Simultaneous recovery of ammonia and volatile fatty acids from dark fermentation effluents via gas-liquid membrane contactor

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ABSTRACT

The increasing interest in sustainable waste management has spurred the development of innovative technologies for resource recovery. In this context, organic waste fermentation generates effluents rich in ammonium and volatile fatty acids (VFAs), both of which represent valuable precursors for the fertilizer and chemical industries. This study introduces and evaluates an innovative membrane-based methodology enabling the simultaneous recovery of ammonia (NH_3) and VFAs from synthetic and real dark fermentation broths. The experimental setup employed a gas–liquid membrane contactor consisting of a 44 cm^2 hydrophobic polytetrafluoroethylene (PTFE) membrane (0.22 μm pore size) housed in a flat-plate module. The effects of different extraction solutions (HCl, H_2SO_4, NaOH, and ionic liquids), their concentrations, and the flow rates of both the fermentation effluent (500 mL min^{-1}) and the extracting solution (250 mL min^{-1}) were systematically investigated, along with the influence of the broth pH (7.0 and 5.5). Among the tested conditions, 2 M NaOH was identified as the most effective extraction medium, achieving simultaneous recoveries of 24.5 % for NH_3, 50 % for propionic, butyric, and valeric acids, and 42 % for acetic acid after 168 h of operation in an acidogenic broth at pH 5.5. Furthermore, higher solvent concentrations and increased recirculation velocities were positively correlated with improved NH_3 and VFA recovery, regardless of the solvent type. Overall, the results highlight the potential of the proposed membrane contactor-based approach as a promising and scalable technology for integrated resource recovery from fermentation effluents.

1. Introduction

Municipal solid waste is expected to generate 2.2 billion tons of waste globally by 2025 and its management cost 375.5 billion USD [1]. The organic fraction of municipal solid waste (OFMSW) can be treated via anaerobic digestion (AD), composting, landfilling, and incineration. The AD of the OFMSW is a reliable and attractive platform to convert the complex organic matter into a clean and renewable source of energy [2]. The AD of food waste (FW) has attracted a great interest in recent years due to its high organic removal rates and positive net energy balance. However, the digestate generated still needs to be managed in order to meet the ecologically acceptable requirements for direct discharge into natural water bodies due to their high nitrogen and phosphorous concentrations [3]. The effective treatment and management of both solid

(DSF) and liquid (DLF) dark fermentation fractions require the adoption of sustainable technologies aimed at recovering valuable by-products such as energy, biofuels, biochar, and nutrients [4]. Both fractions must be treated before being reused in order to handle dark fermentation effluents sustainably. The DSF can be used as a nutrient-rich amendment on land or transformed into energy and biochar through thermochemical processes such as gasification, hydrothermal carbonization, and pyrolysis. In order to concentrate nutrients and lessen the impact on the environment, the DLF can be primarily transformed into fertilizer following physico-chemical and biological treatments, such as membrane filtration, ammonia stripping and struvite precipitation [5–7]. In this context, dark fermentation (DF) stands out as the most promising biological method to produce renewable outputs from organic wastewaters and waste [8] such as biofuels [9] (i.e.,

biohydrogen [10,11]), biogenic carbon dioxide [12], and high-value organic acids [13]. DF effluents typically contain high concentrations of short-chain carboxylates, with total organic acids in food-waste-based dark fermentation effluents commonly ranging from 13.3 ± 1.8 to 18.8 ± 3.4 g L^{-1} (or 15.3 ± 2.4 to 21.5 ± 4.6 g COD$_{eq}$ L^{-1}), and acetate concentrations reaching up to 5.0 g L^{-1} under optimal acidogenic conditions [14], and low concentrations ammonium (NH$_4$), in the range of 0.03–0. 3 g L^{-1} in food waste dark fermentation effluents [15], both of which can be recovered and valorized.

Today, organic acids are key building blocks in the manufacture of foods, drinks, medicines, polymers, resins and chemicals [16]. Of them, volatile fatty acids (VFAs) are monofunctional, linear short-chain aliphatic compounds that can be used as precursors to produce biofuels, reduced chemicals (e.g., alcohols, ketones, aldehydes, and esters), and biopolymers [17]. On the other hand, free ammonia (NH$_3$) induce toxic effects in humans and microorganisms at high concentrations in both aqueous and gas phase, whereas NH$_4$ represents a valuable nutrient for biofertilizer production [18]. High NH$_3$ concentrations may inhibit methanogens and fermentative bacteria, thus causing lower biogas production in AD and lower hydrogen and organic acids synthesis in DF [19]. Therefore, the simultaneous recovery of VFAs and NH$_3$ from fermentation broths can help partially alleviating this inhibition [20].

In this context, membrane-based recovery [21], liquid-liquid extraction [22], adsorption [23] and electrodialysis [24] have been proposed to recover VFAs from fermentation broths. Similarly, multiple NH$_3$ removal and recovery methods have been investigated [19], including physical processes (e.g., stripping, adsorption, ion exchange, etc.), chemical processes (e.g., chemical precipitation, oxidation, and electro-kinetic processes), and other microbial processes (e.g., nitrification-denitrification, anammox) [25,26]. In particular, techniques such as ion exchange, membrane separation, adsorption, and ammonia stripping, have been proposed for the recovery of NH$_3$ from digestates [27]. Membrane-based processes implemented in membrane contactors (MC) are emerging as the most promising technique for a simultaneous VFAs and NH$_3$ recovery [28,29]. The membrane contactor (MC) technology has attracted increasing attention for resource recovery applications due to its low energy requirements and high recovery efficiency [30]. Initially investigated for the removal of carbon dioxide (CO$_2$) from gaseous streams [30], its applicability has since expanded to include the separation of other compounds such as sulfur dioxide (SO$_2$) [31], alcohols [32], ammonia [33], and VFA [33]. Thus, NH$_3$ is typically extracted across membranes by diffusion of un-ionized NH$_3$ driven by a pH gradient, where NH$_3$ volatilizes on the high-pH side and is trapped as NH$_4^+$ in an acidic receiving phase. VFAs are extracted when the neutral (protonated) form of the acid diffuses through the membrane under a pH gradient, after which it dissociates in a higher-pH receiving phase, preventing back-diffusion and enabling separation [27,34]. In particular, the recovery of ammonia and VFAs via MC relies on the establishment of a pH gradient between the feed and permeate phases [35]. This gradient facilitates the volatilization of the compounds in their gaseous form from the feed solution, followed by their absorption into the permeate phase where they are converted back into their dissolved ionic form [36]. In MC, chemical solutions based on acids have been traditionally used as liquid extractants [37]. However, particular attention should be paid to other types of liquids that can be used as extractors, such as basic solutions or ionic liquids (ILs). ILs are considered "green solvents" that exist at temperatures below 100 °C as liquids and exhibit a very low vapor pressure [38]. ILs represent a promising alternative for the replacement of conventional solvents in separation techniques due to their stability, nonvolatility, and changeable miscibility and polarity, which can enhance both safety and environmental friendliness. In ILs, the structures of cations and anions determine whether anions are hydrophilic or hydrophobic [39]. Specific hydrophilic ILs can be selected as extractants because their water-miscibility makes them suitable for the aqueous permeate phase in the MC. Imidazolium-based ILs show strong affinity for short-chain carboxylates

through hydrogen bonding, improving VFA recovery. Testing structurally related ILs also enables a systematic assessment of how small changes in the alkyl substituent influence extraction performance [40]. ILs have been proposed as a promising platform for the extraction of carboxylic acids, but, to the best of the authors' knowledge, never tested for NH$_3$ recovery [41]. In the context of alkaline extracting solutions, Rivera et al. observed that, despite the strong buffering capacity of the anaerobic system, which stabilizes the broth pH, a basic pH in the effluent remains advantageous, as it shifts the NH$_4^+$/NH$_3$ equilibrium toward free NH$_3$, thereby increasing the driving force for its transport and recovery across the membrane [42,43].

This study introduces and systematically evaluates an innovative membrane contactor methodology for integrated resource recovery, pioneering the simultaneous extraction of NH$_3$ and VFAs using a wide array of unconventional media, including basic solutions NaOH and Ionic Liquids (ILs). The comprehensive investigation identifies 2 M NaOH as a superior, non-acidic extraction solvent for this dual recovery, highlighting the first reported application of ILs for NH$_3$ recovery within an MC system. Particularly, this study assesses the influence of i) the pH of the fermentation broth, ii) the type and concentration of the extraction solution (NaOH, H$_2$SO$_4$, HCl, and ILs), and iii) the recirculation flow rates in the MC on the recovery efficiency of both NH$_3$ and VFAs. The selection of the pH range (pH 5.5–7.0) was chosen to reflect the typical pH values of dark fermentation effluents. Similarly, the concentrations of the acidic and basic extraction solutions (0.5 M to 2 M) were systematically varied to ensure excess proton or hydroxide availability to maximize the chemical driving force for NH$_3$ and VFA capture, while IL concentrations were constrained by viscosity and cost for initial comparison. The diverse portfolio of extractive liquids (H$_2$SO$_4$, NaOH, and Ionic Liquids) was intentionally used to rigorously compare the performance of conventional H$^+$-based capture against novel OH$^-$ and physiochemical IL-based capture mechanisms for integrated recovery. Finally, the flow rates (250 mL min^{-1} and 500 mL min^{-1}) were optimized to evaluate the crucial impact of recirculation velocity on minimizing mass transfer resistance in the boundary layer of the membrane, and enhancing overall contactor efficiency.

2. Material and methods

2.1. Synthetic and real fermentation broths

The synthetic fermentation broth mimicked the effluent from the DF of fruits and vegetables waste (FVW). The fermentation effluent composition was as follows: 6.45 g L^{-1} acetic acid; 4.95 g L^{-1} butyric acid; 10.86 g L^{-1} lactic acid; 0.041 g L^{-1} propionic acid; 5.0 g L^{-1} valeric acid; and 1.09 g L^{-1} formic acid [44]. All reagents used were of analytical reagent grade and were utilized as supplied by the manufacturer, with no additional purification steps. NH$_4$Cl was added at an initial concentration of 1 g L^{-1}. The real FVW was characterized by a total COD concentration of 111.5 ± 5.1 g O$_2$ L^{-1}, of which 96.7 g L^{-1} corresponded to soluble COD, the total carbohydrates concentration was 79 g L^{-1} [45].

Real DF broths generated at the Institute of Sustainable Processes of the University of Valladolid from the DF of two different substrates, namely FW and powdered cheese whey (CW). The FW was based on a grinded mixture consisting of 78 % of potato flakes, 14 % of chicken breast, 4 % of white cabbage and 4 % of pork lard (on a dry weight basis), as a source of carbohydrates, proteins, and lipids, respectively [46]. The pH of the FW was 6.2 ± 0.05, while its total solids (TS) concentration accounted for 223 g TS kg^{-1}. The FW digestate contained 0.25 g L^{-1} NH$_3$ and the following VFA concentrations: 6.36 g L^{-1} acetic, 1.63 g L^{-1} propionic, 1.83 g L^{-1} butyric, and 0.00 g L^{-1} valeric acids. CW DF broth was produced in the laboratory via DF of a synthetic CW effluent consisting of NH$_4$Cl 2.4 g L^{-1}, K$_2$HPO$_4$ 2.4 g L^{-1}, MgCl$_2$·6H$_2$O 2.525 g L^{-1}, KH$_2$PO$_4$ 0.6 g L^{-1}, CaCl$_2$·2H$_2$O 0.15 g L^{-1}, FeCl$_2$ 0.0357 g L^{-1}. All reagents used were of analytical reagent grade and were utilized

as supplied by the manufacturer, with no additional purification steps. CW powder at 41 g L^{-1} was purchased from Prolactea S.A, while Corquimia Industrial, S.L. (Barcelona, Spain) provided the PCW. The product had a minimum lactose content of 75 % and a maximum ash content of 8 %, according the manufacturer's standards. Laboratory analysis revealed that the PCW was mostly composed of carbohydrates (76.5 %), followed by proteins (11.5 %) and lipids (0.95 %). The CW digestate showed 0.61 g L^{-1} NH_3 and 1.02 g L^{-1} acetic, 1.01 g L^{-1} propionic, 1.65 g L^{-1} butyric, and 0.12 g L^{-1} valeric acids. The DF process was carried out at a hydraulic retention time (HRT) of 6 h and a pH of 6, utilizing a specialized hydrogen-producing mixed culture previously enriched [47].

2.2. Experimental setup

Fig. 1 shows the experimental set-up, consisting of a 3.5 L glass reactor (CSTR, 3.3 L of working volume) continuously stirred (Agimatic-HS, Selecta®, Spain) at ≈ 200 rpm and located in a controlled temperature room at 37 °C. A pH control system (BSV EVo pH-P 1.5 L, Quimpool, Spain) was connected to the reactor to maintain the pH of the DF broth. The fermentation broth was recirculated tangentially on the active layer of a hydrophobic polytetrafluoroethylene (PTFE) membrane (MF-Millipore™, Germany) via a peristaltic pump (Watson Marlow 520, Spirax-Sarco Engineering plc, United Kingdom) at setted flow rates. The PTFE membrane was characterized by a surface area of 0.0044 m^2, pore size of 0.22 μm, nominal thickness of 175 μm, contact angle of 150 θ and a porosity of 70 %. The extractive liquid was tangentially recirculated on the opposite side of the membrane (support layer) through an identical peristaltic pump (Watson Marlow 520, Spirax-Sarco Engineering plc, United Kingdom). The extraction solution, contained in a 1 L glass bottle, was magnetically stirred (LBX S20, Labbox Labware, Spain).

2.3. Operational conditions

The influence of operational variables such as the pH and flow rate of DF broth, the type of extractant solution, and its flow rate on the extraction efficiency of NH_3 and of acetic acid, propionic acid, butyric acid, and valeric acid was investigated with synthetic and real fermentation broths (Table 1). In test 1, 1 M NaOH was utilized for pH regulation in the fermentation broth (set point: pH 7), while 1 M H_2SO_4 served as the extraction solution, with a flow rate of 250 mL min^{-1}. In

Table 1
Operational conditions tested during the optimization of VFAs and NH_3 extraction.

Test n°	pH control	pH broth	Fermentation broth	Flowrate* (mL min^{-1})	Extractive liquid (g L^{-1})
1	1 M NaOH	7.0	Synthetic	250	H_2SO_4 [98]
2	1 M HCl	7.0	Synthetic	250	NaOH [40]
3	1 M HCl	5.5	Synthetic	250	NaOH [40]
4	1 M HCl	5.5	Synthetic	500	NaOH [40]
5	2 M HCl	5.5	Synthetic	500	NaOH [80]
6	1 M NaOH	5.5	Synthetic	500	1-ethyl-3-methylimidazolium, chloride [10]
7	1 M NaOH	5.5	Synthetic	500	1-ethyl-3-methylimidazolium, chloride [20]
8	1 M NaOH	5.5	Synthetic	500	1-allyl-3-methylimidazolium, chloride [10]
9	1 M NaOH	5.5	Synthetic	500	1-allyl-3-methylimidazolium, chloride [20]
10	2 M HCl	5.5	Real from FW	500	NaOH [80]
11	2 M HCl	5.5	Real from CW	500	NaOH [80]

* Flow refers to the flow rate of fermentation broth and extraction solution on both sides of the membrane.

tests 2 and 3, 1 M HCl was used to maintain the fermentation broth at pH 7.0 and 5.5, respectively, with 1 M NaOH as the extraction solution at a flow rate of 250 mL min^{-1}. Studies on NH_3 recovery using gas-permeable membranes indicate that maintaining a pH of 9.0 is the most effective strategy, balancing high NH_3 transfer efficiency with minimal chemical consumption. Research on NH_3 stripping from digestates also supports this, showing that higher pH and temperature improve removal efficiency, with up to 87 % achieved at 40 °C and pH 9.0 [48]. However, in this study, a lower pH of 5.5 was chosen to ensure compatibility with the biotic conditions of DF, the process used for
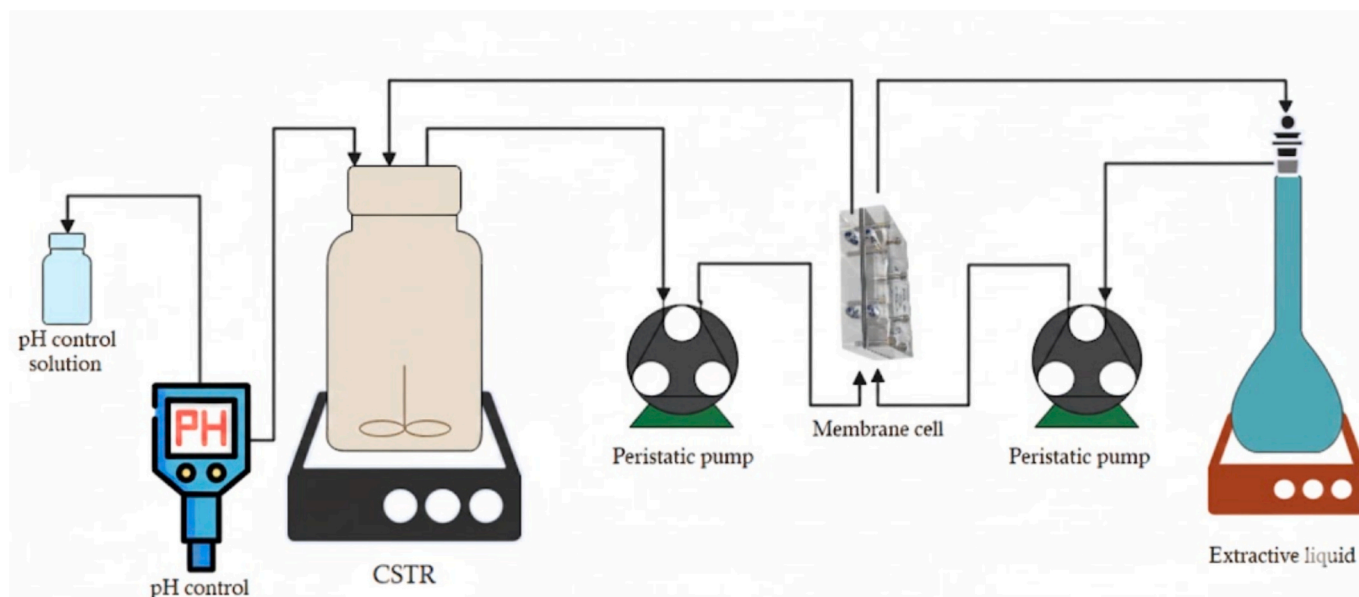

Fig. 1. Experimental set-up for VFA and NH_3 extraction.

hydrogen production. This acidic environment was necessary to support bacterial activity, maintaining optimal conditions for microbial metabolism while still enabling efficient NH₃ and VFA recovery.

Test 4 replicated the conditions of test 3 but was conducted with an increased recirculation flow rate of 500 mL min⁻¹ on both sides of the membrane. Test 5 was performed at pH 5.5, regulated with 2 M HCl, using 2 M NaOH as the extractant solution, and maintaining a recirculation flow rate of 500 mL min⁻¹. Tests 6 to 9 were also conducted at pH 5.5, employing the ionic liquids 1-ethyl-3-methylimidazolium chloride (EMIMCl) (purity >98 %, CAS n.65039–10-3, IoLiTec-Ionic Liquids Technologies GmbH, Germany), and 1-allyl-3-methylimidazolium chloride (AMIMCl) (purity >95 %, CAS n.143314–17-4, IoLiTec-Ionic Liquids Technologies GmbH, Germany) as extractant solutions. EMIMCl and AMIMCl were tested at concentrations of 10 g L⁻¹ (tests 6 and 8, respectively) and 20 g L⁻¹ (tests 7 and 9, respectively). In all these tests, 1 M NaOH was used for pH regulation, and a recirculation flow rate of 500 mL min⁻¹ was maintained. Tests 10 and 11 investigated extraction performance using real fermentation broths derived from FW and powdered CW, respectively, at pH 5.5, regulated with 2 M HCl. In both cases, 2 M NaOH served as the extractant solution, with a recirculation flow rate of 500 mL min⁻¹. All experiments were conducted in duplicate under controlled conditions at 37 °C for seven days. The reproducibility of the measurements was assessed by comparing the two duplicate results for each condition, calculating the difference between them relative to their average value, and expressing it as a percentage. The resulting reproducibility error was below 5 % for both NH₃ and VFA recoveries, confirming the reliability of the experimental data.

Samples (2 mL) of fermentation broth were periodically collected from the reactor to monitor VFA and total ammoniacal nitrogen (TAN) concentrations. For fermentation broths derived from FW and CW, samples were centrifuged at 10,000 rpm for 10 min using a Spectrafuge 24D Microcentrifuge (LABNET, NJ, 08837 USA). The supernatants were then filtered through 0.22 μm membranes, acidified with 20 μL of concentrated H_2SO_4 per mL of sample, and stored at −20 °C until TAN analysis. For VFA gas chromatographic analysis, 1 mL of freshly filtered fermentation broth was diluted 1:10 with Milli-Q water and acidified with 20 μL of concentrated H_2SO_4 per mL of sample prior to injection.

2.4. Analytical methods

TAN was measured by using the Nessler analytical method in a SPECTROstar Nano absorbance 220–1000 nm spectrophotometer (BMG Labtech, Germany) at 425 nm. Acetic, propionic, butyric, and valeric acids were measured using a Gas Chromatograph (Agilent Technologies, Santa Clara, USA) coupled with a Flame Ionization Detector (GC-FID) equipped with a capillary column Heliflex AT-1000 (30 m × 0.53 mm × 1.0 μm film thickness; Alltech associates, Inc., IL, USA). The oven of the GC was maintained at 100 °C for 1 min and then increased at a rate of 15 °C per minute up to 230 °C. This temperature was maintained for 0.4 min. Injector and detector temperatures were 150 and 250 °C, respectively. Helium was used as the carrier gas at a flow rate of 3 mL min⁻¹.

2.5. Calculations

The overall mass transfer of VFAs through the membrane was calculated according to Eq. 1 [49]:

$$ln\left(\frac{[VFA]_{R,0}}{[VFA]_{R,t}}\right) = \frac{KA}{V_R}t \tag{1}$$

where [VFA] stands for the concentration of the VFAs (mg L⁻¹) in the reactor (*R*), at time 0 and time *t*, respectively, *A* is the membrane surface area (m²), V_R is the volume of the reactor (m³), *K* is the experimental mass transfer coefficient [m h⁻¹].

K was calculated by algebraically rearranging Eq. 1 into the inverse form presented in Eq. 2

$$K = \frac{V_R}{A\,t}ln\left(\frac{[VFA]_{R,0}}{[VFA]_{R,t}}\right) \tag{2}$$

The recovery efficiency (RE) of both VFAs and NH₃ was calculated according to Eq. 3:

$$RE = \frac{Mass\ accumulated\ in\ extractive\ liquid}{Initial\ mass\ in\ fermentation\ broth} \times 100$$

$$RE = \frac{C_{extractive,t}\ \times\ V_{extractive}}{C_{broth,t}\ \times\ V_{broth,0}} \times 100 \tag{3}$$

where: $C_{extractive,t}$ is the concentration in the extractive liquid of VFAs or NH₃ (g L⁻¹); $C_{broth,t}$ is the initial concentration in the fermentation broth (g L⁻¹), $V_{extractive}$ is the total volume of the liquid in the permeate circuit, $V_{broth,0}$ is the initial total volume of the fermentation broth.

The concentrations C_0 and C_t were normalized to the initial concentration C_0, thus allowing the recovery efficiency to be expressed as a percentage of the initial amount.

3. Results and discussion

3.1. Influence of the liquid extractor on NH₃ and VFAs removal

In the MC-based NH₃ and VFA recovery process, the fermentation broth containing VFAs and NH₃ was recirculated on the active side of a hydrophobic PTFE membrane, while an extractive liquid with the same recirculation rate was circulated on the support side. In test 1, NH₃ removal remained almost constant over time, reaching a total removal rate of 25.9 % from the fermentation broth by day 7. The peak removal rate of 27.9 % occurred on day 4 (Fig. 2a). Regarding VFA removal, the results were not significant. The alkaline pH (7.0) of the broth inhibited the recovery of VFAs to their protonated forms, leading to an increase in VFA concentration. By the end of the 7-day experiment, the concentrations of acetic, propionic, butyric, and valeric acid increased by 26 %, 19.4 %, 11.1 %, and 0.97 %, respectively, compared to their initial values (Fig. 2b).

3.2. Influence of the pH of the fermentation broth on NH₃ and VFAs extraction

Test series 2 and 3 were conducted to assess the effect of the pH of the acidogenic broth using 1 M NaOH as extractive solution under recirculation rates of 250 mL min⁻¹ in the membrane module. The synthetic VFA broth at pH 7.0 experienced an increase in NH₃ concentration by a factor of 1.8 times, while at pH 5.5, the NH₃ recovery recorded accounted for 6.8 % after 7 days of extraction (Fig. 3). The increase in NH₃ concentration in the enclosed stirred tank under a recirculating NH₃-free NaOH solution suggests the gradual appearance of interfering compounds in the Nessler analytical methodology as a result of Cl-diffusion or side reactions. In this context, Xu et al. (2021) investigated a two-stage direct contact membrane distillation system to aid NH₃ recovery from a simulated anaerobic digestate. The greatest NH₃ recovery occurred under a pH of 12 in the anaerobic digestate, which supported an NH₃-RE of 84,2 ± 1,9 %. Other necessary conditions were a temperature of 60 °C and 0.6 M H_2SO_4 permeate extraction liquid [50].

On the other hand, the recovery efficiencies of acetic, propionic, butyric and valeric acids in the assays carried out at pH 7 accounted for 1 %, 4 %, 13 % and 16 %, respectively, after 7 days of operation (Fig. 4a). Similarly, recoveries of 23 %, 26 % and 34 % (Fig. 4b) were recorded for propionic, butyric and valeric acids, respectively, while acetic acid concentration remained constant in the synthetic fermentation broth at pH 5.5 under NaOH extraction. Jankowska and coworkers (2015) assessed that at low pH (4–5.5), butyrate and acetate are the dominant products, while at high pH (7.5–8), acetate and ethanol prevail due to the presence of *Klebsiella*, which lacks butyrate-related
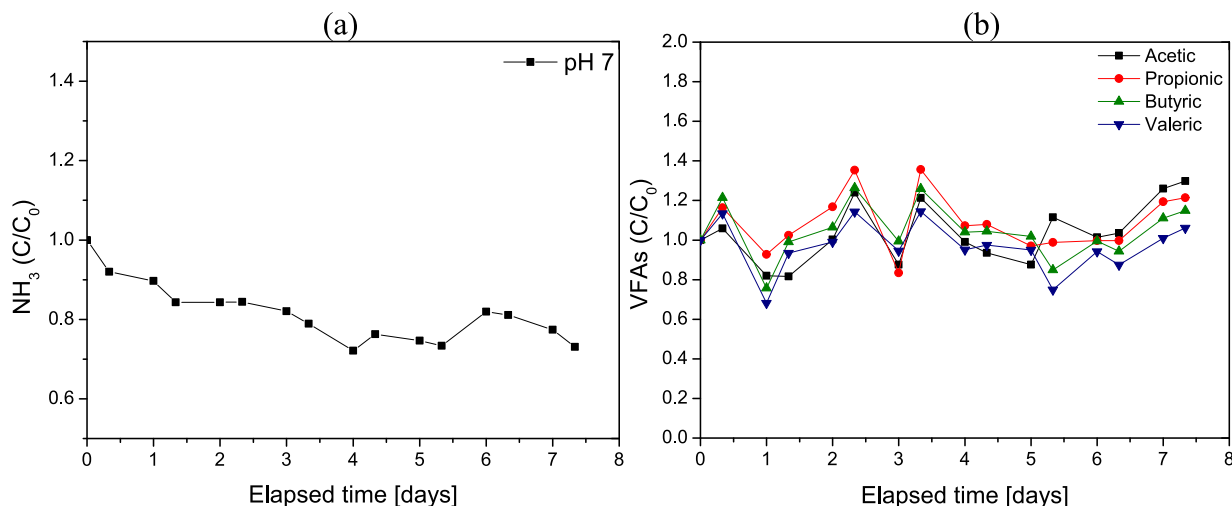
Fig. 2. Time course of: (a) normalized ammonia (NH$_3$) concentration and (b) volatile fatty acids (VFAs) concentration (acetic ■, propionic ●, butyric ▲, valeric ▼) in a synthetic dark fermentation broth. The extraction process was carried out using 1 M H$_2$SO$_4$ as the extractant solution at pH 7, with 1 M NaOH as the extraction solution, under a recirculating rate of 250 mL min^{-1}.
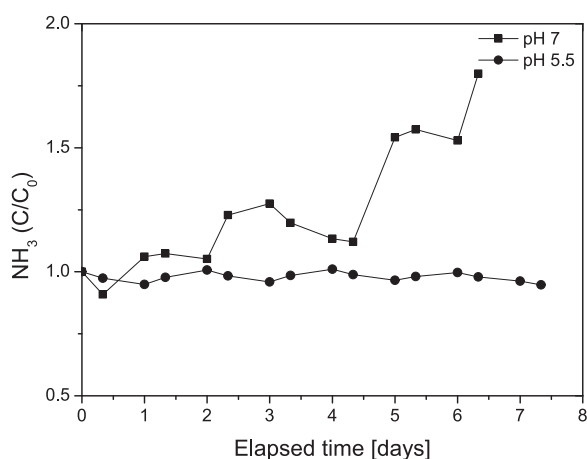

Fig. 3. Time course of the normalized ammonia (NH$_3$) concentration in the synthetic dark fermentation broth at pH 7 (■) and pH 5.5 (●) using 1 M NaOH as extractant solution.

enzymes [51]; in their study they observed a clear shift from butyrate to acetate/ethanol at alkaline pH, though the exact transition depends on the specific mixed culture used [52]. Therefore, acidic fermentation effluents can experience a more effective recovery of NH$_3$ and VFAs using 1 M NaOH as extractive solution. In this context, Yesil et al. (2021), observed that a temperature of 38 °C and a 1 M NaOH solution were the optimal parameters for VFAs recovery in a vapor permeation membrane contactor system [28], although in this study, the highest removal rate (17.9 %) was achieved for valeric acid at pH 7.0 under the same solution concentration and temperature conditions, the other VFAs showed lower removal rates, not exceeding 16 %.

3.3. Influence of the liquid recirculation rates on NH$_3$ and VFAs recovery

The increase in the recirculation flow rate from 250 mL min^{-1} to 500 mL min^{-1} in a fermentation broth at pH 5.5 supported a similar NH$_3$ recovery (6.2 % compared to the 6.8 %) within 7 days (Fig. 4c). In this context, Rivera and co-workers (2022a) demonstrated that higher recirculation flow rates on the membrane feed side resulted in a faster NH$_3$ recovery, which followed first order kinetics [53]. On the other hand, increasing the recirculation rate of the VFA broth and NaOH to

500 mL min^{-1} led to a reduction in propionic and valeric acid concentrations by 52.4 % and 58.9 %, respectively (Fig. 4d). These values compare favourably with the lower recovery rates of 31.1 % and 30.2 % observed at 250 mL min^{-1} after 7 days. The recovery of acetic and butyric acid at 500 mL min^{-1} accounted for 16.8 % and 38.7 % after 7 days of experiment, respectively. Rivera et al. (2022a) evaluated that NH$_3$ fluxes decreased at higher flow rates due to shear-induced fouling. Mass transfer was primarily restricted on the digestate side, while NH$_3$ transfer through membrane pores remained efficient. The overall mass transfer coefficient increased with recirculation flow rate, and results were consistent with literature findings for similar pH conditions [53].

3.4. Influence of the concentration of the NaOH extraction solution on NH$_3$ and VFAs removal

A further tests (test 5) was conducted by increasing the concentration of the NaOH extraction solution from 1 to 2 M, and the HCl solution used to maintain the pH from 1 to 2 M. NH$_3$ recovery at 2 M NaOH concentration accounted for 24.5 % in 7 days (Fig. 5a), which represented a significant enhancement compared to process operation at 1 M NaOH (increase 8.7 % of NH$_3$). Similarly, VFA recoveries were higher with a 2 M NaOH solution, which supported extraction efficiencies of 42.3 %, 49.7 %, 47.5 %, and 53.2 % for acetic, propionic, butyric, and valeric acids, respectively, within 7 days of membrane operation (Fig. 5b). It was assessed that a more concentrated HCl solution increases the chemical gradient between the feed and extraction sides, promoting greater diffusion of VFAs through the membrane. VFAs are weak acids that exist in equilibrium between their dissociated (R-COO$^-$) and protonated (R-COOH) forms. A higher concentrated environment shifts the equilibrium toward the protonated form, which is more lipophilic and crosses the membrane more easily. Additionally, higher acidity on the receiving side reduces the likelihood of VFA back-diffusion, enhancing their retention during the extraction step [54].

In this context, Aydin et al. (2018), investigated the recovery VFAs from a synthetic mixture at pH < 4 using NaOH at 0.5 M as extractive liquid and different several membrane materials. The overall mass transfer coefficient through a PTFE membrane similar to the membranes herein used was 8.4×10^{-3} m h^{-1} for acetic acid, while for propionic, butyric and valeric acid it accounted for 1.2, 1.4, 1.6×10^{-3} m h^{-1} [55]. These values were slightly lower than those estimated in the present work (Table 2) at a NaOH concentration of 2 M for propionic, butyric and valeric acids.
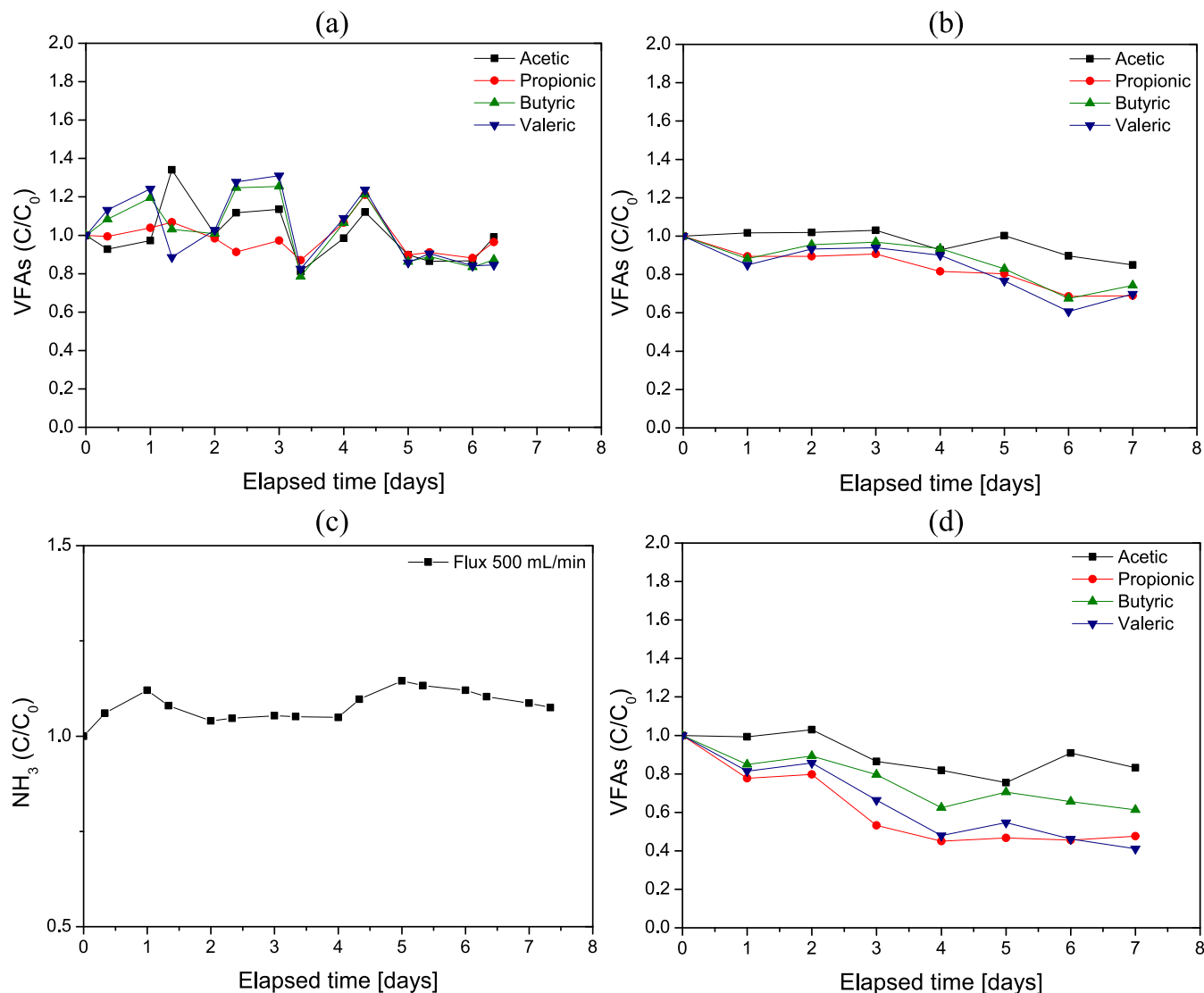
Fig. 4. Time course of volatile fatty acids (VFAs) acetic (■), propionic (●), butyric (▲) valeric (▼) acids concentration in a synthetic dark fermentation broth at (a) pH 7 and (b) pH 5.5 with 1 M NaOH as extraction solution under recirculating rates of 250 mL min^{-1}. Time course of: (c) ammonia (NH$_3$) concentration and volatile fatty acids (VFAs) (d) acetic (■), propionic (●), butyric (▲) valeric (▼) acids in the 5.5 pH synthetic dark fermentation broth at recirculation rates of 500 mL min^{-1}.

3.5. Influence of ionic liquids on NH$_3$ and VFAs recovery

The selection of the concentrations of EMIMCl and AMIMCl (10 and 20 g L^{-1}) was based on preventing plasticizing effects of the ionic liquids in the PTFE material after a 24-h membrane submergence. Unexpectedly, while the use of EMIMCl at 10 g L^{-1} entailed an increase NH$_3$ concentration by a factor of 3 (likely due to interference effects of the compound in the Nestler method or to the release of NH$_3$ from chemical reactions of the EMIMCl diffusing through the membrane), the recirculation of AMIMCl at 10 g L^{-1} induced a recovery of 19 % of the initial ammoniacal nitrogen (Fig. 6 a,b). The test 6, conducted with EMIMCl at 10 g L^{-1}, experienced a sudden rupture of the membrane, which led to an interruption of the experiment at day six.

The recirculation of EMIMCl and AMIMCl at 20 g L^{-1} (tests 7 and 9) also resulted in an increase in NH$_3$ concentration by a factor of 1.6 and 1.7, respectively, likely mediated by interferences in Nessler methodology or by the diffusion and NH$_3$ generating chemical reactions of the ILs (Fig. 6a,b). NH$_3$ recovery is mostly dependent on NH$_3$ solubility selectivity, which is dependent on the interactions between the ILs and NH$_3$ gas molecules. Indeed, Jiang et al., engineered Pebax blended membranes with aprotic IL [EtOHmim][NT$_{f2}$] and protic IL [EtOHim]

[NT$_{f2}$] tailored with hydroxyl groups to improve NH$_3$ separation performance and achieve a high NH$_3$ selectiviy, which suggested that the use of ILs can enhance the performance of membranes during NH$_3$ separation [56]. Hypothetically, the higher viscosity of the ionic liquid AMIMCl gives it lower NH$_3$ recovery power [57,58]. At this point, it is important to stress that both NH$_3$ and VFA must be extracted from the ionic liquids in order to allow extractants recycling, with the subsequent increase in process economics and environmental sustainability.

Fig. 6 (c,d,e,f) reports the fatty acid profile of the tests 6–9. The recirculation of an aqueous solution of EMINC1 at 10 g L^{-1} resulted in a recovery of 18 %, 29 %, 31 % and 33 % of the acetic propionic, butyric, and valeric acids, respectively. Interestingly, the increase in concentration of EMIMCl at 20 g L^{-1} mediated REs of 7.4 %, 15.9 %, 15.7 %, and 18.0 % for acetic, propionic, butyric, and valeric acids, respectively. In addition, AMIMCl at 10 g L^{-1} supported negligible recoveries of acetic acid and limited recoveries for propionic, butyric and acetic acids, which accounted for 11.1 %, 13.5 %, and 14.6 % respectively. AMIMCl at concentrations of 20 g L^{-1} mediated recoveries of 6.5 %, 12.1 %, 1.2 %, and 1.7 % for acetic, propionic, butyric and valeric acids respectively.

Xing et al. (2023) conducted tests on the extraction of acetic acid and butyric acid using membrane processes and ionic liquids as extractants.
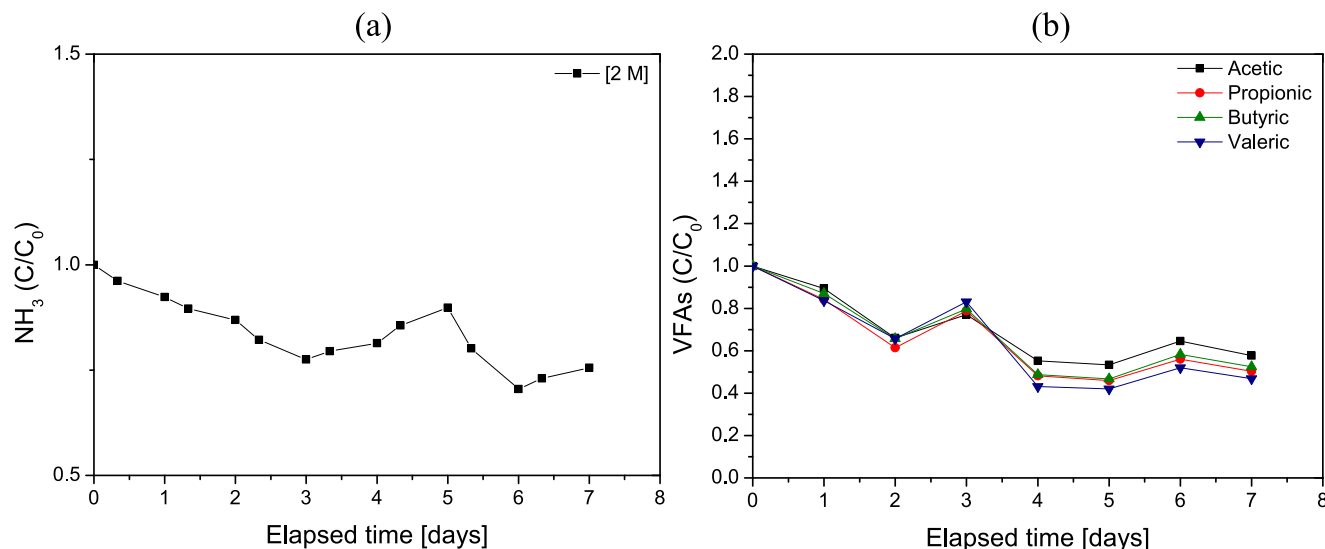
Fig. 5. Time course of (a) ammonia (NH$_3$) concentration and volatile fatty acids (VFAs) (b) acetic (■), propionic (•), butyric (▲) valeric (▼) acid concentration by using 2 M NaOH as the extractant solution.

Table 2
Mass transfer coefficient [m h^{-1}] using a PTFE membrane.

VFAs	Mass transfer coefficient (m h^{-1})	
	Test 5	[55]
Acetic	3.84×10^{-2}	8.4×10^{-2}
Propionic	3.12×10^{-2}	1.2×10^{-2}
Butyric	3.32×10^{-2}	1.4×10^{-2}
Valeric	2.82×10^{-2}	1.6×10^{-2}

They used IL-101$^+$ as the ionic liquid. IL-101 combined with dodecane proved highly effective at pH 6.0, particularly for butyric acid, achieving over 90 % extraction efficiency. The IL-101 ratio in dodecane and the solvent-to-feed (S/F) ratio significantly influenced extraction performance. This solvent also performed well in mixed VFA systems, including real broths from kitchen waste fermentation, showing strong selectivity for butyric acid. Maximum extraction/selectivity rates reached 60.2 %/70.5 % in butyric acid broth and 74.6 %/62.7 % in mixed acid broth [59].

3.6. VFA and NH$_3$ extraction from real DF broth under optimized operational conditions

The extraction of NH$_3$ and VFAs concentrations from real FW and CW DF broths was tested in the same experimental setup using NaOH at 2 M as membrane extractive liquid at a recirculation flow of 500 mL min^{-1}. A recovery of 22,7 % of the initial NH$_3$ was recorded in the FW fermentation broth after 7 days of extraction, while an increase in NH$_3$ concentration was recorded in the particular case of the CW fermentation broth (Fig. 7 a,b). This increase, which was not previously observed in the assays conducted with synthetic fermentate, might be explained by the hydrolysis and ammonification of the organic nitrogen remaining in the cultivation broth. The test fermentation broth from CW was stopped on the fourth day due to a sudden membrane failure. As reported by Rivera and co-workers during a comparative study assessing NH$_3$ extraction in real digestate and synthetic digestate, the greater membrane fouling in the tests with real digestate only reduced NH$_3$ extraction by 1.8 % [53].

Evaluating the VFAs profile shows that in the case of FW, (Fig. 7c), the reduction trends are consistent, with a particular removal effect recorded for valeric acid which reached an RE of 67.9 %, compared to acetic, propionic and butyric recorded at 25.7, 31.0, 33.5 %

respectively. Aydin et al. (2018) reported VFAs recovery from synthetic solutions and fermented organic wastes using air-filled and amine extractant-filled PTFE membranes in vapor pressure membrane contactors. The found that acetic acid recovery exceeded 45 % across all fermented wastes, while the use of trioctylamine-filled membranes enabled the efficient extraction of propionic, butyric, valeric, and caproic acids, achieving over 86 % recovery from landfill leachate and 95 % from anaerobically digested organic waste [55]. (Fig. 7d) shows that propionic and butyric acids decreased, 32.2 and 24.9 % respectively, while acetic acid concentration increased about 75.3 %. Valeric acid concentrations in this fermentate were very low (data not shown). Molinuevo-Salces et al. (2024) reported the use of a gas-based membrane system to recover VFAs from CW fermentation broth. The findings showed that pH control significantly impacts bioconversion efficiency, with sequential control under acidic conditions increasing conversion to 54 %, while alkaline conditions resulted in a lower efficiency of 45 %. Acidic conditions led to a diverse VFA profile, whereas alkaline conditions predominantly produced acetic acid. The novel gas-permeable membrane system enabled VFA recovery, achieving 15 % when multiple VFAs were present and 100 % when acetic acid was the main component [35]. In this study, acetic acid showed an increasing trend despite the acidic pH (5.5), with a total increase of 75.2 % by the end of the experiment. The highest recorded peak reached 97.9 % after 56 h from the start of the experiment.

4. Conclusions

Gas-liquid membrane contactor for the simultaneous recovery of NH$_3$ and VFAs from synthetic and real DF broths was investigated. Various experimental conditions were tested, adjusting key operational parameters such as fermentate pH, recirculation flow rate, and the type and concentration of extractive solution. Using a synthetic fermentation broth, optimal conditions were achieved at pH 5.5, with a recirculation flow of 500 mL min^{-1}, employing 2 M HCl and 2 M NaOH as pH regulator and extractive liquid, respectively. Under the specified experimental conditions, NH$_3$ recovery was 24.5 % with significant VFA recovery rates of 42.3 % for acetic acid, 49.9 % for propionic acid, 47.5 % for butyric acid, and 53.2 % for valeric acid. Using a real dark-fermentation broth from FW, the process achieved a maximum recovery of 22.7 % of the initial NH$_3$ with VFAs recoveries of 67.9 % (valerate), 25.7 % (acetate), 31.0 % (propionate), and 33.5 % (butyrate). This study demonstrates that DF broths can be effectively valorized
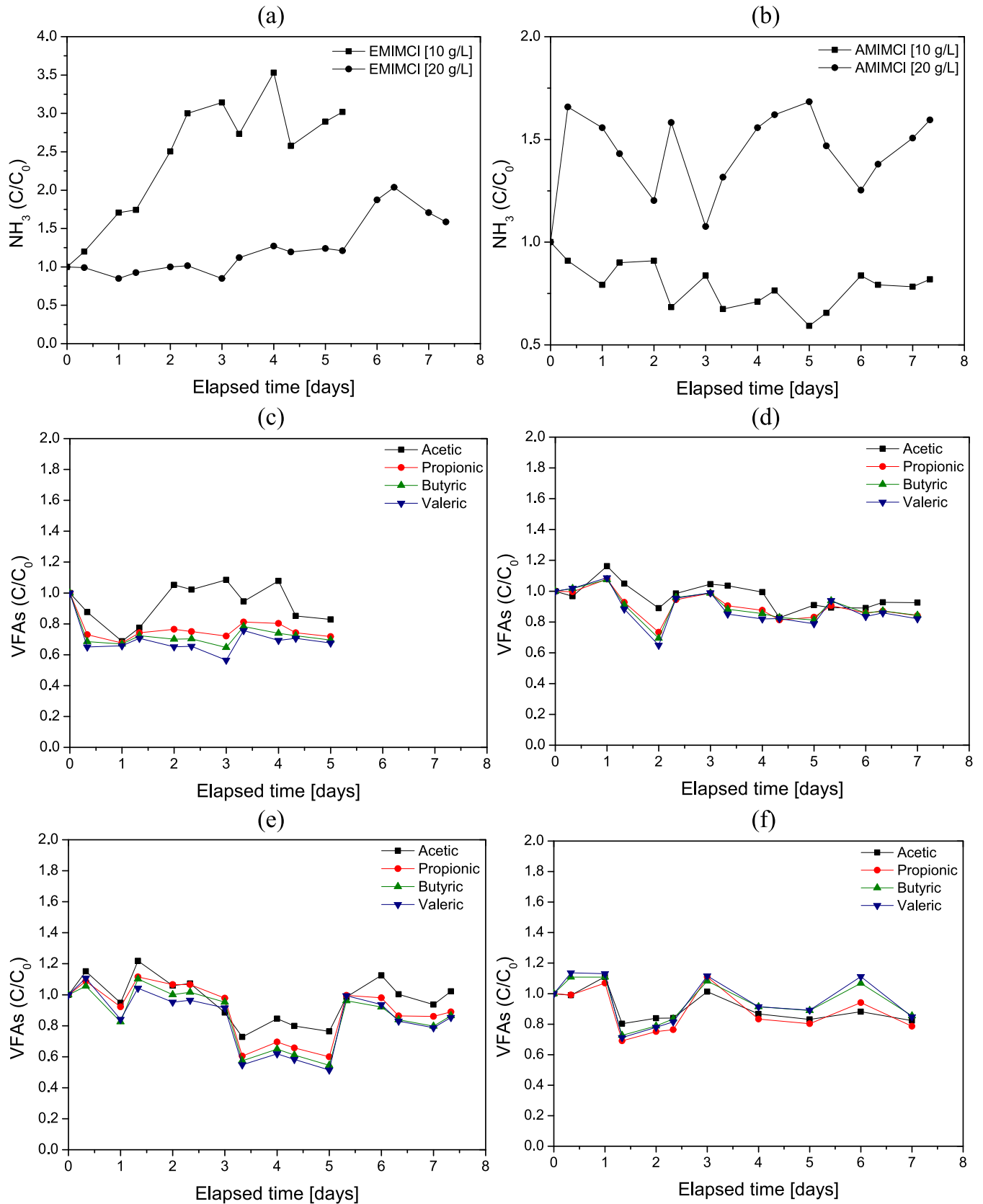
Fig. 6. Time course concentration of ammonia (NH$_3$) concentration using (a) EMIMCl at 10 (■) and 20 g L^{-1} (●), and (b) AMIMCl at 10 g L^{-1} (■) and 20 g L^{-1} (●). Time course of volatile fatty acids (VFAs) acetic (■), propionic (●), butyric (▲) valeric (▼) acid) concentration in synthetic dark fermentation broth during extraction; (c) using EMIMCl [10 g L^{-1}] as liquid extractant; (d) AMIMCl [10 g L^{-1}]; (e) EMIMCl [20 g L^{-1}]; (f) AMIMCl [20 g L^{-1}].
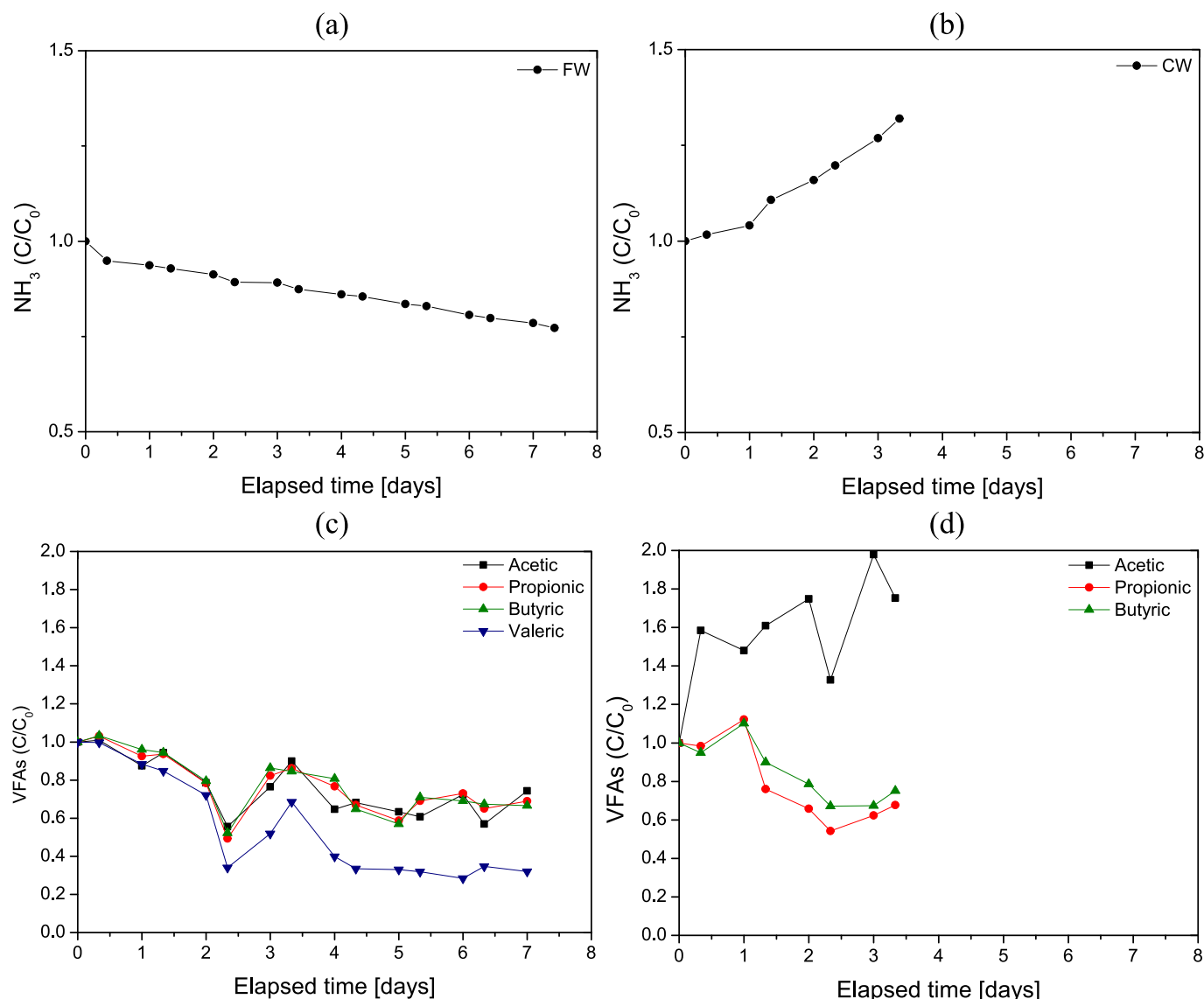
Fig. 7. Time course of ammonia (NH$_3$) concentration (•) and volatile fatty acids (VFAs) acetic (■), propionic (•), butyric (▲) valeric (▼) acid) concentration in FW fermentation broth (a and c) and powdered cheese whey fermentation broth (b and d).

through the simultaneous recovery of NH$_3$ and VFAs. Beyond confirming technical feasibility, these results highlight the potential of membrane contactors as an integrated upgrading step to enhance the circularity and economic value of dark-fermentation processes.

CRediT authorship contribution statement

Fabiana Romano: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Tiziano Zarra:** Writing – review & editing, Supervision. **Laura Palacio:** Writing – review & editing, Resources. **Octavio García-Depraect:** Writing – review & editing, Funding acquisition. **Raúl Muñoz:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

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.

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Data availability

Data will be made available on request.

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