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Ammonia recovery from acidogenic fermentation effluents using a gas-permeable membrane contactor

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Abstract

A gas-permeable membrane (GPM) contactor was used to recover ammoniacal nitrogen from a synthetic and a biowaste fermentation broth under different pH (from 6 to 11) and temperatures (35 and 55 °C). Ammonia mass transfer constant (K_m) increased as pH and temperature increased. For synthetic broth, pH 10 provided the best results, when considering the K_m ($9.2 \cdot 10^{-7}$ m·s^{-1}) and the reagents consumption (1.0 mol NaOH mol^{-1} TAN and 1.2 mol H_2SO_4·mol^{-1} TAN). Biowaste fermentation generated a broth with a high concentration of ammoniacal nitrogen (4.9 g N·L^{-1}) and volatile fatty acids (VFA) (28.5 g·L^{-1}). Experiments using the biowaste broth showed a

lower K_m ($5.0 \cdot 10^{-7}$ $m \cdot s^{-1}$ at pH 10) than the synthetic broth, related to the solution matrix and other species interference. VFAs were not detected in the trapping solution. Overall, these results show that GPM is a suitable technology to efficiently separate ammoniacal nitrogen and VFA from fermentation broths.

KEYWORDS: membrane technology; nitrogen recovery; food waste fermentation; volatile fatty acids; biorefinery

1. Introduction

Gas-permeable membrane (GPM) contactor is an emerging technology to recover ammoniacal nitrogen from wastewater as N-based fertiliser (e.g. $(NH_4)_2SO_4$, NH_4NO_3, $(NH_4)_2HPO_4$), with a market value of 0.4-1.0 €·kg^{-1} N for $(NH_4)_2SO_4$ (Darestani et al., 2017; Menkveld and Broeders, 2018). In GPM, ammonia (NH_3) diffuses across the membrane from the feed-membrane interface to an acidic trapping solution. NH_3 is a non-charged species able to diffuse through a nano-perforated hydrophobic membrane, and its diffusion is driven by the NH_3 concentration difference between the feed and the trapping solution. Once at the acidic solution, NH_3 is protonated and converted to ammonium (NH_4^+), an ionised species unable to diffuse across the membrane. Liquid penetration into the pores (membrane wetting) is prevented by (i) the hydrophobic nature of the membrane and (ii) the small size of the nanopores due to the capillary effect (Boehler et al., 2015).

GPM contactors have been successfully used to recover total ammoniacal nitrogen (TAN) from anaerobic digestion supernatants (Noriega-Hevia et al., 2020; Dube et al., 2016), the effluent of a primary treatment in a municipal wastewater treatment plant

(Lee et al., 2021), concentrates from the regeneration of zeolites (Vecino et al., 2019), human urine (Nagy et al., 2019), and pig slurry (García-González and Vanotti, 2015; García-González et al., 2015; Riaño et al., 2019). However, the recovery of TAN from fermentation broths has not been reported, despite the potential application of this approach in biorefineries schemes that require to decouple easily biodegradable organic matter from TAN. This would be the case of the proposed biorefinery scheme that aims to produce polyhydroxyalkanoates (PHA) from biowaste (Figure 1).

PHA production using mixed-cultures is typically carried out by a 3-stage process (Reis et al, 2011; Frison et al., 2015). In the anaerobic stage, the biowaste is fermented to produce a volatile fatty acids (VFA) rich fermentation broth. In the selection stage, a sequencing batch reactor fed with the fermentation liquid (liquid fraction from fermentation broth solid-liquid separation) produces biomass with high PHA storage capacity by alternating periods with high VFA availability (feast) and periods with absence of VFA (famine). In the accumulation stage, the selected PHA-storing biomass is fed with the VFA-rich fermentation liquid (batch mode and aerobic conditions) to promote the maximum accumulation of PHA. Recovering TAN from the fermentation liquid before using it as carbon source in the selection reactor could enhance the efficiency of PHA production by decoupling the carbon and nitrogen availability in the feast and famine phases. Oliveira et al. (2017), Silva et al. (2017) and Lorini et al. (2020) improved PHA production when carbon and nitrogen were fed separately.

Recovering nitrogen from the fermentation liquid with GPM would also reduce the TAN concentration in the anaerobic digester that treats the unfermented solid fraction and other reject streams of the biorefinery (Figure 1). This feature could alleviate or

avoid NH_3 inhibition of the anaerobic digestion process (Capson-Tojo et al. 2020). In this regard, Lauterböck et al. (2014) reported an improved methane production from slaughterhouse wastewater when the TAN concentration was decreased from 6.5 to 2.5 g TAN·L^{-1} in the anaerobic digester. Shi et al. (2019) achieved a stable operation at high organic loading rates in an anaerobic digester treating food waste after TAN recovery. Bayrakdar et al. (2017) and González-García et al. (2021) also reported a positive impact on the biogas production in an anaerobic digester treating chicken and pig manure, respectively.

Several factors influence TAN recovery by GPM such as pH, temperature, salinity, initial TAN concentration, the feed flowrate, the membrane material and contactor configuration, and membrane fouling (Boehler et al., 2015; Rongwong and Goh, 2020). Among them, pH and temperature are particularly important since they have a noticeable impact on NH_4^+/NH_3 equilibrium. Many studies have evaluated the impact of pH and temperature on the efficiency of GPM contactors (Fillingham et al., 2017; Noriega-Hevia et al., 2020). However, to the best of the authors' knowledge, the impact of pH and temperature on GPM performance has not yet been evaluated for a hybrid process recovering TAN from fermentation broths. This is an important application because fermentation and GPM could be important technologies in future biorefineries. Accordingly, an experimental study evaluating the impact of pH and temperature on the performance of GPM is important to understand how these two operational factors influence the recovery of TAN from fermentation broths.

This work assesses the impact of pH and temperature on the performance of a GPM contactor to separate TAN and VFAs from biowaste fermentation broths. The recovery

of TAN was evaluated for a synthetic and a biowaste fermentation liquid under different pH and temperature conditions. The ultimate goal was to find the optimum pH and temperature condition to integrate a hybrid GPM process that recovers TAN as N-based fertiliser and produces a VFA-rich stream with limited N concentration from fermentation broths.

2. Material and methods

2.1 Synthetic solution and OFMSW

Synthetic and organic fraction of municipal solid waste (OFMSW) fermentation broths were used in this study. The synthetic broth consisted in deionised water containing 7.0 g $NH_4Cl \cdot L^{-1}$ (2.35 g $TAN \cdot L^{-1}$) and 3.0 $g \cdot L^{-1}$ of acetic acid (3.2 g $COD \cdot L^{-1}$). Acetic acid was selected to determine the maximum diffusion of VFA through the membrane since this is the VFA with the lowest molecular weight. The OFMSW fermentation broth was obtained from OFMSW fermentation at 35 °C (see characterisation in e-supplementary material). The OFMSW was collected from a mechanical-biological treatment (MBT) plant of the Barcelona Metropolitan Area (Spain) that treats about 50,000 t per year of source-sorted OFMSW. The OFMSW was collected after the pre-treatment and before its feeding to the anaerobic digesters (see description of the MBT plant in Fernández-Domínguez et al., 2020). The high soluble COD and VFA concentration of the collected OFMSW could be attributed to the pre-fermentation of the OFMSW in the pulper and hydrocyclones system of the MBT plant.

2.2 Experimental set-up

2.2.1 Acidogenic fermenter

A 40-L fermenter at mesophilic conditions (35 °C) was used to produce the OFMSW fermentation broth. The fermenter was equipped with a mechanical stirrer (Triam, 75040), a pH probe system (Crison pH 28), a heating system (AS, Electric Heating Jacket) and an alleviation valve located at the top of the fermenter to avoid overpressure. 30 kg of OFMSW were fed to the reactor without adding external inoculum nor external chemicals since it was considered that the anaerobic digestion supernatant recirculation provided enough fermentative bacteria and alkalinity. The fermentation batch lasted 8 days, when the VFA concentration reached its maximum value. The fermentation broth used in the membrane contactor was obtained after sieving (0.05 mm mesh size), centrifuging (16600 × g, 10 min) and filtering (1.2 µm mesh light filter) the fermentation broth. The resulting fermentation liquid was stored at 4 °C until use.

2.2.2. Membrane contactor

Figure 2 shows the membrane contactor experimental set-up used to recover TAN from the feed solution. Two 2-L jacketed glass tanks were used as chambers for the feed (fermentation broth) and the acidic trapping solution (initial solution of 0.1 M H_2SO_4). The feed and trapping solutions were pumped using a peristaltic pump in a closed loop to a microporous hollow-fibre polypropylene (PP) membrane contactor with an active surface area of 0.50 m^2 (3M, 1.7 x 5.5 MiniModule). The relation between feed solution and trapping solution flow rates was 3:1 according to manufacturer's recommendations. Specifically, the feed solution flow rate was 15 $L \cdot h^{-1}$ (shell side of the membrane) and the trapping solution flow rate was 5 $L \cdot h^{-1}$ (lumen side of the contactor). The operational temperature was achieved by circulating water

from a heated water bath through a jacket surrounding the tanks. These tanks were sealed to minimise NH_3 losses by volatilisation. Each tank was equipped with a magnetic stirrer (180 rpm) and a pH control system consisting of a pH electrode (Crison, code 53 35) and a pH controller (Crison, pH 28), connected to peristaltic pumps (Ismatec, Type ISM827). The peristaltic pumps dosed an acid solution (H_2SO_4 75%) to keep the trapping solution at pH 1.0 and an alkali solution (NaOH 10 M) to keep the feed solution at the targeted set point. The trapping solution needs to be acid enough to retain the NH_3 diffused from the feed solution as NH_4^+, since charged species are not able to diffuse through the membrane. The feed solution needs to be alkaline to displace the TAN equilibrium towards NH_3, which is the non-charged species able to diffuse across the membrane from the feed to the trapping solution. The fermentation liquor was filtered through 1.2 µm filters to prevent membrane clogging.

2.3 Membrane contactor operational conditions

Table 1 summarizes the operational conditions of the experiments carried out with the membrane contactor. Firstly, the effect of pH (6.0, 7.0, 8.0, 9.0, 10.0 and 11.0) and temperature (35 and 55 °C) was evaluated using the synthetic fermentation liquid as a feed solution. These temperatures were selected since both mesophilic (35 °C) and thermophilic (55 °C) conditions are used to ferment OFMSW (Bolzonella et al., 2012; Micolucci et al., 2020; Valentino et al., 2021). Subsequently, considering the results from the synthetic fermentation liquid, experiments at pH of 9.0 and 10.0 and at temperature of 35 and 55 °C were carried out using the OFMSW fermentation liquid as feed solution. The experiments carried out with the synthetic fermentation liquid had 2 L of feed and trapping solution, while the experiments using the OFMSW

157 fermentation liquid were conducted with a lower volume (0.5 L of feed and trapping
158 solutions) due to the difficulty to filter the OFMW fermentation broth through 1.2 µm
159 filters. All conditions were tested by duplicate.

160 The process was monitored by withdrawing several samples from the feed and
161 trapping solution during the experiments (ca. 8 hours). The sampling frequency was
162 once per hour, except the first hour where two samples were withdrawn. In each
163 sampling event, 4 mL were withdrawn from both solutions. For the feed solution
164 sample, 0.1 mL of sulfuric acid (1 M) was immediately added to decrease the pH and
165 prevent TAN losses by volatilisation. All samples were stored at 4 °C prior analysis.

166 The TAN recovery efficiency was calculated using Equation 1, where $TAN_f(0)$ is the
167 initial TAN mass in the feed solution (g), $TAN_t(0)$ is the initial TAN mass in the trapping
168 solution (g), and $TAN_t(t)$ is the TAN mass at a specific time (g). The nitrogen mass
169 balance showed that nitrogen losses by volatilisation where minimal (< 1%).
170 Accordingly, it was assumed that there were no losses of NH_3 by volatilisation.

171 $$\%\ \text{TAN recovery}\ (t) = \frac{g\ TAN_t(t) - g\ TAN_t(0)}{g\ TAN_f(0)} \cdot 100 \quad (1)$$

172 **2.4 Analytical methods**

173 All the analyses were performed according to the Standard Methods for the
174 Examination of Water and Wastewater (APHA, 2017). TAN concentration was
175 determined using a Thermo Fisher Scientific ion-selective electrode (Orion
176 9512HPBNWP) following the procedure 4500-NH3D. Total solids (TS) and volatile solids
177 (VS) were measured according to Standard Method 2540G (APHA, 2017). Alkalinity was
178 determined following the Standard Method 2320B, using an automated titrator (Crison

pH Burette 24) with a 0.1 M HCl solution and a pH endpoint of 4.30. The soluble fraction was obtained by centrifuging the samples at 16600 × g (Sigma 1-14 microcentrifuge) for 10 min and filtering the supernatant through a 1.2 µm mesh light cellulose filter. Soluble COD was determined according to the Standard Method 5220C (APHA, 2017). Cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, $P\text{-}PO_4^{3-}$) were analysed using an 863 Advanced Compact IC Metrohm ionic chromatographer and Metrosep columns (Metrosep C 4-150/4.0 and Metrosep A Supp 17-250/4.0, respectively). VFAs (i.e. acetic, propionic, i-butyric, n-butyric, ivaleric, n-valeric, i-caproic, n-caproic and heptanoic acid) were analysed using a Shimadzu GC-2010 plus gas chromatograph equipped with a Nukol™ capillary column and flame ionisation detector. VFAs were converted to COD equivalents using the theoretical value (mg COD·mg^{-1} compound): 1.07 for acetic acid, 1.51 for propionic acid, 1.82 for butyric acid, 2.04 for valeric acid, 2.21 for caproic acid, and 2.34 for heptanoic acid.

2.5 Ammonia mass transfer constant assessment

NH_3 flux through the membrane contactor was evaluated by the NH_3 mass transfer constant (K_m). K_m is also defined as the conditional permeability of the NH_3 through the membrane and allows quantifying the nitrogen transfer under specific conditions (Ashrafizadez and Khorasani, 2010; Ahn et al., 2011; Reig et al., 2021).

The physicochemical model used to determine K_m considers that: (i) the hydrophobic membrane is only permeable to NH_3, (ii) the pH of the feed and trapping solutions is constant, (iii) the acid-base equilibrium is always fulfilled at both sides of the

membrane, (iv) NH_3 losses by volatilisation are negligible and (v) the volumes of the feed solution (V_f) and the trapping solution (V_t) are constant.

NH_3 transport is described by Fick's law (Equation 2) that considers (i) a behaviour of ideal diluted solution for NH_3 and (ii) no interferences amongst solution components.

$$J_{NH_3,f}(t) = -K_m\left(c_{NH_3,t}(t) - c_{NH_3,f}(t)\right) \quad (2)$$

Where $J_{NH_3,f}(t)$ is the flux of NH_3 (mol·m^{-2}·s^{-1}) from the feed to the trapping solution (at time *t*), K_m ($K_m = D_{NH_3}/\Delta x$) is the NH_3 mass transfer constant through the membrane (m·s^{-1}), D_{NH_3} is the diffusion coefficient of NH_3 (m^2·s^{-1}), Δx is the thickness of the membrane (m), $c_{NH_3,f}$(t) is the concentration of NH_3 in the feed solution (mol·m^{-3}, at time *t*) and $c_{NH_3,t}(t)$ is the concentration of NH_3 in the trapping solution (mol·m^{-3}, at time *t*).

The equilibrium reaction $NH_4^+ \leftrightarrow NH_3 + H^+$, is described by the following acid-base approximate equilibrium constant $K_a(T)$, in each side of the membrane, *i* :

$$K_a(T) \approx \frac{c_{NH_3,i} \cdot 10^{-pH_i}}{\gamma_{NH_4^+,i} \cdot c_{NH_4^+,i}} \quad (3)$$

Where $\gamma_{NH_4^+,i}$ is the activity coefficient for NH_4^+, which could be described by the Davies correction of Debye-Hückel law and depends on the ionic force (assumed to remain constant in both sides of the membrane during the process). Equation 4 correlates the value of $K_a(T)$ for a given temperature (T, K) (Anthonisen et al., 1976).

$$K_a(T) = e^{-6344/T} \quad (4)$$

The TAN mass balance (TAN = $NH_3 + NH_4^+$) expressed in terms of the TAN fraction at time t is kept constant: $z_f(t) + z_t(t) = 1$, where $z_i(t) = x_i(t) + y_i(t)$, and $x_i(t) = \frac{mol_{NH_3,i}(t)}{mol_{TAN,0}}$, $y_i(t) = \frac{mol_{NH_4^+,i}(t)}{mol_{TAN,0}}$. These are the non-dimensional fractions for both NH_3 and NH_4^+ in terms of the initial TAN.

Then, mass transport equation (Equation 2) can be written as Equation 5, which can be arranged in terms of non-dimensional TAN fraction (Equation 6).

$$J_{NH_3,f}(t) = -\frac{1}{A}\left(\frac{dmol_{NH_3,f}}{dt}\right) = -K_m\left(\frac{mol_{NH_3,t}}{V_t} - \frac{mol_{NH_3,f}}{V_f}\right) \quad (5)$$

$$\frac{dz_f(t)}{dt} = \alpha(\omega\,\beta - (1 + \omega\,\beta)\,z_f(t)) \quad (6)$$

Where $\alpha \equiv \frac{K_m\,A}{V_f}$, $\omega \equiv \frac{V_f}{V_t}$; $\beta \equiv \frac{\beta_t}{\beta_f}$, $\beta_i \equiv \frac{\overline{K}_i}{1+\overline{K}_i}$, $\overline{K}_i \equiv \gamma_{NH_4^+,i}\,10^{pH_i - pKa}$

With the initial solution $z_f(0) = 1$, the solution of this ordinary differential equation is:

$$z_f(t) = \frac{(\omega\,\beta + \exp(-\alpha\,(1+\omega\,\beta)\,t))}{1+\omega\,\beta} \quad (7)$$

With limit solutions that depends on ω and β: $\lim_{t\to\infty} z_f(t) = \frac{\omega\,\beta}{1+\omega\,\beta}$ and $\lim_{t\to\infty} z_t(t) = \frac{1}{1+\omega\,\beta}$

As β depends on pH_t,pH_f,pKa, an approximate solution can be derived depending on the trapping solution pH. When the pH of the trapping solution is 1: pH_t << pKa, $\overline{K}_t \equiv \gamma_{NH_4^+,t}\,10^{pH_t - pKa} \approx \gamma_{NH_4^+,t}\,10^{-8} \ll 1$, then $\overline{K}_t \to 0$, and $\beta \to 0$. Therefore, Equation 8 could be simplified to Equation 8.

$$z_f(t) = \exp(-\alpha\,t) \quad (8)$$

A complete recovery of TAN could be reached for operation times long enough ($\lim_{t\to\infty} z_f(t) = 0$). Then, Equation 8 in terms of TAN concentration can be written as Equation 9, a well-known equation to describe TAN recovery in GPM studies.

$$\frac{C_{TAN,f}(t)}{C_{TAN,f}(0)} = \exp\left(-\frac{K_m A}{V_f} t\right) \quad (9)$$

This model was coded in 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 TAN concentration of the feed and trapping solution in the tanks over time.

3. Results and discussion

3.1 Ammonia recovery from the synthetic fermentation liquid

Figure 3 illustrates the TAN concentration evolution of the experiments carried out with synthetic fermentation liquid and Table 2 summarises their performance parameters. Experimental results show that the performance (i.e., TAN recovery rate, flux, K_m) of the membrane contactor improves as the pH of the feed solution increases from 6.0 to 11.0. At pH 10.0 and 11.0, TAN was completely recovered after 4 hours of experiment at both temperatures, while at pH 6.0 the percentage of TAN recovery was lower than 10% after 8 hours. The greater performance of the membrane at higher pH can be directly related to the higher amount of NH_3 in the solution due to the displacement of the NH_4^+/NH_3 equilibrium (Equation 3). pH values higher than the pKa (8.94 and 8.45 at 35 and 55 °C, respectively) implies that the percentage of NH_3 represents more than the 50% of the TAN. The process performance was better at 55

°C than at 35 °C. However, at pH of 10.0 and 11.0, no statistical difference was observed between tests carried out at 35 and 55 °C. These results can be explained by the minimal difference on NH_3 concentration between pH 10.0 and 11.0 (far above the pKa). The improved membrane performance at 55 °C can be attributed to the lower pKa values at higher temperatures, which increases the NH_3 concentration and the driving force through the GPM. Besides changes in the pKa value, temperature can also affect the K_m since it can modify the membrane properties with a slight impact on NH_3 diffusivity.

TAN flux across the membrane was enhanced as the pH and temperature of the feed solution increased (Table 2). At 35 °C, increasing the pH from 9.0 to 10.0 doubled the TAN flux from 62 to 115 g $N \cdot m^{-2} \cdot day^{-1}$, while a less noticeable improvement was obtained when the pH was further increased to 11.0 (138 g $N \cdot m^{-2} \cdot day^{-1}$). The change in TAN flux at higher pH was also evident in the fitted K_m values, which sharply increased with pH. The fitted K_m values was slightly lower at pH 10.0 than at pH 11.0 with values of $0.92 \cdot 10^{-6}$ and $1.13 \cdot 10^{-6}$, respectively. However, there was no significant difference in K_m values when comparing 35 and 55 °C (Table 2). The superior performance of NH_3 membrane contactors at pH 10.0 and 11.0 is in accordance with the results reported by Ashrafizadeh and Khorasani (2010) and Noriega-Hevia et al. (2020), who reported a K_m of $10.9 \cdot 10^{-6}$ and $2.4 \cdot 10^{-6}$ $m \cdot s^{-1}$ at pH 10, respectively. Vecino et al. (2019) and Reig et al. (2021) also reported similar K_m values when operating the same membrane module under similar conditions ($0.7 \cdot 10^{-6}$ and $1 \cdot 10^{-6}$ $m \cdot s^{-1}$, respectively). NH_3 diffusion through the membrane was not affected by the presence of acetic acid since similar K_m were observed for experiments carried out with and without acetic acid (data not shown).

This observation is in accordance with Daguerre-Martini et al. (2018), who assessed the effect of humic acids concentration in the feed solution on the TAN transfer using an e-PTFE membrane.

Acetic acid concentration in the feed solution remained constant during all the experiments at 3.2 g COD·L^{-1} while its concentration in the trapping solution was below the detection limit for all experiments (<10 mg·L^{-1}). These results are in line with the results of Molinuevo-Salces et al. (2018), who reported a minimal transfer of soluble organic matter (5-20 mg COD·L^{-1}·day^{-1}) and cations (0-20 mg·L^{-1}·day^{-1}) through an e-PTFE membrane when recovering TAN from pig manure. The retention of acetic acid allows hypothesising that VFAs with higher molecular weight (e.g., propionic acid, butyric acid) would not diffuse across the membrane and would not affect the nitrogen recovery efficiency under the tested operating conditions.

The specific reagent consumption (mol reagent spent·mol^{-1} N recovered) after 8 hours was lower when working with higher feed pH values for both NaOH and H_2SO_4 (Table 2). These results show that the process is more reagent efficient at higher feed solution pH values. Reagent consumption during the test did not consider the reagents needed at the beginning of the process to reach the initial pH. Considering that only NH_3 was able to diffuse the membrane, the theoretical maximum consumption during the test would be 1 mol NaOH·mol^{-1} N recovered and 0.5 mol H_2SO_4·mol^{-1} N recovered. Since these experiments were performed using a synthetic solution without extra alkalinity, it is observed that the total reagents consumption approached to the theoretical value in those tests where a complete nitrogen recovery was obtained (e.g., Experiment 1F, 2E).

These experimental results allowed considering pH 10.0 as the preferable pH for this GPM contactor. In comparison with other pH values, pH 10.0 provides (i) a high TAN flux across the membrane and (ii) a lower consumption of reagents (alkali and acid) per unit of nitrogen recovered. This conclusion agrees with Ashrafizadeh and Khorasani (2010), who reported that pH above 10.7 did not improve NH_3 removal. However, a recent study by Lee et al. (2021) suggested that the application of moderate alkaline pH values (i.e., 9.0) could be beneficial to prevent inorganic fouling on the membrane.

3.2 OFMSW fermentation

Figure 4 shows the VFAs, sCOD, TAN and pH values during OFMSW fermentation. The VFA concentration steadily increased from 21.7 g COD·L^{-1} up to a maximum concentration of 41.1 g COD·L^{-1} (day 7), with a concomitant pH decrease (from 6.96 to 6.47). The VFA yield was 0.63 g COD_{VFA}·g^{-1} VS, slightly higher than the fermentation yield reported by Fernandez-Domínguez et al. (2020), who fermented OFMSW from the same MBT plant. During the fermentation batch, the proportion of acetic and propionic acids remained nearly constant, while the proportion of valeric and caproic acids increased to the detriment of butyric acid (Figure 4a). At the end of the batch (day 8), the proportion of acetic, propionic, and butyric acids were 34%, 25% and 27%, respectively (Figure 4b). The COD_{VFA}/sCOD ratio increased over time reaching a final value of 0.92±0.05 (Figure 4c). This COD_{VFA}/sCOD ratio is higher than the reported by Fernandez-Domínguez et al. (2020) but aligns with Valentino et al. (2021) results. The latter reported a COD_{VFA}/sCOD ratio of 0.90 when treating screw pressed OFMSW. The high acidification efficiency (percentage of sCOD as COD_{VFA}) reached in this study is a

positive feature for the proposed biorefinery (Figure 1). On one hand, a fermentation broth with a low concentration of non-VFA soluble COD is preferable for PHA production, since it provides a good selection of PHA-storing microorganisms (Valentino et al., 2017). On the other hand, the low concentration of non-VFA sCOD implies that the organic matter that has not been converted to VFA is diverted to the anaerobic digester for biogas production. Finally, it is worth mentioning that the TAN concentration increased from 3.8 to 4.9 $g \cdot L^{-1}$ due to ammonification of organic nitrogen (Figure 4d). The resulting TAN/COD_{VFA} ratio is 0.12 mg $N \cdot mg^{-1}$ COD, which is unfavourable to produce PHA (Sriyapai et al., 2021; Lee et al., 2014). Therefore, removing TAN from the fermentation broth is paramount to utilise this stream for PHA production.

3.3 Ammonia recovery from the OFMSW fermentation liquid

Figure 5 shows the TAN concentration evolution of the experiments carried out with the OFMSW fermentation liquid and Table 3 summarises their performance parameters. It can be observed that the operation time required to reach the same TAN recovery is much shorter than the time required for the synthetic fermentation liquid (Figure 3), which is attributed to the operation of the system at a higher area to volume ratio (membrane area to feed solution volume). The higher TAN fluxes obtained in these experiments compared to the ones obtained with the synthetic solution can be attributed to higher initial TAN concentration of the OFMSW fermentation liquid (higher concentration gradient). K_m will be the parameter used to compare these results with those obtained from the synthetic solution since it does

not depend on the operation time, the initial TAN concentration, nor the volumes of the feed and trapping solution as well as its ratio.

The K_m values obtained with the OFMSW fermentation liquid showed the same trend than those obtained with the synthetic solution: (i) a higher NH_3 mass transfer at pH 10 than at pH 9, and (ii) a higher NH_3 mass transfer at 55 °C than at 35 °C. However, the K_m values obtained using the OFMSW fermentation liquid were lower than those obtained with the synthetic solution. At 55 °C, the K_m values at pH 9.0 and 10.0 were $3.3 \cdot 10^{-7}$ and $5.4 \cdot 10^{-7}$ $m \cdot s^{-1}$, respectively, while the equivalent K_m for the synthetic solution were $5.9 \cdot 10^{-7}$ and $9.3 \cdot 10^{-7}$ $m \cdot s^{-1}$. The lower performance of the GPM contactor using the OFMSW fermentation liquid cannot be attributed to membrane fouling since the tests conducted with the synthetic solution before and after operating the GPM with the OFMSW fermentation liquid reached the same K_m values (data not shown). The low membrane fouling observed in these experiments could be attributed to: (i) the low fouling propensity of PP membranes compared with other membranes such as PTFE membranes (Zarebska et al., 2015) and (ii) the low duration of the experiments (< 8 h). Accordingly, the loss of performance could be related to the interference (e.g., ionic interaction) of other species and the complex matrix of the fermentation liquid.

As for the synthetic solution experiments, the specific reagent consumption per unit of TAN recovered was higher at pH 9 than at pH 10. The total NaOH and H_2SO_4 consumption in the OFMSW fermentation experiments was almost the same than the consumption in the synthetic feed experiments (Table 2 and 3). The NaOH required to adjust the pH at the beginning of the experiment was higher, but the amount of NaOH required to keep the pH at the set point was noticeably lower. This behaviour can be

370 explained by the alkalinity of the OFMSW fermentation liquid (9.1 g $CaCO_3 \cdot L^{-1}$) that
371 acted as a buffer making the pH of the feed solution harder to raise, but also harder to
372 decrease during the operation. The total consumption of H_2SO_4 was similar to
373 synthetic feed solution experiments, but its addition during the experiment was lower.
374 It is worth noting that H_2SO_4 consumption was slightly higher than the stoichiometric
375 values of 0.5 mol $H_2SO_4 \cdot mol^{-1}$ TAN recovered, probably caused by the excess of acid in
376 the trapping solution at the end of the test due to the limited accuracy of the dosing
377 pump controlling the trapping solution pH. .

378 Figure 6 shows the VFA concentration during each experiment treating OFMSW
379 fermentation liquid. The initial concentration was slightly lower (37.5-38.8 g $COD_{VFA} \cdot L^{-1}$)
380 than the measured at the end of the fermentation batch (41.1 g $COD_{VFA} \cdot L^{-1}$). This
381 implies that a VFA loss occurred during sample post-treatment (i.e., filtration and
382 centrifugation). During the experiments, none of the VFAs were detected in the
383 trapping solution (detection limit of 10 $mg \cdot L^{-1}$), which demonstrates that VFAs are
384 unable to diffuse across the membrane under the tested conditions. However, a small
385 VFA loss in the feed stream (8.7-10.7% on COD basis) was recorded during the
386 experiments. The authors attribute this phenomenon to the biological aerobic
387 degradation of these compounds. The feed tank was closed but it was not flushed and
388 sealed with an inert gas (e.g. N_2) to prevent the presence of oxygen. Strategies to
389 minimize VFA losses should be considered in future research.

390 Finally, it is worth mentioning that no increase in ions concentration (i.e., Ca^{2+}, Mg^{2+},
391 K^+, Na^+, Cl^-) was detected in the trapping solution (detection limit of 0.5 $mg \cdot L^{-1}$).
392 Similarly, the ions concentration in the feed solution at the beginning and at the end of

393 the experiments remained constant. Thus, it can be stated that ions did not diffuse
394 through the membrane from the feed to the trapping solution, at least, at short-term
395 conditions.

396 Overall, the results of these experiments show that the combination of acidogenic
397 fermentation with a membrane contactor unit could be a technological solution to
398 separate TAN and VFA.

399 **Conclusions**

400 A gas-permeable membrane contactor was used to recover ammoniacal nitrogen from
401 fermentation broths. Nitrogen recovery efficiency improved at higher pH and
402 temperatures. The optimum pH was 10 since high K_m were achieved at expenses of low
403 reagent consumption. For the OFMSW fermentation liquid, the K_m values were lower
404 than for the synthetic liquid, although the K_m followed the same trend with pH and
405 temperature. Ions and VFA present in the fermentation liquid were not detected in the
406 trapping solution. Overall, the results showed that membrane contactors can
407 efficiently separate ammoniacal nitrogen and VFAs from fermentation broths.

408 **Supplementary material**

409 E-supplementary data for this work can be found in e-version of this paper online.

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539 **Authors contribution statement**

540 **Andreu Serra-Toro:** Methodology, Investigation, Formal analysis, Writing - original draft,
541 Visualisation. **Sergi Vinardell:** Methodology, Writing - review & editing, Visualisation.
542 **Sergi Astals**: Conceptualization, Writing - Review & Editing, Supervision, Visualisation,
543 Funding adquisition. **Sergio Madurga**: Formal analysis, Writing - Review & Editing,
544 Visualisation, **Joan Llorens**: Methodology, Writing - Review & Editing. **Joan Mata-**
545 **Álvarez:** Writing - Review & Editing, Funding adquisition. **Francesc Mas:**
546 Conceptualization, Methodology, Formal analysis, Writing - Review & Editing,
547 Supervision, Visualisation, Funding adquisition. **Joan Dosta:** Conceptualization,

Methodology, Investigation, Writing - Review & Editing, Supervision, Visualisation, Funding adquisition.

39.

Declaration of interests

☐ 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.

☒ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

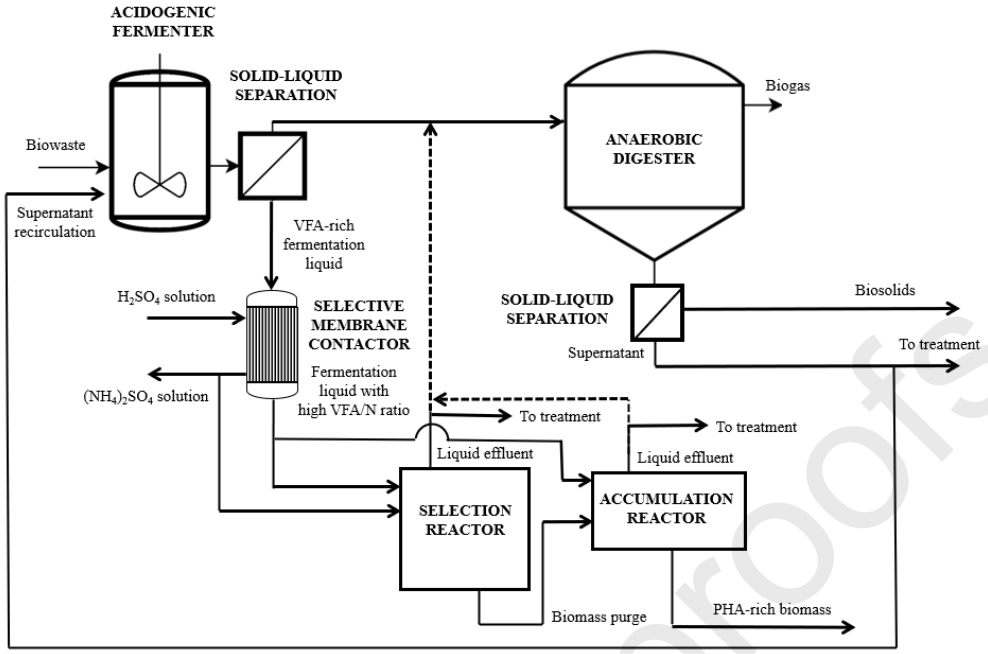
Andreu Serra-Toro reports financial support was provided by Indukern company (Barcelona).

40.

Highlights

- Membrane contactor efficiently recovered NH_3 from a biowaste fermentation broth
- Membrane contactor allowed a complete separation of NH_3 from volatile fatty acids
- Higher operating temperatures and pH enhanced NH_3 mass transfer rate
- NH_3 was successfully recovered at alkaline pHs (9, 10 and 11) at 35 and 55 °C
- Ions present in the fermentation broth were not detected in the trapping solution

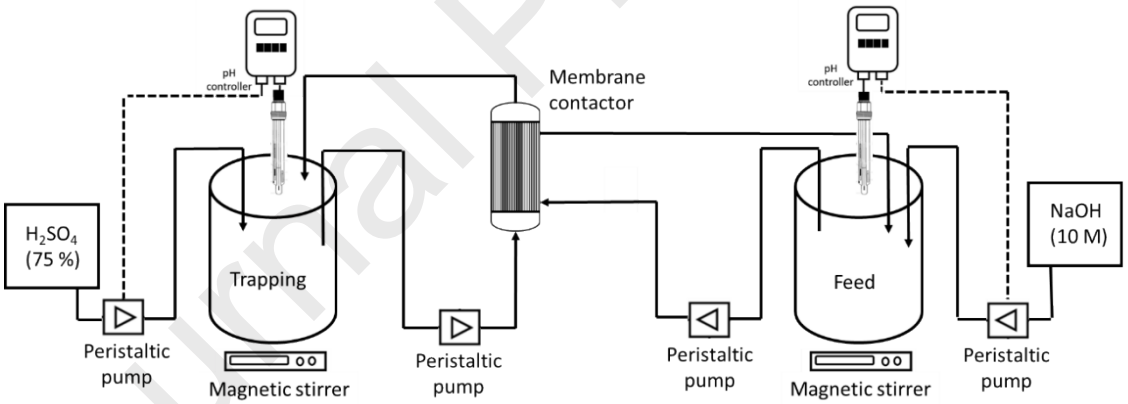
41.



573

574 **Figure 1.** Scheme of the proposed biorefinery scheme for PHA production from biowaste using
575 a GPM contactor to separate TAN from the fermentation liquid.

576 42.



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578 **Figure 2**. Schematic representation of the lab-scale membrane contactor set-up.

579 43.

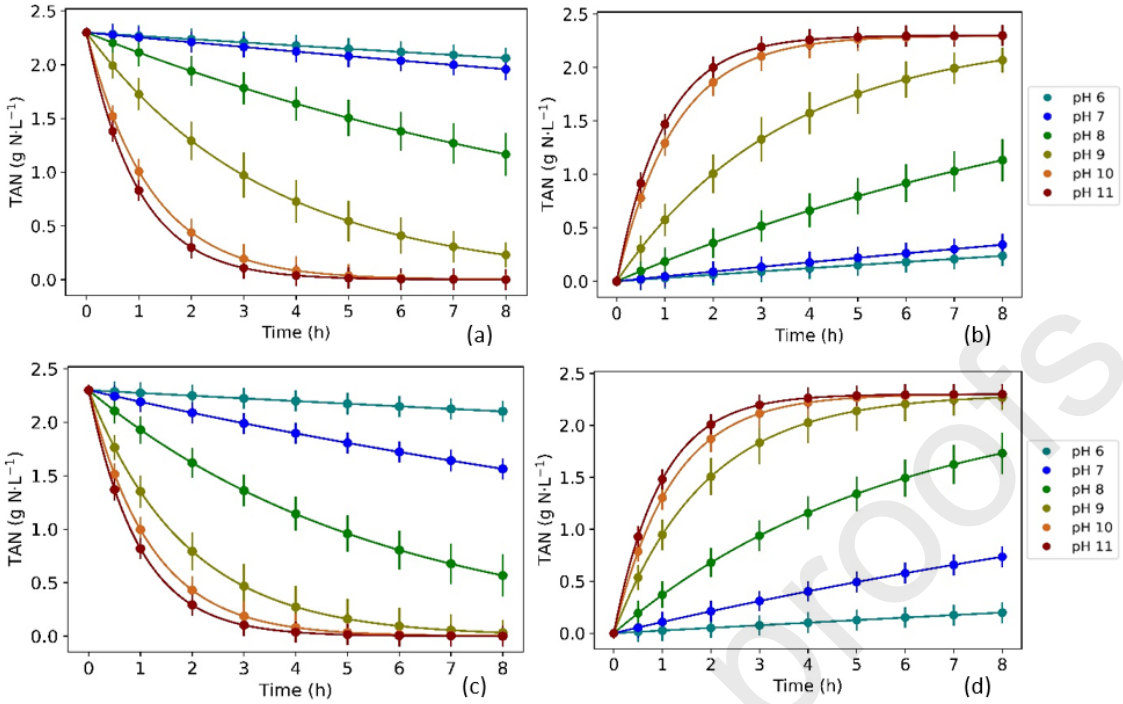

Figure 3. Experimental (dots) and modelled (solid lines) TAN concentration over time at different synthetic solution pH and temperature. (top) experiments at 35 °C (a) feed solution and (b) trapping solution, and (bottom) experiments at 55 °C (c) feed solution and (d) trapping solution. Error bars represent the standard deviation.

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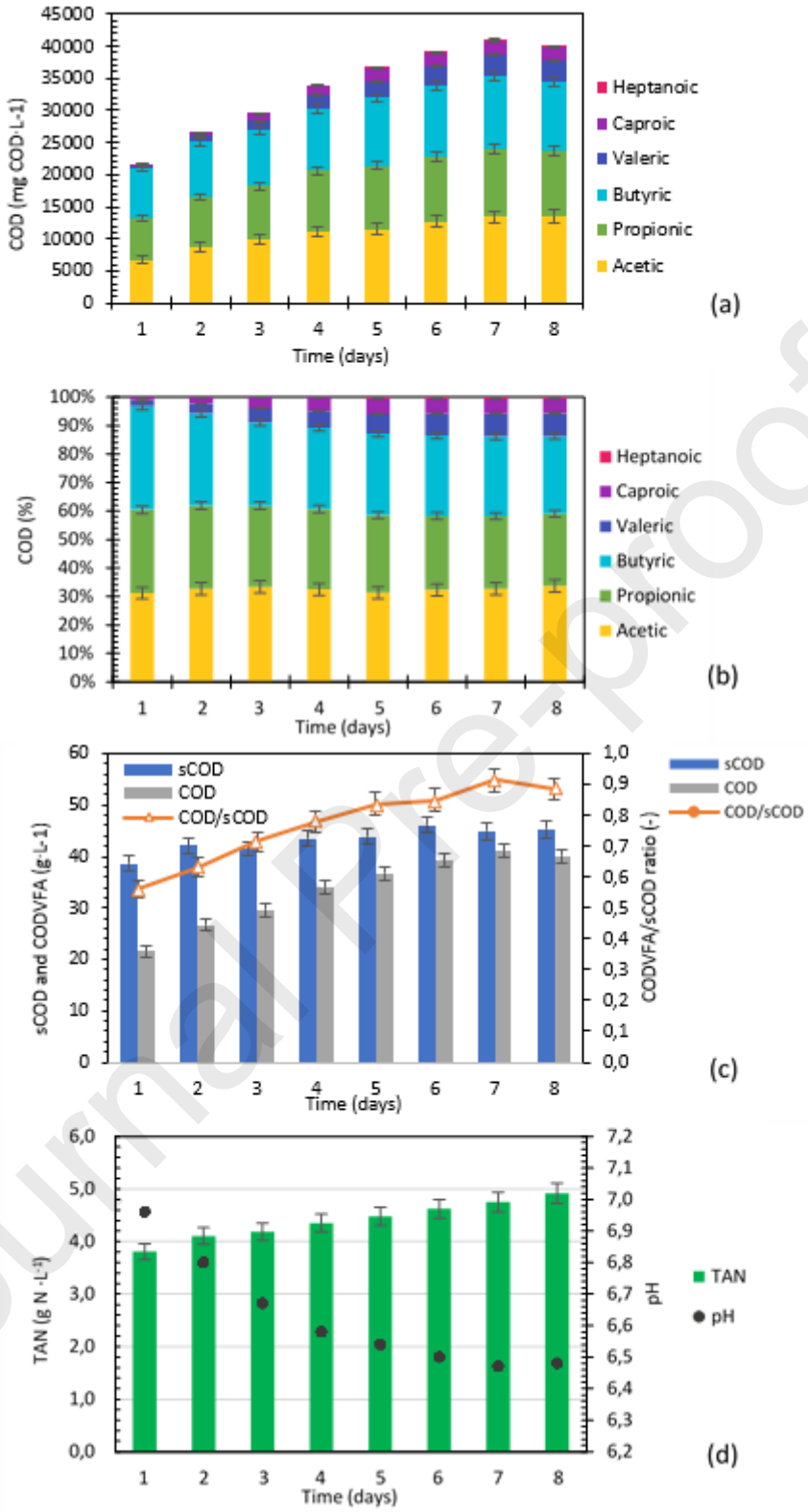

586

587 **Figure 4.** OFMSW fermentation performance, (a) VFA concentration, (b) proportion of the VFA,
588 (c) concentration of COD_{VFA}, sCOD and its ratio, (d) concentration of TAN and pH. Error bars
589 represent the standard deviation.

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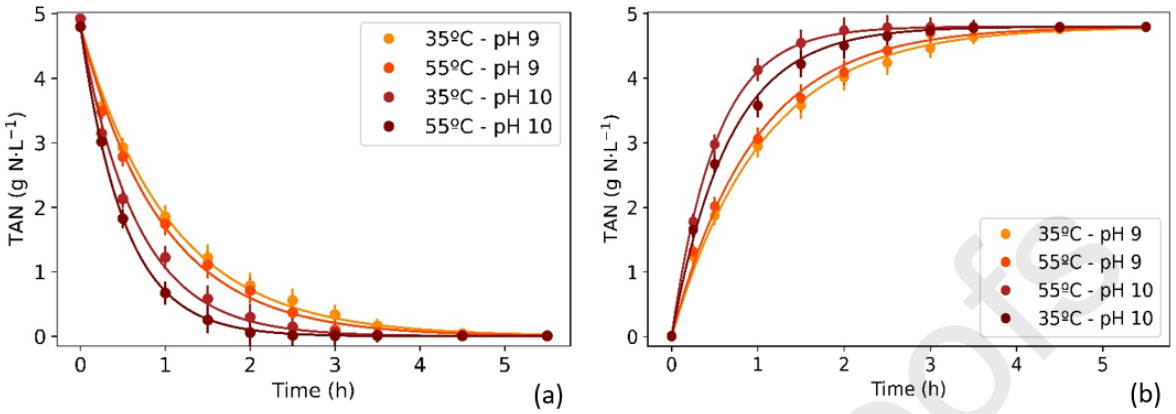
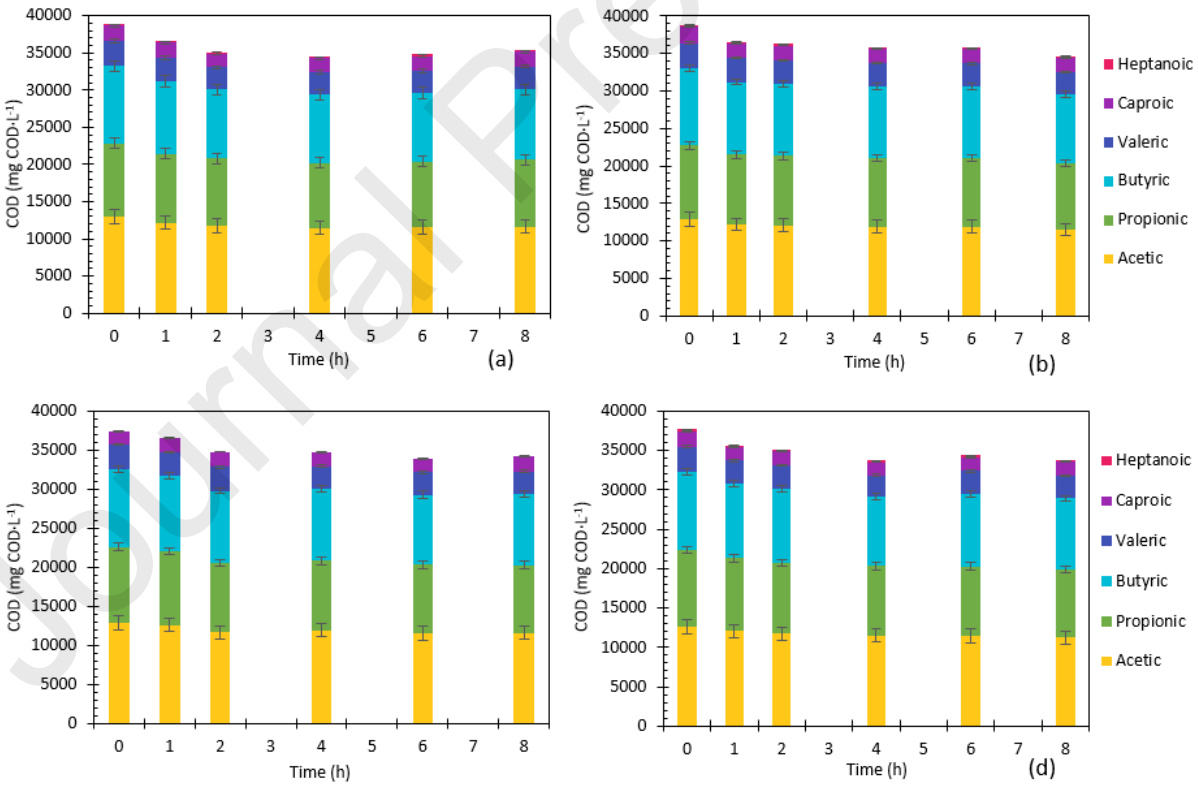


592

593 **Figure 5.** TAN concentration evolution of the (a) feed solution and (b) trapping solution for the
594 experiments carried out with OFMSW fermentation liquid. Error bars represent standard
595 deviation.

596 46.



597

598 **Figure 6.** Evolution of the VFA concentration in the feed solution for experiments (a) 3A at pH
599 9.0 and 35 °C, (b) 3B at pH 9.0 and 55 °C, (c) 3C at pH 10.0 and 35 °C and (d) 3D at pH 10.0 and
600 55 °C. Error bars represent the standard deviation.

601 47.

602 **Table 1.** Operational conditions of the experiments carried out in this study.

Feed solution	Test	Feed solution pH (-)	Temperature (°C)
Synthetic fermentation liquid	1A	6.0	35
	1B	7.0	35
	1C	8.0	35
	1D	9.0	35
	1E	10.0	35
	1F	11.0	35
	2A	6.0	55
	2B	7.0	55
	2C	8.0	55
	2D	9.0	55
	2E	10.0	55
	2F	11.0	55
OFMSW fermentation liquid	3A	9.0	35
	3B	10.0	35
	3C	9.0	55
	3D	10.0	55

603

604 48.

605 **Table 2.** Operational conditions and performance parameters in experiments using synthetic
606 fermentation liquid (average values ± standard deviation).

Exp.	T	pH	TAN recovery at 8h	Average flux at 8h	K_m	Alkali consumption		Acid consumption	
	°C	-	%	g N·day^{-1}·m^{-2}	m·s^{-1}	mol NaOH·mol^{-1} TAN recovered		mol H_2SO_4·mol^{-1} TAN recovered	
						Total*	Test**	Total*	Test**
1A	35	6.0	8	2.5 ± 0.3	(2.2 ± 0.5)·10^{-8}	4.5 ± 0.5	0.64 ± 0.06	2.32 ± 0.27	1.03 ± 0.10
1B		7.0	16	4.3 ± 0.6	(2.8 ± 0.4)·10^{-8}	2.5 ± 0.3	0.60 ± 0.06	2.14 ± 0.25	1.14 ± 0.11
1C		8.0	65	17 ± 3	(9.5 ± 1.3)·10^{-8}	1.4 ± 0.1	0.64 ± 0.06	0.87 ± 0.09	0.64 ± 0.07
1D		9.0	91	62 ± 10	(3.2 ± 0.3)·10^{-7}	1.0 ± 0.1	0.55 ± 0.06	0.63 ± 0.07	0.52 ± 0.06
1E		10.0	100	115 ± 16	(9.2 ± 0.4)·10^{-7}	1.0 ± 0.1	0.12 ± 0.03	0.61 ± 0.07	0.52 ± 0.06
1F		11.0	100	138 ± 17	(1.13 ± 0.03)·10^{-6}	1.1 ± 0.1	0.02 ± 0.01	0.61 ± 0.07	0.50 ± 0.05
2A	55	6.0	10	2.8 ± 0.3	(1.3 ± 0.3)·10^{-8}	4.1 ± 0.5	0.65 ± 0.06	2.41 ± 0.25	1.15 ± 0.12
2B		7.0	36	10 ± 2	(5.8 ± 1.0)·10^{-8}	1.8 ± 0.2	0.69 ± 0.06	0.95 ± 0.11	0.61 ± 0.07
2C		8.0	73	32 ± 5	(1.9 ± 0.1)·10^{-7}	1.2 ± 0.1	0.68 ± 0.06	0.67 ± 0.08	0.56 ± 0.07
2D		9.0	99	84 ± 11	(5.9 ± 0.5)·10^{-7}	1.2 ± 0.1	0.33 ± 0.04	0.65 ± 0.09	0.54 ± 0.06
2E		10.0	100	121 ± 16	(9.3 ± 0.3)·10^{-7}	1.2 ± 0.1	0.18 ± 0.02	0.50 ± 0.04	0.48 ± 0.05
2F		11.0	100	133 ± 16	(1.15 ± 0.04)·10^{-6}	1.1 ± 0.1	0.00 ± 0.00	0.63 ± 0.04	0.52 ± 0.05

607 * NaOH and H_2SO_4 including the initial reagent consumption and the consumption during the experiment
608 ** NaOH and H_2SO_4 consumption during the experiment to keep the pH at the set point.

609 49.

610 **Table 3.** Operational characteristics and results obtained in experiments using OFMSW
611 fermentation broth as feed solution (average values ± standard deviation).

Exp.	T	pH	TAN recovery at 8h	Average flux at 8h	K_m	Alkali consumption		Acid consumption	
	°C	-	%	g N·day^{-1}·m^{-2}	m·s^{-1}	mol NaOH·mol^{-1} TAN recovered		mol H_2SO_4·mol^{-1} TAN recovered	
						Total*	Test**	Total*	Test**
3A	35	9.0	100	78.4 ± 11.0	(2.8 ± 6.0)·10^{-7}	1.02 ± 0.10	0.25 ± 0.04	0.63 ± 0.06	0.25 ± 0.03
3B		10.0	100	120.1 ± 14.4	(5.0 ± 9.2)·10^{-7}	0.94 ± 0.10	0.10 ± 0.02	0.65 ± 0.06	0.14 ± 0.02
3C	55	9.0	100	91.0 ± 12.7	(3.3 ± 6.3)·10^{-7}	0.97 ± 0.11	0.21 ± 0.03	0.67 ± 0.07	0.21 ± 0.03
3D		10.0	100	138.8 ± 16.7	(5.4 ± 5.7)·10^{-7}	0.86 ± 0.08	0.05 ± 0.02	0.63 ± 0.06	0.17 ± 0.02

612 * NaOH and H_2SO_4 including the initial reagent consumption and the consumption during the experiment
613 ** NaOH and H_2SO_4 consumption during the experiment to keep the pH at the set point.

614 50.