

Recovery of ammonia from acidogenic fermentation effluents using a hydrophobic membrane contactor

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Keywords: Acidogenic fermentation; Ammonia; Fertilizer; Membrane contactor; Nitrogen.

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Abstract: Hydrophobic gas-permeable membrane contactors represent a promising solution for NH₃ recovery from wastewaters or organic wastes to obtain valuable N-based fertilizers (i.e. (NH₄)₂SO₄) in the so-called resource recovery facilities (Dube *et al.*, 2016; Rongwong and Goh, 2020). Volatile Fatty Acids (VFAs) are also identified as high-added value products that could be produced from a wide variety of feedstocks, such as sewage sludge and/or Organic Fraction of Municipal Solid Waste (OFMSW). Among other applications, these VFAs could be used as platform chemicals for Polyhydroxyalkanoates (PHA) production (Reis *et al.*, 2011; Conca *et al.*, 2020). Recent studies have revealed that decoupling carbon (VFA) and nitrogen feeding could enhance PHA storing microorganisms selection, thereby increasing the PHA production in the accumulation reactor (Lorini *et al.*, 2020; Nguyenhuynh *et al.*, 2021). However, the VFA-rich effluent obtained in acidogenic fermenters using mixed microbial cultures and treating organic wastes is usually characterised by a high total ammonium nitrogen (TAN) concentration. The objective of this study is to evaluate the use of a gas-permeable membrane contactor operated under six pH (6 to 11) and two temperatures (35 and 55°C) conditions to recover ammonia from the liquid fraction of fermented OFMSW.

The experimental set-up consisted of a nanoporated Polypropylene (PP) hollow fiber membrane contactor. The feed solution enriched in TAN and VFAs was pumped in a closed loop from a stirred feed tank (maximum working volume of 2 L) to the shell side of the contactor, while a sulphuric acid extraction solution was pumped from a stirred tank (maximum working volume of 2 L) to the lumen side of the contactor to strip the TAN of the feed solution and produce (NH₄)₂SO₄. In this study, the volume of the feed and the trapping solution were the same, although other authors have successfully recovered ammonia using a volume of trapping solution 1/120 times lower than the feed solution (Vecino *et al.*, 2019). The pH of both the feed and the trapping solution tanks were controlled to a set point value using pHmeters connected to peristaltic pumps to supply NaOH and H₂SO₄, respectively. Moreover, the temperature of the feed tank was controlled using a thermostatic bath. All the analyses were performed according to the standard methods for the examination of water and wastewater (APHA, 2005).

Figure 1 shows the TAN concentration evolution in the feed and trapping solution for experiments carried out at 35 °C with controlled pH in the feed tank (ranging from 6 to 11) using synthetic wastewater with 2.4 g NH₄⁺-N/L and 3.0 g/L of acetic acid (2 replicates for each condition). Higher TAN recovery rates were achieved as the pH in the feed tank was increased. However, similar TAN recovery rates were obtained at pH 10 and 11, reaching a N recovery above 99% for contact times lower than 5 h. When temperature was increased to thermophilic conditions (55 °C), higher recovery rates were obtained than when working at mesophilic conditions, especially for pH values lower than 10 (data not shown). In all these tests, acetic acid was not detected in the trapping solution.

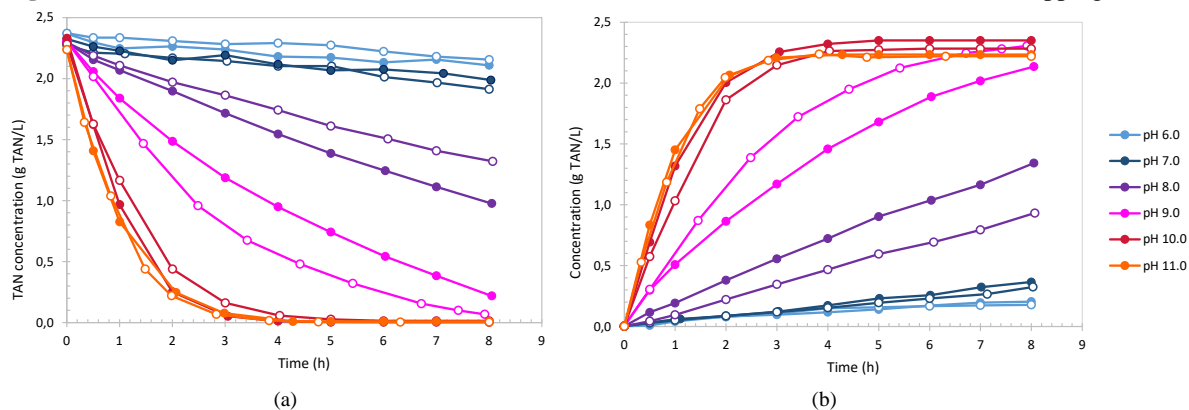


Figure 1 – Evolution of the TAN concentration in the feed synthetic solution (2 L) (a) and the trapping solution (2 L) (b) working with 2 replicates for each pH value in the range of 6-11 (feed solution) and mesophilic conditions (35 °C).

To test the nitrogen recovery from fermentation liquids, source sorted OFMSW was collected in a mechanical-biological treatment plant of the Barcelona Metropolitan Area. This substrate was treated in batch conditions in a 30 L fermenter at 35 °C and without external inoculum. During the fermentation process, the decrease of pH due to VFA production was monitored and when a slight rise in this pH was observed (after 8 days of fermentation) thus indicating VFA consumption, the fermentation process was stopped. Figure 2(a) shows the evolution of the VFA concentration and its distribution, which reached 28g VFA/L, with a predominance of acetic (12.6 g/L), butyric (6.0 g/L) and propionic (6.7 g/L) acids. VFA production was accompanied by an increase in TAN concentration from 3.8 to 4.9 g TAN/L.

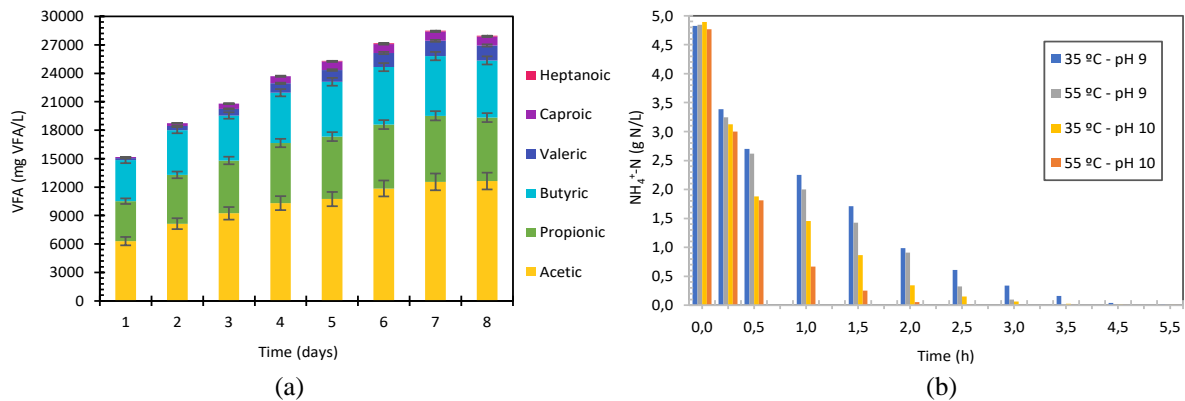


Figure 2 – Evolution of the VFA concentration during a mesophilic fermentation batch test (30 L) of OFMSW collected in a MBT plant (a) and TAN recovery in real liquid fraction of fermented OFMSW (0.5 L) at two temperatures (35 and 55 °C) and pH values for the feed solution (pH 9 to 10) (b).

The fermentation effluent was meshed and filtered using 1.2 μm filters to separate the liquid fraction enriched in VFA and TAN. Subsequently, 0.5 L of the fermentation liquid were treated in the membrane contactor unit to recover nitrogen without affecting VFA concentration. Figure 2(b) shows the evolution of TAN in the fermentation liquid when working at 35 and 55°C, respectively and at a pH of 9 and 10. As observed in Figure 2b, TAN was completely recovered before 3.5 h in all the conditions tested (it should be noted that in these tests only 0.5 L of fermentation liquid was treated). No losses of TAN were detected in all these experiments. VFAs were not detected in the trapping solution, although approximately a loss (always below 14%) of VFAs were observed during these tests, probably due to biological reactions in the feed tank. Thermophilic conditions slightly favoured the nitrogen uptake rate due to the lower pKa of $\text{NH}_4^+/\text{NH}_3$ equilibrium at higher temperatures. Although a higher TAN uptake rate was monitored at pH 10, the use of pH 9 lead to lower NaOH consumption to adjust the pH.

In conclusion, this study demonstrates that ammonia can be completely recovered from the liquid fraction of OFMSW acidogenic fermentation at both mesophilic and thermophilic temperatures and at pH values above 9, yielding a $(\text{NH}_4)_2\text{SO}_4$ solution with fertilizing value and a VFA-rich liquid without ammonia nitrogen

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