fed to the SAMBRs. The HR and SAMBR1 were connected in series: the leachate containing particulates was fed to SAMBR1 and the permeate from SAMBR1 was recycled to the HR in order to maintain the moisture and alkalinity of the system. On day 45, SAMBR2 was fed on leachate in parallel with SAMBR1 in order to compare the effect of inoculum on the start-up of SAMBR. The HR, SAMBR1 and SAMBR2 were maintained at 35 ± 1 °C.). The submerged anaerobic membrane bioreactors (SAMBRs) had a working volume of 3 litres, and were made of acrylic panels. They contained a standing baffle designed to direct the fluid to the upcomer and downcomer regimes. The biomass was continuously mixed using headspace biogas that was pumped (Charles Austen Pumps, Model B100SEC) through a stainless steel tube diffuser to generate coarse bubbles. The bubbles pushed the sludge flow upward between the membrane module and the reactor wall in the upper section. The sparging rate was controlled by a gas flowmeter (2 - 20 LPM, ColeParmer, USA) to minimize cake formation on the membrane. A more detailed schematic of the SAMBR and a description of the equipment can be found elsewhere (Hu and Stuckey, 2006). The biogas sparging rate was set at 5 L/min (LPM) to minimize cake

formation on the membrane and three drops of anti-foaming agent were added[every day-when?]. On day 130 an AMBR operating at ambient temperature (21-22°C) was started up to treat the permeate of SAMBR2. The permeate of the AMBR was then returned to the HR. The two SAMBRs and the AMBR were fitted with a Kubota polyethylene flat sheet membrane with 0.1 m^2 total surface and a pore size of 0.4 microns.

Inoculation and start-up of reactors

The HR was inoculated with 4L of biomass from a previous batch test in the HR. The inoculum was sieved through a 180 micron screen and its TSS and VSS were 2.74 and 2.07 g/L, respectively. The HR was initially loaded with 400 g OFMSW on a dry matter basis (≈340 g VS) in order to stimulate the growth of hydrolytic bacteria, and the volume was adjusted to 10L with tap water containing $NaHCO_3$ so that the HR was started up at 4,000 mg equivalent $CaCO_3$/L of alkalinity. The HR was then fed semi-continuously with a feedstock of 10% Total Solids that was prepared by adding leachate from the HR to the simulated OFMSW in order to blend the mixture and obtain a homogeneous slurry, and also to minimize fresh water consumption. Fresh tap water was only added to the HR to keep a constant working volume. Until day 159 the HR was fed once every two days, however, from day 160 onwards it was fed every day.

SAMBR1 was inoculated with 0.5 L of seed from a SAMBR fed on leachate from the same simulated OFMSW at a HRT of 4 days. The volume was adjusted to 3 L with the anaerobic biomedium defined in Owen *et al.* (1979) so that the initial TSS and VSS were 3.31 and 2.54 g/L, respectively. SAMBR2 was inoculated with biomass from a 4 litre chemostat batch-fed (once a week) on a 8 g COD/L feed with a composition given elsewhere (Nachaiyasit and Stuckey, 1995). The feed consisted of peptone and meat extract (25% on a COD basis) and a synthetic VFA mixture (75% on a COD basis). The ratios of the VFAs compared to acetic acid were 1.2, 0.05, 0.22, 0.08,

0.23 for propionate, iso-butyrate, n-butyrate, iso-valerate, n-valerate, respectively. These ratios were typically observed in the raw leachate obtained in previous tests from the simulated OFMSW. The supernatant of the chemostat was discarded and the settled solids were used to inoculate SAMBR2. The volume was adjusted to 3L with the anaerobic biomedium defined in Owen *et al.* (1979) so that the initial TSS and VSS were 2.56 and 1.78 g/L, respectively. The AMBR was inoculated with an aerobic biomass from a dye wastewater plant at an initial MLTSS and MLVSS of 3 and 2.3 g/l, respectively. Air was used to mix the reactor content at 1.4 LPM.

Analytical Methods

The measurement of pH (Jenway) was accurate to within ±0.02 units. The Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Fixed Suspended Solids (FSS), Soluble Chemical Oxygen Demand (SCOD) and Total Chemical Oxygen Demand (TCOD) were measured as described in Standard Methods (APHA, 1999). Their coefficient of variation (COV) for ten identical samples was 4%, 3.1%, 7.1%, 2.6% and 9.9%, respectively. Volatile fatty acids (VFAs) were measured using a Shimadzu Gas Chromatograph with a flame-ionized detector and a SGE capillary column (12mx53mm ID-BP21 0.5µm). The COV was 3% for ten identical samples. The composition of biogas was determined using a Shimadzu GC-TCD fitted with a Porapak N column (1500×6.35 mm). The COV for 10 identical samples was 2%. Ammonia-Nitrogen was measured using the Nesslerization method by reading absorbance at 425 nm. The COV was equal to 6.6% for 10 identical samples. Nitrite and nitrate were analyzed by Dionex Ion Chromatography. The COV for 5 identical samples was 1.8%.

For the GC-MS analysis, the analytes of interest were extracted using a solid phase extraction (SPE) procedure. The Oasis HLB cartridge (Waters Corporation) was first conditioned with 3 mL methyl tertiary-butyl ether (MTBE), 3mL methanol and 3 mL deionized water (DW). A sample (500 mL)

at pH2 was then loaded onto the cartridge and filtered dropwise. The cartridge was then washed with 3 mL of 40% methanol in DW to remove organic interferences, re-equilibrated with 3 mL DW, washed with 3 mL 10% methanol/2% NH_4OH to remove humic interferences and finally 6 mL 10% methanol/90% MTBE. The final matrix was then evaporated to 200 µL. The samples were then analyzed using a 5890 Series gas chromatograph equipped with an autosampler and a 5970 mass spectrometry detector (Hewlett-Packard, USA). Analytes were separated using a SGE HT5 column of 25m x 0.22mm with a film thickness of 0.1 µm . The temperature program was: 50°C, hold 2 min, rate 8°C min^{-1} to 350°C, hold 30 sec. Helium was used as a carrier gas at a flowrate of 2 ml/min . The injector temperature was set at 270°C. The MS was operated in the electron impact ionisation mode (70eV). The transfer line and ion source temperatures were 290°C and 220°C, respectively, and the quadrupole was not heated. Scan runs were made with a range from *m/z* 33 to 500.

RESULTS

Hydrolytic Reactor

The TCOD in the leachate varied over a wide range, between 4000 and 26,000 mg/L, due to the HR being fed every two days until day 159, intermittent mixing, and occasional stirring difficulties. It can be seen from Figure 1 that the TCOD did not change with changes in OLRs from 0.5 to 16 g VS/L.day. However, the value of TCOD did depend upon the occasional presence of solid particles in the sampling line at the time of sampling. Similarly, the SCOD did not vary significantly when a step increase in OLR was effected in the HR, and was always in the range 530 – 2900 mg/L. The evolution and composition of VFAs over time in Figure 2 shows that acetate was the main VFA at steady-state, but propionate temporarily became the main acid after the shock at 4, 8 and 16 g VS/L.day on days 101, 146 and 164, respectively, which is a few days after the organic shocks took

place. From day 160 onwards, the HR was fed every day at 16 g VS/L.day at an HRT averaging 2.2 days, and propionate remained the main acid until the end of the run. Gallert *et al.* (2003) observed a higher and longer-lasting propionate accumulation when the HRT was reduced from 7.1 days to 5.7 days at an OLR of 15 kg COD/m³.day. They correlated this with 1% hydrogen in the off-gases. Propionate oxidation is know to be the bottle neck reaction during the methanogenesis of complex substrates because the organism carrying out this reaction only has a growth rate of $0.13 d^{-1}$ (Wallrabenstein et al., 1995), and can be washed out at an HRT below 8 days (Gallert et al., 2003). The pH was then between 6 and 6.5 but with the accumulated alkalinity (5,000 mg equivalent $CaCO_3$/L on day 199) the pH did not drop any further.

The low SCOD observed in the leachate was thought to be due to poor hydrolysis because of the inadequate amount of inoculum used to seed the HR. The initial inoculum to substrate ratio was 0.02 based on the initial load of 340 g volatile solids fed during start up. Then the HR was fed continuously at an OLR of 0.5 g VS/L.day but with intermittent mixing as well as occasional stirring difficulties at TS above 5 %. Table 2 presents the VS removal percentages at the various OLRs and HRTs tested. The VS removal % was calculated as follows:

$$\text{VS removal \%} = 100\% \cdot \left(1 - \frac{mass\ VS\ \ removed + mass\ VS\ \ accumulated\ \ in\ \ HR}{mass\ VS\ \ \ fed\ \ in\ \ HR}\right)$$

Where the masses were considered over a period longer than 15 days so that steady-state can be assumed and the mass of VS accumulated in the HR is the difference between the mass of VS in the HR at the beginning and the end of the period considered. The VS removal percentages shown in Table 2 are 65.4, 43.8, 35.5, 22 and 13.8 % VS destruction at 0.5, 2, 4, 8 and 16 g VS/L.day, respectively, assuming that the volatile solids production due to bacterial growth and the transfer of volatile solids to the SAMBR were negligible. The transfer of volatile solids to the SAMBR was very limited thanks to the separation between coarse solids and leachate by the perforated stainless

steel mesh within the HR. Nevertheless a small fraction of solids could still pass through and be pumped to the SAMBRs. This fraction over 200 days was estimated as 37.8 and 69.3 g VS for SAMBR1 and SAMBR2, respectively, which can be considered as negligible. For instance, during the period at 16g VS/L.day (day 159 to day 199) the total VS mass transferred to SAMBR1 and SAMBR2 together equaled 91 g changing the VS removal % in the HR to 12.4 instead of 13.8. The former is the actual VS removal in the HR, while the later could be named the "apparent VS removal" and in this study they were similar and thus the difference was neglected.

The low VS removal percentages were also due the low volatile solids retention times calculated as the ratio of mass of volatile solids in the HR that is equal to $X \cdot V$ where X is the VS concentration in g/L and V is the reactor volume in L, and the mass of volatile solids removed per day (W in gVS/day): VS RT (days) = $\frac{X.V}{W}$ (Cecchi *et al.*, 2003). Consequently, the anaerobic biodegradability of the compost of solid digestate that was taken out of the HR was consistent with the lower VS removal observed as the OLR was increased. The BMP of the digestate was 167.7, 229.7 and 296.6 mL CH_4/g VS fed at OLRs of 0.5, 8 and 16 g VS/L.day, respectively.

Table 2 also contains the HRT of the HR, i.e. the hydraulic retention time or leachate retention time, which is the average retention time of a unit volume of liquid in the reactor and is calculated as the ratio of the reactor volume and the leachate flowrate to the SAMBRs. Longer lasting propionate accumulation was observed from day 146 when the HRT was 4 days and also when the HRT dropped to 2 days on day 164. This is in line with Gallert *et al.* (2003) who stated that propionate oxidizers wash out at HRTs below 8 days.

SAMBR1

276 *COD removal*. The OLR to the SAMBR was not constant because of fluctuations in the TCOD of
277 the leachate from the HR (Fig. 1), and as a result the SCOD in SAMBR1 (Fig. 3) sometimes
278 increased sharply over time. For instance, an OLR to the SAMBR of 8.14 g COD/L.day was
279 observed temporarily on day 164, and a simultaneous decrease of the HRT to 2.1 days led to a sharp
280 peak of SCOD in the reactor but this was not due to VFAs building up, indicating that hydrolysis
281 was rate limiting. On day 185, a maximum OLR of 19.8 g COD/L.day was observed with stable
282 COD removal. Despite the varying OLR, the permeate SCOD (effluent SCOD in Figure 3)
283 increased steadily and stabilized at around 500 mg /L, but from day 178 onwards it slowly
284 decreased to 354 mg/L. This can be partly attributed to the greater consumption of fresh water
285 towards the end of the run to keep up the volume in the HR (see Table 2), but the decline of SCOD
286 was also due to the very high MLTSS (28.7 g/L) at the end of the run, and was not due to the
287 enhanced rejection by the membrane because the SCOD in the bulk liquid was also found to
288 decrease slowly. The SCOD inside the reactor remained higher than the effluent values throughout
289 the experiment, which demonstrates that the presence of a cake/gel layer on the membrane surface
290 considerably improves the effluent quality: this is in line with previous work on the SAMBR
291 (Akram, 2006). Nevertheless, membrane rejection did not increase with time but varied according
292 to the bulk SCOD. Membrane rejection was expressed as a percentage:

293 $$\text{Rejection} = 100\% \ \frac{SCOD_{bulk} - SCOD_{permeate}}{SCOD_{bulk}}$$

294 In this study it was observed that the higher the bulk SCOD, the higher the rejection (Figure 4),
295 which suggests that the high molecular weight COD is kept in the reactor and only when it is
296 degraded in the bulk can it pass through the membrane pores. The COD removal was 93% on
297 average while the VFA concentration was virtually zero, indicating that the methanogenic
298 population could cope with an HRT as low as 1 day. However, SAMBR1 could not be operated in a
299 sustainable way at a HRT below 1.6-2.3 days due to a membrane flux limitation of 0.54-0.78 LMH.
300 At an HRT below 2 days, the rate of particulate COD destruction became less than the feeding rate,

resulting in the build up of solids at the bottom of the reactor which eventually blocked the diffuser and, on day 182 there were no bubbles scouring the membrane. At the same time, the MLTSS increased to 28.7 g/L (Figure 5) which also adversely affected the flux. This indicates that the performance of the SAMBR treating leachate containing particles was limited to 1.6-2.3 days HRT by particulate hydrolysis and not VFA degradation.

SAMBR2 coupled with AMBR

Effect of inoculum on start-up of SAMBR2. Previous studies (Akram, 2006) have shown that a shorter start-up period and higher COD removal in SAMBRs can be obtained by increasing the organic load at a lower constant HRT rather than gradually decreasing the HRT at constant high feed strength. This approach was followed to start up a SAMBR, although Akram (2006) used a sucrose-based wastewater that is easily degradable, while the leachate used in this study was partially refractory. For an easily degradable substrate, VFA accumulation can occur in the SAMBR due to overloading of the methanogens and possibly the lack of syntrophic associations necessary to degrade reduced intermediates. For this reason, prior inoculation into a CSTR is helpful for the development of an active inoculum enriched in methanogens (Akram, 2006). With this in mind, an inoculum was fed on synthetic VFAs as their main carbon source (75% on a COD basis) in a 4 litre chemostat prior to inoculating SAMBR2. Prior to inoculating SAMBR2, a specific acidogenic activity test was conducted on the two different inocula, the one from SAMBR1 and the one from the chemostat batch fed with synthetic VFAs. The same amount of glucose was fed to both sets of bottles to result in 2 g COD/L for the test, and Figure 6 reveals that indeed the acidogenic and methanogenic biomass of the inoculum fed with synthetic VFAs was more active than the inoculum taken from SAMBR1 on a same MLVSS basis. This is due to the large fraction of non-living MLVSS in the inoculum from SAMBR1 that contained lignocellulosic fibers resistant to hydrolysis.

VFA concentrations in SAMBRs1 and 2 were both virtually zero. This indicates that an inoculum acclimatized to VFAs such as the one used to start up SAMBR2 does not bring further advantages because both SAMBRs at similar initial MLVSS could start-up at a HRT of 5.2-5.7 days with no VFA accumulation. Thus, for a lignocellulosic-based feed, the rate-limiting step is the hydrolysis, and not VFA degradation as it is for a sucrose-based feed. Moreover, the methane content of the biogas in SAMBR2 gradually increased to a maximum of 61% after 50 days (Figure 7), whereas in SAMBR1 it reached 60% after four days of operation and then slowly stabilized at values between 69 and 71%, which suggests that the inoculum fed on synthetic VFA was not optimal for start-up because initially it did not contain enough hydrolytic and acidogenic bacteria for a leachate medium. Previous work (O'Sullivan and Burrell, 2007) on leachate from MSW has also shown that microorganisms grown in another medium are unable to out-compete native solid waste microorganisms for the cellulose in a foreign (leachate based) medium. In this study, the methanogens enriched with synthetic VFAs may have been inhibited when fed suddenly with leachate explaining why the methane content displayed such a long lag phase before reaching normal value of 60% CH_4 in the biogas.

COD removal. The HRT of the AMBR was equal to the HRT of SAMBR2 because the two reactors were connected in series. The COD removal in SAMBR2 was 94.5% on average, and only 1.6% in the AMBR so that a total COD removal of 96.1% was achieved. The VFA concentration was virtually zero in SAMBR2 and the permeate, and thus were omitted from Figure 8. No significant change in the contribution to the total COD removal efficiency of both reactors was observed when the HRT was decreased from 5.2-5.7 to 0.37 d. At such a low HRT, particulate solids in the leachate built up at the bottom of the SAMBR eventually leading to the diffuser blocking. The MLTSS reached 46 g/L on day 195 (data not shown) which lowered the available flux to 0.4 LMH.

In a moving-bed biofilm reactor system with an anaerobic-aerobic arrangement, Chen *et al.* (2008) observed that at 1.5 days HRT the COD removal of the anaerobic reactor dropped to 81%, whereas the aerobic COD removal increased to 11%, but nonetheless the total COD of the system remained stable. Although the contribution of the aerobic step to the total COD removal of the system was low in this study (1.6 % on average) because of the membrane rejection in SAMBR2, it should be emphasized that on average 26% of the recalcitrants from SAMBR2 could be degraded aerobically in the AMBR. The COD in the permeate of the AMBR was approximately 300 mg/L at the end of the experiment, which is close to the 390 mg/L reported by Agdag and Sponza (2005).

Nitrification in the AMBR. The sequential oxidation of NH_4^+ to NO_3^- involves autotrophic NH_3 and NO_2^- oxidizers. In addition, heterotrophic bacteria can oxidize reduced forms of organic N to NO_3^- (Prosser, 2007). Figure 9 shows the evolution of inorganic nitrogen species in the AMBR. Because the inoculum used in this study came from a dye wastewater plant, it is assumed that it did not contain any nitrifiers. As a result, ammonia-nitrogen was initially not converted to nitrite or nitrate. Ammonia oxidizers may also have been inhibited by undissociated ammonia (NH_3) which was in the range 14 – 23 mg NH_3/L between days 136 and 146. Anthonisen *et al.* (1976) have observed that free ammonia can inhibit ammonia oxidation to nitrite by *Nitrosomonas* and nitrite oxidation to nitrate by *Nitrobacter* in the range 10-150 and 0.1-1 mg NH_3/L, respectively. The nitrite build-up may be explained by the inhibition of nitrite oxidizers due to the free ammonia ranging from 0.1 to 0.4 between days 146 and 167. Inhibition of nitrifying organisms by free nitrous acid (HNO_2) is unlikely to have occurred as the concentration remained in the range 0.00084-0.0052 mg HNO_2/L, which is far below the inhibitory range of 0.22 to 2.8 mg/L reported by Anthonisen *et al.* (1976). The growth of *Nitrobacter* was confirmed by the slow decrease in nitrite which was correlated with a slow increase in nitrate. Nitrite was not completely consumed and plateaued around 60 mg N/L

due to HRTs shocks. The ammonia-nitrogen in the permeate of SAMBR2 was typically 45-135 mg/L. From day 171 onwards, 97.7% of the NH_4-N was converted in the AMBR at a maximum nitrogen loading rate of 0.18 kg NH_4-N/m^3.day. The nitrite-nitrate rich permeate was recycled to the HR where denitrification took place because no nitrate was detected in the HR effluent. In this study, the SCOD fed to the AMBR was relatively low (400-600 mg/L) which promoted the growth of autotrophic bacteria. Because of the low organic content and high DO (1.6 mg/L) optimal conditions were met for the growth and retention of autotrophic ammonia oxidizers in the AMBR at a HRT as low as 0.37 day. In contrast, Chen *et al.* (2008) and Im et al. (2001) could not maintain nitrification at 1.5 and 2.7 days HRT, respectively, because the COD concentration in the feed to the aerobic step increased sharply. Jokela *et al.* (2002) also observed that nitrification efficiency dropped to below 20% when the COD concentration suddenly increased at 1.4 d HRT. The authors stated that heterotrophs competed for oxygen with the autotrophs leading to a decrease in nitrification activity.

In this study, in addition to ammonia removal in the AMBR, the analysis of Total Nitrogen (TN) revealed that between 7 and 35% of the TN in the permeate of the AMBR was organic N and that organic N was slowly building up in the AMBR. Hence, heterotrophs could very likely have coexisted in the AMBR using organic N for growth and recalcitrant SCOD as a sole carbon source.

GC-MS Analysis

The GC-MS analysis performed in thus study was qualitative and not quantitative, although comparison between the abundance of the components detected can lead to conclusions regarding the biodegradability in anaerobic (HR, SAMBR1 and 2) and aerobic (AMBR) reactors. Figure 10 shows the chromatographs obtained. The sample referred to as anti-foaming agent consisted of 500 mL DW in which few drops of anti-foaming agent were added. The sample called ‘SCRAP’

consisted of 500mL of DW in which small pieces of the plastic used to make the reactor were added and the mixture shaken for few weeks at 30°C in order to determine which components if any could leach from the reactor's construction material. Table 3 gathers all the information collected, i.e. the name of the components that were detected in the effluent of each reactor, but not in the blank (DW that followed the same SPE protocol) or the sample with plastic scraps. The second and third columns contain the abundance and the biodegradability, respectively.

HR effluent. The analysis revealed that butylated hydroxytoluene and tridecanoic acid, 12-methyl-, methyl ester found in the HR effluent and in the anti-foaming agent were completely degradable because they were not found in both SAMBRs and the AMBR effluents, which explains why the effect of the anti-foaming agent was noticeable only for a limited period of time in the SAMBRs. Previous work has shown that butylated hydroxytoluene can leach from plastic and tubing (Shpiner, 2007). Similarly, methyl 9-methyltetradecanoate and pentadecanoic acid, 14-methyl, methyl ester were two aliphatic molecules were not detected in the SAMBR permeates due to their complete degradation in this reactor. Surprisingly, 1-phenanthrene carboxylic acid 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-,methylester, [1R(1alpha,4abeta,10aalpha)]- that is polyclyclic and thus considered difficult to biodegrade was successfully degraded in SAMBRs due to the complete retention of bacteria and the high MLVSS.

SAMBR1 permeate. Table 3 shows that o-hydroxybiphenyl and phenol 4,4'-(1 methylethylidene)bis can be considered as non biodegradable because their abundance was very close to those in the HR effluent (about 600000 and 4800000, respectively). On the other hand, Bis (2-ethylhexyl)phthalate which is a common plasticizer was not detected in the blank and scrap, and its abundance more than doubled from the HR effluent to SAMBR1 and 2 permeates, suggesting that it could be secreted by bacteria themselves, or is the catabolic end product of non detected compounds. Some molecules

were found to be slowly biodegradable because their abundance decreased when passing through both SAMBRs. These molecules were tributyl phosphate, benzophenone, diisooctylmaleate and 2,6-di-tert-butyl-4-(dimethylaminomethyl)phenol. The last three molecules were also found to be slowly degradable when passing through SAMBR2.

SAMBR2 and AMBR. In comparing the SAMBR2 and AMBR permeates it can be seen that phenol 2,4-bis(1,1-dimethylethyl) and benzenesulfonamide N-butyl were not degraded aerobically because their abundance was found to increase when passing through the AMBR. Benzenesulfonamide N-butyl is a common plasticizer that was not found in the blank, scrap or anti-foaming agent, but was produced in both SAMBRs at an abundance of 3 million and at an abundance of 7.5 million in the AMBR. Previous work has shown that this compound can originate from the tubing used in our lab (Shpiner, 2007).

Interestingly, some molecules were found to be non biodegradable in an anaerobic environment but could be slowly biodegraded in the AMBR such as diphenylamine and Bis (2-ethylhexyl)phtalate. The former had an abundance of 550000 in the SAMBR2 permeate which decreased to 350000 in the AMBR permeate (36% reduction), whereas Bis (2-ethylhexyl)phthalate had an abundance of 10900000 and 6600000 in SAMBR2 and AMBR permeate, which is 40% degradation. Nevertheless, new molecules appeared in the AMBR permeate such as thiophene,2,5-bis(2-methylpropyl), 1,2-benzenedicarboxylic acid,bis(2-methylpropyl)ester, tetracosamethyl-cyclododecasiloxane and 2,6 di-t-butyl-4-[3(2,3epoxypropylthio)propyl]. The molecules 1,2-benzenedicarboxylic acid, bis(2-methylpropyl)ester and Bis (2-ethylhexyl)phthalate have a very similar structure with a common ring and two carboxylic groups attached to the ring in ortho and meta positions. Since the abundance of Bis (2-ethylhexyl)phthalate decreases in AMBR and since 1,2-benzenedicarboxylic acid, bis(2-methylpropyl)ester is a new molecule formed in the AMBR, it is presumed that Bis (2-

ethylhexyl)phthalate can lose 2 butyl groups in the two chains attached to the ring to form 1,2-benzenedicarboxylic acid, bis(2-methylpropyl)ester under aerobic conditions which is not possible in an anaerobic environment.

Phtalates and Plasticisers. Plasticisers are compounds that are added to polymers in order to improve the properties of a plastic such as increasing its flexibility, and several phtalates were detected in this study. For instance dimethylphtalate was found in the blank and scrap but was not detected in the reactor indicating that it could be readily biodegraded. Diethylphthalate was also found in the blank and scrap but also in the HR effluent and all at a similar abundance of 2100000 for the blank and scrap and 2040000 for HR effluent. The fact that it was not detected in the SAMBR permeates indicates that it could be biodegraded completely thanks to the high MLVSS in SAMBRs.

Dibutylphtalate was found in the anaerobic reactors but also in the blank and scrap suggesting that it might come from the reactor plastic. Interestingly, its abundance decreased greatly in the SAMBRs (from 6250000 in HR effluent to 1400000 and 1200000 in SAMBR1 and 2 permeate, respectively) and was absent in the AMBR, indicating that a great proportion of it can be degraded anaerobically and totally degraded aerobically.

CONCLUSIONS

The main results of the two-stage membrane process continuously treating the OFMSW are:

- The HR was treating the OFMSW at OLRs ranging from 0.5 to 16 g VS/L.day without process instabilities. The main acid in the leachate was acetic acid at steady state, while propionic acid became temporarily predominant when the OLR was increased and was the main acid at 16g

476 VS/L.day. Unfortunately the VS removal was not greater than 13.8% at these high OLRs. pH
477 drops were avoided due to the permeate containing alkalinity that was recycled back to the HR.
478 This procedure also minimized the use of fresh water to slurry the feedstock.

479 • The use of a membrane in the second reactor had several advantages; the complete retention of
480 bacteria allowed for stable operation, and no VFAs accumulated even when propionate was the
481 predominant acid. TCOD removal was greater than 90% at a HRT of 1.6-2.3 days in SAMBR1,
482 and recalcitrant SCOD did not build up over 200 days of operation. Reasons for this are the high
483 MLTSS obtained in MBRs towards the end of the run. The slow SCOD decline was not due to the
484 enhanced rejection by the membrane because the SCOD in the bulk liquid was also found to
485 decrease slowly. The permeate of the SAMBR was low in COD thereby providing a stabilized
486 leachate from the very first days of continuous treatment.

487 • Inoculation of the SAMBR with a bacterial consortium enriched in methanogens in a synthetic
488 biomedium with VFAs as a main carbon source did not bring further advantage compared to
489 SAMBR1 that was inoculated with a mixed consortium acclimatized to the leachate biomedium.
490 The inoculum fed on synthetic VFAs was not optimal for start-up because initially it did not
491 contain hydrolytic and acidogenic bacteria specifically active in a leachate medium.

492 • SAMBR2 achieved COD removals of greater than 95% at HRTs as low as 0.4 days. The SCOD
493 permeate was low and constant which did not inhibit autotrophic bacteria in the AMBR even at
494 such low HRT. The membrane promoted the growth of autotrophic bacteria in the subsequent
495 AMBR so that 97.7% of the NH_4-N was removed at a maximum nitrogen loading rate of 0.18 kg
496 NH_4-N/m^3.day.

497 • GC-MS analysis revealed that the HR effluent contained a number of aliphatic molecules but they
498 were all degraded in the SAMBRs. The permeate of the SAMBRs only contained mainly aromatic
499 recalcitrants molecules, and amongst these Bis (2-ethylhexyl)phthalate was found to build up in
500 the permeate of SAMBRs but was slowly degraded in the AMBR.

ACKNOLEDGEMENT

The authors would like to thank Professor Charles Banks from Southampton University (UK) for a gift of the hydrolytic reactor. This research was supported by a grant from the Department of Environment, Food and Rural Affairs (DEFRA) in the UK.

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Type of paper	**%**
Newspaper	21.2
Magazine	12
Office paper	7.9
Card and paper packaging	10.5

Cardboard	15.06
Card non packaging	0.6
Liquid carton	1.4
Tissue paper	15.06
Paper plate	15.06
Toilet paper	15.06

Table 1. Composition of paper waste used in this study.

OLR (g. VS/L.day)	0.5	2	4	8	16
Duration (days)	63	17	47	14	40
VS RT (days)	67.8	n.a.	16.6	6.4	3.3
VS removal %	65.4	43.8	35.5	22	13.8
Average Fresh water consumption (mL/day)	3.7	n.a.	68	202	652
HRT (days)	15	9	7.8	4	2.2
Digestate methane Potential (mL CH4/g VS)	167.7 ± 6.2	n.a.	n.a.	229.7 ± 6.9	296.6 ± 24

Table2. Comparison of volatile solids retention times, volatile solids removal percentages, fresh water consumption, hydraulic retention times and digestate methane potential at different organic loading rates in the hydrolytic reactor. n.a. = not applicable

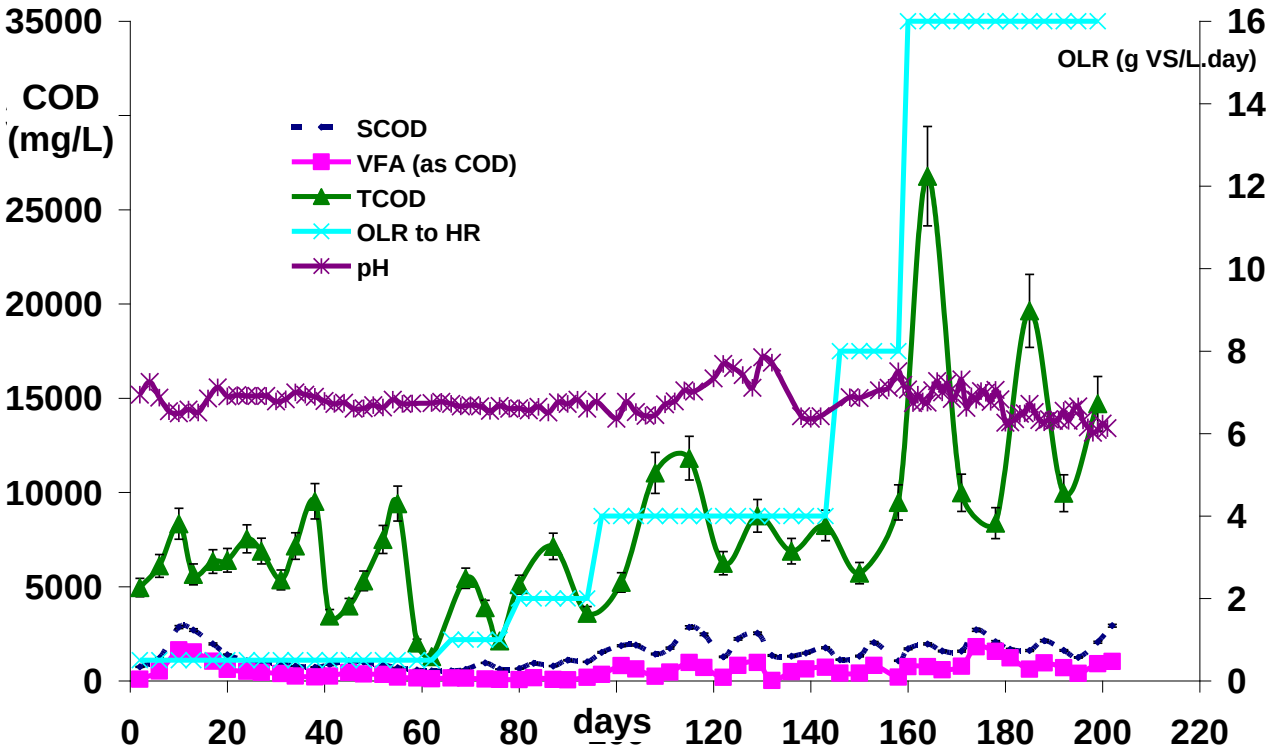

Figure 1. Evolution with time of TCOD, SCOD and VFAs in the effluent of the HR on the left axis, and OLR and pH on the right axis.

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666 **Figure 2**. VFA distribution in the effluent of the HR.

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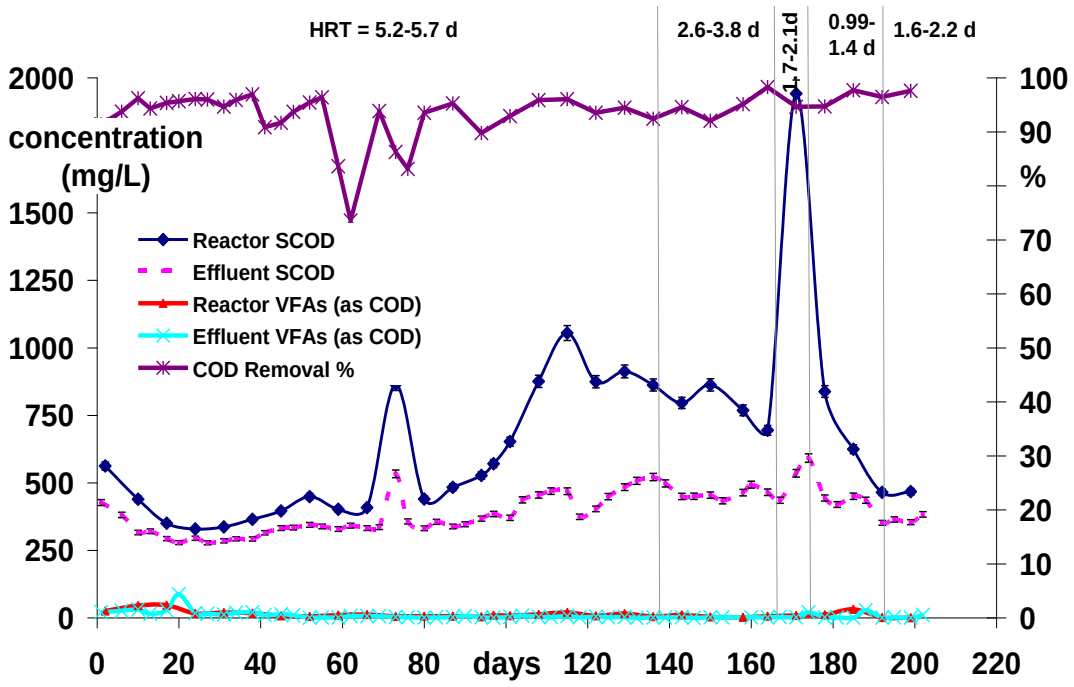


Figure 3. SCOD and VFAs inside SAMBR1 and in its permeate (left axis). COD removal in SAMBR1 (right axis).

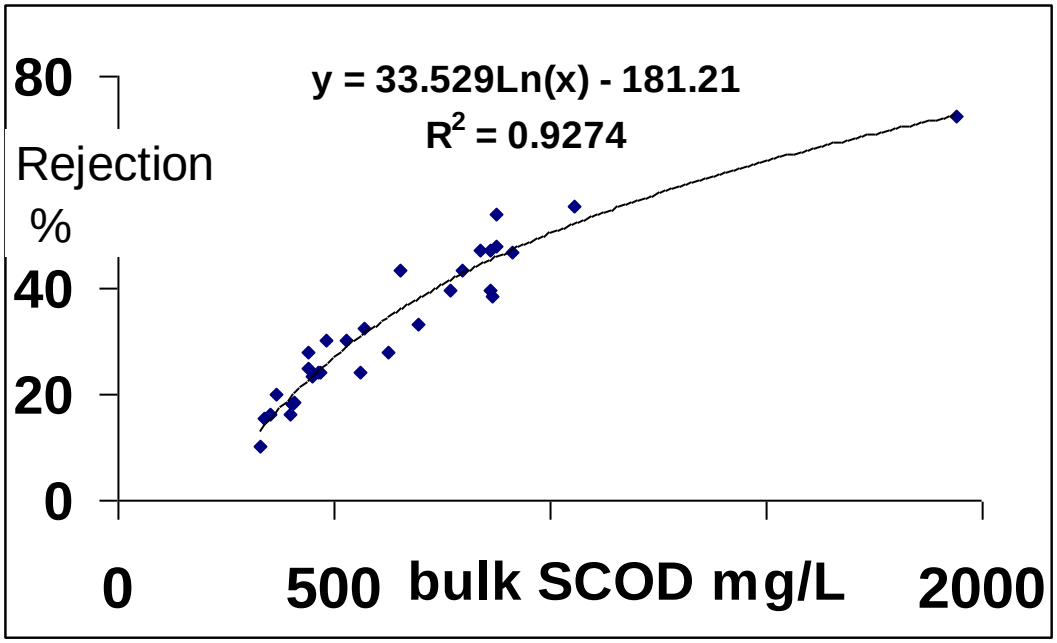


Figure 4. correlation between the bulk SCOD in SAMBR1 and the membrane rejection.

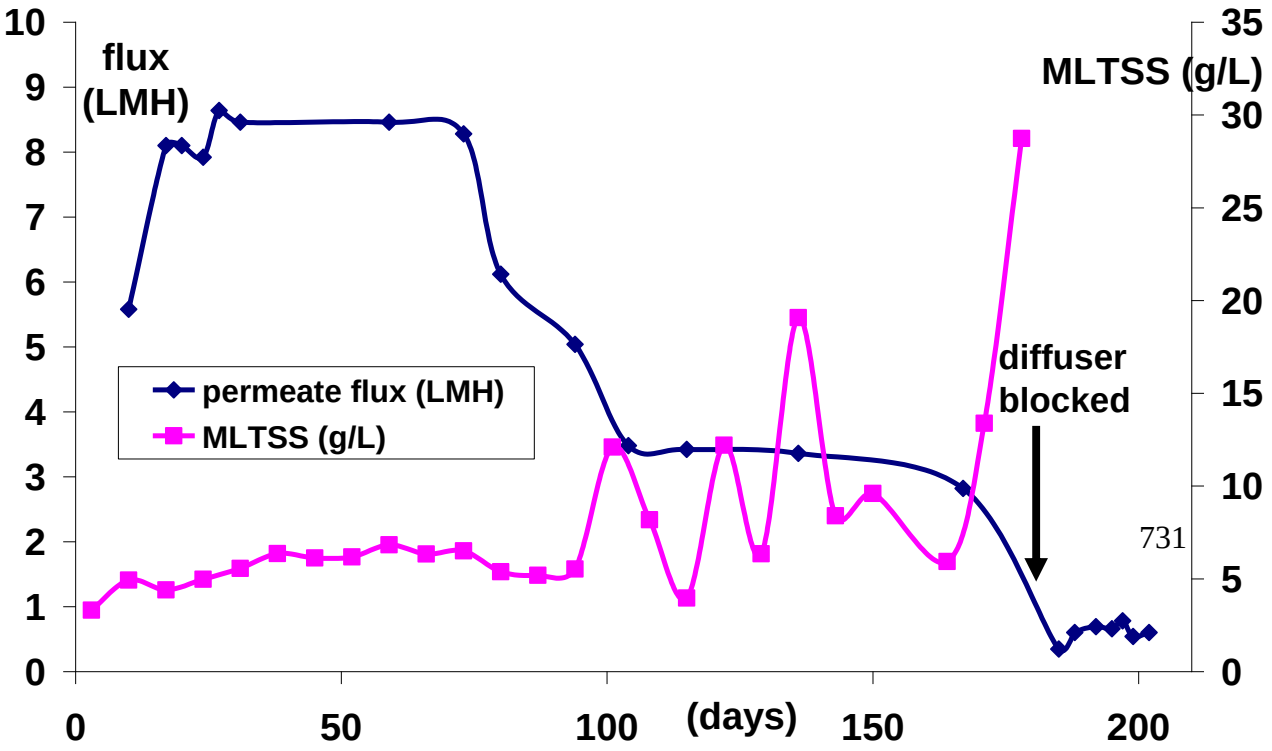


Figure 5. Evolution with time of the MLTSS (right axis) in SAMBR1 and the membrane flux (left axis) .

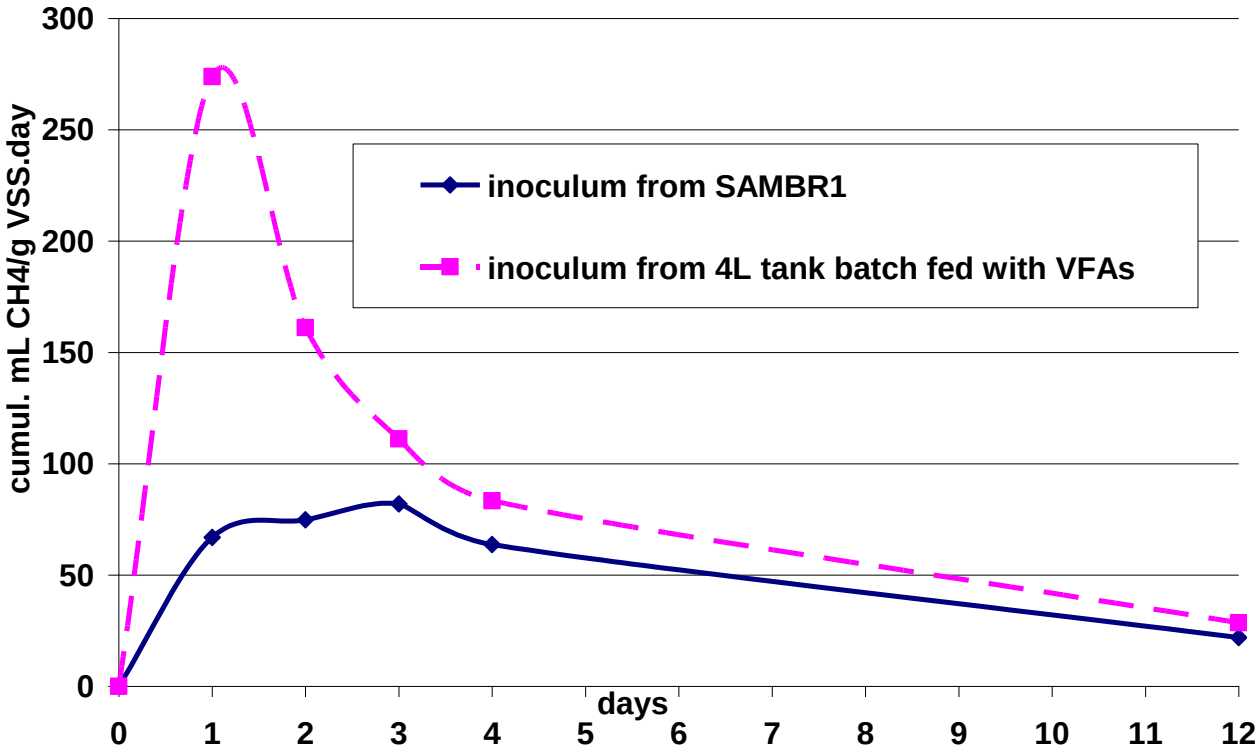


Figure 6. Specific acidogenic activity test on the inoculum from SAMBR1 acclimatized to the leachate medium and the inoculum from a 4 litres chemostat enriched with methanogens in a synthetic medium of peptone, meat extract and VFAs.

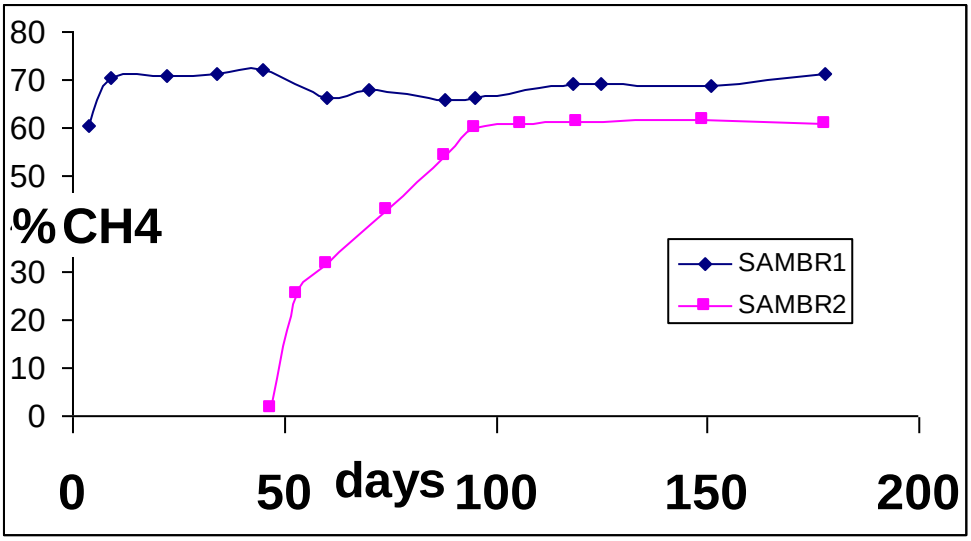


Figure 7. Evolution with time of the methane content of the biogas in a SAMBR inoculated with a biomass acclimatized to the leachate medium (SAMBR1) and a SAMBR inoculated with a inoculum acclimatized to a synthetic biomedium aiming at enriched methanogens (SAMBR2).

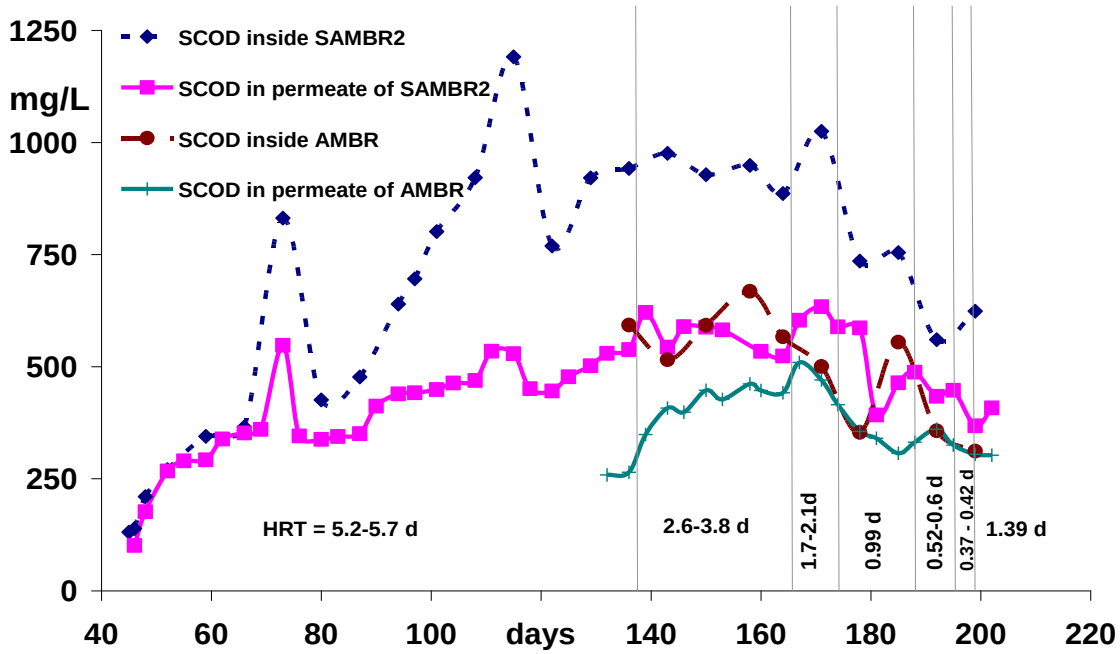


Figure 8. SCOD inside and in the permeate of SAMBR2 and AMBR at different HRTs.

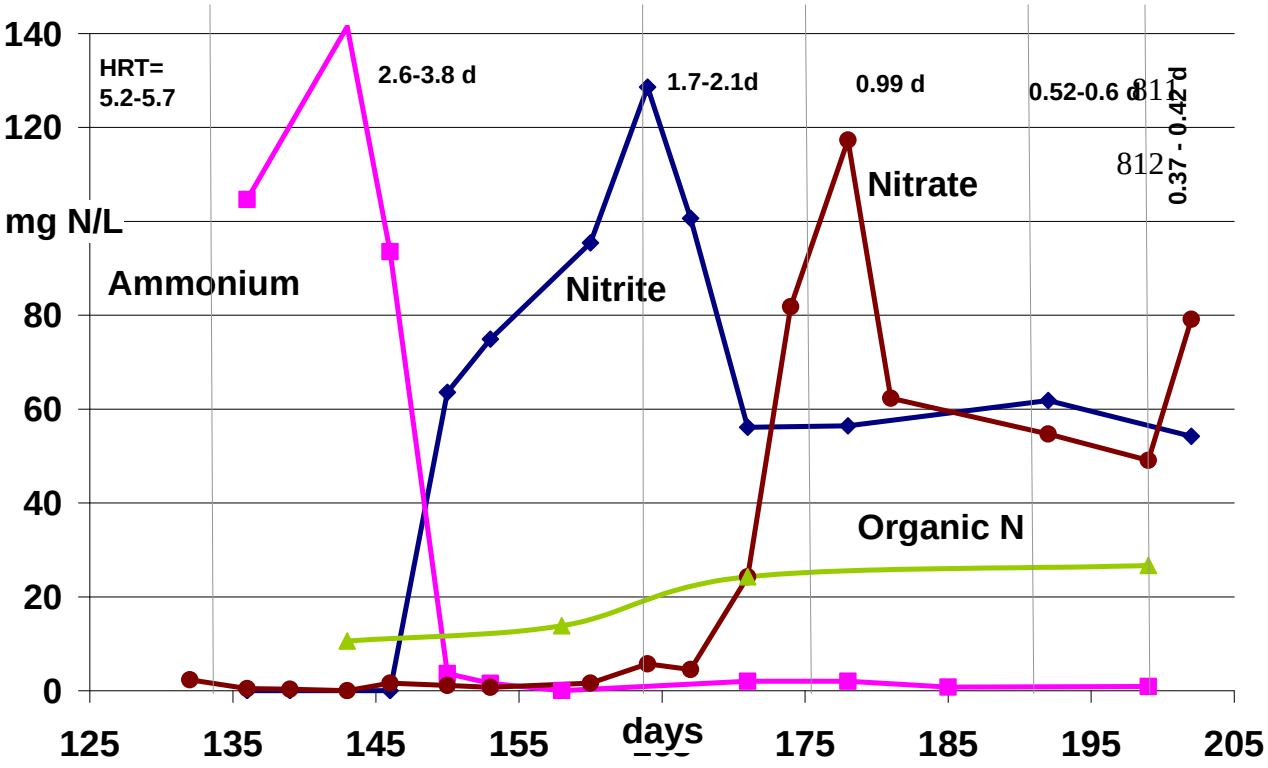


Figure 9. Evolution of inorganic nitrogen with time in the AMBR.

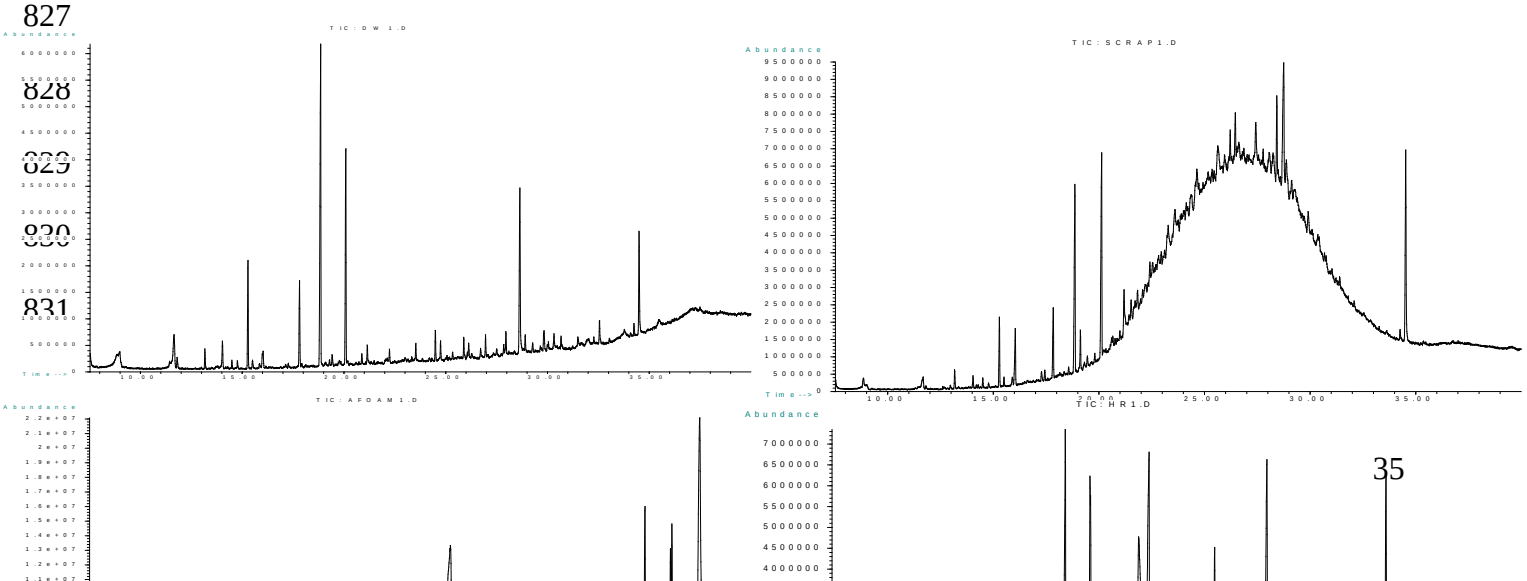
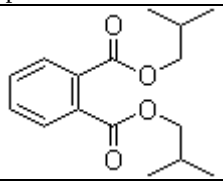


Figure 10. GC-MS chromatographs. From left to right: blank, reactor's plastic scrap, deionized water with anti-foaming agent, effluent of the hydrolytic reactor, SAMBR1 permeate, SAMBR2 permeate, AMBR permeate.

Recalcitrants in HR effluent	abundance	biodegradability	comments
butylated hydroxytoluene	660000	Fully biodegradable	Found also in anti-foaming agent but at higher abundance
o-hydroxybiphenyl	580000		
tributyl phosphate	870000		
benzophenone	3300000		
tridecanoic acid, 12-methyl-, methyl	1700000	Fully biodegradable	Found also in anti-foaming

ester			agent but at higher abundance
methyl 9-methyltetradecanoate	2480000	Fully biodegradable	aliphatic
pentadecanoic acid, 14-methyl, methyl ester	2850000	Fully biodegradable	aliphatic
phenol 4,4'-(1 methylethylidene)bis	4800000		
diisooctylmaleate	9500000		Epoxy resin (used as a plastisizer)
1-phenanthrene carboxylic acid 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-,methyl ester,[1R(1alpha,4abeta,10aalpha)]-	2550000	Fully biodegradable	Polycyclic aromatic
Bis (2-ethylhexyl)phtalate	4550000		
2,6-di-tert-butyl-4-(dimethylaminomethyl)phenol	3700000		
Recalcitrants in SAMBR1 permeate			
2,4,7,9-tetramethyl-5-decyn-4,7-diol	600000	new	
phenol 2,4-bis(1,1-dimethylethyl)	200000	new	
o-hydroxybiphenyl	600000	non biodegradable	
tributyl phosphate	400000	slowly biodegradable	
benzophenone	800000	slowly biodegradable	
1,3,6,9b-tetraazaphenalene-4-carbonitrile,7,9-dichloro-2methyl	750000	new	
benzenesulfonamide N-butyl	3200000	new	
7,9-di-tert-butyl-oxaspiro(4,5)deca 6,9-diene-2,8-dione	2200000	new	
phenol 4,4'-(1 methylethylidene)bis	4800000	non biodegradable	
diisooctylmaleate	4400000	slowly biodegradable	
Bis (2-ethylhexyl)phtalate	11600000	non biodegradable	plastisizer
2,6-di-tert-butyl-4-(dimethylaminomethyl)phenol	1900000	slowly degradable	
Recalcitrants in SAMBR2 permeate			
phenol 2,4-bis(1,1-dimethylethyl)	450000	new	
o-hydroxybiphenyl	1100000	non biodegradable	
diphenylamine	550000	new	
benzenemethanol, alpha-phenyl	600000	new	
benzophenone	1200000	slowly biodegradable	
benzenesulfonamide N-butyl	3000000	new	plastisizer
phenol 4,4'-(1 methylethylidene)bis	4900000	non biodegradable	
diisooctylmaleate	7700000	slowly biodegradable	
Bis (2-ethylhexyl)phtalate	10900000	non biodegradable	plastisizer
2,6-di-tert-butyl-4-(dimethylaminomethyl)phenol	500000	slowly biodegradable	
Recalcitrants in AMBR permeate			
phenol 2,4-bis(1,1-dimethylethyl)	700000	non biodegradable	
Thiophene,2,5-bis(2-methylpropyl)	200000	new	
diphenylamine	350000	slowly biodegradable	
benzenesulfonamide N-butyl	7550000	non biodegradable	plastisizer
1,2-benzenedicarboxylic acid,bis(2-methylpropyl)ester	900000	new	
tetracosamethyl-cyclododecasiloxane	500000	new	

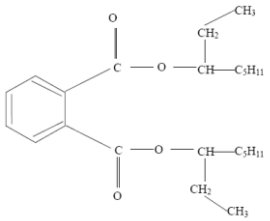
Bis (2-ethylhexyl)phtalate	6600000	slowly biodegradable	Plastisizer 
2,6 di-t-butyl-4-[3(2,3epoxypropylthio)propyl]	8400000	new	
Plastic scraps			
dimethylphtalate	150000		plastisizer
hexadecane	160000		
2-p-tolylpyridine	400000		
Tri(2-chloroethyl)phosphate	700000		
hexadecanoic acid, methyl ester	1800000		
dibutylphtalate	2650000		plastisizer
9-octadecenoic acid, methyl ester, e	2950000		
1,2 benzene dicarboxylic acid, dicyclohexyl ester	7900000		
decanedioic acid, bis (2 ethylhexyl)ester	8450000		
Erucylamide	5900000		

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Table 3. Compounds found by GC-MS analysis in the HR effluent, SAMBR1 permeate, SAMBR2 permeate, AMBR permeate and plastic scraps.