18th International Conference on Environmental Science and Technology

Athens, Greece, 30 August to 2 September 2023

Nutrients recovery from liquid anaerobic digestate by combining nanofiltration and struvite precipitation - The case of dairy effluents valorization

TSARIDOU C.[1], KARANASIOU A.[1,*], SIOUTOPOULOS D.[1], PLAKAS K.[1], TZIOUMAKLIS C.[2], PATSIKAS N.[3], GLIAOS P.[3], KARABELAS A.J.[1]

[1] Natural Resources & Renewable Energies Laboratory, Chemical Process and Energy Resources Institute, Centre for Research and Technology-Hellas, 6th km Charilaou-Thermi Road, Thermi-Thessaloniki, GR 57001 GREECE

[2] BIZIOS S.A., Vodiana, Elassona, GR 40200 GREECE

[3] TEDRA, 23 Papanastasiou str., Larisa, GR41222 GREECE

*corresponding author:
e-mail: akaranasiou@certh.gr

Abstract. Results are reported herein of a study aiming to develop an integrated process for valorizing liquid digestate (LD) from an industrial anaerobic digestion (AD) plant treating dairy-processing effluents. The investigated approach involves LD treatment by nanofiltration (NF) membranes, at pilot-scale on-site, followed by precipitation/recovery of struvite in the retentate stream. The obtained NF permeate, for a typical 60% recovery, meets the required standards for restricted irrigation. The significant concentration of nutrients in the NF-retentate (~500 mg/L NH_4-N, ~230 mg/L PO_4-P) allowes the investigation of struvite precipitation and the determination of near optimum process conditions, through lab- and pilot-scale testing. The results show that the maximum removal of nutrients and production of struvite-rich precipitate is obtained at molar ratio of N:Mg:P = 1:1.5:1.5 and pH=10 in the retentate stream. Additionally, almost complete struvite precipitation can be achieved within ~30 min, whereas solids drying at modest/ambient temperature is desirable to avoid struvite degradation. Under the aforementioned conditions, a significant amount of dry precipitate (~11 g dry mass/L of treated retentate) including crystalline struvite is obtained. The results of this study warrant further development of this integrated process as well as its overall sustainability assessment in comparison to alternative LD valorization approaches.

Keywords: dairy-industry effluents; anaerobic digestion; liquid digestate; nanofiltration; struvite recovery

1. Introduction

Anaerobic Digestion (AD) is an established technology, of increasing applicability in recent years, as it provides a renewable energy source (biogas), in accord with the European Union de-carbonization goals. In fact, the number of such biogas plants in Europe exhibited a sharp increase (from 10,500 to ~17,000) in the years 2010 to 2014 (EBA, 2022). A variety of AD feedstocks are currently used, of significant organic content, although those of agricultural origin (i.e. assorted agricultural residues) dominate.

In an AD plant, in addition to biogas, the valorization of resulting digestate is currently pursued; the latter is a mixed liquor consisting of biomass, nutrients (nitrogen, N, phosphorus, P and potassium, K) volatile fatty acids (VFA) and metals. The rather high nutrient content of these streams has raised interest in their application for soil fertilization, in particular because the use of secondary raw materials in manufacturing fertilizers is foreseen by the new European Union regulation on fertilizers (2019/1009) (EU, 2019). A rather common practice is to apply LD directly on cultivated land, however raising serious concerns by the farmers (Sheets et al., 2015). Additionally, several nutrient-recovery technologies (NRTs) have been employed for the treatment of LD in order to concentrate and efficiently utilize it in fertilizers. The most common NRTs, applied to various waste streams, are ion exchange and adsorption, ammonia (NH_3) stripping, chemical precipitation and membrane processes (Barampouti et al., 2020). However, the valorization of LD tends to be challenging and the integration of two or more operations may be necessary, to recover both appropriate fertilization products and adequately treated effluents, suitable for discharge or reuse (Lorick et al., 2020, Saliu and Oladoja, 2021, Wu and Vaneeckhaute, 2022).

Nanofiltration (NF) has been previously assessed for the concentration of LD and concurrent production of a sufficiently clean effluent for recycling or safe disposal (Tsaridou et al., 2023). A comprehensive methodology was followed, comprising laboratory tests with synthetic and real effluents accompanied by reliable simulations, in order to design and construct an appropriate NF pilot unit. In the present study, the NF-pilot is used for pre-concentration of LD from an industrial AD plant, operating in Central Greece (Elassona, "BIZIOS S.A."), treating dairy-processing effluents. Moreover, recovery of nutrients from the NF concentrate in the form of struvite ($NH_4MgPO_4 \cdot 6H_2O$) is systematically examined.

2. Materials and methods

2.1. Liquid Effluent (LD)

Table 1 summarizes the characteristics of the LD from the AD plant (obtained after membrane ultrafiltration of the raw digestate to remove sludge), which was employed in the concentration tests conducted with the NF pilot unit. In general, the effluent is characterized by moderate nutrients content (NH_4-N~250 mg/L, PO_4-P~100 mg/L) and relatively high ionic strength and alkalinity, which render it inappropriate for safe disposal.

Table 1. Composition of LD and NF-concentrate

	LD 1	NF_ Conc 1	LD2	NF_ Conc 2
Pilot test No	**PS01**		**PS02**	
Operation of AD plant, months	16.5		20	
pH	7.4	7.0	7.1	7.4
eC, mS/cm	8.3	18.3	8.3	18.8
PO_4-P, mg/L	102	246	126	161
NH_4-N, mg/L	213	509	268	546
Cl^-, mg/L	635	1549	791	1318
SO_4^{2-}, mg/L	91	4230	152	2950
Na^+, mg/L	1758	4079	1657	3323
K^+, mg/L	231	547	294	618
Ca^{2+}, mg/L	18	35	<40	26
Mg^{2+}, mg/L	20	62	25	44
Alkalinity, mg $CaCO_3$/L	3710	4185	3703	4612
TOC, mg/L	151	274	24	118

2.2. Nanofiltration (NF) pilot tests

The systematic design of the industrial nanofiltration (NF) pilot unit (Fig. 1) is reported elsewhere (Tsaridou et al., 2023), where design parameter values are also included. The pilot is equipped with two pressure vessels (Phoenix ltd, UK), a horizontal multistage pump (1HM22N11T, LOWARA, Xylem Inc., USA), three vessels (1000 L) for the feed, concentrate and permeate and systems for pH adjustment and clean in place (CIP). Two NF90-2540 (DuPont) spiral wound membrane (SWM) modules are placed in each pressure vessel. A human–machine interface (HMI) with a touch screen (MT8090XE, WEINTEK, Taiwan) is installed for the supervision and control of pilot tests.

Two pilot tests were conducted (PS01 and PS02) for LD concentration in batch mode, with full recycle of condensate and collection of permeate. Test conditions were adjusted to achieve an initial recovery of 13% per pass. Therefore, the feed flow rate was adjusted to 15 L/min (cross-flow velocity u~0.25 m/s) and the permeate flow rate to 2 L/min. The system inlet pressure applied under these conditions was 9.3-10.5 bar and the total permeate recovery at the end of each test was ~56%. Between the tests a cleaning protocol was applied (DuPont™, 2021). During the tests acidification with 6N sulfuric acid was necessary to counteract the high alkalinity of the feed solution.

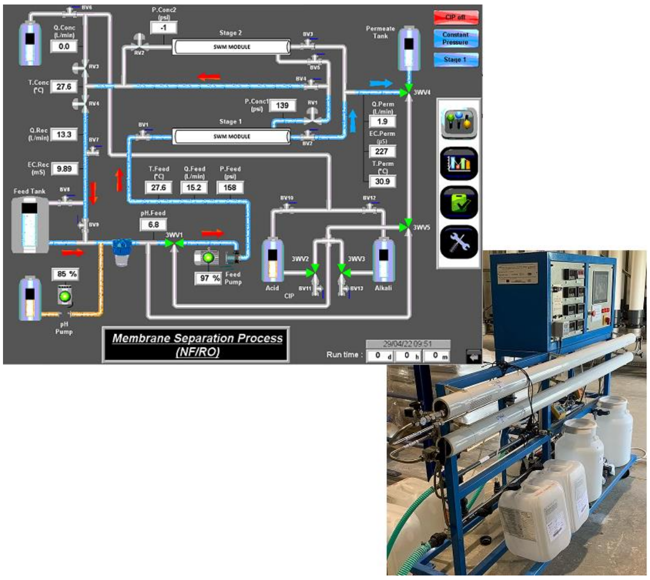


Figure 1. NF pilot unit: at the premises of BIZIOS S.A. and HMI screen of the dynamic flow diagram.

2.3. Struvite precipitation tests

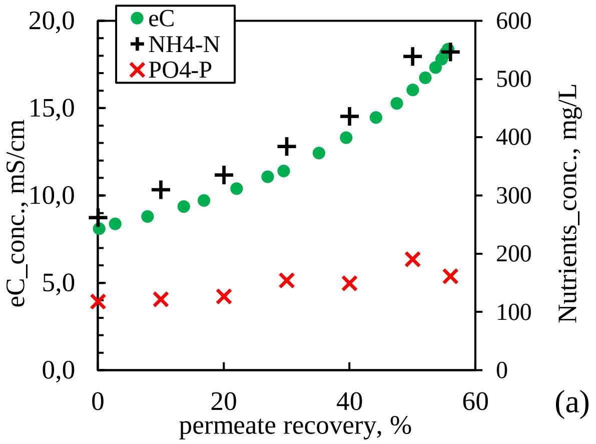
The concentrate (NF_Conc 1 & NF_Conc 2) of the NF-pilot tests (Table 1) was used for the study of struvite precipitation. A bench-scale parametric study (with NF-pilot test PS01 concentrate) was conducted with a JarTest system (AMF4, I.S.Co srl, Italia) with four agitators. The precipitation protocol was as follows: (a) 1L beakers were filled with 900mL of concentrated LD, (b) solutions of K_2HPO_4 58.7% w/v (Honeywell, USA) and $MgCl_26H_2O$ 68.3% w/v (Baker, Poland) were added under constant agitation at 200 rpm (rapid stirring) for a period of 5 min, (c) pH was adjusted with NaOH 5N (Riedel-de-Häen, Germany), (d) agitation rate was set at 45 rpm for 10 min for aggregation of the precipitate, (e) the mixture was left to settle for 30 min, filtered after 24h and (f) the precipitate was dried at ambient temperature. The parameters studied were the pH range (8-11), method of precipitate separation from the supernatant and NH_4:Mg:PO_4 molar ratio (1:1:1, 1:1:1.5, 1:1.5:1.5 and 1:2:2). Finally, a pilot test with 100L of NF concentrate (from NF-pilot test PS02) was conducted under near-optimal conditions.

2.4 Analytical methods

All liquid effluents were analyzed in terms of ion concentration (IC - Ion Chromatography, Prominence, Shimadzu, Japan), pH and electrical conductivity (eC) (multi-parameter bench meter AD8000, Adwa, Hungary) and alkalinity (Titrator 877 Titrino Plus, Metrohm AG, Switzerland). TOC was determined with a TOC analyzer (TOC-L, Shimadzu, Japan). The solid precipitates were characterized with Scanning Electron Microscopy (SEM, JSM-6300 SEM, JEOL Ltd., Japan), Energy Dispersive X-ray Spectrometry (EDS, Link ISIS, Oxford Instruments, UK) and X-Ray Diffraction (XRD D500 Siemens, Germany). The precipitates were dissolved with HCl 0.06N for nutrients and metals determination employing IC and an Inductively Coupled Plasma (ICP) unit (Optical Emission Spectrometer, Model Optima 4300 Dv, PerkinElmer, USA).

3. Experimental Results

Table 1 shows that LD was concentrated approximately 2 times during the NF pilot tests, with an exception of orthophosphate ions in test PS02, probably due to oversaturation and precipitation of phosphate salts (Fig. 2a). The continuous concentration of LD and the resulting increase of osmotic pressure led to the reduction of the permeate flux (Fig. 2b). The sharp decrease of the permeate flux at the end of test No PS02 is attributed to membrane-scaling phenomena, which is confirmed by the reduction of PO_4^{3-} concentration.



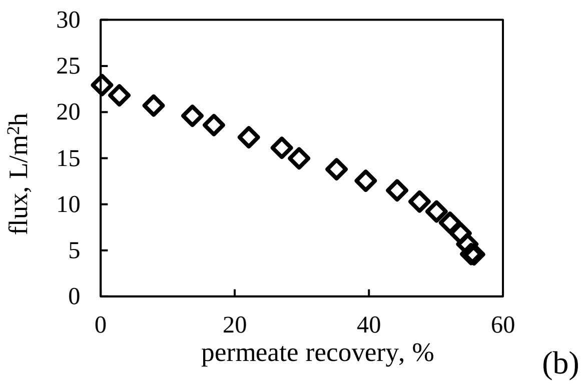


Figure 2. Effect of permeate recovery on (a) eC and nutrients' concentration and (b) permeate flux; Test No PS02: inlet pressure 11 bar, feed flow ~15 L/min (u~0.25 m/s)

The concentrate of test No PS01 was employed in the parametric study of struvite precipitation with jar tests. Initially, the effect of pH was studied on nutrients rejection/binding from the NF-concentrate for equimolar concentration of NH_4, Mg and PO_4. Increase of pH had a positive effect on Mg^{2+} removal from 80% (pH 8) to ~97% (pH 11) (Fig. 3). Rejection of PO_4^{3-} remained high (>99%), in the pH range tested, which implies complete binding to the precipitate. NH_4^- rejection is rather limited (60-69%) and seems to be unaffected by pH. Increasing pH from 10 to 11 had insignificant effect on the process performance. Therefore, pH 10 was selected for the following experiments, to limit NaOH consumption (and cost) for pH adjustment.

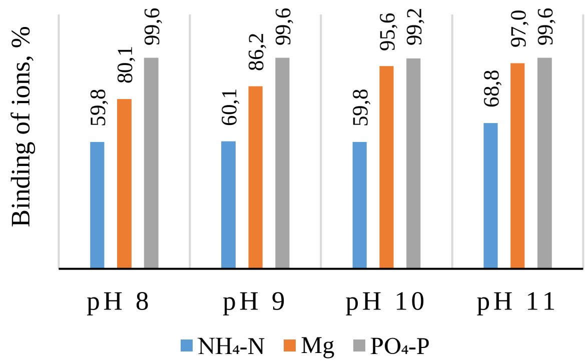


Figure 3. Effect of pH on ions binding in the filtrate during struvite precipitation. NH_4:Mg:PO_4 = 1:1:1

As depicted in Fig. 4, the concentration of the three ions of interest (NH_4^+, Mg^{2+}, PO_4^{3-}) in the supernatant remains almost constant after 30 minutes of precipitation and does not differ from the concentration of the filtered supernatant, indicating that no special separation /filtering is needed to recover struvite after precipitation. Nevertheless, the concentration of NH_4^- in the supernatant remains high. For this reason, the effect of the molar ratio of NH_4:Mg:PO_4 on the removal of nutrients was investigated. It is clear from Fig. 5 that the increase of Mg and PO_4 molar ratio to NH_4, has led to increased rejection of the three ions. Molar ratio 1:1.5:1.5 appears to be more effective, since the increase to 1:2:2 leads to a reduction of phosphates rejection, indicating that they are in excess. Consequently, no extra phosphates source is needed.

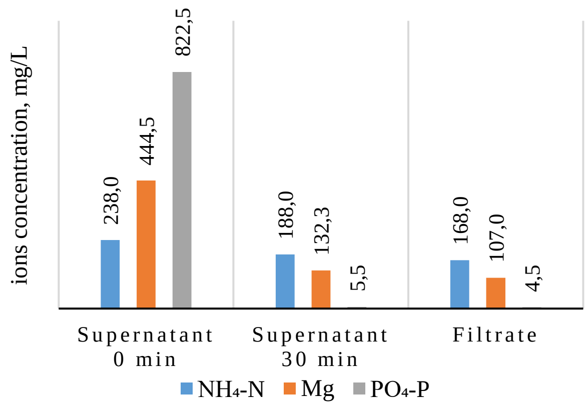


Figure 4. Effect of precipitate separation method on supernatant composition. NH_4:Mg:PO_4 = 1:1:1. pH=10.

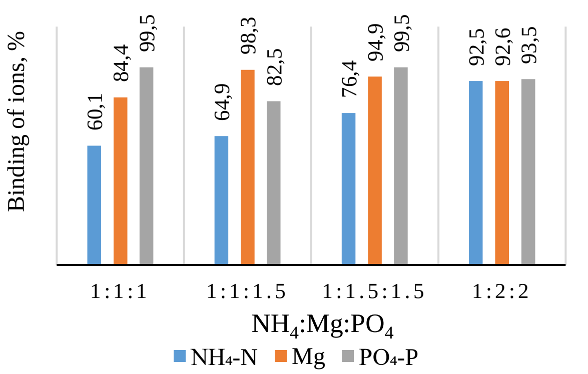


Figure 5. Effect of NH_4:Mg:PO_4 molar ratio on ions rejection from NF-concentrate. Supern. 30 min. pH=10.

Based on the results obtained from bench-scale tests, a pilot test was designed for recovery of struvite from 100 L of NF-concentrate (pilot test No 02PS). The conditions selected were pH 10, NH_4:Mg:PO_4 1:1.5:1.5 in the feed solution and precipitation for 30 min. Recovered precipitate was left at ambient temperature to remove moisture. With this procedure, ~11g precipitate (dry mass)/L of NF concentrate was produced. Through SEM, EDS and XRD studies, struvite was identified (Fig. 6).

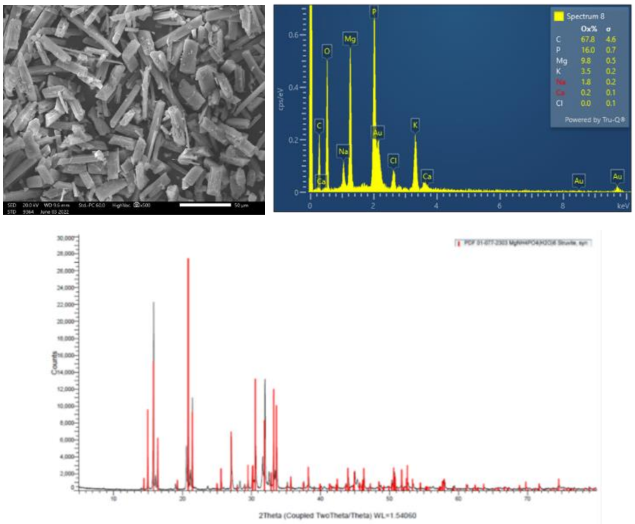


Figure 6. Characterization of precipitate: (a) SEM, (b) EDS, (c) XRD. Crystal form identified: struvite.

4. Assessment of the process products / effluents

Recovered product-streams appear to meet specifications for reuse/recycling (Table 2). Regarding the NF-permeate, the disposal limits especially to sensitive receiving water-bodies are not satisfied in respect of NH_4-N ($\leq$ 2 mg/L); however, it can be utilized for industrial use or restricted irrigation (GreekGovernment, 2011). Unrestricted irrigation can be also implemented after proper dilution. The produced struvite can be used for fertilization, while the supernatant after precipitation (~ 40% in volume of the initial effluent) needs further treatment before disposal (e.g. blending with effluent of municipal/local WWT plant).

Table 2. Characterization of the products/effluents of the proposed integrated process (optimal conditions considered).

Precipitate[1]	Supern. 30 min[1]	NF-permeate[3]
TN : 5.1 % wt TP : 11.8 % wt Mg : 10.7 % wt K : 3.2 % wt Ca : 1.5 % wt Zn : 7.6 mg/kg Fe : 14.4 mg/kg pH[2] : 9.9 (1:1000 v/v) eC[2] : 163 mS/cm (1:1000 v/v)	NH_4-N: 120 mg/L PO_4-P: 7,8 mg/L Mg^{2+}: 62 mg/L K^+: 2754 mg/L Na^+: 6168 mg/L Cl^-: 4128 mg/L NO_3^-: 200 mg/L SO_4^{2-}: 4023 mg/L Alkalinity: 5208 mg $CaCO_3$/L pH: 10 eC: 28.2 mS/cm	NH_4-N: 16.2 mg/L PO_4-P: 4.6 mg/L Mg^{2+}: 1.4 mg/L K^+: 18.0 mg/L Na^+: 135.3 mg/L Cl^-: 45.0 mg/L NO_3^-: 9.8 mg/L SO_4^{2-}: 46.9 mg/L Alkalinity: 258.4 mg $CaCO_3$/L pH: 5.7 eC: 736 μS/cm

[1] Bench scale test NH_4:Mg:PO_4 1:1.5:1.5, [2] Pilot scale test NH_4:Mg:PO_4 1:1.5:1.5, [3] NF-pilot test PS01

In conclusion, it is emphasized that important issues in the management of agro-industrial wastewater effluents are the variability of composition as well as the relatively high conductivity and alkalinity of the digestate, which make it necessary to combine appropriate processes (such as those presented in this work) to cope with operating problems and achieve a sustainable process.

5. Acknowledgements

This research was funded by the European Regional Development Fund of European Union and Greek National Funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation", under the call "Research–Create–Innovate", project ANATHREPSIS (project code: T1EDK-04825). Acknowledgement is also made of Mssrs A. Lekkas and M. Lekkas for their expert technical support.

References

Barampouti E. M., Mai S., Malamis D., Moustakas K. and Loizidou M. (2020), Exploring technological alternatives of nutrient recovery from digestate as a secondary resource, *Renewable and Sustainable Energy Reviews*, **134**.

DuPont™, 2021, FilmTec™ Reverse Osmosis Membranes Technical Manual, https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/RO-NF-FilmTec-Manual-45-D01504-en.pdf, [12 April 2023].

EBA, 2022, EBA Statistical Report 2022, Brussels, Belgium, [24 March 2023].

EU (2019), REGULATION (EU) 2019/1009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing No 2003/2003, *Official Journal of the European Union*, **62**.

GreekGovernment (2011), MD 145116/2011: Determination of measures, conditions and procedures for the reuse of treated wastewater and other provisions, *Official Government Gazette*, **OGI 354/B/8-3-2011,** p. 5229-5243, Athens.

Lorick D., Macura B., Ahlström M., Grimvall A. and Harder R. (2020), Effectiveness of struvite precipitation and ammonia stripping for recovery of phosphorus and nitrogen from anaerobic digestate: a systematic review, *Environmental Evidence*, **9**.

Saliu T. D. and Oladoja N. A. (2021), Nutrient recovery from wastewater and reuse in agriculture: a review, *Environmental Chemistry Letters*, **19,** 2299-2316.

Sheets J. P., Yang L., Ge X., Wang Z. and Li Y. (2015), Beyond land application: Emerging technologies for the treatment and reuse of anaerobically digested agricultural and food waste, *Waste Management*, **44,** 94-115.

Tsaridou C., Karanasiou A., Plakas K. V. and Karabelas A. J. (2023), Valorization of Anaerobic-Fermentation Liquid Digestates - Membrane-Based Process Development, *Membranes*, **13,** 297.

Wu H. and Vaneeckhaute C. (2022), Nutrient recovery from wastewater: A review on the integrated Physicochemical technologies of ammonia stripping, adsorption and struvite precipitation, *Chemical Engineering Journal*, **433**.