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Acidogenic fermentation of biowaste coupled with nitrogen recovery using selective membranes to produce a VFA-rich liquid with a high C/N ratio

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ABSTRACT

This research focuses on the production of a liquid stream rich in volatile fatty acids (VFAs) and low ammoniacal nitrogen content (<0.1 g N/L) from biowaste. The liquid stream was obtained by combining (i) mixed culture acidogenic fermentation to maximise VFA production and (ii) gas-permeable membrane (GPM) contactor to recover ammoniacal nitrogen. Three batch fermentation tests of biowaste collected in a full-scale mechanical-biological treatment plant provided high and stable VFA concentrations (37–39 g COD_{VFA}/L). VFAs represented 73–81 % of the soluble chemical oxygen demand (sCOD) concentration, with a predominance of acetic, propionic and butyric acids. A highly specialized microbial community was observed in all batch tests, with *Bacteroidota* and *Firmicutes* as predominant phyla (>90 % of relative abundance). The GPM contactor recovered more than 99 % of the ammoniacal nitrogen in the fermentation liquid without VFA losses. The suitability of the produced fermentation liquid with a high C/N ratio for downstream applications was evaluated using biomethane potential tests (BMP) at different total ammonium nitrogen (TAN) concentrations (0.76–3.15 g N/L) and circumneutral pH. Despite achieving similar ultimate methane yields (279–314 NmL CH_4/g COD_{feed}), lower TAN concentrations in the biowaste fermentation liquid improved anaerobic biodegradation kinetics, enhancing its potential applicability for methane production.

1. Introduction

Anaerobic bioprocesses using mixed microbial cultures (MMC) can handle a wide variety of organic wastes to valorise them into value-added bioproducts within the biorefinery concept and circular economy framework. Volatile fatty acids (VFAs) are linear short-chain aliphatic mono-carboxylate compounds, having from two (acetic acid) to six (caproic acid) carbon atoms [65]. VFAs can be produced through MMC acidogenic fermentation by means of different metabolic routes that depend on the composition of the substrates and the operating conditions applied, while restricting methanogens proliferation [30,72,73]. In recent years, biobased VFA production from organic wastes using MMC fermentation is gaining attention due to its increasing market demand as chemical products as well as precursors of chemicals (esters, ketones, aldehydes, alcohols and alkanes), biopolymers (such as polyhydroxyalkanoates) and bioenergy (biomethane, biodiesel, biohydrogen, electricity via microbial fuel cells), among others [4,52,68,71]. Biobased VFAs stand as an alternative to petroleum-based VFAs which currently supply the majority of VFAs market demand. Nonetheless, biobased VFAs are key building blocks in waste processing biorefineries that can contribute to the transition from a linear to a circular economy and increase the sustainability of their supply chain [22,27].

A great variety of biodegradable organic wastes originated at urban level have been successfully used to produce VFAs by means of MMC fermentation [12]. Importantly, fermentation reactors and auxiliary equipment could be easily adopted and integrated into the existing waste processing plants such as mechanical-biological treatment (MBT) plants for biowaste treatment and wastewater treatment plants (WWTPs). Biowaste, also known as organic fraction of municipal solid waste (OFMSW), is one of the most abundant organic-rich wastes produced at urban level. In low and middle-income communities, OFMSW constitutes approximately 50–70 % of the total Municipal Solid Waste (MSW), whereas in high-income communities, it comprises for about

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20–40 % of the total MSW [1,37,69]. OFMSW has a remarkably high VFA yield with literature values ranging between 0.25 and 0.87 g COD_{VFA}/g VS [20,33,32,53,66].

Continuous fermenters fed with OFMSW at mesophilic conditions, pH of 5.6–6.3 and retention time of 3.5 days reached a VFA yield of 0.34–0.36 g COD_{VFA}/g VS dominated by acetic, propionic, butyric and valeric acids [20]. The VFA yield reported in continuous operation [20] was lower than the VFA yield of 0.49–0.59 g COD_{VFA}/g VS reported under batch operation [28], probably due to a shorter retention time. When OFMSW is treated in two-stage anaerobic digestion (TSAD) processes, comprising a fermentation and an anaerobic digestion unit with digestate recirculation, the VFA yield of the fermentation unit working at pH values around 5.5–6.0 usually falls within the range reported by Cheah et al. [20]. Specifically, the VFA yield of the thermophilic fermentation unit was 0.31–0.32 g COD_{VFA}/g COD_{feed} (pH around 5.5) [48] and 0.45 g COD_{VFA}/g VS (pH 5.0–5.6) [70], dominated by acetic, propionic and butyric acids. In another study operating a TSAD plant (mesophilic fermentation followed by thermophilic anaerobic digestion) treating screw pressed OFMSW, a VFA yield of 0.49 g COD_{VFA}/g COD was obtained but dominated by propionic and valeric acids, probably due to the higher operating pH (around 6.6) in the fermentation reactor [71]. Gottardo et al. [33] reported a VFA yield up to 0.87 g COD/g VS (effluent pH 6.6), enriched in acetic, butyric and caproic acids, during mesophilic fermentation of squeezed food waste after combined thermal-alkaline pretreatment. Qin et al. [56] also studied the impact of seasonal variations of food waste on the VFA yield in mesophilic acidogenic fermentation (0.316–0.353 g COD_{VFA}/g VS) and the distribution of fermentation products, that were mainly composed by acetic (3.8–22.4 %), propionic (16.2–38.7 %) and butyric (42.2–79.9 %) acids. Independently of the VFA yield and VFA profile obtained, all these VFA-rich liquids from OFMSW fermentation (14–41 g COD_{VFA}/L) had a considerable total ammoniacal nitrogen (TAN) concentration (up to 5.1 g N/L) due to the ammonification of organic nitrogen [20,28,32,48,71].

A high TAN concentration in fermentation liquids represent a limitation for some VFA downstream applications such as polyhydroxyalkanoates synthesis [21,4] and biogas production [19,49,58], among others. Recent studies have demonstrated that coupling gas-permeable membrane (GPM) technology to anaerobic bioreactors can improve biogas production by mitigating ammonia inhibition while recovering ammonia as a liquid fertiliser [49,58]. GPM technology consists of recirculating an acidic liquid flow (e.g. diluted H_2SO_4) through one side of a selective hydrophobic membrane that receives a nitrogen-rich liquid on the other side of the membrane. The selective membrane only allows gas-phase molecules (such as free ammonia) to diffuse through the pores of the membrane [5]. This technology exhibits a high potential for sustainable upcycling of ammoniacal nitrogen from wastewater effluents as it is relatively simple to operate, consume little energy and could produce a sealable liquid fertiliser product [13,23]. Serra-Toro et al. [62] reported TAN recovery efficiencies above 98 % when controlling the pH of the feed solution at 9.0 by using a GPM contactor. Under these operating conditions, Serra-Toro et al. [62] reported negligible VFA losses since only unionized VFAs could pass through hydrophobic membranes [9]. Therefore, the combination of acidogenic fermentation and TAN recovery through selective membranes could lead to an improved resource recovery scenario, since not only nitrogen could be recovered as a saleable fertiliser (e.g. $(NH_4)_2SO_4$ solution) but also a VFA-rich stream with a high C/N ratio could be generated, which in turn could enhance the efficiency of downstream applications.

The main objective of this research was to evaluate the acidogenic fermentation of OFMSW for VFA production combined with GPM technology for ammoniacal nitrogen recovery. This process aims to produce a VFA-rich stream with high C/N ratio suitable for downstream applications and a $(NH_4)_2SO_4$ rich solution with fertilising value. This research also conducted a comprehensive characterization of the microbial community involved in the acidogenic fermentation process. Finally, the benefits that this treatment train could entail for downstream bioprocesses was assessed by evaluating the mitigation of ammonia inhibition in anaerobic digestion.

2. Materials and methods

2.1. Substrate and inoculum origin

OFMSW was collected in three different sampling events in a mechanical-biological treatment plant of the Barcelona Metropolitan Area that treats over 50,000 t per year of source-sorted OFMSW. The samples collected were the feedstock to the full-scale anaerobic digester, after their maceration in a pulper and its treatment through a hydrocyclone system (see details in Fernández-Domínguez et al. [28]). Table 1 summarizes the main characteristics of the collected OFMSW (from March to July 2022), which had a relatively high VFA concentration (20–22 g COD/L) enriched in acetic, propionic and butyric acids. This high initial VFA concentration is mainly attributed to unintended pre-fermentation taking place during OFMSW pre-treatment in the pulper and hydrocyclones units. Pre-fermentation is also favoured by the fact that supernatant from the anaerobic digesters is recirculated to the pulper to adjust the volatile solids (VS) content of this stream and to provide alkalinity to maintain circumneutral pH values.

For the biomethane potential (BMP) tests, two batch of inoculum were collected from a mesophilic anaerobic digester in a municipal wastewater treatment plant (WWTP) treating sewage of about 400,000 population equivalents in the Barcelona metropolitan area (Spain). After collection, the inoculum was stored at 4 °C until use (< 7 days).

2.2. Experimental set-up and methodology

A three-stage process was carried out including (i) acidogenic fermentation, (ii) TAN recovery using a gas-permeable membrane contactor and (iii) anaerobic digestion. In this study, stages (i) and (ii) were carried out in batch operation for the OFMSW collected in three sampling events. Stage (iii) was performed in duplicate testing a range of TAN concentrations.

2.2.1. Acidogenic fermentation batch tests

The acidogenic fermentation of OFMSW was carried out in a 30 L digester equipped with a pH probe, a mechanical stirrer, and a temperature control system to maintain mesophilic conditions (35 °C). Due to VFA production, pH started to decrease and the process was stopped when a slight increase of pH was detected. During each fermentation test, samples were daily withdrawn to analyse the evolution of pH, VFA concentration and profile, soluble COD (sCOD) and TAN. Samples were immediately centrifuged after withdrawal and stored at 4 °C prior to

Table 1
Characterization of the OFMSW samples.

Parameter	Units	Value		
		1st sampling	2nd sampling	3rd sampling
TS	g/L	76.1 ± 1.7	87.8 ± 0.8	69.1 ± 0.9
VS	g/L	56.4 ± 0.9	66.8 ± 1.1	48.7 ± 0.6
% VS/TS	%	74.0 ± 2.8	76.1 ± 1.9	70.5 ± 0.2
TAN	g N/L	3.3 ± 0.2	3.6 ± 0.2	3.2 ± 0.2
pH	-	6.66 ± 0.01	7.13 ± 0.01	7.55 ± 0.01
soluble COD	g COD/L	38.7 ± 0.2	47.9 ± 0.7	42.3 ± 1.2
total VFA	g COD/L	20.23 ± 0.22	21.13 ± 1.36	21.88 ± 2.19
Acetic acid	g COD/L	6.36 ± 0.09	5.44 ± 0.41	7.18 ± 0.79
Propionic acid	g COD/L	6.30 ± 0.05	4.59 ± 0.29	4.58 ± 0.51
Butyric acid	g COD/L	6.88 ± 0.03	10.03 ± 0.59	8.98 ± 0.80
Valeric acid	g COD/L	0.34 ± 0.01	0.41 ± 0.03	0.60 ± 0.04
Caproic acid	g COD/L	0.35 ± 0.04	0.67 ± 0.05	0.54 ± 0.05
Conductivity	mS/cm	32.2 ± 0.7	16.9 ± 0.1	25.6 ± 1.1

their analysis. To analyse the microbial community in the fermenter, samples were withdrawn daily and stored at −20 °C until analysis. Once the fermentation batch finished, the OFMSW was sieved (0.05 mm mesh size), centrifuged (16,600 × g, 10 min) and filtered (using a 1.2 μm mesh light filter) to prevent the clogging of the subsequent membrane treatment. The manipulation of the fermentation liquid led to a decrease in the total VFA content that never exceeded 6 %.

2.2.2. Gas-permeable membrane tests

The TAN of the fermentation liquid was recovered as $(NH_4)_2SO_4$ using a hydrophobic hollow fibre polypropylene (PP) membrane contactor with 0.5 m^2 active surface area (3 M™ Liqui-Cel™ MM-1.7×5.5 MiniModule). The membrane contactor experimental set-up consisted of two sealed and stirred tanks connected to a GPM module using closed loops for each stream [62]. Specifically, a tank with 0.5 L of effective volume was used for the trapping solution (diluted H_2SO_4 that never exceeded a pH value of 2.0) and a tank with 1.7–1.8 L of effective volume was used for the feed (controlled at 35 °C and pH 9.0). The pH was controlled in both the feedstock (pH of 9) and the trapping solution (pH of 2) tanks by adding NaOH 10 M and H_2SO_4 75 % w/w, respectively. The selected pH of the feedstock (9.0) and the volume of the trapping solution, which was 3.4–3.5 times lower than that of the feedstock was based on Serra-Toro et al. [61]. Each test had a duration of 17–18 h and finished when more than 99 % of TAN was removed from the fermentation liquid. Samples (3 mL) were withdrawn from the feed and trapping solution tanks to monitor the process. A drop of sulfuric acid 1 M was immediately added to the samples withdrawn from the feed tank to decrease the pH and prevent TAN losses by volatilization. All samples were stored at 4 °C prior to their analysis.

2.2.3. Biomethane potential tests

BMP tests were used to assess the anaerobic biodegradability of the fermentation liquid at ten different TAN concentrations. BMP tests were carried out in 250 mL Wheaton® serum bottles as described in Holliger et al. [36] under mesophilic (35 °C) conditions. Each bottle contained 175 mL of an inoculum-substrate mixture to reach the fixed inoculum-to-substrate ratio (ISR) of 2 g VS/g COD. A test containing microcrystalline cellulose and inoculum at an ISR 2 g VS/g VS was used as positive control [36]. A blank test containing only inoculum was used to correct the background methane production from the inoculum endogenous respiration. NH_4Cl was added to reach the desired TAN concentrations. The headspace of each bottle was flushed with 99.9 % N_2 gas for 30 seconds (ca. 4 L/min). The bottles were sealed with a chlorobutyl septum, retained with a screw cap, and stored in an incubator at 35 ± 1 °C (MEMMERT UF750). The bottles were mixed by swirling before each sampling event. All BMP tests and blanks were carried out in quadruplicate. Cumulative methane production was measured using the gas density method [40]. At each sampling event, the biogas volume and density were measured using a 100 mL syringe connected to a bench-top water-manometer and a precision balance (FZ-500i, accuracy ± 0.002 g). The biogas density was calculated considering the mass loss and the standardised dry biogas volume [40]. The mole fraction of CH_4 in biogas was calculated from the normalised difference in density of CO_2 and biogas [40]. BMP tests were run for 29–35 days, until the daily methane production during three consecutive days was <1 % of the accumulated volume of methane [36]. Cumulative volumetric gas production was calculated at standard conditions (0 °C, 1 atm, dry) using the OBA web application [35].

Two distinct sets of BMP tests were carried out to assess the reproducibility and validate the results: A first exploratory set (experiment A) testing three TAN concentrations (0.9, 2.5 and 2.9 g N/L) and a second set (experiment B) with seven TAN conditions into the range of 0.8–3.1 g N/L. pH was adjusted in all the tests to maintain the value of the non-adjusted nitrogen condition (7.2–7.4). Table 2 summarizes the main operating conditions of the BMP tests performed in both tests.

Table 2
Initial conditions of the BMP tests performed in experiment A and B to assess the impact of TAN recovery in the biomethane production.

Test	Fermentation liquid		Batch test	
	COD_{VFA}/sCOD	TAN (g N/L)	TAN (g N/L)	initial pH (-)
A1	0.81 ± 0.10	0.87 ± 0.05	0.94 ± 0.07	7.20 ± 0.01
A2	0.81 ± 0.10	7.65 ± 0.01	2.47 ± 0.04	7.30 ± 0.02
A3	0.81 ± 0.10	9.87 ± 0.01	2.91 ± 0.06	7.20 ± 0.01
B1	0.79 ± 0.09	0.76 ± 0.06	0.76 ± 0.03	7.40 ± 0.01
B2	0.79 ± 0.09	1.12 ± 0.01	1.00 ± 0.02	7.40 ± 0.02
B3	0.79 ± 0.09	2.25 ± 0.01	1.26 ± 0.02	7.30 ± 0.01
B4	0.79 ± 0.09	3.39 ± 0.01	1.54 ± 0.04	7.40 ± 0.02
B5	0.79 ± 0.09	5.65 ± 0.01	2.07 ± 0.12	7.50 ± 0.03
B6	0.79 ± 0.09	7.90 ± 0.01	2.61 ± 0.04	7.30 ± 0.01
B7	0.79 ± 0.09	10.16 ± 0.01	3.15 ± 0.10	7.40 ± 0.02

2.3. Analytical methods

Total solids (TS) and VS concentration were analysed following the 2540 G procedure of the Standard Methods [7]. pH was measured with a pH-meter (CRISON pH basic 20) equipped with a pH electrode. For the analysis of soluble compounds, samples were centrifuged (16,600 × g for 15 min) and filtered through a nylon syringe filter (0.45 μm pore size). Soluble COD was analysed following the 5220D Standard Methods procedure [7]. VFAs (i.e. acetic, propionic, i-butyric, n-butyric, i-valeric, n-valeric, i-caproic and n-caproic) were analysed using a gas chromatograph (Shimadzu GC-2010 Plus) equipped with an Agilent J&W DB-FFAP column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. VFA isomers (normal and iso) concentrations were summed in a single species and transformed into COD using the COD equivalents theoretical value based on their elemental composition. TAN was analysed following the Standard Methods procedure 4500-NH3D, using a Thermo Fisher Scientific ammonium ion-selective electrode (Orion 9512HPBNWP).

2.4. Microbial community analysis

Duplicate samples of biomass from fermentation batch tests were collected daily (from 0 to 6 days), centrifuged to remove supernatant, and stored at −20 °C for microbial community analysis. Total genomic DNA was extracted from 250-mg aliquots of centrifuged biomass using the DNeasy PowerSoil Pro Kit (Qiagen, USA). DNA samples were submitted to 16S rRNA amplicon sequencing at Novogene Co. (Cambridge, UK). Paired-end reads (2×250 bp) of the V4 region of the 16S rRNA gene were obtained using Illumina NovaSeq 6000 equipment and reagents. Forward and reverse reads were truncated at 250 bp to retain sequences with a quality score >30. Reads with >5 expected errors were discarded. Dereplication, amplicon sequence variants (ASVs) inference and chimera removal were run with DADA2 default parameters. Taxonomic assignment of the ASVs was performed using assign Taxonomy function in DADA2 with a minimum bootstrap confidence of 80 %, using the MiDAS 4.8 database [26]. Downstream statistical analyses were performed in R studio [10] using the in-built functions from following packages: ampvis2 v.2.7.32 [6] and tivyverse v.1.3.2 [76]. To evaluate alpha-diversity, samples were rarefied at 35,000 reads. Differences in overall microbial community structure were explored by principal component analysis (PCA) where the ASV reads were Hellinger transformed prior to ordination. Functional prediction of the microbial community was performed using PICRUSt2 v2.5.2 [25] using default settings. Predicted functional abundances were assigned based on the KEGG orthologs (KOs) database and further classified at KEGG pathway level 1 and 3 by the categorized.by.function.py R code. A heatmap depicting relative abundance of the functional data was constructed using the pheatmap function v1.0.12 in R.

Abundance of total *Bacteria*, methanogenic *Archaea* and members of

Prevotella within the acidogenic fermentation batch reactors was estimated by quantitative PCR (qPCR) analysis. All qPCR reactions were carried out on an Applied Biosystems QuantStudio 1 Real-Time PCR system using PowerUp SYBR Green Master Mix (Applied Biosystems, CA, USA), 1 μL of template and 4 pmol of each primer in a final volume of 20 μL. Total bacterial abundance was estimated by amplification of 16S rRNA genes using universal primers 341 F and 534 R [50], while methanogenic *Archaea* were quantified by amplification of the methyl-coenzyme M reductase (*mcrA*) genes using primers mlas and mcrA-rev [64]. Specific primers targeting the 16S rRNA genes of the members of the genus *Prevotella* detected within the fermenters were designed using Primer-BLAST and experimentally validated by PCR (Prevo5F (5'-GCCGTGGGTTAAGTGTGTTG3–3')/Prevo5R (5'-CCTTC GCAATCGGAGTTCCT-3'). For quantification, six-point 10-fold standard dilution series were used. Amplification efficiency for all qPCR reactions ranged between 84 % and 110 % with a slope between −3.1 and −3.7. Primer specificity was assessed by the observation of a single peak during melt curve analysis. Standards were prepared by cloning the gene amplicons using the pGEM-T Easy Vector System (Promega, WI, USA). Plasmids were purified with the GeneJET Plasmid Miniprep Kit (Thermo Scientific, USA), and validated by sequencing.

2.5. Calculations

To assess the fermentation performance, the VFA yield (g COD/g VS) was calculated by means of Eq. (1), where it is only considered the increase of VFA concentration during the fermentation batch (the feedstock already had a high VFA concentration). The overall VFA yield (expressed as g COD/g VS) was calculated by means of Eq. (2), considering the final VFA concentration independently of the initial VFA concentration of the substrate. In these equations, VFA_i and VFA_e are the VFA concentration in the feedstock and at the end of the fermentation process (g COD/L), respectively, and VS_i is the VS concentration of the feedstock (g VS/L).

$$VFA \quad yield = (VFA_e - VFA_i)/VS_i \tag{1}$$

$$Overall \quad VFA \quad yield = VFA_e/VS_i \tag{2}$$

To assess the GPM performance, the TAN removal and recovery (expressed in %) were calculated using Eqs. (3) and (4), respectively. In these equations, TAN_i and TAN_e stand for the TAN concentration in the feed solution at the beginning and at the end of the test (g N/L), respectively. TAN_t refers to the TAN concentration in the trapping solution at the end of the test (g N/L), V_i, V_e and V_t represent feed volume at the beginning of the test, feed volume at the end of the test and the trapping solution volume at the end of the test, respectively.

$$TAN \quad removal = ((TAN_i \quad V_i - TAN_e \quad V_e)/TAN_i)\cdot 100 \tag{3}$$

$$TAN \quad recovery = (TAN_t \quad V_t/TAN_i \quad V_i)\cdot 100 \tag{4}$$

The ammonia mass transfer constant (K_m) was used to evaluate the ammonia flux through the membrane [62,8]. This parameter quantifies the ammonia transfer under specific conditions. Eq. (5) determines the K_m value (m/s) from the experimental TAN concentration data assuming that the NH_3/NH_4^+ equilibrium is fulfilled during the operation. In Eq. (5), A is the area of the membrane (0.5 m^2), V_f is the volume of the feed solution (m^3) and t is the time (s). The K_m depends on the pH and temperature of the feed solution, among other operating factors. The model was adjusted with the programming language Python using the curve fit function of the SciPy.Optimize library, which uses the Levenberg-Marquardt algorithm to perform non-linear least squares estimates. The algorithm estimates K_m by fitting the nitrogen concentration of the feed and trapping solution over time.

$$TAN_{treated,feed} \Big/ TAN_{feed} = \exp \quad \left(\frac{-K_m \quad A}{V_f} \quad t\right) \tag{5}$$

The Gompertz model (Eq. (6)) was used to describe methane generation kinetics in BMP tests due to its capability to adjust BMP curves with a sigmoidal profile [54,82]. In Eq. (6), B(t) is the time-dependent specific cumulative methane production (NmL CH_4/g COD_{feed}), B_0 is the ultimate methane yield (NmL CH_4/g COD_{feed}), R_{max} is the maximum specific methane production rate (NmL CH_4/g COD_{feed} d), λ is the lag phase (d), e is the number e=exp (1) and t is time (d).

$$B(t) = B_0 \cdot \exp\left(-\exp\left(\left(\frac{R_{max}\cdot e}{B_0}\right)\cdot(\lambda - t) + 1\right)\right) \tag{6}$$

The model parameters were derived by employing the least-squares method using MATLAB's lsqcurvefit function (R2022b). This process was achieved by reducing the mean squared differences between the collected experimental data and the forecast outcomes of the model. Confidence intervals at the 95 % confidence level were computed using the *nlparci* function. The calibration fitness of the model was evaluated using the coefficient of determination (R^2) and root mean square error (RMSE).

3. Results and discussion

3.1. OFMSW acidogenic fermentation

Fig. 1 shows the individual VFA concentration, TAN and pH over time of the three OFMSW fermentation tests. At the beginning of the batch, the pH decreased due to the accumulation of VFAs followed by a slight rise in pH on the 6th day, which usually occurs when the VFAs concentration stabilises [16]. However, the pH remained within circumneutral values (6.30–7.55) in all fermentation tests due to the high buffering capacity of the influent, which is related to the recirculation of supernatant from the OFMSW anaerobic digestion [32,77]. Having a pH stability inherent in the influent is ideal for acidogenic fermentation, as pH plays a critical role in ensuring consistent performance during the fermentation process [33]. Therefore, the three fermentation tests performed similarly as shown in Table 3, with a final VFA concentration ranging 37.0–39.3 g COD_{VFA}/L.

The VFA profile was dominated by acetic (32–39 % COD basis), propionic (21–27 % COD basis) and butyric (24–34 % COD basis) acids. These values are similar to other studies on OFMSW fermentation [24,28,30,39,56,62,63]. An increase of TAN concentration was observed from 3.2 to 3.6 g N/L up to 4.1–5.0 g N/L due to protein hydrolysis and acidification [75]. The final VFA to sCOD ratio was in the range of 0.73–0.81 g COD_{VFA}/g sCOD, indicating that most of the sCOD was in the form of VFAs. These ratio values are in accordance with the reported values of Bolzonella et al. [16] (0.5–0.9 g COD_{VFA}/g sCOD). The VFA yield of the fermenter (without considering the initial VFA concentration) ranged between 0.25 and 0.34 g COD_{VFA}/g VS. The overall VFA yield (considering the total VFA concentration at the end of the fermentation batch) ranged between 0.57 and 0.76 g COD_{VFA}/g VS, similar to those reported by Fernández-Domínguez et al. [28] and Serra-Toro et al. [62]. It is worth noting that the VFA yields obtained are higher than those reported in literature [12], which could be related to (i) the batch operation, (ii) the high biodegradability of source-sorted OFMSW and (iii) the buffer capacity of this substrate due to the recirculation of supernatant from the anaerobic digester.

Changes in feedstock physical and chemical properties due to seasonal variation could affect the VFA yield and profile [44,56,73]. However, the OFMSW samples used in this study had similar characteristics (Table 1) and yielded consistent VFA yield and profile.

3.2. Microbial community structure and dynamics during OFMSW acidogenic fermentation

The bacterial and archaeal community present in the fermentation batch tests were analysed by 16S rRNA amplicon sequencing to identify

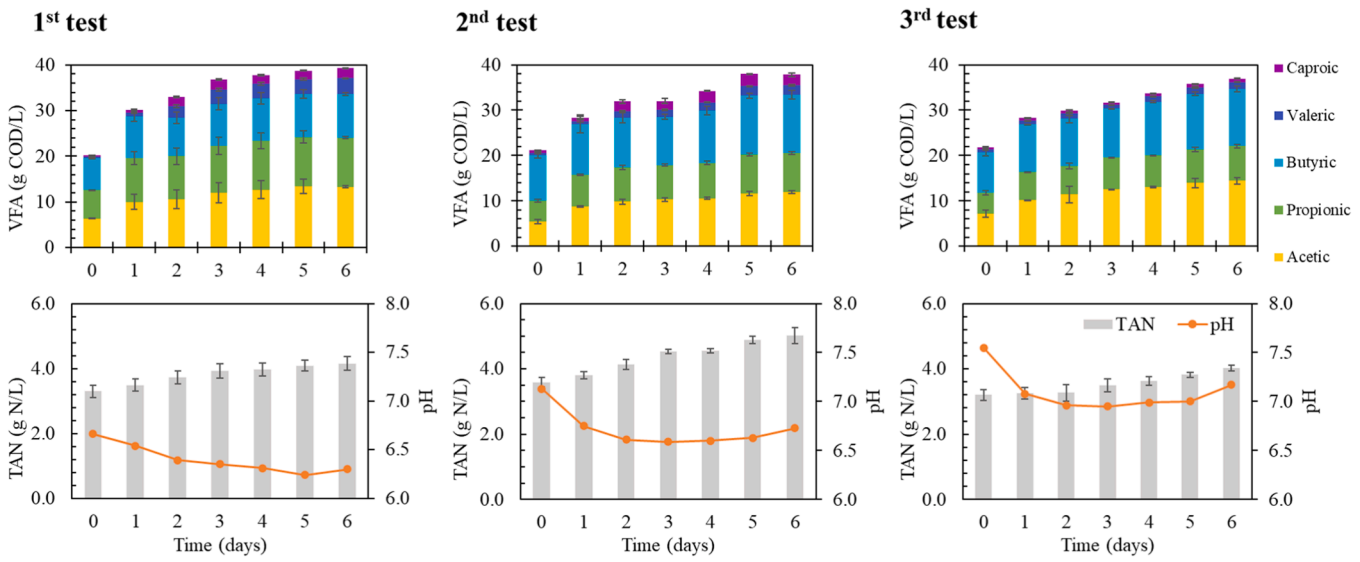

Fig. 1. Evolution of VFA, TAN and pH over time during the three fermentation batch tests.

Table 3
Composition of the fermentation liquid after each fermentation test.

Parameter	Units	Value		
		1st test	2nd test	3rd test
pH	-	6.30 ± 0.01	6.73 ± 0.01	7.17 ± 0.01
TAN	g N/L	4.2 ± 0.2	5.0 ± 0.2	4.1 ± 0.1
sCOD	g COD/L	48.6 ± 3.6	48.0 ± 1.92	48.7 ± 1.4
VFA/sCOD	g COD/g sCOD	0.81 ± 0.10	0.79 ± 0.08	0.73 ± 0.05
VFA yield	g COD/g VS	0.34 ± 0.04	0.25 ± 0.08	0.31 ± 0.07
Overall VFA yield	g COD/g VS	0.70 ± 0.04	0.57 ± 0.08	0.76 ± 0.07
total VFA	g COD/L	39.30 ± 0.89	37.80 ± 2.16	36.95 ± 1.87
Acetic acid	g COD/L	13.33 ± 0.26	11.96 ± 0.26	14.42 ± 0.79
Propionic acid	g COD/L	10.70 ± 0.26	8.53 ± 0.30	7.65 ± 0.37
Butyric acid	g COD/L	9.61 ± 0.30	12.91 ± 1.02	12.60 ± 0.59
Valeric acid	g COD/L	3.45 ± 0.02	2.02 ± 0.14	1.50 ± 0.07
Caproic acid	g COD/L	2.20 ± 0.03	2.38 ± 0.43	0.78 ± 0.05

the communities responsible of OFMSW fermentation. After filtering low-quality reads and trimming adapters, barcodes, and primers, a total of 4,039,264 reads (96,173 ± 22,043 reads/sample) were obtained and further classified into 3456 ASVs. Despite the time variation of the collection periods, microbial community structure was highly similar in the three fermentation tests. Only minor differences were observed at the beginning of the incubation of the first test, which were drastically reduced after one day of operation under the fermentation conditions (Fig. 2a). The microbial community was mainly composed of *Bacteria*, with only a minor presence of methanogenic *Archaea* (<0.03 % in all samples), indicating a successful inhibition of methanogenesis. *Bacteroidota* and *Firmicutes* were the most predominant bacterial phyla in all fermentation batches, accounting for more than 90 % of the total microbial relative abundance (Fig. 2b). These results are consistent with those reported in the literature for other acidogenic fermentation systems [41,46,78]. The genus *Prevotella* (phylum *Bacteroidota*), represented by three different ASVs, was the most abundant genus within the bacterial community, reaching maxima of relative abundance between 37.2 % and 56.5 % in the three batch tests, and suggesting a high degree of specialization of the microbial community. Quantitative analysis (qPCR) using genus-specific primers targeting the 16S rRNA gene of members of *Prevotella* and primers targeting the mcrA gene as a proxy of methanogenic *Archaea*, confirmed (i) the predominant role of *Prevotella*, with increasing abundances during the first two days of incubation associated with major VFA production (from $1.03{\cdot}10^{10}$ to $5.14{\cdot}10^{10}$ gene copy number/g), and (ii) the effective inhibition of methanogens (<0.03 % of relative abundance relative to total microbial community) (Figure S1).

The functional potential of the microbial community present at the time of maximum VFA accumulation (3 days) was predicted for the three batch tests. A total of 7396 KOs (KEGG Orthologies) were predicted and grouped into 267 level 3 categories. Among them, 61 categories predominated (relative abundance >0.6 %) (Fig. 3) and were classified in the KEGG modules metabolism (33.3 %), genetic information processing (24.5 %), environmental information processing (9.1 %) and cellular processes (4.4 %) (Figure S2). The obtained predicted categories were selected based on their relevance to acidogenic fermentation. Out of the 61 predominant predicted categories, 9 were related to the metabolism of lipids and carbohydrates (8.3 %) and 9 to the hydrolysis of proteins and metabolism of aminoacids (10.3 %) (Fig. 3 and S2), all of which are linked to the initial hydrolysis and further break down of complex polysaccharides and proteins. Remarkably, within the predominant KEGG pathways related to carbohydrate hydrolysis, it was observed fructose and mannose metabolism, amino sugar and nucleotide sugar metabolism, galactose metabolism, and starch and sucrose metabolism. The most abundant KEGG pathway related with protein processing was the presence of peptidases (2.3 %), which was accompanied by specific pathways for the further processing of most individual aminoacids (Fig. 3).

The enrichment of these pathways was associated to the detected predominance of members of *Bacteroidota* (genus *Prevotella*) and *Firmicutes* in the microbial community. Members of these two phyla are well known by their capability to produce a wide range of hydrolytic enzymes, and thus to decompose complex biodegradable organic substrates into fermentation products such as acetate, propionate, and succinate [46,47,59,80]. Members of *Firmicutes*, mainly affiliated to *Clostridiales*, are major contributors to protein, lipid and polysaccharide hydrolysis in fermentation systems [46]. Polysaccharide hydrolysis is associated to their capacity to produce cellulosomes, large multi exo-enzyme complexes whose purpose is the efficient degradation of lignocellulosic materials to fermentable sugar monomers [29]. Members of *Prevotella* are anaerobic bacteria known by their proteolytic activity associated to the presence of peptidases, responsible for the hydrolysis of proteins to aminoacids [74]. During amino acid degradation, formation

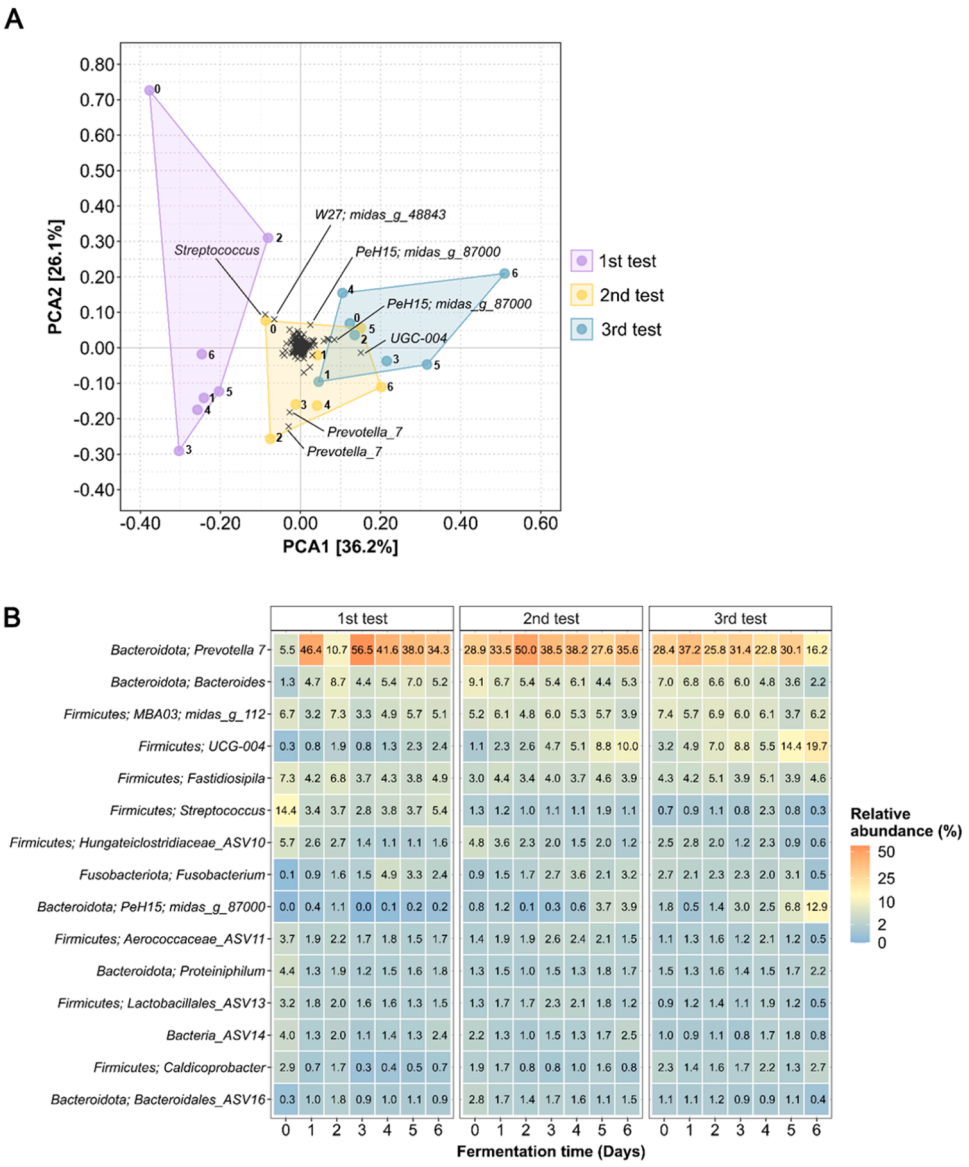

Fig. 2. (a) Principal component analysis (PCA) plot of the microbial community structure at the ASV level (Hellinger transformed) for the three fermentation tests. The distribution of samples is shown with coloured circles, and adjacent numbers indicate the time of sampling in days. Crosses show the distribution of ASVs. (b) Heatmap showing the relative abundance of 15 predominant taxa (the lowest possible taxonomic assignment is shown) within the microbial community of the fermentation batches. In both graphs, values represent the average of two replicate samples.

of organic acids and ammonia has been observed [67]. Recent genomic and metagenomic analyses have also identified that *Prevotella* encompass in their genomes polysaccharide utilization loci (PUL), which are gene clusters encoding enzymes specialized in the hydrolysis of complex carbohydrates [34]. *Prevotella* can better adapt to the low pH conditions caused by the higher replacement ratio and has a high acidogenesis capacity, which contributes significantly to the production of VFAs [38, 43,45]. Metagenomic analysis of anaerobic digestion systems exposed to acidosis revealed an enrichment in carbohydrate utilization pathways associated to *Bacteroidetes*, that outcompeted members of *Firmicutes* [14]. Therefore, the enrichment of *Prevotella* in this study likely played an important role in the production of acetic acid, propionic acid, and butyric acid due to polysaccharides and protein degradation.

3.3. Ammoniacal nitrogen recovery using a gas-permeable membrane

Fig. 4 shows the evolution of TAN concentration in the feed and trapping solution tanks. The results were quite similar for the three tests, each for one of the fermentation liquids obtained from the fermentation batch. Nitrogen removal and recovery were above 98.9 % and ammonia losses were below 0.1 % during the treatment (Table 4), which is consistent with the results of several studies on the nitrogen recovery from anaerobic digestion effluents [2,81]. Final TAN concentrations of the trapping solution were up to 19 g N/L depending on the initial TAN concentration of the fermentation liquid. The ammonia mass transfer constant (K_m) was also calculated to compare the GPM performance with literature values. The K_m values for the three tests performed in this study were similar to those reported by Serra-Toro et al. [62]. The sulphuric acid consumption was 0.6–0.7 mol H_2SO_4/mol N recovered, which is slightly higher than the theoretical value (0.5 mol H_2SO_4/mol N recovered) to keep an acidic pH in the trapping solution tank. The alkali consumption was set around 1.1 mol NaOH/mol N recovered, which is close to the theoretical value (1 mol NaOH/mol N recovered) considering that extra alkali was needed to raise the pH of the fermentation liquid from 6.3-7.2 to 9.0. These chemicals consumption values are also in line with Serra-Toro et al. [62]. VFA losses in the treated

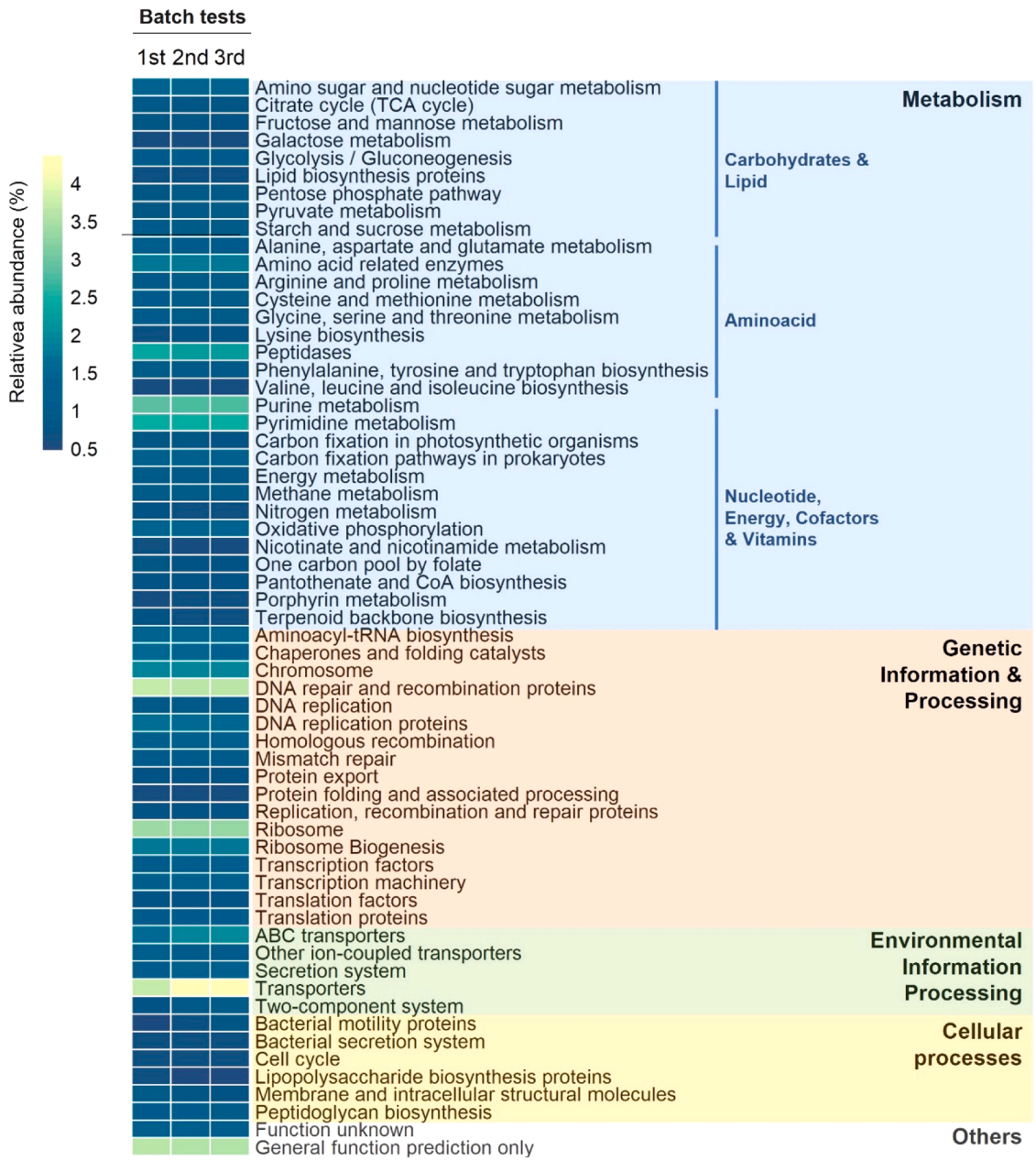

Fig. 3. Heatmap of the sixty-one predominant metabolic pathways at KEGG level 3 (relative abundance > 0.6 %) predicted using PICRUSt2 in the three fermentation batch tests. Prediction was conducted based on 16S rRNA amplicon sequencing data obtained from batch fermentation tests at 3 days. KEGG pathways are distributed in their corresponding KEGG modules indicated by color boxes.

effluent were below 5 % and no VFAs were detected in the trapping solution. Accordingly, the slight VFA reduction in the fermentation liquid during the GPM contactor treatment was attributed to their oxidation as a result of the presence of air in the headspace volume of the feed tank at the beginning of the test.

It is important to highlight that the treated fermentation liquid contained a TAN concentration as low as 10–50 mg N/L and a high VFA concentration (up to 35.3 g COD_{VFA}/L), making it an ideal feedstock for downstream applications where a high C/N ratio is required. In addition to the economic value of biobased VFAs [11,55], the recovery of TAN as a concentrated $(NH_4)_2SO_4$ solution represents another potential source of revenue for the treatment plant [17]. The demand of fertilizers is expected to increase at an annual growth rate of 1.5 % over the coming decade [79], which would increase the future economic expectation of GPM technology. Rongwong et al. [60] concluded that recovering 90 % of nitrogen as solid $(NH_4)_2SO_4$ using GPM technology to treat anaerobic effluents with TAN concentrations ranging from 300 to 700 mg/L could be attractive from an economical point of view. Rongwong et al. [60] also highlighted that the total costs of this treatment was highly influenced by the wastewater pH and alkalinity, the percentage of N recovery and the wastewater flowrate. Noriega-Hevia et al. [51] performed an economic analysis of the implementation of GPM to treat supernatant from anaerobic digestion of sewage sludge concluding that the cost of reagents and membranes composed the 94.5 % of the total costs. Aguilar-Moreno et al. [3] also concluded that GPM technology has the potential to be an economically competitive alternative for nitrogen recovery from anaerobic digester supernatants. Nevertheless, to the best of the authors knowledge, more research is needed to optimize the TAN recovery using GPM under long-term operation for the treatment of complex liquid streams such as OFMSW fermentation liquids, including pre-treatment methods and membrane cleaning protocols that would enhance its cost-effectiveness.

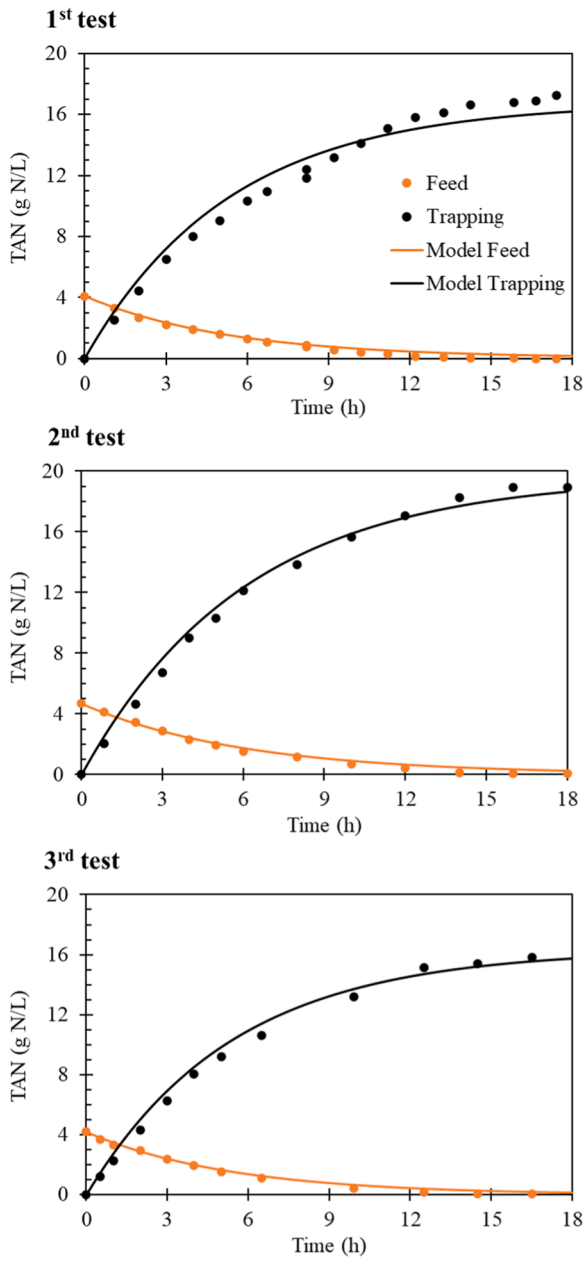

Fig. 4. Evolution of TAN concentration in the feed solution and the trapping solution during the nitrogen recovery process from the fermentation liquids in each test. Dots represent the experimental data and solid lines represent the model best fit.

3.4. Biomethane production tests

Fig. 5 shows the specific cumulative methane production from the VFA-rich fermentation liquids under various TAN concentrations for the two experiments (A and B). Table 5 summarizes the experimental methane yield at the end of the experiment and the fitted parameters of the Gompertz model.

Experimental results show that as the TAN increased from 0.76 to 3.15 g N/L at a working pH near neutrality, the maximum specific methane production rates (R_{max}) decreased from 48.36 to 24.52 NmL CH_4/(g COD_{feed} d) and the lag phase (λ) increased from 0.59 up to 1.37 d (Table 5). These results are in accordance with Berzal de Frutos et al. [15], who reported a 67 % reduction in R_{max} (98–32 mL biogas/(g VS d)) and a lag phase increase (0–2.4 d) when TAN increased from 0.586 to 2.946 g/L. Therefore, for a given pH, lower TAN content lead to higher R_{max} as well as a lower lag time that could increase the overall methane production in continuous digesters [31,42]. More concisely, in the present study, the highest TAN conditions tested lead to a 5–9 % decrease of the methane yield when compared to those monitored when using fermentation effluents previously treated in a GPM for TAN recovery. It is also important to highlight that unionized ammonia (NH_3) has been reported as the most toxic form of ammonia nitrogen [18,57] and, consequently, working at higher pH values would have led to a decrease of methanogens activity.

Finally, considering the theoretical specific methane yield from completely biodegradable COD (350 NmL CH_4/g COD), the biodegradable fraction of the sCOD present in fermentation liquids was estimated at 78–90 %. These percentages are slightly higher than the COD_{VFA}/sCOD ratios obtained in the fermentation liquids used (81 % and 73 % in experiment A and B, respectively), which suggests that other organic compounds present in the fermentation liquid were converted into methane in addition to VFAs.

Overall, these results reveal that recovering TAN from fermentation liquors could improve the kinetics of the subsequent anaerobic digestion process. Therefore, the production of a VFA-rich fermentation liquid from OFMSW and the subsequent recovery of its ammoniacal nitrogen content using gas permeable membranes would potentially enhance or even widen the downstream applications of acidogenic fermentation liquids.

4. Conclusions

OFMSW batch fermentation at mesophilic conditions resulted in volatile fatty acids (VFAs) production in the range of 37–39 g COD_{VFA}/L, with VFAs representing the 73–81 % of the sCOD. The main VFAs were acetic, propionic and butyric acids. The microbial community composition showed a remarkable stability between batches, in agreement with the consistent results in VFA production. Members of *Bacteroidota* and *Firmicutes* predominated in the microbial community, with a high relative abundance for three members of the family *Prevotellaceae*. Functional predictions revealed an enrichment in carbohydrate and protein utilization pathways, identifying the potential for hydrolysis and further break down of complex polysaccharides and proteins. The fermentation liquid was also characterised by a high TAN concentration in the range of 4.1–5.0 g N/L. A gas-permeable membrane was successfully used to recover 99 % of the TAN in the fermentation liquid without affecting its VFA concentration. Biomethane potential tests of the fermentation liquid with a wide range of TAN concentration (0.76–3.15 g N/L) at pH near neutrality showed that moderate TAN concentrations do not affect the ultimate methane yield but do decrease the degradation kinetics. Therefore, the combination of acidogenic fermentation with ammonia recovery using GPM contactors could lead to the valorisation of TAN as a concentrated $(NH_4)_2SO_4$ solution and the generation of a VFA-rich stream with high C/N ratio. Further research is needed to optimize the combined process under long-term continuous operation and to evaluate the potential downstream applications of the obtained fermentation liquid enriched in acetic, propionic and butyric acids.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Table 4
GPM performance for the nitrogen recovery of fermentation liquids in each test.

Parameter	Units	1st test	2nd test	3rd test
Fermentation liquid (feed)				
Initial feed volume	L	1.8	1.8	1.7
Final pH	-	9.20	9.06	9.14
Initial VFA concentration	g COD/L	37.1 ± 2.9	33.0 ± 2.6	32.5 ± 2.5
Final VFA concentration	g COD/L	35.3 ± 2.7	31.4 ± 2.5	30.5 ± 2.3
Initial TAN concentration	g N/L	4.1 ± 0.1	4.7 ± 0.1	4.1 ± 0.1
Final TAN concentration	g N/L	0.01 ± 0.01	0.05 ± 0.01	0.04 ± 0.01
NaOH consumption	mol NaOH/mol N recovered	1.09 ± 0.11	1.04 ± 0.11	1.18 ± 0.13
N removal	%	99.8	98.9	99.0
k_m	(m/s)	$(2.07 \pm 0.08)\cdot10^{-7}$	$(1.83\pm0.08)\cdot10^{-7}$	$(2.05\pm0.09)\cdot10^{-7}$
Trapping solution				
Initial trapping volume	L	0.5	0.5	0.5
Final pH	-	1.50	1.69	1.02
Final VFA concentration	g COD/L	b.d.l.	b.d.l.	b.d.l.
Final TAN concentration	g N/L	17.3 ± 0.2	19.0 ± 0.2	15.8 ± 0.2
H_2SO_4 consumption	mol H_2SO_4/mol N recovered	0.65 ± 0.07	0.63 ± 0.07	0.70 ± 0.08
TAN recovery	%	99.8	98.9	99.0

* b.d.l. stands for below detection limit (<0.01 g COD/L).

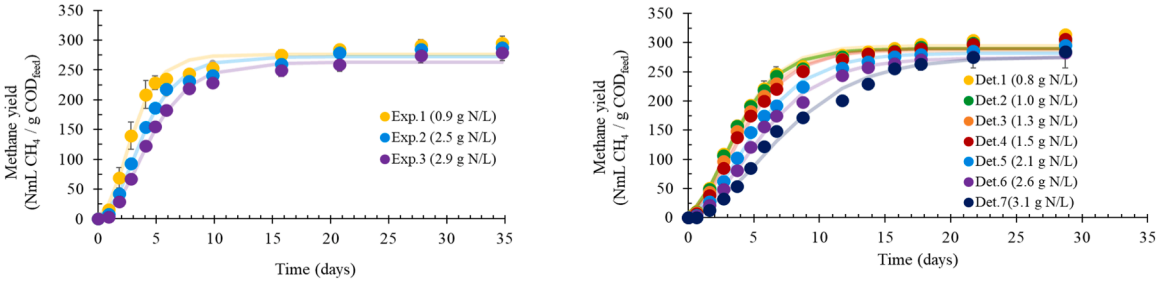

Fig. 5. Biomethane potential curves of the treated fermentation liquids at different TAN concentration in (left) experiment A and (right) experiment B. Dots represent the experimental data and solid lines represent the model best fit.

Table 5
Experimental results and Gompertz model parameters of the BMP tests.

Test	Experimental results		Modelled results				
	TAN (g N/L)	Bo (NmL CH_4/g COD_{feed})	Bo (NmL CH_4/g COD_{feed})	R_{max} (NmL CH_4/g COD_{feed} d)	λ (d)	R^2	RMSE
A1	0.94 ± 0.07	295 ± 12	275.88	63.25	0.67	0.98	14.29
A2	2.47 ± 0.04	288 ± 4	272.25	48.27	0.93	0.99	11.96
A3	2.91 ± 0.06	279 ± 21	262.84	40.91	1.17	0.99	9.86
B1	0.76 ± 0.03	314 ± 4	294.89	48.36	0.59	0.99	9.87
B2	1.00 ± 0.02	305 ± 2	289.69	48.21	0.62	0.99	8.93
B3	1.26 ± 0.02	302 ± 7	286.49	45.38	0.67	0.99	8.40
B4	1.54 ± 0.04	306 ± 5	290.03	43.00	0.76	0.99	8.67
B5	2.07 ± 0.12	295 ± 7	281.93	36.23	0.97	0.99	7.81
B6	2.61 ± 0.04	283 ± 7	274.09	31.83	1.15	0.99	7.59
B7	3.15 ± 0.10	285 ± 28	276.27	24.52	1.37	0.99	11.06

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.112352.

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