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Anaerobic Digestion of the Organic Fraction of Municipal Solid Waste in a two-stage membrane process¹.

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Abstract A batch of the Organic Fraction of Municipal Solid Waste (OFMSW) was treated in a two-step process with effluent recirculation comprising a novel hydrolytic reactor (HR) followed by a Submerged Anaerobic Membrane Bioreactor (SAMBR) operating at a stable permeate flux of 5.6 L/m².hr (LMH). A soluble COD removal higher than 95% was obtained from the SAMBR. The soluble COD as well as the Total Suspended Solids (TSS) did not build up due to efficient hydrolysis inside the SAMBR, and no VFA accumulation occurred due to the complete retention of methanogens by the membrane as well as the formation of syntrophic associations. Because of the microfiltration membrane in the second reactor a stabilized leachate was obtained from the very first days of the treatment and the highly stable process enabled shorter treatment periods compared to traditional leach bed processes. This experiment showed that the recycle of the stabilised leachate does not lead to a build up of SCOD. Size exclusion chromatography analysis confirmed that high molecular weight compounds were completely degraded and did not appear in the SAMBR permeate, and that low molecular weight fulvic-like and medium MW material were present in the permeate of the SAMBR but their concentration remained stable with time.

Keywords: Anaerobic digestion (AD); Submerged Anaerobic Membrane Bioreactor (SAMBR); Organic Fraction of Municipal Solid Waste (OFMSW); refractory organics; membrane fouling.

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INTRODUCTION

A major issue in the UK is the shortage of landfills where MSW is dumped. Another issue which is a consequence of landfills is the percolating rainwater that leads to the generation of a highly contaminated wastewater called leachate. Current technologies for treating leachates include aerobic biological reactors but this technology requires large footprints and high costs (Li and Zhao, 2003). Unlike aerobic composting, anaerobic digestion (AD) is an energy producing process that is becoming very attractive due to more restrictive legislation.

Many studies on the OFMSW involve the treatment of a batch in two successive tanks where the leachate from the first one (called a leach-bed or landfill cell) is sprayed over the top of the second tank after acidification has taken place (Vieitez and Ghosh, 1999). Leach bed systems are technically simple but require a large footprint which make them comparable to aerobic composting. Moreover, they suffer from a slow and limited solubilization because of channelling problems (Vandevivere *et al.*, 2003), and the absence of mixing which has been shown to be good because it ensures intimate contact between microorganisms and substrate, and because it can break the physical association existing in ligno-cellulosic material (Yadvika *et al.*, 2004). One technical shortcoming of leach bed and other batch systems, is the plugging of the perforated floor, resulting in the blockage of the leaching process. However, this can be alleviated by means of a bulking material such as wood chips (Vandevivere *et al.*, 2003). Another disadvantage is the instabilities resulting from an unbalanced population of microorganisms leading to souring of these reactors. A consequence is the very long period in order to stabilize the OFMSW. For instance, Vieitez and Ghosh (1999) took 295 days to treat a batch of OFMSW, Viéitez *et al.* (2000) took 524 days, He *et al.* (2005) took 105 days, Poggi-Varaldo *et al.* (2005) took 180 days, and Wang *et al.* (2006) took 98 days. They suggested that the long time required was possibly due to inhibition from low pH and end-product accumulation such as fatty acids. In contrast, shorter times and more reliable process performance can be achieved in a Sequential Batch Anaerobic Composting Process (SEBAC) as an inoculum from a mature landfill cell is used to provide a balanced population of acidogenic and methanogenic bacteria, and alkalinity to buffer pH (O'Keefe and Chynoweth, 2000). Some of these batch processes combine a UASB with a packing material or a membrane module in order to retain more bacteria. For instance, Jans *et al.* (1992) used an UASB combined with reverse osmosis and they achieved almost complete removal of COD. Another pertinent question related to 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. Recirculation of stabilised leachate in membrane bioreactors is not very well documented and it could significantly reduce the use of fresh water, and reduce the environmental impact of MSW disposal. On the other hand, there is little data regarding the flux that can be obtained in a SAMBR treating landfill leachate. Van Zyl *et al.* (2007) reported a flux of 2-3 LMH at 36 g TSS/L when treating synthetic petrochemical effluent using a submerged Kubota membrane. Zayen *et al.* (2008) have investigated the treatment of landfill leachate in an anaerobic side-stream MBR and the maximum flux through the ultrafiltration membrane was only 2.5 LMH. Rautenbach and Mellis (1994) also observed a flux drop from 27 to 7 LMH in 50 days operation with a spiral wound nanofiltration module external to an anaerobic MBR treating landfill leachate. The flux for a SAMBR treating leachate has been reported to be normally in the range 5-10 LMH (Robinson, 2005).

Based on these considerations, the aim of this work was to investigate: (i) the use of a novel anaerobic hydrolytic reactor where a stirrer moves inside a cylindrical perforated mesh enabling the HRT to be uncoupled from the SRT; (ii) the use of a microfiltration membrane submerged in the second anaerobic reactor where the leachate is stabilized and (iii) how is

that related to the degree of humification of the leachate in terms of size exclusion chromatography. The aim of this study was also to investigate the evolution with time of these refractory organics to see whether their concentration increases with time due to the oxidation of side-chains of lignin structures.

MATERIAL AND METHODS

Feedstock

The simulated OFMSW mixture used in this study consisted of 41% kitchen waste (KW), 11 % garden waste (GW) and 48% paper waste (PW) on a wet basis. Kitchen waste came from a canteen in Southampton University, UK. The left-overs were passed through a kitchen grinder and mixed in a large tank with a drill mixer and then frozen until the experiment. Garden waste was collected from the Downend Quarry centralised composting site near Fareham (Hampshire, UK) and were kept at 4°C until the experiment. The composition of the simulated paper waste used for the study is listed in Table 1. This composition comes from an assessment scheme for kerbside collection of dry recyclables undertaken by the district of Eastleigh in the UK (RRF, 2001). It was deemed a representative paper waste composition because Eastleigh has a good mix of socio-economic groups. Moreover, data of KW, GW and PW were given for summer and winter months, allowing us to see the variation (Mainly in garden waste) over the seasons and to calculate an annual average. Finally, Eastleigh has a well established dry recyclables collection of card, newspaper, cans, bottles etc and the data is set out so that actual refuse (Total MSW minus recyclables) is available. This is desirable as legislation says that all city councils in the UK now have to pick up at least 2 dry recyclables in their waste collections, meaning that Eastleigh refuse MSW is representative of future MSW in the UK. A feedstock of 10% Total Solids was then prepared by adding tap water in order to blend the mixture and obtain a homogeneous slurry. In other words, to prepare 1kg of feedstock at 10%TS, about 830 g of tap water was mixed with 18.6g of PW, 71g of KW and 82g of PW. About 84% of the dry matter was organic and the COD/VS ratio was found to be in the range 1.2 – 1.6 g COD/gram of volatile solid as listed in Table 2 with other properties.

Experimental Setup

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

Type of paper	%
Newspaper	21
Magazine	12
Office paper	8
Card and paper packaging	11
Cardboard	1
Card non packaging	0.6
Liquid carton	1.4
Tissue paper	15
Paper plate	15
Toilet paper	15

Table 2. Properties of the simulated feedstock of the Organic Fraction of Municipal Solid Waste.

Parameter (unit)	Value (standard deviation)
TS (%)	9.9
VS (%)	8.2-8.6
COD/VS	1.2-1.6
pH	6.3-6.9
TN (mg/g TS)	13.1 (0.4)
TP (mg/g TS)	1.3 (0.1)
Ca (ppm of TS)	38698.66 (4733.6)
Fe (ppm of TS)	2325.39 (266.3)
Na (ppm of TS)	2256.59 (265.5)
K (ppm of TS)	1848.02 (208.5)
Mg (ppm of TS)	821.34 (93.9)
Zn (ppm of TS)	588.17 (66.3)
Al (ppm of TS)	551.94 (66.9)
Mn (ppm of TS)	88.75 (10)
Cu (ppm of TS)	47.79 (5.4)
Co (ppm of TS)	45.16 (5.1)
B (ppm of TS)	25.73 (4.4)
Pb (ppm of TS)	8.93 (3.6)
W (ppm of TS)	6.83 (0.9)
Ni (ppm of TS)	4.73 (0.9)
Cr (ppm of TS)	4.2 (0.5)
Cd (ppm of TS)	2.1 (0.2)
V (ppm of TS)	<2.6
Mo (ppm of TS)	<2.6
Biodegradability (L CH ₄ STP/g VS)	0.216 (0.01)

The HR (12.2L 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 (Figure 1). Typical full scale plant include several consecutive units such a mechanical pre-treatment step where the particle size is reduced, a hydropulper where the process water is added to the waste and a post treatment step where the sludge is dewatered and the liquid process is further treated or recycled (Vandevivere *et al.*, 2003). The HR used in this work is novel in the sense that the particle size reduction, the anaerobic digestion and the dewatering steps were all combined in the same unit; the mechanical pre-treatment is effected by the action of the stirrer that tear up the fibers against the perforated mesh. The sludge is continuously separated from the process liquid due to the perforated stainless steel that only let pass small particles to the outer zone around the mesh where it is pumped to the SAMBR, hence achieving the uncoupling of the HRT and SRT. The excess leachate is returned to the top of the HR where it is mixed with the non solubilised waste in the inner zone of the HR. The stirrer moved inside the mesh allowing two pieces of rubber to rub against the perforated mesh. The speed of the stirrer was 40 rpm (Heidolph). In order to decrease further the particles size in the leachate an additional polypropylene mesh of 150 micron pore size (Spectrum Laboratories Inc.) was fitted to the existing stainless steel one. The HR was inoculated with 3 liters of sludge (TSS=2.7g/L, VSS=2.1g/L) from a CSTR fed on the same substrate at 10 days HRT.

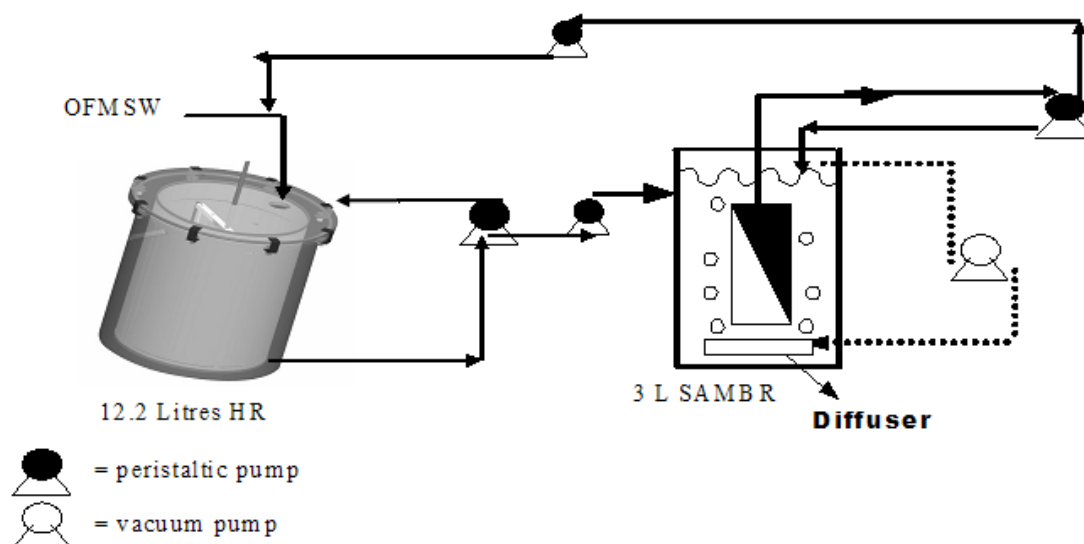


Fig 1. Schematic diagram of the 2-phase process. The full lines show the liquid line and the dashed lines show the biogas line.

The SAMBR was a 3 litre reactor fitted with a Kubota polyethylene flat sheet membrane of 0.1 m² of total surface and a pore size of 0.4 micron (Trzcinski and Stuckey, 2009). The biogas sparging rate was set at 5 L/min to minimize cake formation on the membrane. The Transmembrane Pressure (TMP) was recorded on a computer by means of a pressure transducer (Druck) fitted in the permeate line of the SAMBR. A more detailed schematic diagram of the SAMBR and a description of the equipment can be found elsewhere (Hu and Stuckey, 2006). The SAMBR was started up with an inoculum from a 4L stirred tank batch-fed on leachate from a 4 litre hydrolytic reactor at a HRT of 28 days. The TSS and VSS of the inoculum were 8.3 and 5.7g/L, respectively. The reactors used in this study were connected in series with the permeate of the SAMBR being recycled to the HR (Figure 1) in order to maintain the moisture and alkalinity of the system. Both reactors were maintained at 35 ± 1°C. The HR was loaded with 615 g of dry matter on day 1 (520 g VS), and with alkalinity

(NaHCO₃) at a concentration of 4g equivalent CaCO₃/L. The SAMBR was operated at a hydraulic retention time of 4.4 days and a solid retention time of 300 days.

Analytical Methods

The measurement of pH (Jenway), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Fixed Suspended Solids (FSS), and Chemical Oxygen Demand (COD) was carried out as described in Standard Methods (APHA, 1999). The Soluble COD is defined as the fraction centrifuged at 13,000 rpm for 20 minutes and then filtered through a 0.2 microns filter. For the heavy metals of the feedstock the solid sample and blank were firstly digested in Aqua Regia according to the Standard Methods and then analyzed with PerkinElmer Optima 2000 DV Inductively Coupled Plasma - Optical Emission Spectrometer in triplicate. For the Total Phosphorus (TP) content of the feedstock, the solid sample was first digested in Aqua Regia and then analyzed using the vanadomolybdophosphoric acid colorimetric method described in Standard Methods. The absorbance was read on a spectrophotometer at 470 nm and the coefficient of variation for three replicates was 0.6%. The measurement of Total Nitrogen (TN) was carried out according to the TN kit manual instruction from Hach Lange GmbH. The coefficient of variance for ten identical samples was 5.5%. Volatile fatty acids (VFAs) were measured using a Shimadzu Gas Chromatograph with a flame-ionised detector and a SGE capillary column (12mx0.53mm ID-BP21 0.5µm). The composition of biogas was determined using a Shimadzu GC-TCD fitted with a Porapak N column (1500x6.35 mm). For size exclusion chromatography (SEC), an Aquagel OH-40 column (Polymer Labs) was used with deionised water as eluent delivered at a flowrate of 0.5 mL/min. The sample volume was 50µL, and the column was maintained at ambient temperature with a Shimadzu UV detector set at 254 nm. Unbranched standards of polyethylene oxide (PEO) and polyethylene glycol (PEG) and glucose were used to calibrate the system, hence the results obtained are quoted relative to these linear standards detected by a refractive index detector. The anaerobic biodegradability or Biochemical Methane Potential (BMP) of the feedstock and the leachate was analyzed in triplicate by Owen *et al*'s. (1979) bioassay method.

RESULTS AND DISCUSSION

Performance of the HR

The soluble COD (SCOD), total COD (TCOD) and VFAs in the HR effluent peaked together around day 12 (Figure 2, Panel A). From day 12 onwards, the total VFA concentration decreased slowly, as well as the SCOD, but the TCOD remained in the range of 15 to 20 g/L. This is due to the lignin that is recalcitrant to hydrolysis and the remaining cellulose bonded to the lignin which is only slightly accessible to enzymes. After day 34, the percentage of acidification calculated as the ratio of VFAs (expressed as COD) to Soluble COD (data not shown) also dropped suggesting that the remaining soluble organics were hardly being hydrolysed any further into fermentable sugars and subsequently converted to VFAs. The pH in the HR dropped to 5.85 when the VFAs peaked and then returned slowly to neutral as the VFAs decreased. A more severe pH drop was avoided due to the recycle of the accumulated alkalinity from the SAMBR, which highlights the advantage of recycling the effluent. The main VFA produced was acetate at the beginning of the batch (Figure 3) and its concentration (≈3g/L) was far from inhibitory, while the pH of 6 did not inhibit acidogenesis as propionate still increased until day 15. During the fermentation step, 80% (on a COD basis) of the amino acids and sugars are converted to acetate, H₂ and CO₂, whereas 20% are converted to intermediary products such as propionate and butyrate (Pavlostathis and Giraldo-Gomez, 1991).

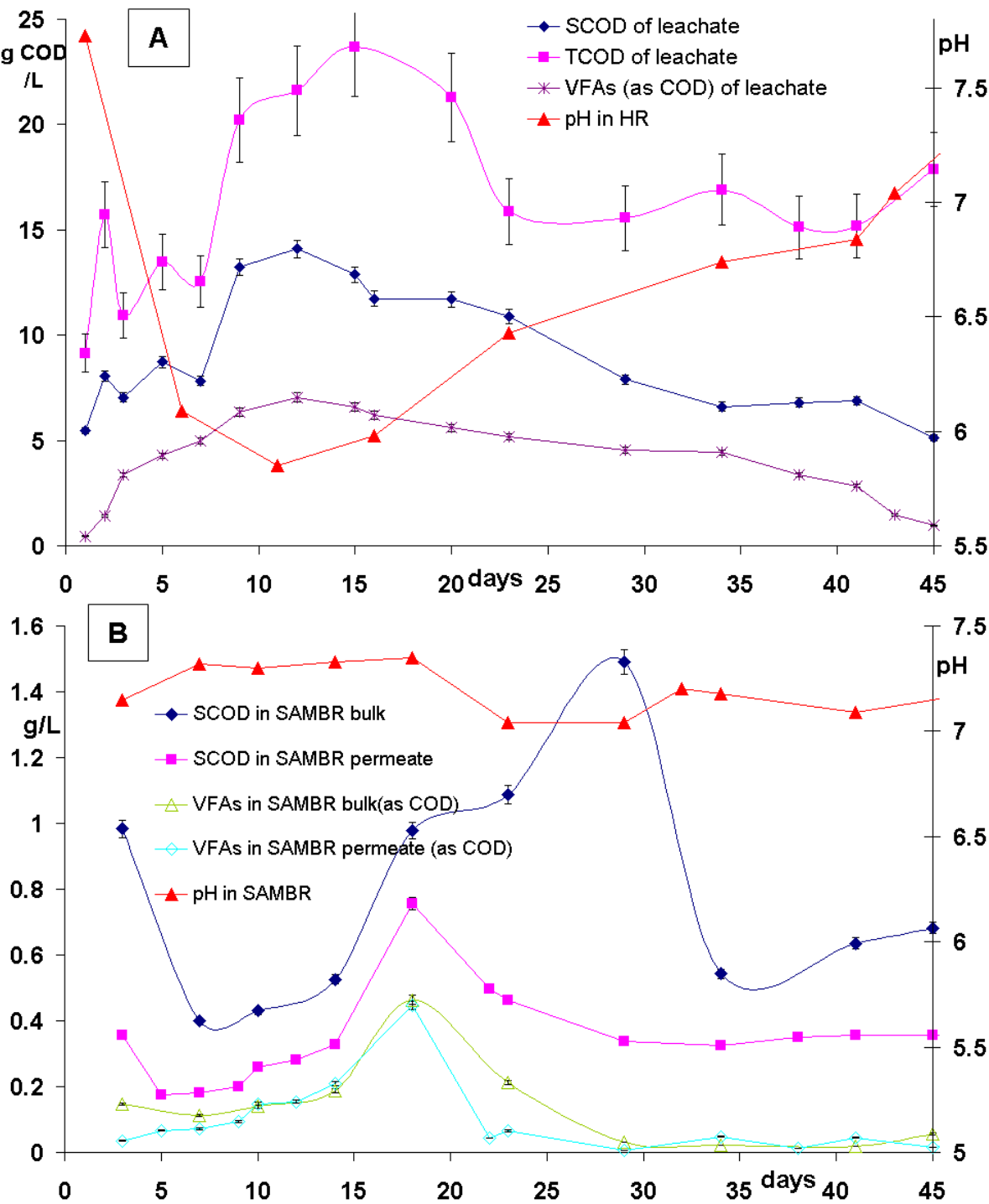


Fig. 2. (A) SCOD, TCOD and VFAs (as COD) concentrations in the hydrolytic reactor effluent (left axis). pH in the HR (right axis). (B) SCOD and VFAs (as COD) in the SAMBR bulk and permeate (left axis). pH in the SAMBR (right axis).

226 Propionate concentration was constant (2 g/L) from day 12 until day 34 as it is degraded at a
227 lower rate than acetate. This also indicates that during those 2 weeks, propionate utilisers
228 might not have been sufficient in the HR and could not cope with the load due to their slow
229 growth kinetics (Houwen *et al.*, 1990). Propionate oxidation is know to be the bottle neck
230 reaction during the methanogenesis of complex substrates because their growth rate is only

0.13 d⁻¹ (Wallrabenstein *et al.*, 1995). As the H₂ partial pressure increases, the NADH is used to produce more reduced products such as propionic and butyric acids as the conversion of

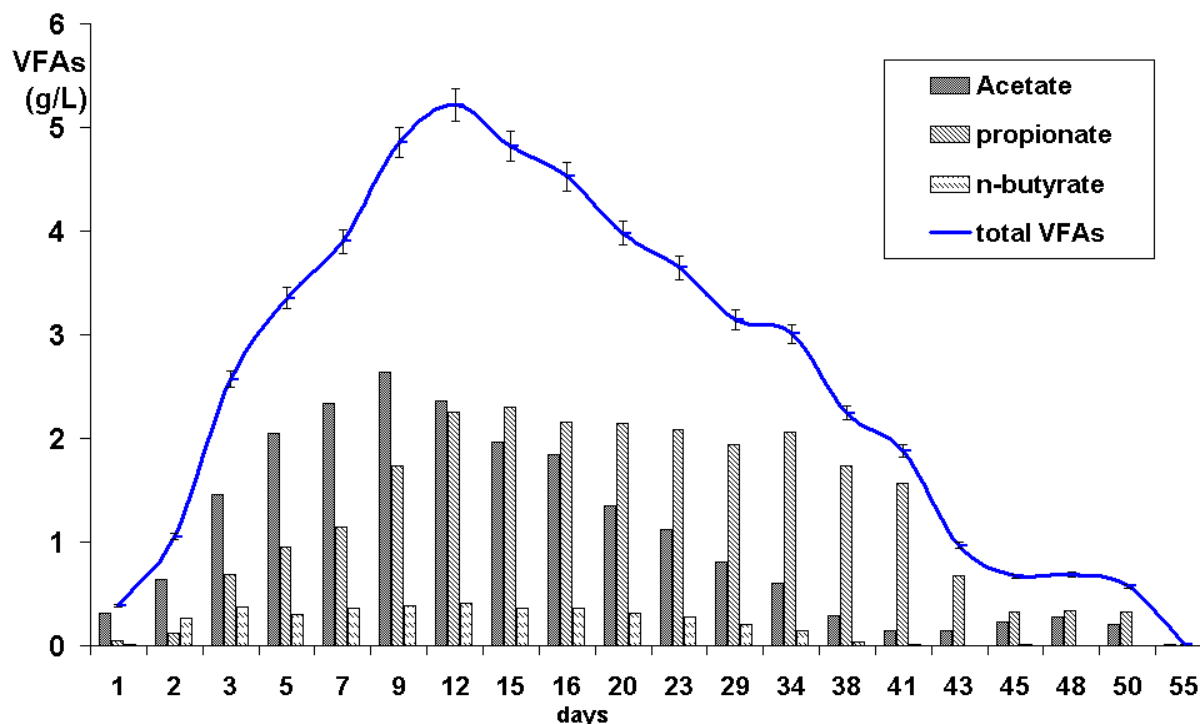


Fig 3. Total Volatile Fatty Acids concentration and distribution in the hydrolytic reactor effluent.

acetate become energetically unfavourable. With elevated hydrogen levels the production of propionic acid predominates at neutral pH values, but as the pH level becomes acidic then the production of butyric acid will begin to predominate (McCarty and Mosey, 1991). The levels of propionic and n-butyric acids in the HR are due to large interspecies distances that reduced the conversion rate of hydrogen. This can in turn be explained by the shear and agitation existing in the HR for hydrolysis purposes and this can cause aggregate disruption. Another explanation for the stable propionate concentration could be a dilution effect as the VFA rich effluent was continuously fed to the SAMBR and the SAMBR permeate was low in VFAs: maximum 450 mg/L (as COD) on day 18 (Figure 2, Panel B). Acetic acid concentration started to decrease after day 9 due to acetoclastic methanogens and this was associated with the methane percentage in the HR headspace that increased linearly from 0% on day 7 to 20% on day 36 (data not shown). This evolution could however not be correlated with an increase in the gas production rate because it was not measured. Propionate concentration started to decrease after day 34. Among the other VFAs, n-butyrate never exceeded 410 mg/L on day 12. The other VFAs were insignificant with concentrations below 100 mg/L throughout the batch (data not shown). After day 43, very few VFAs were produced, and eventually VFA concentrations dropped to zero on day 55.

BMP of the total and soluble fraction of the leachate. Biochemical methane potential (BMP) analyses (Owen *et al.*, 1979) were carried out on the leachate from the HR on day 9 to assess its biodegradability, and to gain more insight on the fate of particulate COD present in the

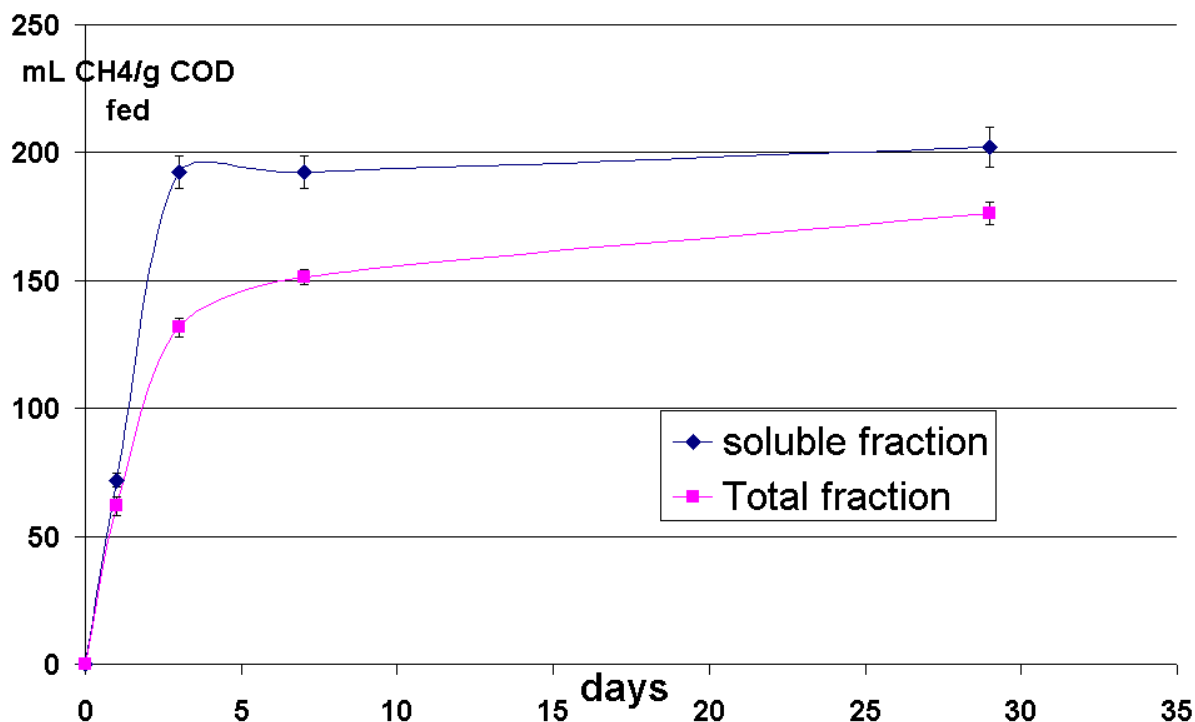


Fig 4. BMP of the soluble fraction and the total fraction of leachate on day 9 of the batch test. The error bars show the standard deviation.

leachate. The characteristics of the leachate on that day were a TCOD concentration of 20,220 mg/L, a SCOD/TCOD ratio of 0.65 and a VFAs/SCOD ratio of 0.48. Figure 4 shows the BMP of the soluble fraction and the total fraction of the leachate containing particles. Based on the theoretical methane value of 1 g COD (395 mL at 35°C), the BMP test revealed that 51% (=202/395) of the SCOD in the leachate was converted to methane and moreover 93.4% of the methane produced was converted from the VFAs initially present in the sample, while only 6.6% was converted to methane through the degradation of fermentable sugars present in the leachate. This evidences the refractory character of the SCOD. Regarding the total fraction of the leachate, all the methane produced originated from the VFAs and no methane was produced from the particulate COD nor the remaining SCOD. This confirms the refractory character of the ligno-cellulosic fibers in the leachate which means that the suspended solids in the leachate were likely to build up in the SAMBR. Nevertheless, the BMP test showed also that the SCOD and particulate COD were not inhibitory to the methanogens as no lag phase was observed during the test and the two curves displayed a similar initial rate of production.

Performance of the SAMBR

In the SAMBR, the pH remained very stable with values ranging from 7.04 to 7.35 (Figure 2B). The comparison with the pH drop in the HR in Figure 2A shows that the SAMBR was not affected by the VFAs production in the HR and a physical and temporal separation of the acid production and degradation stages leads to a stable process. The pH higher than 7 in the SAMBR is essentially due to the VFAs degradation in the SAMBR that takes place without any washout of methanogens thanks to the membrane.

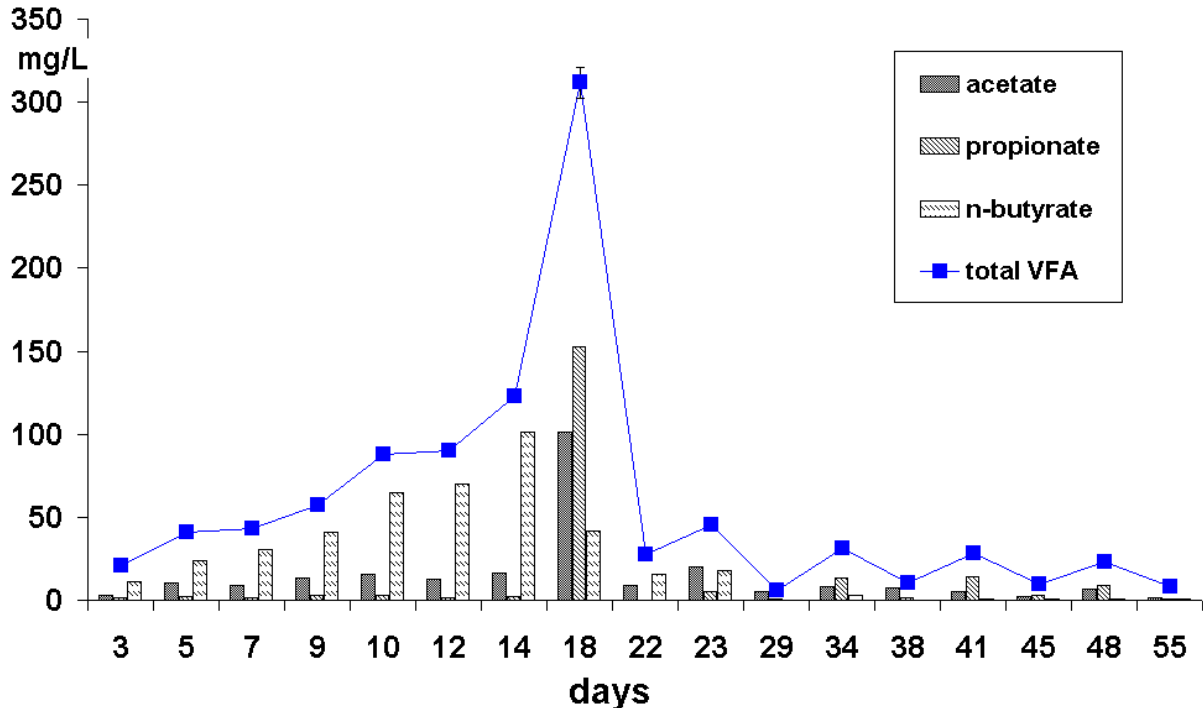


Fig 5. Total VFAs concentration and distribution in the permeate of the SAMBR.

The VFAs concentration in the permeate of the SAMBR is shown on Figure 5 and it can be seen that n-butyrate slowly increased during the first two weeks of the batch to reach a maximum of 100 mg/L on day 14, and then it decreased indicating that the acetogens such as *Syntrophomonas wolfei* were not in sufficient amount to convert all the n-butyrate present in the leachate. Acidogens are known to be fast-growing bacteria with a minimum doubling times of around 30 minutes (Mosey, 1983). Therefore, the slow build up of butyrate was very likely to be due to a hydrogen partial pressure superior to 10^{-4} atm, but no attempt was made to measure hydrogen. The decrease in n-butyrate associated with a rapid increase in acetate and propionate can be explain by the growth of hydrogen-consuming acetogenic bacteria such as *Clostridium aceticum* or by the formation of small granules where the hydrogen-producing acetogenic bacteria and hydrogen-consuming bacteria are close enough to create syntrophic associations. The data demonstrate that butyrate and propionate could be degraded after 2 weeks due to the complete retention of bacteria in the SAMBR. The formation of successful hydrogen interspecies transfer and the resulting butyrate and propionate degradation was thus successful in the SAMBR which was not possible in the HR as demonstrated by the VFAs profiles.

Throughout the batch, the SCOD inside the SAMBR and in its permeate remained below 1500 and 800 mg/L, respectively (Figure 2B). Furthermore, after day 18, the permeate SCOD remained below 370 mg/L. The SCOD removal in the SAMBR (based on the SCOD in the HR effluent and the SAMBR permeate SCOD in Figure 2) was greater than 95% throughout the experiment. The methane content of the biogas reached 57% after only seven days emphasizing the rapid start up of the SAMBR, and progressively increased through the experiment to reach 67% from day 26 onwards,.

TSS, VSS and FSS

The suspended solids were measured in the bulk of the SAMBR and are shown in Figure 6. The inorganic fraction (FSS) increased at the beginning of the batch which indicates that inorganic salts were transferred to the SAMBR as well as volatile suspended solids. In the

SAMBR, TSS, VSS and FSS increased significantly from 8.3 to 21, 5.7 to 14.7 and 2.5 to 6.3 g/L, respectively, which is almost a threefold increase. This was undoubtedly due to the lignin that is difficult to solubilise and build up in the SAMBR. Then around day 20, the three

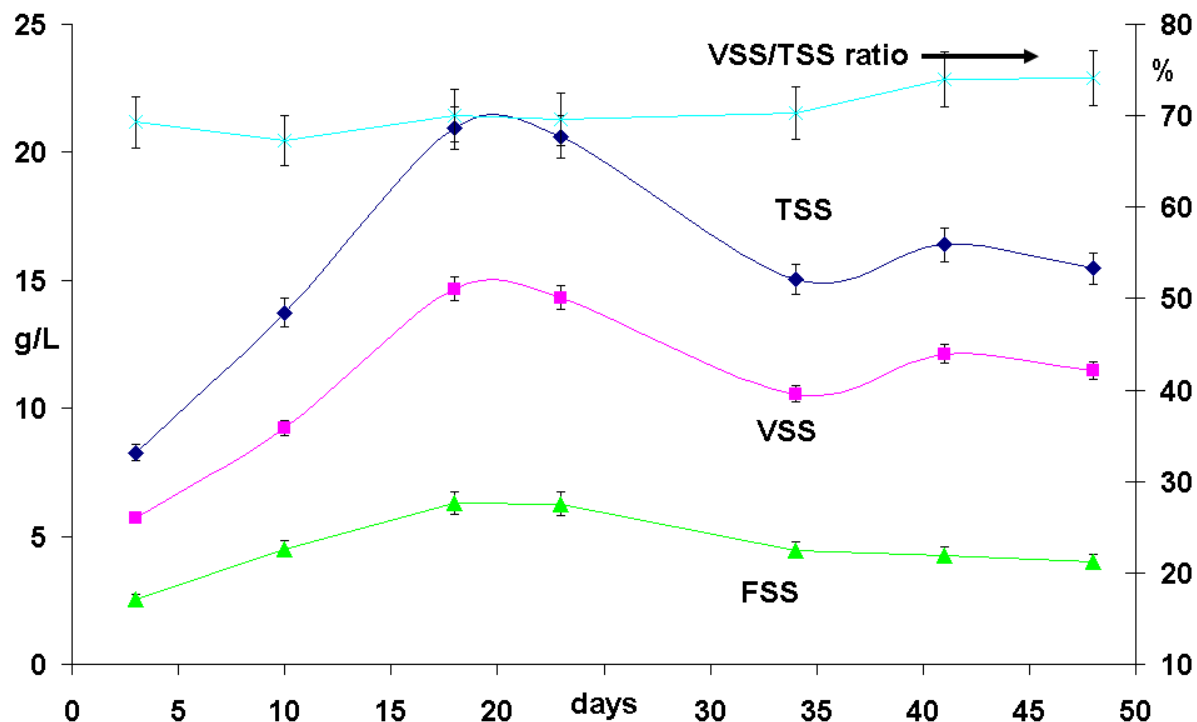


Fig 6. Evolution with time of TSS, VSS and FSS in the SAMBR.

parameters decreased and plateaued, indicating there was a further hydrolysis taking place in the SAMBR. This was linked with an increase in the SCOD in the bulk of the SAMBR (Figure 2B). Eventually, the solids in suspension and the SCOD in the SAMBR remained constant demonstrating the refractory character of the particulate remaining COD, which is consistent with the BMP test performed on the total fraction of the leachate in Figure 4. Interestingly, FSS did not accumulate in the MBR as they seemed to stabilize at 4 g/L. This means that inorganic compounds are solubilised and returned to the HR at the same rate as the FSS enter the SAMBR. Based on the FSS in both reactors, it was found that FSS in the overall process decreased with time because only the inorganics in suspension were measured. With time, the inorganics are transformed into their soluble forms and thus become part of the FDS fraction (Fixed Dissolved Solids) which was not measured.

Size exclusion chromatography

It is well known that landfill leachate contains lignins, humic and fulvic acids which have a wide molecular range distribution that might vary from as low as 2 to perhaps 300 kDa

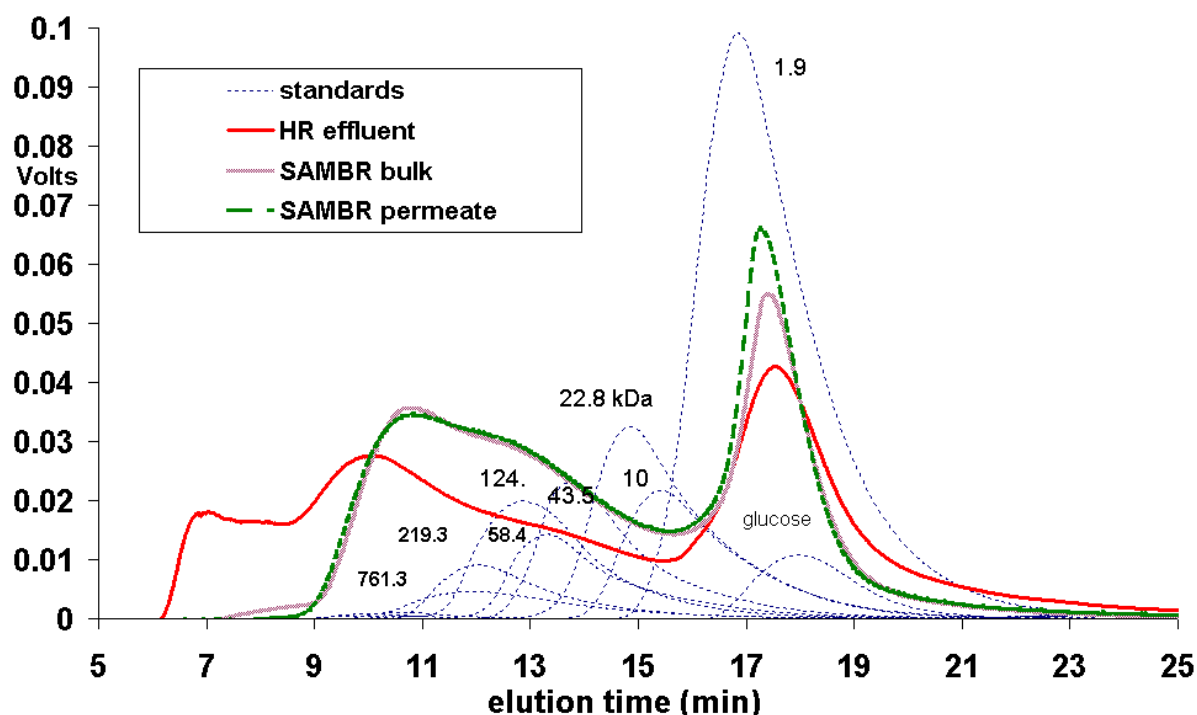


Fig 7. Size exclusion chromatograms of standards, HR effluent, SAMBR bulk and SAMBR permeate taken on day 29 of the batch treatment of the OFMSW.

(Stevenson, 1982). Figure 7 shows the size exclusion chromatograms of the HR effluent, SAMBR bulk and permeate on day 29 of the batch treatment which was deemed representative. Standards of PEO and PEG up to 761.3 kDa were run to calibrate the system and a standard of glucose (0.18 kDa) was run as well. In size exclusion chromatography (SEC), high molecular weight (MW) compounds should elute from the column first and hence appear at low retention times, whilst small molecules, because of their deeper diffusion into the gel, should take longer to elute, therefore appearing at longer retention times. It should be born in mind that only the organics that absorb UV light at 254 nm could be detected in the results. These organics are aromatic molecules and are refractory to anaerobic degradation. It can be seen from Figure 7 that the leachate produced by the HR contained very high MW compounds (less than 7 minutes elution time) as these were out of the calibration range. Interestingly, these high MW were not present in the SAMBR and its permeate which means that these were degraded in the SAMBR. Molecules eluting at 8 minutes were present at a low concentration in the bulk of SAMBR but not in its permeate due the membrane rejection. Medium MW molecules (between 9 and 13 minutes elution time, i.e. down to 58.4 kDa) were also detected but not as a nice peak such as the linear standards because of the aromatic properties of the samples. Although the Y-axis in Figure 7 represents the voltage recorded by the UV detector, it can be assumed that the signal is proportional to the concentration of molecules absorbing light at 254nm. With this in mind, the medium MW (between 9 and 13 minutes elution time) concentration was greater in the SAMBR due to the hydrolysis of the high MW components present in the HR effluent. Low MW (between 16.9 and 18 minutes elution time, i.e. between 1.9 kDa and 180 Da) appeared as a narrow peak with a higher concentration in the SAMBR permeate due to a further stabilization of the fulvic-like materials in the SAMBR.

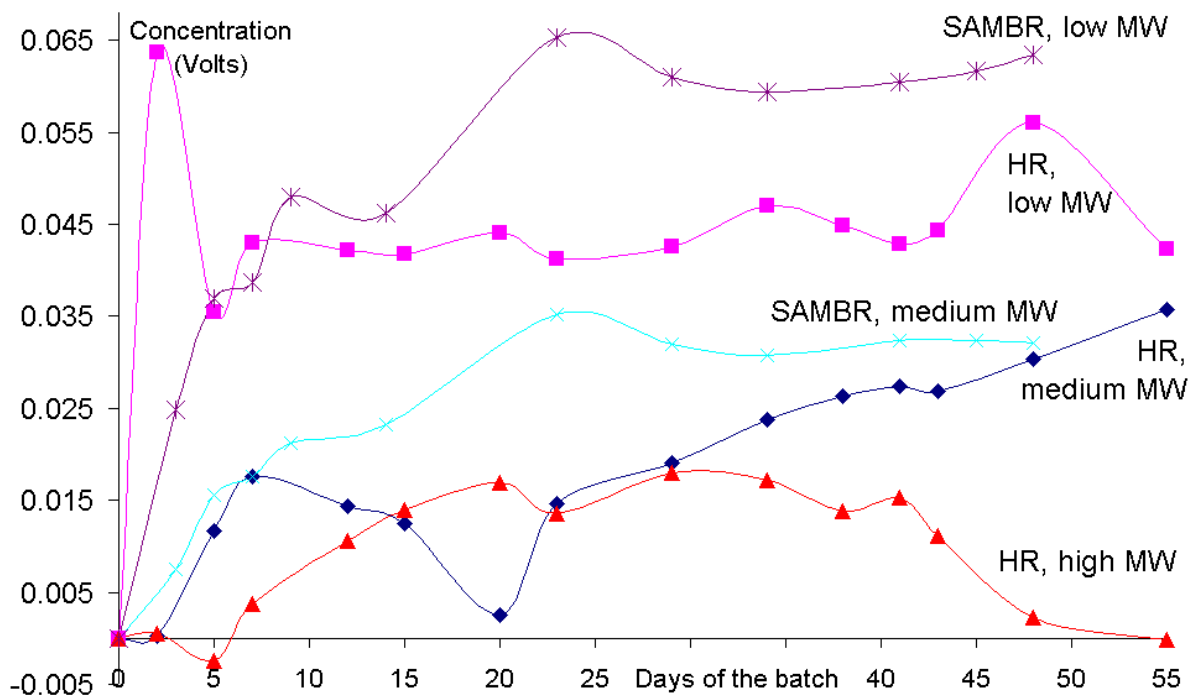


Fig 8. Evolution of concentration of different groups of molecules during the batch treatment of the OFMSW.

Samples of the HR effluent and SAMBR permeate were taken regularly during the batch in order to investigate the evolution with time of the molecular weight (MW) distribution of the reactors effluent. Figure 8 reveals that high MW compounds (less than 7 minutes elution time) were present in the HR effluent but they were slowly degraded throughout the batch. These molecules are carbohydrates and hydrolysable amino acids with unknown MW as they were out of the calibration range. These high MW molecules did not appear in the SAMBR permeate which was due to their complete hydrolysis to fermentable sugars or to recalcitrants molecules with lower MWs. Molecules of medium MW (between 9 and 13 minutes elution time) slowly appeared in the HR effluent but appeared first and at higher concentrations in the SAMBR permeate due to the long solid retention time in the SAMBR (300 days), and possibly because of the greater enzymatic activity resulting from the stable pH in the SAMBR (Figure 2B). Furthermore, the concentration of these medium MW molecules kept increasing in the HR effluent whereas their concentration remained stable in the SAMBR permeate after about 20 days which shows that they were slowly hydrolyzed in the bulk of SAMBR. Low MW compounds (between 1.9 kDa and 180 Da) were also observed in the HR effluent throughout the batch treatment but their concentration remained relatively constant. Their concentration remained also relatively constant with time in the SAMBR permeate, but at a higher concentration than in the HR effluent demonstrating again that the leachate was further stabilized in the SAMBR.

Flux and Transmembrane pressure

Several flux experiments were carried out regularly during the continuous feeding of the SAMBR. The experiment consisted in increasing stepwise the flux until a rapid increase in TMP was observed. This stepwise increase in the flux has been used by other researchers to determine the critical flux (Jeison and Van Lier, 2006). High TMPs should be avoided as it translates into the formation of a cake layer. This would mean that for the same pumping costs less permeate can be extracted from the SAMBR, thus less leachate would be treated per

unit of SAMBR volume. Therefore, it is important to minimize the TMP during the treatment of leachate in the SAMBR.

Determination of the critical flux. Figure 9A displays the evolution with time of the TMP between days 21 and 29 during which the MLTSS remained relatively constant between 15 and 20 g/L so that a proper flux/TMP analysis could be performed. The TMP before day 21 was virtually zero and was thus omitted from Figure 9A. On day 21 the TMP rose sharply when it was attempted to operate at a flux of 7.2 LMH. When the flux was restored to 3 LMH, the TMP went back to low values. On day 23, the flux was set at 5.6 LMH for a few hours and the TMP reached a plateau at about 175 mbar. But when it was shocked to 7LMH, the TMP more than doubled suggesting that this flux was above the critical flux. After a few hours the flux was set back at 5.6 LMH and even though the TMP remained high for several hours, it eventually returned to 100 mbar but at a lower rate than on day 21. This indicates that a fouling layer had taken place but after few hours of scouring it could be removed even at a flux of 5.6 LMH which indicates a reversible fouling at that specific flux.

Effect of the sparging rate on the flux. After returning at steady state at low TMP values at a flux of 5.6 LMH, the effect of the sparging rate was investigated on days 25 and 26. A lower sparging rate would be an advantage as it will lower the operating costs of the SAMBR. This reduction in sparging rate also led to a sharp increase in TMP values to 450 and 300 mbar on day 25 and 26, respectively. This highlights the importance of the sparging rate in the SAMBR to promote turbulence and decrease the resistance associated with polarization layer (Choo and Lee, 1998). Eventually, the TMP returned to low values after lowering the flux to 3 LMH and set the sparging rate back on 5 LPM. From day 40 to day 44, the SAMBR was operating at a flux of 5.6 LMH with virtually zero TMP and this was obtained with a relatively high MLTSS of 16.4 g/L. This flux was sustainable with no TMP change and can therefore be considered as below the critical flux. When operating at a flux of 7 LMH the TMP always skyrocketed which indicates that the critical flux was around 6 LMH.

Effect of operation time on the flux. On day 44, an identical experiment was carried out according to the same stepwise increase in flux (Figure 9B). The TMP rose suddenly but returned to 50 mbar when the flux was reset at 5.6 LMH. On day 47, the flux measured manually was exactly the same as on day 40 meaning that the experiment on day 44 did not have any detrimental impact on the flux. In contrast, on day 50 the TMP could not return to 0 but remained around 100 mbar even 2 days after that the shock took place, indicating an irreversible fouling (Figure 9B). This is typical of several cycles where the flux is increased and then decreased and this is called the hysteresis effect (Howell *et al.*, 2004). The hysteresis effect means that fouling will slowly occur because there is a residual layer of fouling that remains after each cycle. Li *et al.* (2003) also concluded that the removal of the cake strongly depend on its age; if the cake existed for a short period of time, the lift forces due to surface shear can break some of the enmeshed bonding between the bacteria, allowing the removal of the cake in the form of flocks. On the other hand, if the cake has been built up for a longer period, the possibility of breaking the enmeshment is reduced.

A comparison of the TMP curve on days 21, 44 and 50 in Figure 9C shows that the rate of increase is similar for the three days, but nonetheless the extent of fouling is getting worse with time as indicated by the TMP that reached 500 mbar in the case of day 50. Due to the compaction of the cake, the TMP did not return to 0, but remained at 150 mbar showing the slow and irreversible fouling occurring during the leachate treatment in the SAMBR. The progressive fouling was due to the colloids and recalcitrants low molecular weight COD that

are produced in the SAMBR as demonstrated by the SEC data. The fouling can also be explained by non homogeneous scouring of the membrane. Figure 10 shows the Kubota membrane at the end of the run and it can be seen that only one side was properly scoured by the rising bubbles. This was due to the holes in the diffuser that was clogged by an aggregate of sludge and stone which could be an inorganic precipitate such as struvite or calcium carbonate. Only the first hole remained unclogged which explain why the membrane was unevenly scoured, which is the reason why the working flux was limited to 5.6 LMH.

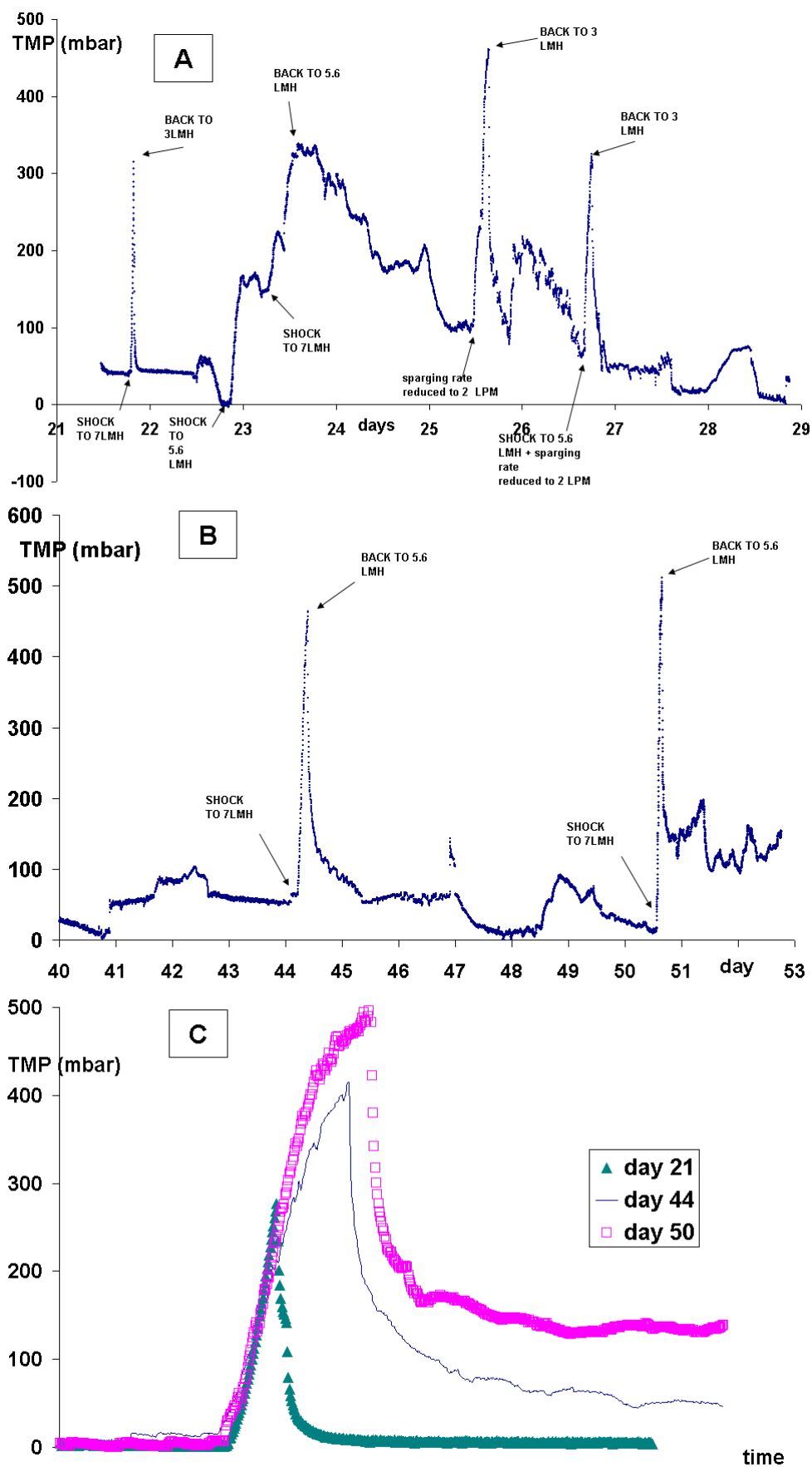


Fig 9. (A) Evolution with time of the transmembrane pressure (TMP) between days 21 and 29. (B) Comparison of TMP evolution after a flux step increase on day 44 and day 50. (C) Comparison on the same time scale of the TMP slope during the flux step increase and the final TMP value.



Fig 10. (left) Kubota partially scoured by biogas bubbles. (right) diffuser located at the bottom of the SAMBR with only the far left hole remaining open for gas bubbles formation.

CONCLUSIONS

The results showed that the treatment of a batch of OFMSW can take place quicker than conventional leach-bed because of an efficient hydrolysis in both reactors, and the complete retention of the slow-growing microorganisms using a membrane in the second reactor without significant flux decline. In particular,

- A very stable process is obtained due to the time and space separation in two different reactors; while the solids were hydrolyzed in the first reactor and VFAs concentration was increasing during the first ten days of the batch, the slow-growing microorganisms have time to build up in the SAMBR.
- The pH in the SAMBR showed that the SAMBR was not under stress, and the VFA concentration showed that propionate and butyrate could be completely degraded after 2 weeks of operation because syntrophic associations were formed in the SAMBR. Hence, the SAMBR could be added to existing designs to accelerate the start-up.
- An irremediable pH drop in the HR was avoided thanks to the recycling of the SAMBR permeate containing the alkalinity.
- SCOD did not build up in the SAMBR showing that the membrane acted as a barrier against large molecules and allowed only the non degradable ones to pass, thereby providing a stabilized leachate from the very first days of the treatment whatever the SCOD and VFAs content of the HR leachate.
- Size exclusion chromatography revealed that high MW compounds were completely degraded and did not appear in the SAMBR permeate. The end-products of the process were medium MW humic acids as well as low MW fulvic acids, but their concentration remained constant with time.
- The tests on the flux have shown that the operation at a flux of 7.2 LMH was not sustainable as TMP rose systematically to 350 - 450 mbar. However, a sustainable flux of 5.6 LMH was obtained with low TMP.

ACKNOWLEDGMENTS

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Figure 1

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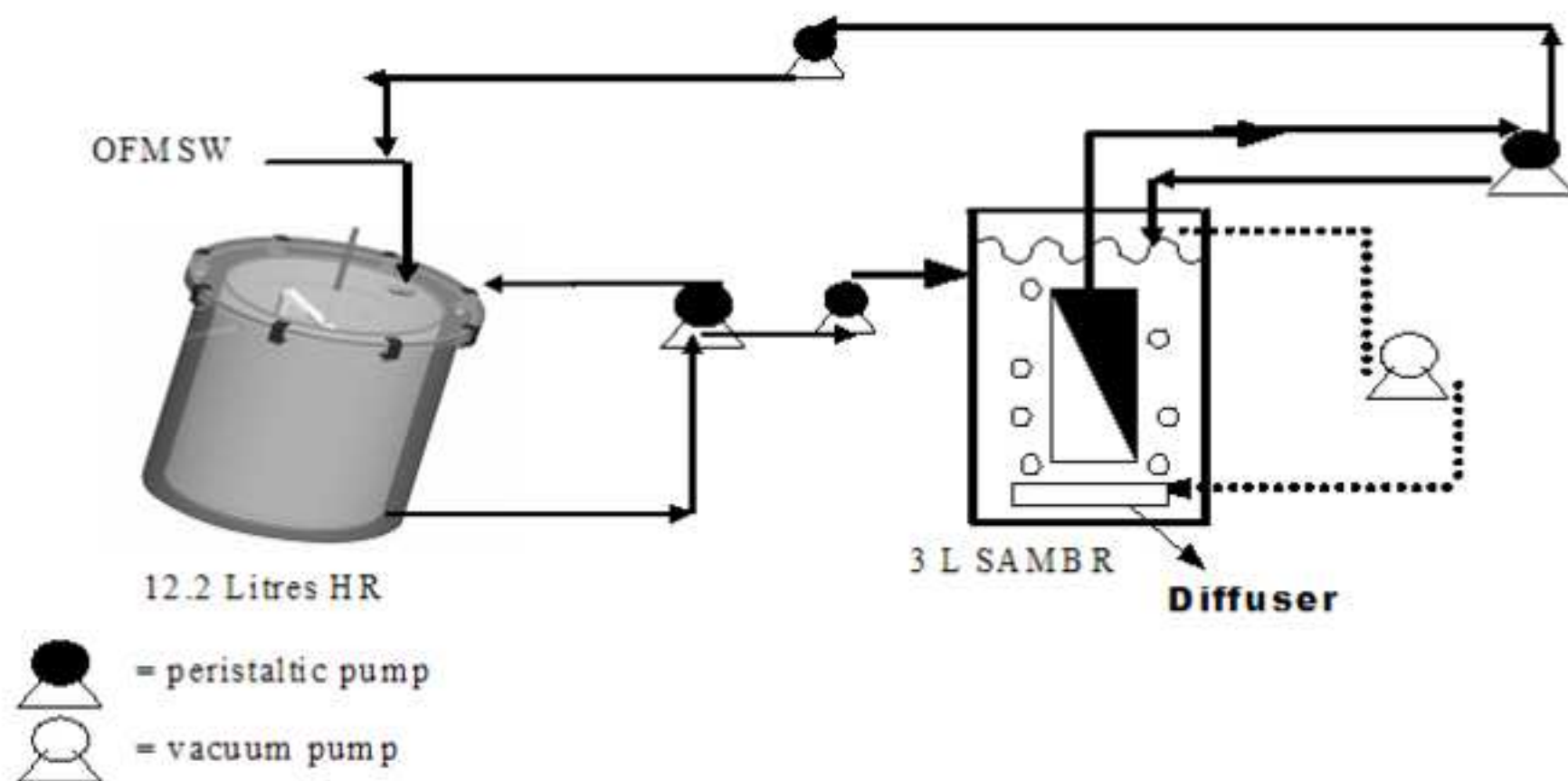


Fig 1. Schematic diagram of the 2-phase process. The full lines show the liquid line and the dashed lines show the biogas line.

Figure 2
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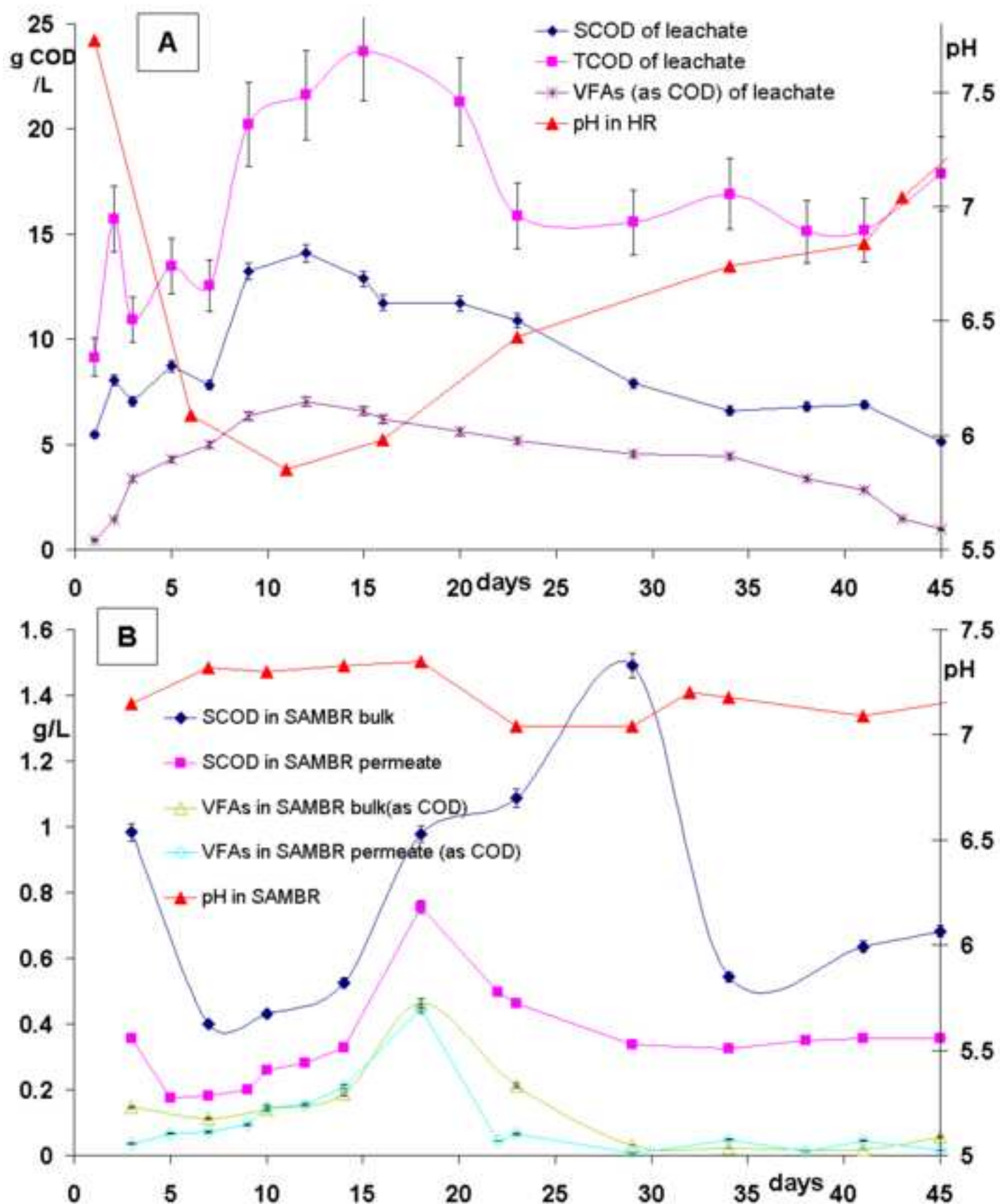


Fig. 2. (A) SCOD, TCOD and VFAs (as COD) concentrations in the hydrolytic reactor effluent (left axis), pH in the HR (right axis). (B) SCOD and VFAs (as COD) in the SAMBR bulk and permeate (left axis), pH in the SAMBR (right axis).

Figure 3
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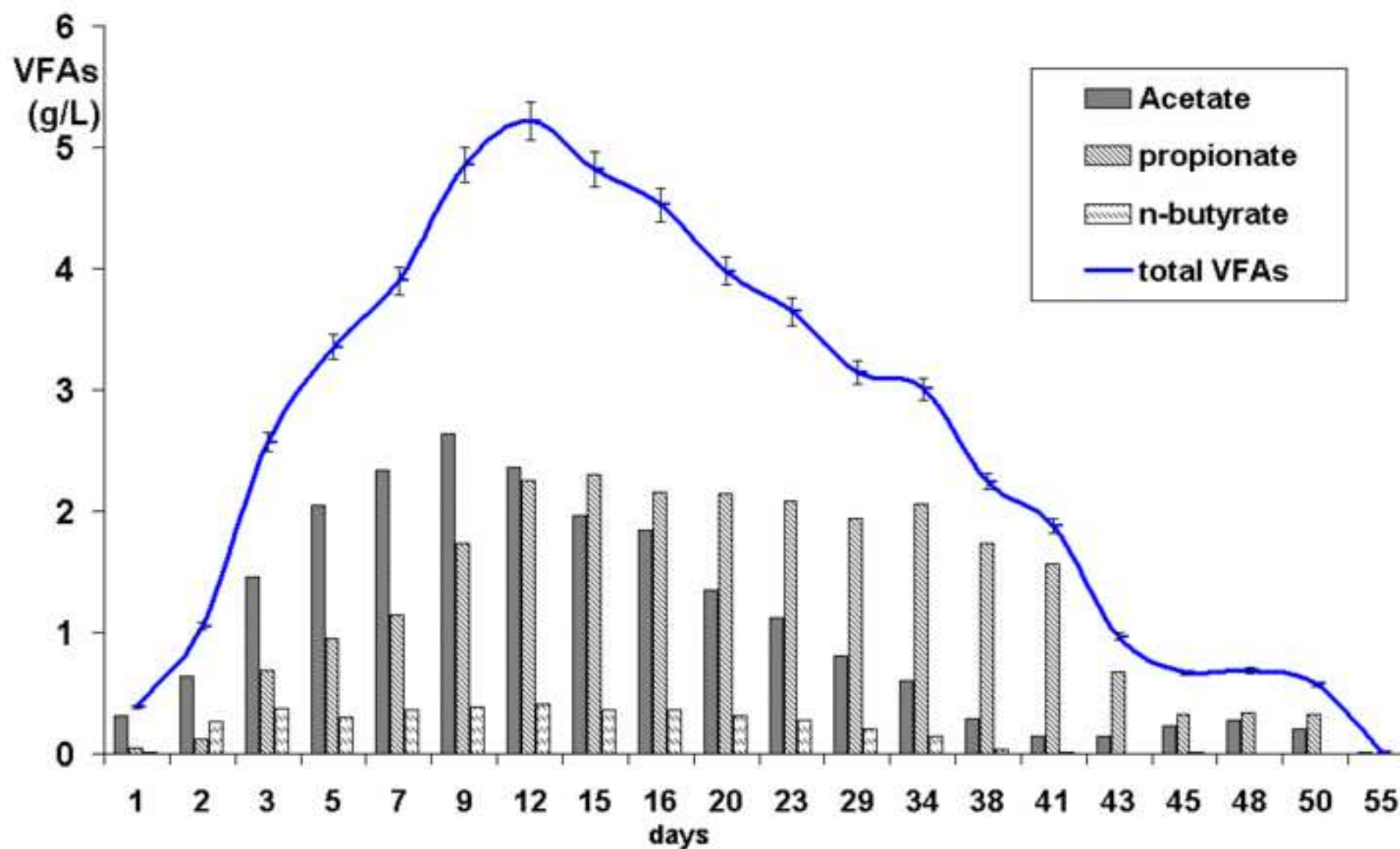


Fig 3. Total Volatile Fatty Acids concentration and distribution in the hydrolytic reactor effluent.

Figure 4
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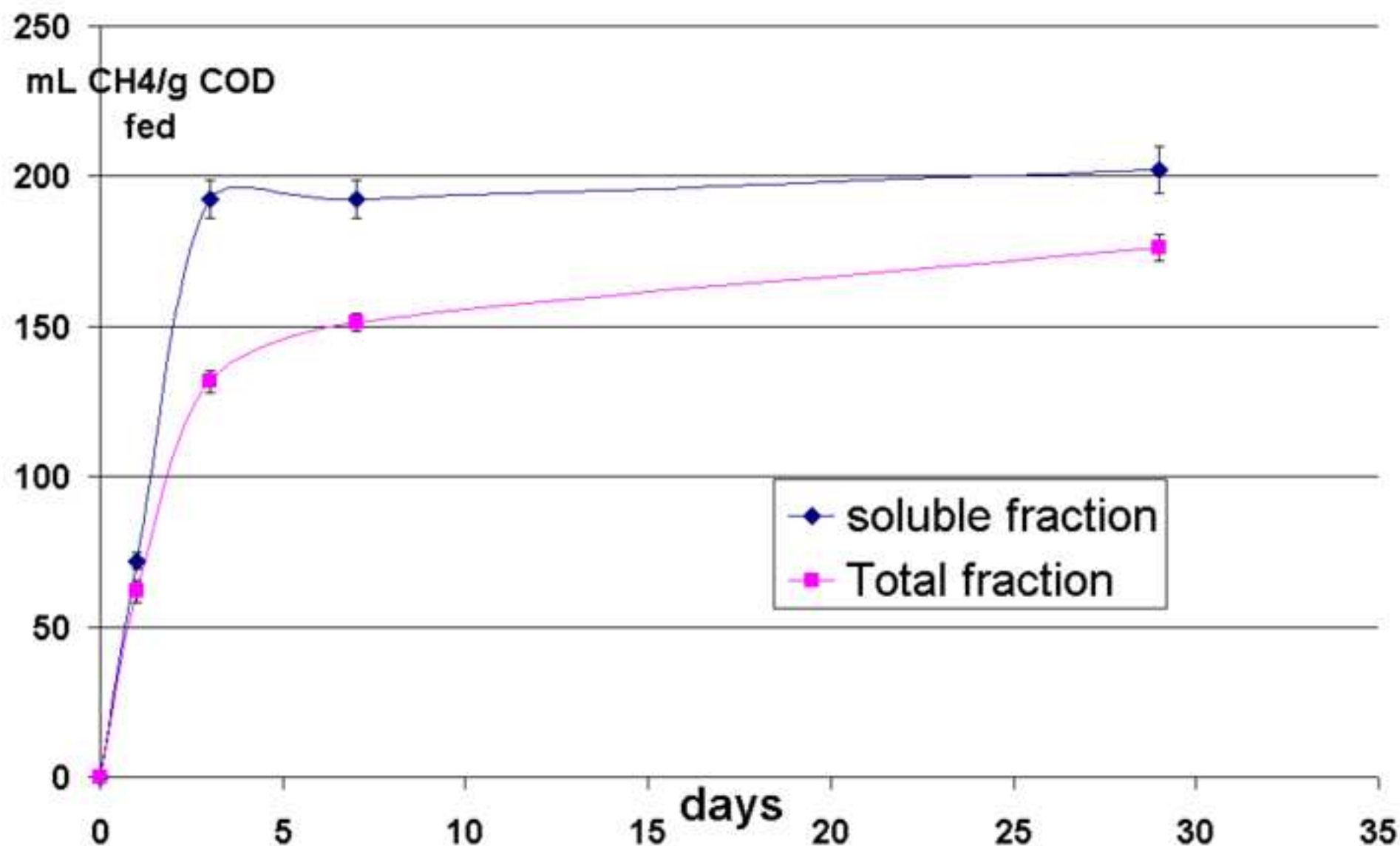


Fig 4. BMP of the soluble fraction and the total fraction of leachate on day 9 of the batch test. The error bars show the standard deviation.

Figure 5
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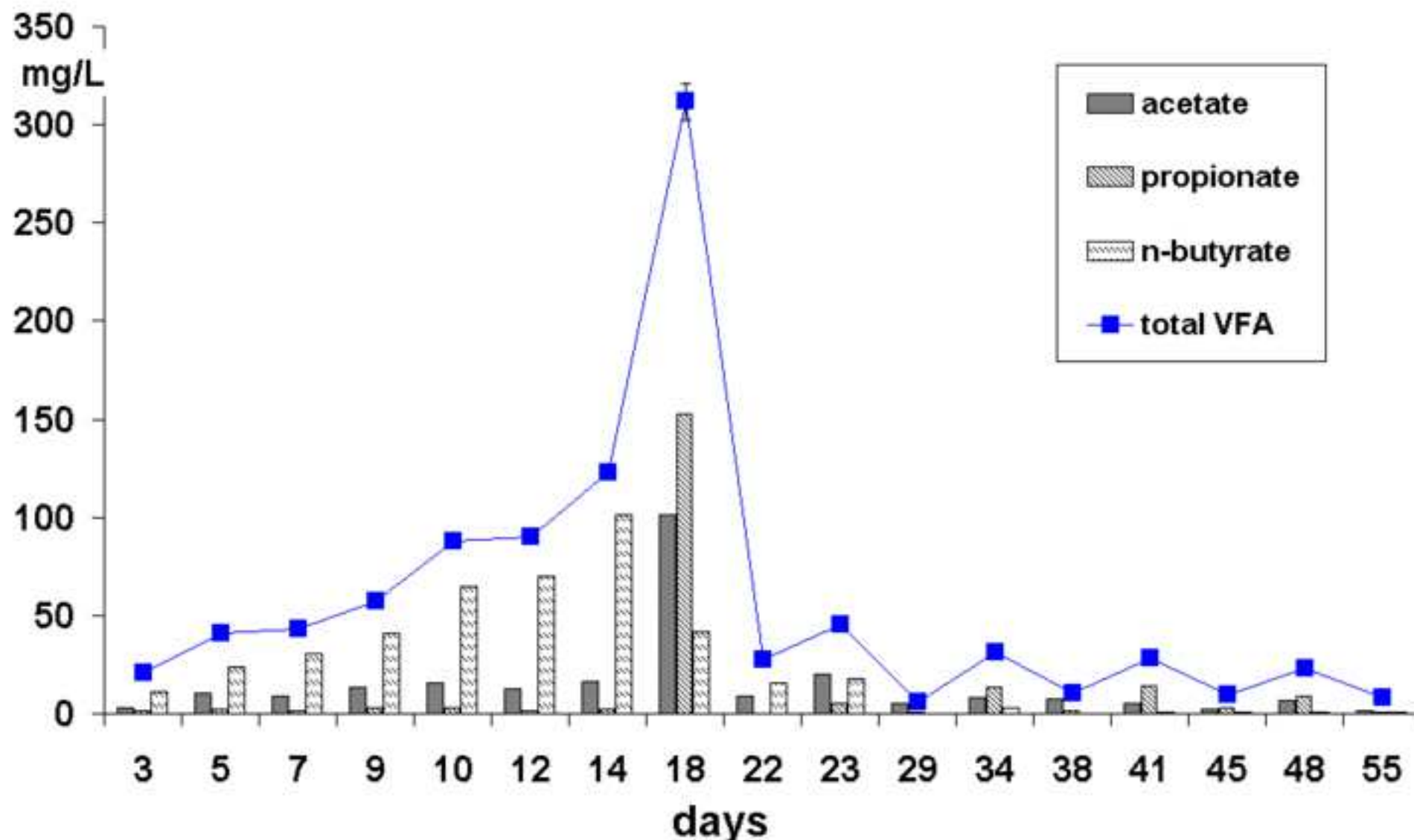


Fig 5. Total VFAs concentration and distribution in the permeate of the SAMBR.

Figure 6
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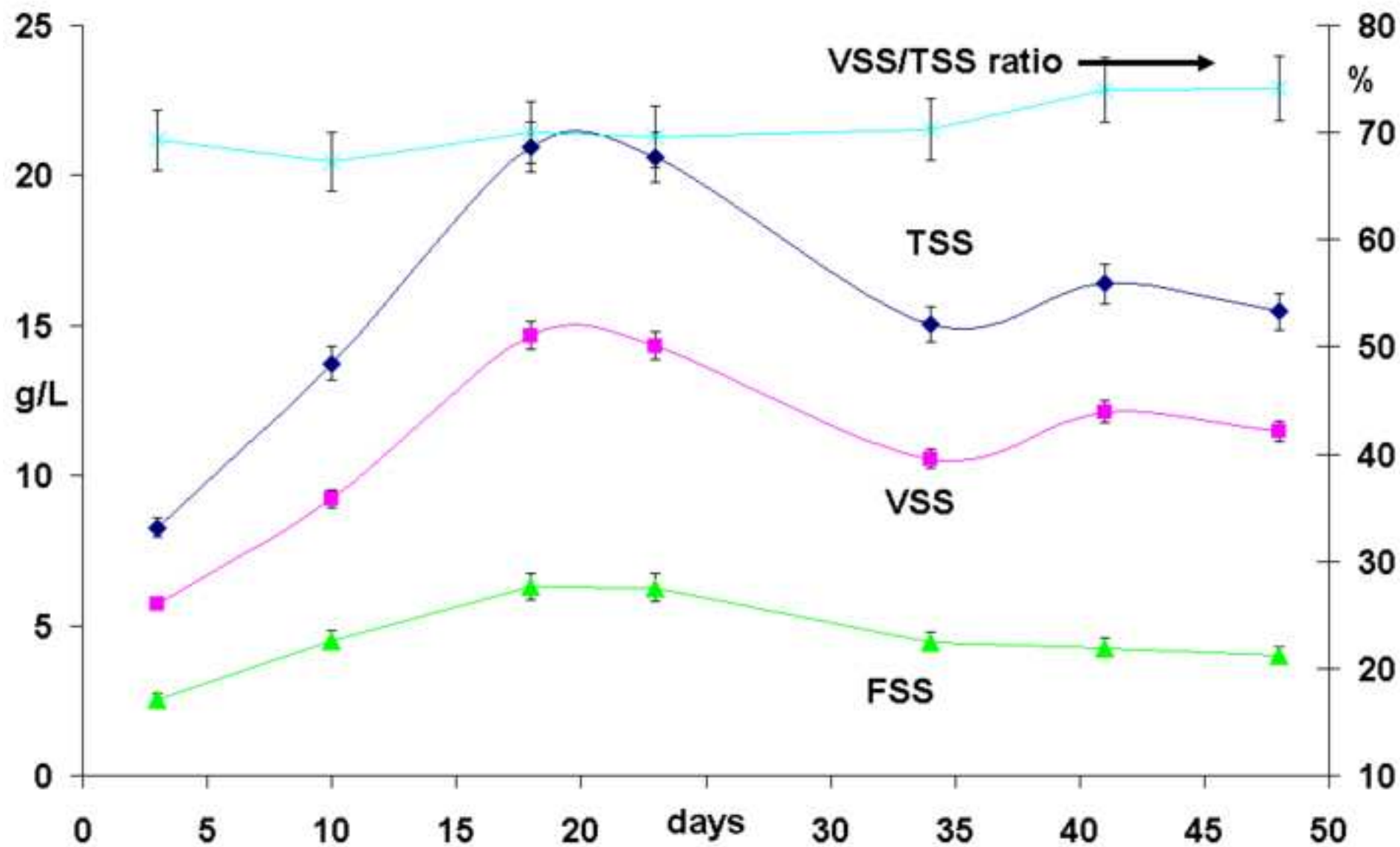


Fig 6. Evolution with time of TSS, VSS and FSS in the SAMBR.

Figure 7
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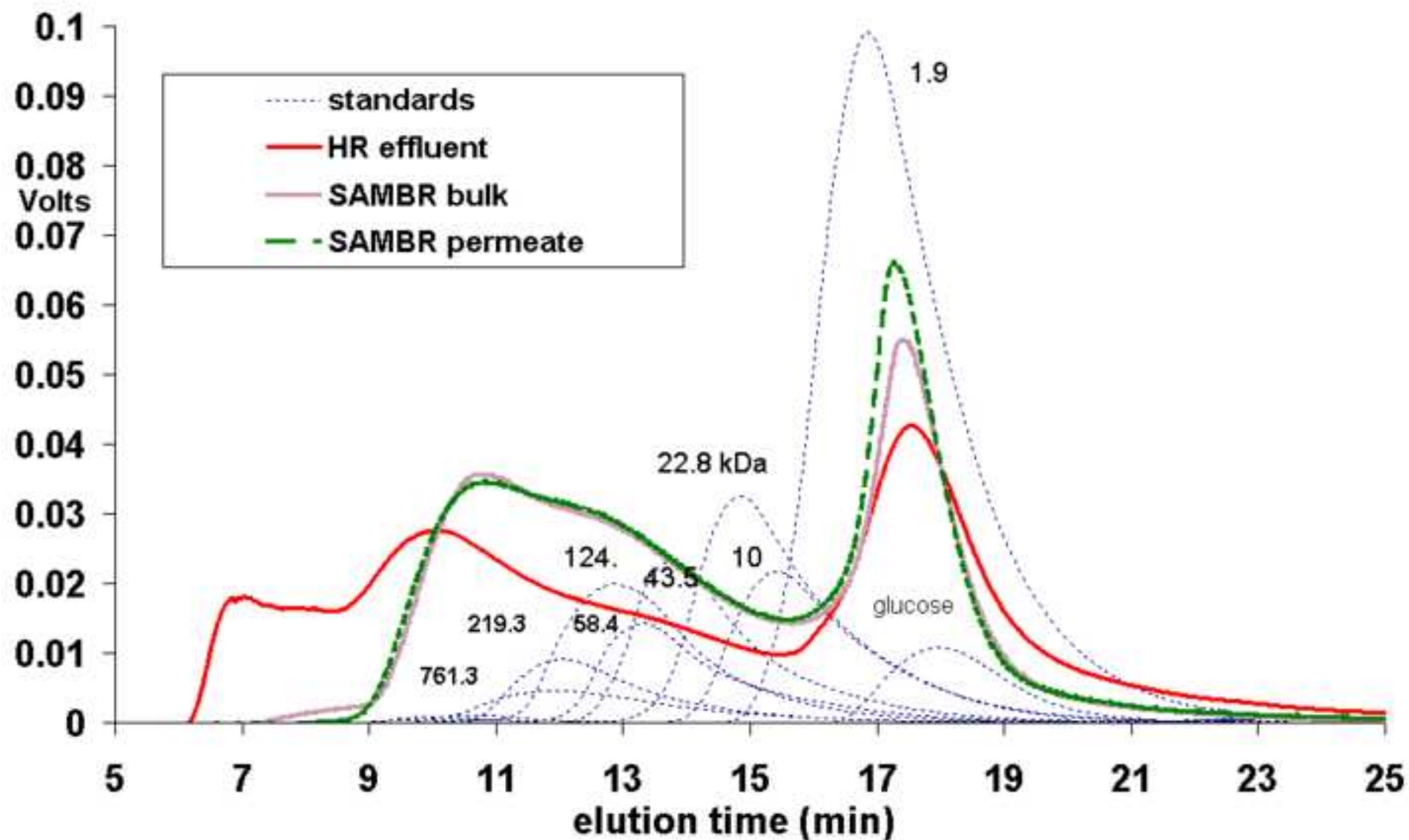


Fig 7. Size exclusion chromatograms of standards, HR effluent, SAMBR bulk and SAMBR permeate taken on day 29 of the batch treatment of the OFMSW.

Figure 8
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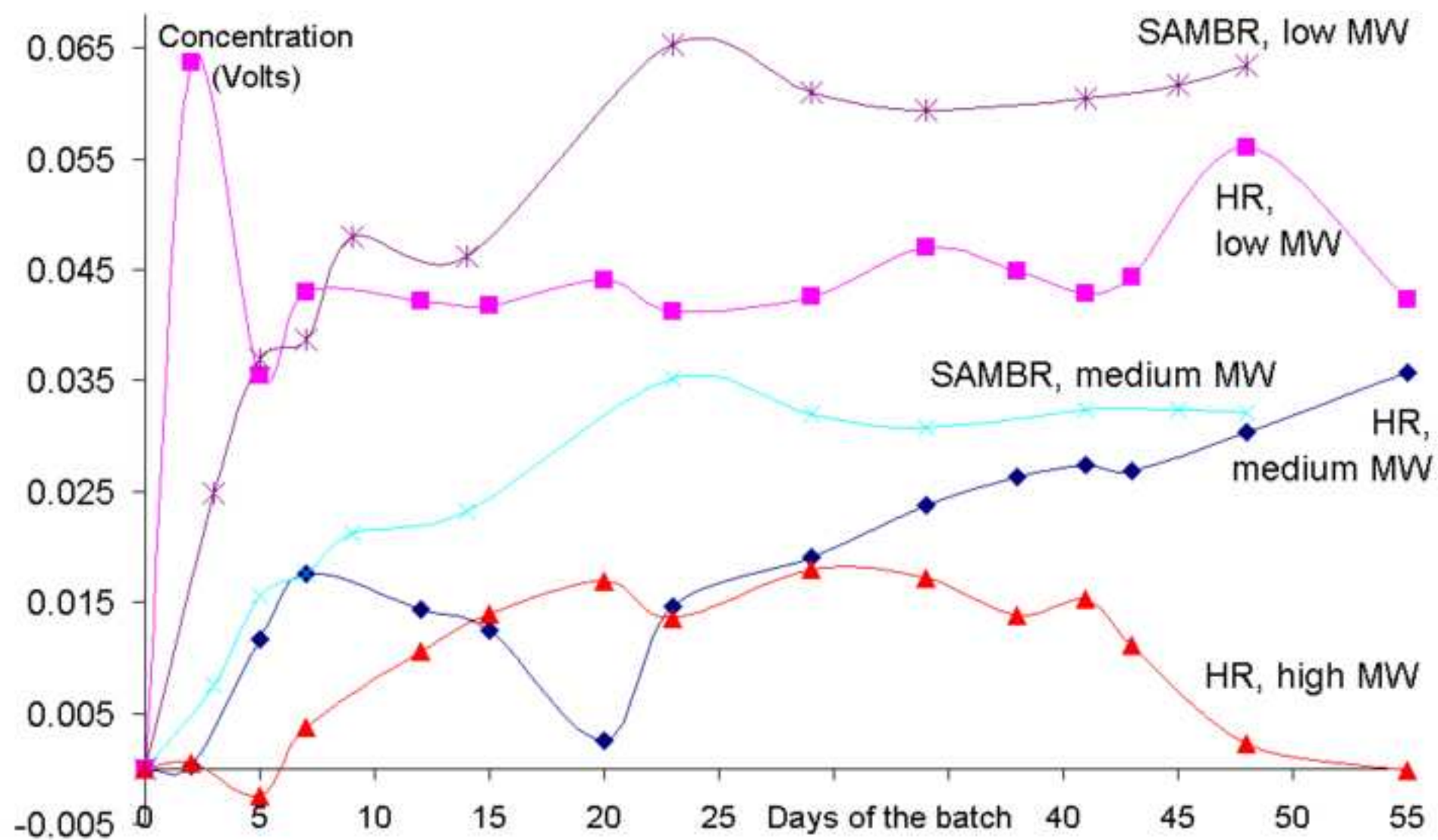


Fig 8. Evolution of concentration of different groups of molecules during the batch treatment of the OFMSW.

Figure 9
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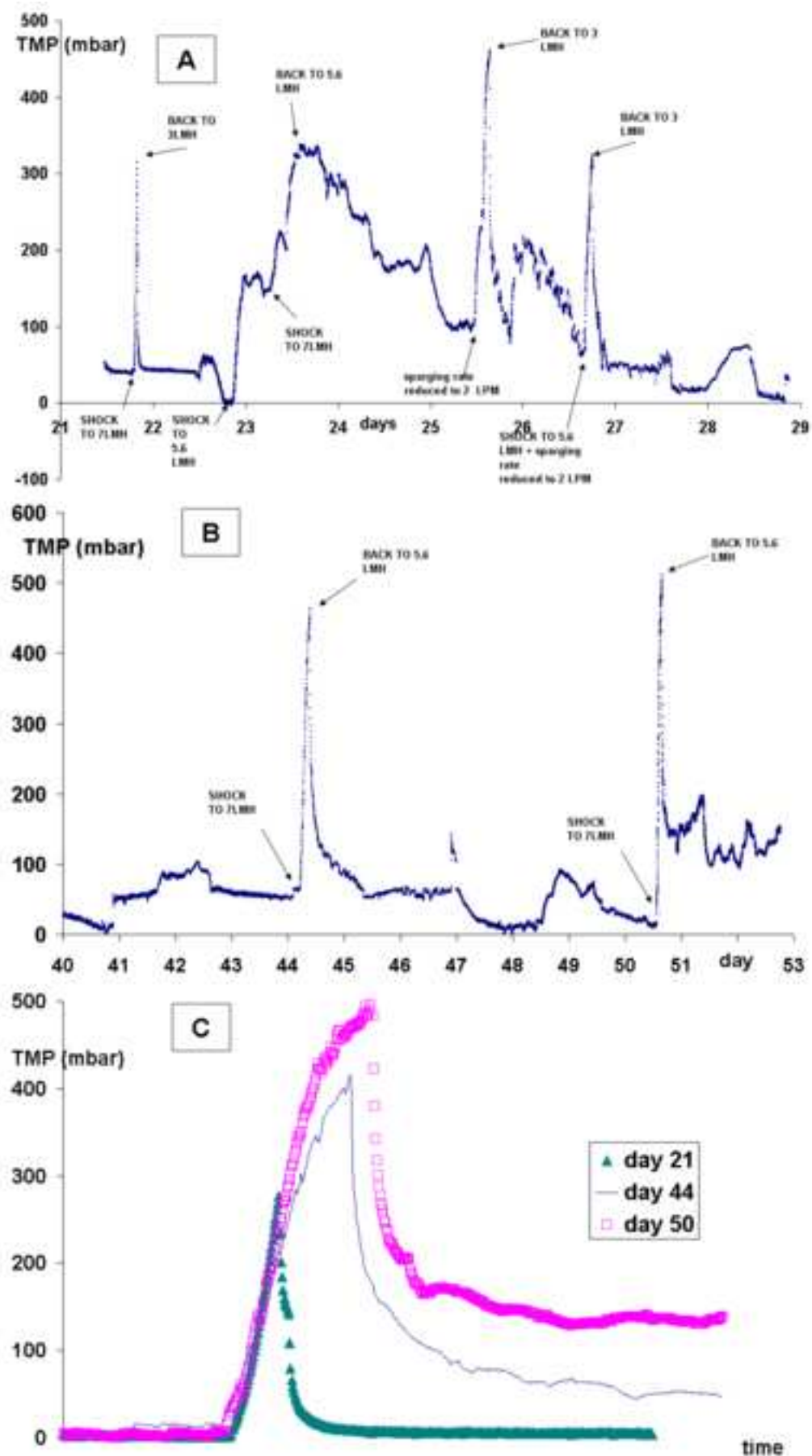


Fig 9. (A) Evolution with time of the transmembrane pressure (TMP) between days 21 and 29. (B) Comparison of TMP evolution after a flux step increase on day 44 and day 50. (C) Comparison on the same time scale of the TMP slope during the flux step increase and the final TMP value.

Figure 10

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Fig 10. (left) Kubota partially scoured by biogas bubbles. (right) diffuser located at the bottom of the SAMBR with only the far left hole remaining open for gas bubbles formation.

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

Type of paper	%
Newspaper	21
Magazine	12
Office paper	8
Card and paper packaging	11
Cardboard	1
Card non packaging	0.6
Liquid carton	1.4
Tissue paper	15
Paper plate	15
Toilet paper	15

Table 2

[Click here to download high resolution image](#)**Table 2.** Properties of the simulated feedstock of the Organic Fraction of Municipal Solid Waste.

Parameter (unit)	Value (standard deviation)
TS (%)	9.9
VS (%)	8.2-8.6
COD/VS	1.2-1.6
pH	6.3-6.9
TN (mg/g TS)	13.1 (0.4)
TP (mg/g TS)	1.3 (0.1)
Ca (ppm of TS)	38698.66 (4733.6)
Fe (ppm of TS)	2325.39 (266.3)
Na (ppm of TS)	2256.59 (265.5)
K (ppm of TS)	1848.02 (208.5)
Mg (ppm of TS)	821.34 (93.9)
Zn (ppm of TS)	588.17 (66.3)
Al (ppm of TS)	551.94 (66.9)
Mn (ppm of TS)	88.75 (10)
Cu (ppm of TS)	47.79 (5.4)
Co (ppm of TS)	45.16 (5.1)
B (ppm of TS)	25.73 (4.4)
Pb (ppm of TS)	8.93 (3.6)
W (ppm of TS)	6.83 (0.9)
Ni (ppm of TS)	4.73 (0.9)
Cr (ppm of TS)	4.2 (0.5)
Cd (ppm of TS)	2.1 (0.2)
V (ppm of TS)	<2.6
Mo (ppm of TS)	<2.6
Biodegradability (L CH ₄ STP/g VS)	0.216 (0.01)