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Evaluation of Pressure-Driven Membrane Processes for Nutrients Recovery from Dilute Effluents

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Abstract Results are presented from an ongoing R&D project, aiming at full utilization of dairy-industry effluents. Development of a membrane-based method is pursued, for treatment of digestate (after fermentation yielding bio-gas) to recover nutrients (N-NH_4, P-PO_4) and water for reuse/recycling or safe disposal. The performance is investigated herein of four commercial nanofiltration/ultra-low-pressure reverse osmosis membranes, employed in dead-end filtration mode, for nutrients recovery from solutions simulating the liquid digestate/effluent of an anaerobic membrane-bioreactor (AnMBR). Best-performing membranes, regarding nutrients' rejection, were assessed within a sufficiently broad range of all key process parameters, including trans-membrane pressure and feed-composition. Further testing took place in a cross-flow set-up, simulating real operating conditions. For ~80% permeate recovery, the concentrate was significantly enriched in nutrients; i.e. compared to feed-solution, N-NH_4 was concentrated twice, whereas P-PO_4 was concentrated by 3- to 4-times. Research with real AnMBR effluent is on-going, for process improvements/optimization, mainly focusing on composition of concentrate/nutrients (for use in liquid fertilizers), membrane-fouling mitigation and quality of permeate/water for possible reuse.

Keywords: nanofiltration, ultra-low-pressure reverse osmosis, dairy industry effluents, anaerobic digestate, ammonium and phosphorous recovery

1. Introduction

Large amounts of effluent streams, composed of diluted products (lipids, proteins, lactose) and cleaning chemicals (acids, alkalis and detergents), are generated in dairy processing plants, which represent a waste of water and nutrients as well as environmental burden. In particular, cheese production effluents are characterized by high organic content, high levels of dissolved or suspended solids, including fats, nutrients such as ammonia or minerals, and phosphates (Carvalho et al., 2013). Anaerobic biological treatment is a sustainable and environmentally friendly solution for the treatment of wastes from agricultural industries such as dairy, with a very high organic content (Amaya et al., 2013). The solids in the anaerobic digestate are usually separated from the liquids through centrifugation, conventional filtration techniques and in some cases, ultrafiltration (UF), which is considered to produce effluent with better physicochemical characteristics (Gupta και Ali, 2013). However, the liquid effluent from anaerobic digestion is rich in nutrients (Vaneeckhaute et al., 2017) and its disposal in surface waters can cause eutrophication.

Considering established and quite effective biological and chemical technologies for nutrients removal, the current research efforts are concentrated on their effective recovery in accord with the principles of circular economy (Vaneeckhaute et al., 2017), because nutrients can be used in the production of chemical fertilizers. Typical methods for nutrients recovery are chemical precipitation of ammonium and phosphate ions for the production of struvite ($MgNH_4PO_4 \cdot 6H_2O$), hydroxyapatite ($Ca_5(PO_4)_3OH$) or brucite ($CaHPO_4 \cdot 2H_2O$) and acidic air scrubbing with H_2SO_4 solution (Vaneeckhaute et al., 2017).

Membrane processes are also employed, producing concentrates of ammonium and phosphates that could be used as fertilizers' substitutes. Among the membrane technologies applied are nanofiltration and reverse osmosis (RO) (Yan et al., 2018). However, the literature, on the recovery of nutrients from liquid digestates produced by the anaerobic treatment of agro-industrial wastewaters, is rather limited. In the work of Van Voorthuizen et al. (2015) very high rejection was reported of ammonium and phosphate from the anaerobic effluent of domestic wastewater, by commercial NF and RO membranes. In particular, NF90 and XLE (Dow-Filmtec) membranes retained N-NH_4 and P-PO_4 by more than 90% and 98%, respectively. Adam et al. (2018) evaluated two industrial-scale membrane filtration pilot units for the separation of organic matter, nutrients and water from the liquid fraction of anaerobic digestate, produced at two biogas plants processing substrates of agricultural residues, cow and chicken manure, food industry waste and cow slurry. The study showed a good performance for COD and TSS retention but the system needed to be optimized for final permeate quality regarding monovalent ions (ammonium and potassium).

In the present study, two commercial NF and two RO membranes were tested for ammonium and phosphate recovery from a synthetic nutrient solution simulating the liquid fraction of the anaerobic MBR effluent of a major Greek dairy industry, after solids separation. Parameters such as membrane permeability, ion selectivity and rejection were investigated as a function of clean water recovery and operating pressure, leading to the selection of the best performing membrane for further testing with real anaerobic effluent.

2. Materials and Methods

2.1. Membranes

Four types of commercial flat sheet RO and NF membranes were used; i.e., NF90 and XLE (DU PONT, former DOW-FilmTec™) and TS80 and ACM2 (MICRODYN-NADIR GmbH). According to the manufacturers' specifications, these membranes are promising in terms of monovalent and divalent ion rejection (~90 and 99%, respectively) and permeation rate. The chosen membranes are tolerant of modest temperatures (ca. 35°C) and exhibit good performance in the presence of other inorganic and organic constituents.

2.2 Chemical reagents and analytical methods

The test solutions simulated the composition of the liquid effluent of the AnMBR plant, installed at BIZIOS S.A. dairy industry facilities (located in Elassona, Greece), (N-NH_4 and P-PO_4 of 150 mg/L, each), after sludge removal. They were obtained by the dissolution in deionized water of ammonium chloride (NH_4Cl) and potassium dihydrogen phosphate, purchased from Lachner S.R.O. (Slovakia) and PENTA S.R.O. (Czech Republic), respectively. The ion concentrations of N-NH_4 and P-PO_4 in the feed, concentrate and permeate solutions were analysed with Ion Chromatography (IC) (Prominence, Shimadzu, Japan). All solutions were characterized in terms of pH and electrical conductivity (eC) with a multi-parameter bench meter (AD8000, Adwa, Hungary).

2.3 Experimental set-ups and procedures

Dead-end filtration tests under constant agitation were performed first with the aim to investigate the ion rejection and water permeability performance of the selected NF/ULPRO membranes. An experimental set-up comprising a pair of high pressure thermostated stirred cells (SEPA-ST cells, Osmonics Inc., Minnetonka U.S.A.) was used for this purpose (Mitrouli et al., 2010). Each cell had a capacity of 0.3 L, with inner diameter of 4.7 cm and effective membrane area of 12.7 cm^2. A second pressure vessel of 0.7 L was connected with each cell in order to increase the total feed volume to 1.0 L. The rejection tests were performed under constant stirring rate 250 rpm, which result in a space-average shear stress at the membrane surface that is close to that prevailing in spacer-filled channels of spiral wound membrane modules, at usual cross-flow velocity ~15 cm/s (Koutsou και Karabelas, 2012). The test cells were connected to a nitrogen cylinder to impose/control a constant filtration pressure. The water temperature in the test cells was kept constant at 25 ± 0.2 °C by a water cooling system (PolyScience®, 9106, U.S.A.). A new membrane specimen was used in each filtration test. Electronic balances connected to PCs were used to monitor permeate fluxes.

The *cross-flow filtration tests* (quite representative of local conditions prevailing in real membrane elements) were performed under constant pressure (5 bar) and full recycling in a laboratory unit, similar to the one described in previous work (Karabelas et al., 2014). This unit was comprised of two test sections of narrow (1 mm) gap, employing flat sheet membrane pieces of filtration area 130.35 cm^2 (5.5 cm × 23.7 cm) as well as a common commercial net-type spacer.

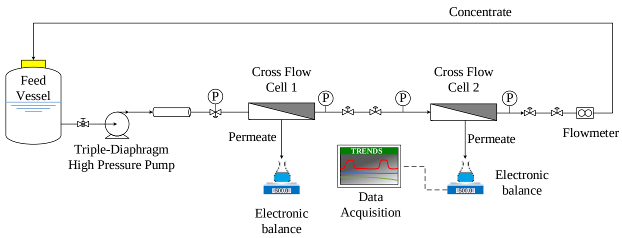

Figure 1. Experimental set-up employed in the cross-flow tests

The synthetic solution was recirculated via a triple-diaphragm high-pressure pump. The permeate mass was continuously recorded with an electronic balance (PL602-S, Mettler-Toledo AG) connected to a computer for automatic data acquisition (GeniDAQ, Advantech Co. Ltd., Taipei, Taiwan).

3. Experimental Results

3.1 Dead-end filtration tests

Characterization of the four membranes was carried out first by measuring (a) pure water permeability (at applied pressures 2, 4, 6, and 8 bar), and (b) rejection of N-NH_4 and P-PO_4 at a concentration of 150 mg/L for each ion and pressure 5 bar. Prior to all rejection tests, the membranes were compacted at 10 bar for 1 h, without agitation. The results are depicted in Fig. 2. The two DU PONT membranes exhibited the highest permeation rates (XLE, 7.6 L/m^{2}h followed by NF90, 6.6 L/m^{2}h) and the highest rejection of nutrients (i.e., N-NH_4 84% and 89% and P-PO_4 99% and 98%, for XLE and NF90, respectively) which was in accordance with the manufacturer's specifications for NaCl.

XLE and NF90 membranes were selected for additional single ion rejection experiments (N-NH_4 or P-PO_4) in an effort to better evaluate the effects of coexisting compounds on ion rejection and permeate flow (Table 1). The effect of the operating pressure (tests at 3, 5 and 7 bar) on the rejection efficiency of the two membranes for the mixture of N-NH_4 and P-PO_4 was also examined.

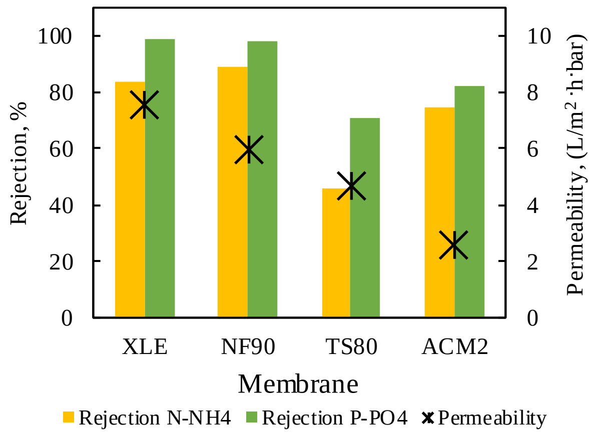

Figure 2. Performance of XLE, NF90, TS80 and ACM2 membranes regarding permeability and nutrients rejection

According to Table 1, the XLE membrane exhibited the best performance in terms of permeate flux (32.6 L/m²h) followed by NF90 (29.7 L/m²h). In the absence of P-PO_4 permeate flux increased for both XLE and NF90 due to the lower osmotic pressure of the N-NH_4 solution. No significant differences in nutrients rejection were observed when one or two components are filtered, which proved the rather negligible effect of the concentration polarization (induced by the retained ions) on solute rejection. As expected, for both the membranes, the increase of the operating pressure resulted in higher water permeation, but had no significant effect on nutrients' rejection, indicating that these membranes can be used at various operating conditions.

Table 1. N-NH_4 and P-PO_4 rejection (%) results in single and binary solutions

	Binary solution	N-NH4 solution	P-PO4 solution
XLE			
Flux, L/m²h	32.6	38.2	31.4
N-NH4 Rejection	84	84	-
P-PO4 Rejection	99	-	95
NF90			
Flux, L/m²h	29.7	45.4	40.3
N-NH4 Rejection	89	75	-
P-PO4 Rejection	98	-	97

The performance of NF90 and XLE membranes was further investigated for high recovery rates of clean water (ca. 80%). All tests were conducted under agitation (250 rpm) and constant pressure (5 bar) at 25 °C. Permeate flux was progressively reduced, for both membranes, in a similar way, reaching 50% of the initial value (i.e. from 31.5 to 14.5 L/m²h and from 33 to 16.5 L/m²h for XLE and NF90, respectively), due to the increase of the solution osmotic pressure. On the other hand, the rejection of nutrient ions was constantly high (P-PO_4 > 90% and N-NH_4 > 80%), even at 80% permeate recovery. The highest rejection values were measured for P-PO_4 ions by NF90 (ca. 95%). The high rejection led to a 5-times concentration of phoshate ions with NF90 and a 4-times concentration with XLE, while ammonium ions were concentrated 3.9 and 3.6 times, with NF90 and XLE, respectively (Fig. 3). The significant concentration of the two nutrient ions in the reject stream of the two membranes justify its potential utilization as liquid fertilizer in agriculture.

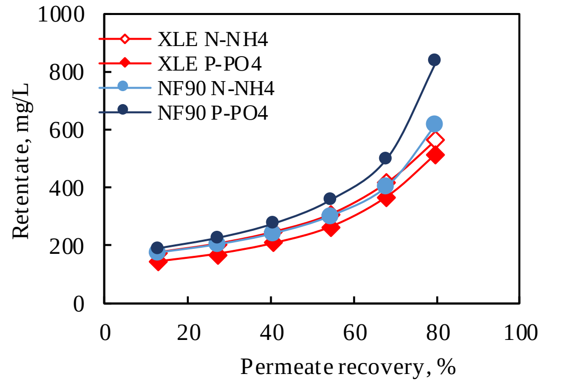

Figure 3. Temporal evolution of nutrients concentration during filtration with NF90 and XLE membranes (dead-end mode)

3.2 Cross-flow filtration tests

Cross-flow tests with NF90 and XLE membranes were conducted up to 77% water recovery. The applied pressure was 5 bar, the temperature remained constant at 25 °C and the cross-flow velocity was ~20 cm/s. The flux profiles of both membranes are depicted in Fig. 4, according to which NF90 displays the best performance in terms of permeate flux at all stages of the filtration process.

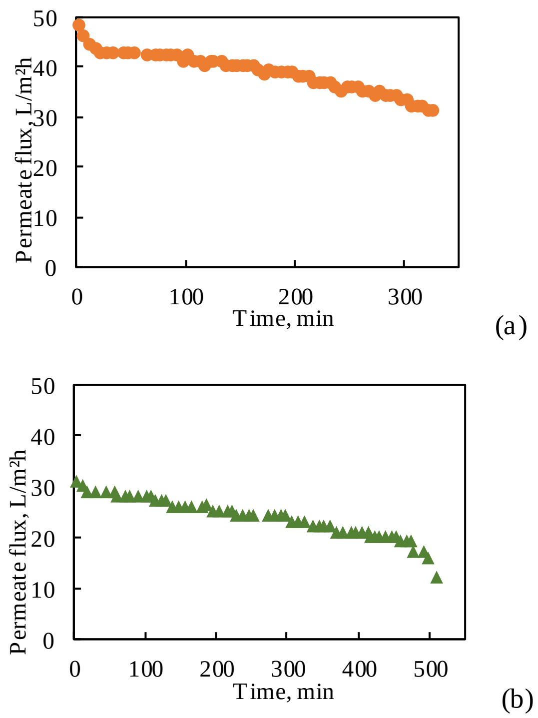

Figure 4. Permeate flux temporal variation for (a) NF90, (b) XLE membranes; cross-flow mode, 150 mg/L N-NH_4, 150 mg/L P-PO_4, 76-77% water recovery

Compared to dead-end filtration, the flux decline in the case of NF90 seems to be lower, despite the increase of feed solution osmotic pressure. The rejection of nutrients remains high during all tests, with the highest values measured for P-PO_4 (98.5% and 97.1% with XLE and NF90, respectively), while N-NH_4 rejection is almost identical for both membranes tested (~83%). Furthermore, higher concentration of P-PO_4 is achieved with NF90 membrane (C_f=4.2) in comparison to XLE (C_f=3.1). N-NH_4 concentration in the retentate is also slightly improved for NF90 compared to XLE (C_f=2.2, contrary to C_f=2.0 for XLE) (Fig. 5).

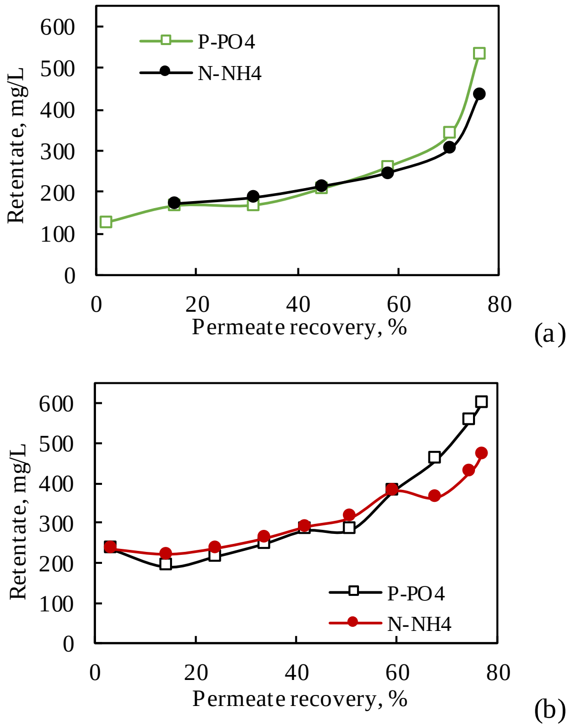

Figure 5. Temporal evolution of nutrients concentration during filtration with (a) NF90 and (b) XLE membranes (cross-flow mode)

4. Conclusions

Among the four commercial NF/ULPRO membranes tested for N-NH_4 and P-PO_4 removal from aqueous solutions, simulating the concentrations encountered in liquid digestates of the dairy industry, XLE and NF90 exhibited the best performance. The clean water permeability was 7.6 L/m^{2}h and 6.6 L/m^{2}h for XLE and NF90, respectively, while the rejection of ammonia and orthophosphate ions was very high (84-89% and 98-99%, respectively), achieving permeate concentrations of 17 mg/L N-NH_4 (NF90) and 2.2 mg/L P-PO_4 (XLE). It is noted that for orthophosphates the desirable limit for disposal of the treated liquid digestate in surface water bodies is met ($\leq$ 4 mg/L). The increase of the applied pressure had a positive effect on water permeation rate; however, no substantial difference was observed in the rejection rates of both ions. The desirable high recovery rates (ca. 80%) of clean water did not affect the rejection of both ions, which remained high (PO_4-P> 90% and NH_4-N> 80%) throughout the filtration period for both membranes. Cross-flow tests with NF90 and XLE showed that NF90 exhibited stable nutrients rejection, higher permeate flux throughout the process and greater nutrients concentration, rendering it suitable for future applications in downstream membrane separation processes for the effective recovery of water and nutrients (N-NH_4, P-PO_4), in accord with the principles of circular economy.

5. Acknowledgements

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