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Nutrient recovery from anaerobic digestate by different combination of pressure driven membranes

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ABSTRACT

Anaerobic digestate, the main by-product from anaerobic digestion process, will increase in the next years arriving at 177 Mt dry matter from the current level of 31 Mt by 2050. This huge amount cannot be directly applied on the soil as the EU "Directive Nitrate" limits this option at 170 kgN/ha for year. Considering the high content of nitrogen, phosphorous and potassium compounds in agricultural digestate, innovative and green methods have been investigated by the scientific community to exploit the digestate for bio-fertilizers production. This work tested different combinations of pressure driven membrane steps (micro, ultra, nanofiltrations and reverse osmosis) to maximize the nutrients and water recovery from agricultural digestate. The microfiltration (MF) step was ineffective in fully separating nutrients and removing colloids and suspended solids. As a result, it can be skipped to prevent nutrient loss in the reverse osmosis (RO) concentrate. Nanofiltration (NF) also underperformed due to rapid membrane fouling caused by its small mesh size. Conversely, ultrafiltration (UF) successfully removed fine and colloidal particles while allowing ammonium and potassium compounds to pass through. Consequently, the nutrients recovery in the concentrate of the RO and the total water recovered in the combination including the UF step was 40–50% w/w and 32.7% w/w, respectively. Moreover, the UF concentrate was also adopted as inoculum for biogas production tests, whose performances were compared to the conventional inoculum represented by the liquid fraction of the agricultural digestate. The performances were similar, but the kinetics were higher with the UF concentrate, as an effect of the higher microorganisms and nutrient concentrations.

1. Introduction

The European countries are leading in the Anaerobic Digestion (AD) technology for biogas production from organic wastes. Currently they produce about 20 billion cubic meters (bcm) of biogas every year, but the most recent forecasts estimate this amount will increase to 100-160 bcm by 2050 (EBA, 2022) as effect of the new EU energetic policies. In particular the "REPowerEU" plan promotes biomethane production to increase the EU energetic resilience and independence from third Countries, preventing the geo-political shocks (European Commission, 2022). Agricultural residues and livestock wastes are the most abundant feedstocks treated by AD which converts most of the carbon content into valuable biogas. Besides carbon, agricultural wastes contain some nutrients, in particular nitrogen, phosphorus and potassium, which are essentially preserved during the AD process and can be found in the main by-products of the AD process, the digestate. The digestate is essentially composed by: i) poorly biodegradable or stable organic fraction, which can serve as a precursor of humus material, ii) microorganisms and iii) the mineral fractions from N, P and K compounds which are interesting for the synthesis of mineral fertilizers (European Biogas Association, 2024).

According to the Fertilizers Europe report (Fertilizers Europe, 2024), the EU nutrients demand in 2022 was 17.4, 6.7 and 12.3 million tonnes of N, P and K based fertilizers, respectively. By 2050 the annual digestate production will arrive to 177 Mt dry matter from the current level of 31 Mt. Considering the average content of these nutrients in agricultural digestate, it is possible to estimate a N, P and K nutrients amounts of 9.7, 1.7 and 0.8 Mt, respectively (European Biogas Association, 2024). It means that digestate, if opportunely valorized, can potentially cover a consistent deal of the fertilizers demand of the EU countries. The main usage of digestate is the direct application on soil as biofertilizer: this practice is applied on the 73% of the total European digestate, while only the 15% is upgraded before agricultural applications (European Biogas Association, 2024).

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At first glance, this can be regarded as a positive consequence due to the higher biobased nutrients available. However, the direct application of the digestate on the soil is associated to negative effects too: the nutrients leachate in the underground waters, the emission of greenhouses gases, the possible contamination of the soil with eventual heavy metals or other contaminants and the diffusion of pathogens. Moreover, the areas with the highest concentration of farms and livestock in the EU are often designated as "Nitrate Vulnerable Zones", or NVZs, by the Nitrates Directive. According to this normative, the quantity of nitrogen which can be applied on the in NVZs must not exceed 170 kgN/ha annually (European Council, 1991). This means that every year, an increasing quantity of digestate must be managed and, due to its instability and residual biogas production, cannot be stored or transported for long periods of time. Anyway, recently the European Commission is discussing the possibility of not considering three products deriving from digestate in the account of the nitrogen limit for the NVZs: i) ammonium sulphate from ammonium stripping, ii) mineral nitrogen and potassium from concentrate of the RO and iii) struvite by precipitation (Phosphorus Platform, 2024). The first option, i.e. ammonium stripping, is the most conventional method to recover nitrogen from digestate. Specifically, the digestate is pretreated with strong bases to volatilize NH_3 under negative pressure and high temperature. Then, ammonia is recovered with a sulphuric acid scrubber to obtain ammonium sulphate, a commercial fertilizer (Battista et al., 2021). This technology is characterized by high energy and chemical demand. Alternatively, the digestate can be treated using pressure driven filtration processes composed of multiple solid/liquid separation steps which gradually removes all the solid particles, leaving a nutrient-rich liquid fraction which will be concentrated with a Reverse Osmosis (RO) step at the end of the process (Gienau et al., 2018a). The final products will be: (i) concentrated, stable, and nutrient-rich liquid which, although does not meet the legal requirements to be considered a proper fertilizer, can reduce classic fertilizers applications; (ii) nitrogen-depleted solid part, rich in phosphorus and recalcitrant fibers that can be used as soil conditioner; (iii) pure water from the RO permeate and iv) a RO concentrate rich in ammonium and potassium, known to be the precursors for fertilizers production. This process, compared to the classic ammonia stripping, can be scaled to single biogas plant. Consequently, the whole digestate refining process can be done *in loco*, without further transportation costs and handling fees which the single farmer or small company must address in order to treat the digestate through ammonia stripping.

To date, few articles have been published on sequential filtration steps of the digestate. Gienau et al. (2018b) performed the nutrient recovery through an ultrafiltration (UF) step followed by a RO step of agricultural digestate a pilot scale from a 2.5 MW_e biogas plant. The process was able to recover 70 % w/w of Total Solids (TS) and 80 % w/w of phosphorus during the first solid/liquid separation test, with a concentration of 5.5 g kg^{-1} of P_2O_5. The liquid part was concentrated through UF and RO, achieving 38% w/w of water recovery and a final retentate concentration of 4 and 10 g kg^{-1} of NH_4-N and K_2O respectively. Van Puffelen et al. (2022) investigated a similar process at full-scale adopting an anaerobic digestate from the AD of animal residues. This process used two steps of centrifugation with $MgCl_2$ and polymeric flocculant addition, followed by a step of microfiltration (MF) and two RO steps. The two centrifugation steps recovered most of the phosphorus in the solid fraction (63 %w/w), while the RO concentrate achieved 8.0 and 7.9 g kg^{-1} of NH_4-N and K_2O respectively.

The aim of this work was the selection of the best combination of different mechanical separations and pressure-driven membrane filtrations able to maximize the nutrients and water recovery from all the process and from the concentrate of the RO at laboratory scale. Moreover, the possibility to recirculate the UF concentrate, rich in microorganisms, into the AD process as inoculum for biogas production was also considered. The results from the laboratory scale will be adopted for the design of a demonstrative plant able to treat about 20 tons/d of agricultural digestate.

2. Materials and methods

Nutrients and water recovery from an agricultural digestate (AGRD) were performed by a combination of mechanical separation and pressure-driven membranes at laboratory scale. By this way, it was possible to identify the best assembly to be scaled-up at demonstrative plant (TRL 7) for the treating of about 20 tons/d of AGRD.

2.1. *Characterization of the agricultural digestates*

The AGRD adopted to test the nutrients and water recovery was obtained from a full-scale AD plant in Isola della Scala (Italy), having a capacity of 1000 kW and treating a mixing of cow manure and lignocellulosic residues from the energy crops at mesophilic condition (35 °C). The main characterization of AGRD was reported in Table 1.

2.2. *Tests on different combinations of mechanical and pressure drive membranes steps*

Three different combinations of sequential filtration steps were tested in order to evaluate the best one in term of nutrients and water recovery from an initial mass of AGRD of 2.00 kg. The mechanical separation of AGRD was provided by a combination of: i) a preliminary solid/liquid separation (PSLS) with the consequent obtaining of a solid (PSLS-SF) and a liquid fraction (PSLS-LF) and ii) a centrifugation step (CENTR) of the resulting LF from the PSLS. Specifically, the PSLS was performed through the adoption of 3 different filters having the mesh sizes of 2 mm, 500 µm, and 100 µm. Solid fraction was recollected and analyzed. Liquid fraction was centrifugated at 4000 rcf for 20 min, obtaining a sedimented fraction (CENTR-SED) and a supernatant (CENTR-SUR). By this way, the biggest solid particles, the fibers and the colloidal particles and the main phosphorus compounds in order to avoid the fouling of the next pressure driven membranes. The centrifuge used for the PSLS was an Eppendorf® 5810R (Germany).

The CENTR-SUR was further treated by three different combinations of pressure driven membranes with the aim to recover the remaining organic nitrogen and phosphorous compounds and the microorganisms. For the microfiltration (MF) step, DuraPES 450 (3M Membranes), PES membrane with 0.45 µm pore size was used; the filtration area was 35 cm^2 with an operative Trans-Membrane Pressure (TMP) of 2 bar. The ultrafiltration (UF) step used a 300 kDa PES membrane, LX MAX (Synder Filtration), with 35 cm^2 of filtration area and operative TMP of 2 bar. The nanofiltration (NF) step used a FilmTec™ NF270 (Dupont), polypiperazine-amide thin film composite (PA-TFC) membrane, with 17 cm^2 of filtration area and operative TMP of 4.5 bar.

Finally, the permeate from the previous steps was sent to the RO which operated at 30 bar and at a filtration area of 17 cm^2. This step used Polyamide TRISEP® ACM2 High Rejection membrane, supplied by MANN + HUMMEL. RO was able to recover the mineral form of nitrogen and phosphorous compounds in the concentrate fraction (or retentate, RO- RET) and water from the permeate (RO- PER).

MF and UF were performed in crossflow-mode with Vibro-Lab 35P

Table 1
Physical and chemical main characterization of raw AGRD.

Raw Agricultural Digestate	
Total Solids (TS) (% w/w)	7.76 ± 0.16
Volatile Solids (VS) (% w/w)	5.45 ± 0.24
VS/TS (%)	70.23 ± 0.05
pH	7.93 ± 0.02
Electrical Conductibility (EC) (mS/cm)	15.31 ± 0.14
Total Kjeldahl Nitrogen (gN/L)	4.08 ± 0.30
NH_4^+-N (gN/L)	3.52 ± 0.19
PO_4^{3-}-P (gP/L)	0.21 ± 0.02
Total Phosphorus (gP/L)	1.05 ± 0.09
Total Potassium (gK/L)	4.01 ± 0.23

filtration system by SANI membranes A/S (Denmark). NF and RO were conducted in dead-end mode using Sterlitech (United States) HP4750 High Pressure Stirred Cell, a technical-grade nitrogen cylinder was used to pressurize the filtration cell. All filtration trials were made at room temperature (~24 °C).

Specifically, the three filtration lines tested were the following:

a) Line #1: PSLS + CENTR + MF + UF + RO;
b) Line #2: PSLS + CENTR + UF + RO;
c) Line #3: PSLS + CENTR + NF + RO.

No more filtration lines were considered as one of main goals of the project was the achieving of a recovery rate of 40–50% for ammonium in the retentate phase of the RO process. Considering the results from the three filtration lines, specifically from Line #1 (MF + UF), introducing multiple separation steps would hinder the achievement of this goal. Such steps would lead to the generation of an additional retentate stream, resulting in the dispersion of nutrients that would no longer be available in the RO retentate.

When the permeability decreased under 10% of the steady state value, the membranes were cleaned following the factory guidelines of the filtration system, which involved a caustic wash at pH 11 for 30 min, followed by an acid wash at pH 2 for 15 min, both steps at 55 °C temperature.

2.3. Parameters for the evaluation of the three filtration lines

The following parameters were used for the selection of the best filtration line:

$$a)\ \text{Nutrient recovery}\ (\%\ w/w) = 100\,\frac{\textit{Mass of each nutrient recovered from the concentrate streams, from PSLS} - \textit{SF and CENTR} - \textit{SED}}{\textit{initial mass of each nutrient in the AGRD}} \qquad /\text{Equation 1}/$$

$$b)\ \text{Nutrient recovery from RO} - \text{RET}\ (\%\ w/w) = 100\,\frac{\textit{Mass of each nutrient recovered from RO} - \textit{RET}}{\textit{initial mass of each nutrient in the AGRD}} \qquad /\text{Equation 2}/$$

$$c)\ \text{Water recovery from RO} - \text{PER}\ (\%\ w/w) = 100\,\frac{\textit{Mass of water recovered from RO} - \textit{PER}}{\textit{initial mass of AGRD}} \qquad /\text{Equation 3}/$$

$$d)\ \text{Volume Reduction Factor, VRF}\ (-) = \frac{PER, i-1}{RET, i} \qquad /\text{Equation 4}/$$

where $PER_{,i-1}$ represents the permeate volume coming from the previous filtration or the supernatant volume from the centrifuge step in the case of MF in Line #1 and UF in Line #2, and $RET_{,i}$ is the volume of the retentate flux of each pressure driven membranes step. (Macedonio and Drioli, 2017)

e) Crossflow Velocity, CFV (m/s), is the linear velocity of the flow in the cross section of the feed channel.

$$\text{CFV} = \frac{\textit{Volumetric inlet flux}\left(\frac{m^3}{s}\right)}{\textit{cross section surface area of the feed channel}\ (m^2)} \qquad /\text{Equation 5}/$$

Finally, the best filtration line emerged from the evaluation of the previous parameters (Equations (1)–(3)) were also tested in terms of permeability to verify the stability of the permeate flux over the time. The permeability of the permeate was compared with the deionized water one. Specifically, the permeability can be determined though Equation (4):

$$\text{Permeability} = \frac{\textit{Flux of the permeate or water}\left(\frac{L}{h}\right)}{\textit{filtration surface}\ (m^2) * \textit{pressure}\ (bar)} \qquad /\text{Equation 6}/$$

2.4. Comparison of the Specific Methane Activity (SMA) of AGRD and the UF retentate

The UF retentate from Line #2, which emerged as the best for the nutrients recovery, was tested as possible inoculum for biogas and methane production. Coming from the PSLS and centrifugation steps, the UF membrane should favor microorganisms separation in the retentate stream. Consequently, the activity of these microorganisms was verified through Specific Methane Activity (SMA) tests performed both with acetic acid and cellulose, in order to simulate the kinetics degradation of simplest and most complex compounds, respectively. The SMA tests were also performed of the PSLS-LF, usually used as inoculum, to observe eventual improvements of the kinetic performance with the UF concentrate adoption. The SMA tests were all performed in triplicate following the methodology described in van Loosdrecht et al. (2016).

2.5. Analytical methods

Total (TS) and volatile solids (VS), the Chemical Oxygen Demand (COD), the Total Kjeldahl Nitrogen (TKN) ammonium content and the Total Phosphorous (TP) compounds of the AGRD and the derived streams from the different filtration steps were analyzed according to APHA Standards Methods (APHA, 1998). pH and electrical conductibility (EC) were measured using CO 3000H portable analyzer by VWR. While potassium (TK) content was measured by a spectrophotometric method supplied by Hach Lange.

3. Results and discussion

3.1. TS and water recovery from the three filtration lines

The removal of solids, fibrous and colloidal materials represented a fundamental operation to avoid membrane fouling in the MF, UF, NF and RO steps, characterized by mesh sizes in the range of 0.1–10 μm, 0.01–0.1 μm, 0.001–0.01 μm and 0.0001 μm, respectively (Van der Bruggen, 2018). The TS parameter was used in order to evaluate the removal of these compounds and their distribution in the different output streams of the three filtration lines.

The TS removal was almost complete in all the filtration lines: the residual TS amount in the RO permeate was 0.26, 0.34 and 0.06% w/w for the filtration line #1, #2 and #3, respectively. Fig. 1 shows the TS distribution on the different output streams of the three filtration lines.

It is interesting to note that the PSLS and the CENTR stages were able to remove the 53 and 24% w/w, respectively, of the TS amount initially present in the AGRD. Specifically, PSLS step allowed the retention of the

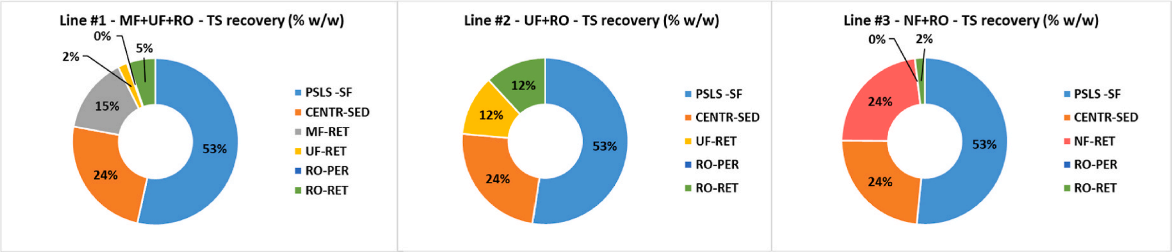

Fig. 1. The distribution of the Total Solids along the three filtration lines.

largest solid particles, such as lignocellulosic fibers from AGRD, composed by a mixture of the energy crops residues and bovine manure, which also includes fibers derived from the animal feeding. The PSLS separation can remove the phosphorus-based compounds too, as commented in the next paragraph of the manuscript. The PSLS-LF was then treated by the CENTR step, which was able to retain in the CENTR-SED the colloidal and fine particles (Van Puffelen et al., 2022). Colloidal materials are compressible, have a density close to the water and are viscous. These features could make them a problem for the MF and UF membranes as they can cause fouling (Bowen and Jenner, 1995). Consequently, their preventive removal can help the next pressure driven filtration units, mitigating membrane fouling and assuring a constant permeability over time. It is important to emphasize that a CENTR step cannot assure the full removal of the colloids as their dimensions range is very large: from 0.1 to 10 μm (Bowen and Jenner, 1995). It means that their retention requires a further MF or UF step to avoid the fouling of the RO membrane.

The distribution of the remaining TS depended on the configuration of the next steps of the filtration lines. Line #1 assured the recovery of about 15% w/w of the TS in the MF retentate, while the next steps of UF and RO completed the TS removal with a recovery yield of 2 and 5% w/w, respectively. Specifically, the MF step led the removal of the suspended solids and microorganisms (Popova et al., 2024), and of the organic nitrogen, contained in the microorganism in form of proteins, allowing the passage in the permeate flux of the inert compounds, such as the ammonium and potassium salts, which can be recovered and concentrated through the final RO stage (Fig. 1) (Bolzonella et al., 2018). Considering the performance of Filtration Line #1, the UF step can be neglected as it recovered only the 2% w/w of the TS.

Instead, Line #2 excluded the MF step and involved only the UF. The TS recovered in the UF retentate were 12% w/w, similar to the 15% w/w achieved by the MF in Line #1. The following RO step led to a TS retention of 12% w/w, more than double what was obtained by RO in Line #1. It demonstrated that Line #2 allowed a better fractioning of the TS based on their nature: suspended solids and microorganisms were blocked by the UF membranes, while the ammonium and potassium salts were mainly recovered in the RO step. Instead, the presence of two pressure driven membranes (MF and UF) in Line #1 reduced the quantity of salts arriving to the RO step, reducing the overall process yield as RO concentrate can be considered the high added value products from AGRD (Phosphorus Platform, 2024). Finally, Line #3 adopted NF after the PSLS and CENTR steps. However, CENTR-SUR, which had a 3% w/w TS content, caused a rapid fouling of the NF membrane, mainly due to accumulation of colloidal solids and small particulate material on the membrane surface (Mohammad et al., 2015). This led to a permeating stream which was only 12% w/w of the inlet stream. On the contrary, in the previous filtration lines #1 and #2, the permeate represented the 70–75% w/w of the inlet stream both for the MF and UF processes. Consequently, all the residual TS content from the CENTR-SUR was in the NF retentate, meaning that the RO led to the recovery of only the 2% w/w of TS in the AGRD.

Another important issue in the digestate treating is represented by water, which is another element to be recovered, especially in arid and semi-arid regions. The RO step, while concentrating the nutrients in RO retentate and reducing the transport costs of these compounds, allowed the recovery of water in the permeate stream. The three filtration lines were different in terms of water recovery yields from the AGRD: the best one was the Line #2 with about the 33% w/w, then Line #1 achieved a 25% w/w, while the worst yield belonged to Line #3 with a recovery water amount lower than 5% w/w. These results confirmed that: i) higher are the membrane units in a filtration line, lower is the water (and the nutrients amount, see next paragraph) which arrived at the RO step. It was a consequence of the increasing number of streams generated from each membrane. Moreover, ii) NF membrane is rapidly clogging without a previous step able to act a prior removal of colloids, suspended solids and lower particles, such as MF or UF.

3.2. Nitrogen, potassium recovery and EC trend in the three filtration lines

The distribution of the TKN, ammonium and potassium compounds in the output streams of the three filtration lines was reported in Fig. 2a–c, respectively.

The distributions of the TKN, ammonium and potassium compounds were very similar along all the filtration lines. It can be explained by considering that ammonium represented more than 85% w/w of TKN in the AGRD (Table 1), while potassium compounds followed the same distribution of ammonium being both little molecules.

As commented above, Line #2 was the best one for the recovery of these compounds in the RO retentate (Table 2). Specifically, Line #2 was the only able to reach the project target of minimal ammonium recovered in the range of 40–50% w/w in the retentate phase of the RO.

The recovery yields for TKN, ammonium and potassium from the RO concentrate were 41.0, 46.5 and 44% w/w, respectively. The UF-PER had an ammonium-TKN ratio in the range of 97–99% (Table 4), which demonstrated that organic nitrogen, characterized by a lower solubility in the aqueous phase, was separated already in the PSLS and CENTR steps and in a little fraction in the UF-RET. Finally, the ammonium-TKN ratio remained constant in the RO-RET, meaning that the final step allowed almost exclusively the water molecules passage (Carter et al., 2015). Potassium recovery had no significative difference compared to ammonium one as they are both small molecular weight compounds: consequently, it was recovered mainly in the RO-RET. The ammonium and potassium concentrations in the RO-RET were similar too: 11.20 and 12.50 g/L.

The filtration Line #1 led to lower performances with TKN, ammonium and potassium recovery yields in the range of 23.0–26.5% w/w for the three parameters. Even if the filtration mechanism for these compounds was similar to the one described for Line #2, the addition of a filtration membrane, the MF was negative as it created a further output stream, the MF-RET, causing the loss of about 15–20% w/w of the recovery performances in the RO concentrate. Being composed mainly by water, MF concentrate also retained a quote of ammonium and potassium compounds, characterized by high solubility in aqueous medium (Fechter et al., 2023).

Finally, the worst recovery performances belonged to Line #3. As already mentioned, it can be explained by the low permeation amount

Fig. 2. Distribution of Total Kjeldahl Nitrogen (Fig. 2a), ammonium (Fig. 2b) and Potassium as K_2O (Fig. 2c).

Table 2
Recovery yields of nutrients and water from the filtration lines.

	LINE #1 - MF + UF + RO		LINE #2 - UF + RO		LINE #3 - NF + RO	
	Total Recovery (%)	Recovery from RO-RET (%)	Total Recovery (%)	Recovery from RO-RET (%)	Total Recovery (%)	Recovery from RO-RET (%)
Water (from RO permeate)	25.09 ± 1.25		32.75 ± 1.86		4.75 ± 0.14	
TKN	92.65 ± 3.69	26.29 ± 1.27	91.18 ± 3.29	41.01 ± 1.87	94.15 ± 2.25	5.63 ± 0.21
$N\text{-}NH_4^+$	96.55 ± 3.21	26.36 ± 0.25	97.42 ± 1.30	46.50 ± 1.14	99.97 ± 0.01	6.41 ± 0.75
TP	92.78 ± 4.85	7.77 ± 0.04	94.54 ± 3.58	14.98 ± 0.70	94.49 ± 3.01	10.00 ± 0.04
K as K_2O	93.99 ± 3.55	22.95 ± 1.31	99.98 ± 0.00	44.32 ± 0.42	99.21 ± 0.02	4.59 ± 0.33

Table 3
Characterization of the different streams in Line #1. "n.d." stays for "not determined".

Line #1	TS (% w/w)	COD (g/kg)	TKN (g/kg)	Ammonium (g/kg)	TP (g/kg)	K_2O (g/kg)	EC (mS/cm)
AGRD	7.76%	718.39	4.08	3.52	1.05	4.10	15.30
PSLS -LF	5.01%	621.34	4.19	3.78	0.38	4.00	15.28
PSLS -SF	11.80%	919.28	3.44	2.92	2.45	4.20	n.d.
CENTR-SUR	2.92%	512.33	4.05	3.97	0.35	4.10	15.04
CENTR-SED	14.43%	1127.12	3.82	2.67	0.50	3.50	n.d.
MF-PER	1.30%	422.90	4.29	3.99	0.33	4.40	14.99
MF-RET	4.97%	612.56	3.81	3.78	0.30	3.40	n.d.
UF-PER	1.16%	337.11	3.87	3.79	0.32	3.60	14.61
UF-RET	1.53%	638.45	3.60	4.80	0.29	5.50	n.d.
RO-PER	0.07%	6.27	0.87	0.57	0.08	0.65	3.10
RO-RET	5.60%	1507.07	17.10	16.80	1.30	15.00	41.83

generated from the NF step due to the rapid membrane fouling, demonstrating that the direct application of this filtration was not convenient. Anyway, some authors (Ma et al., 2024; Mohammad et al., 2015) emphasized that NF can be very useful for the fractioning of divalent and monovalent ions. Specifically, The NF and RO membranes consist both of micropores. NF membranes can remove less than 50% of

Table 4
Characterization of the different streams in Line #2. “n.d.” stays for “not determined”.

Line #2	TS (% w/w)	COD (g/kg)	TKN (g/kg)	Ammonium (g/kg)	TP (g/kg)	K_2O (g/kg)	EC (mS/cm)
AGRD	7.76%	718.39	4.08	3.52	1.05	4.10	15.36
PSLS -LF	5.01%	621.34	4.19	3.78	0.38	4.00	15.21
PSLS -SF	11.80%	919.28	3.44	2.92	2.45	4.20	n.d.
CENTR-SUR	2.92%	512.33	4.05	3.97	0.35	4.10	14.98
CENTR-SED	14.43%	1127.12	3.82	2.67	0.50	3.50	n.d.
UF-PER	1.40%	337.11	3.87	3.79	0.38	3.80	14.44
UF-RET	6.73%	1175.32	3.60	4.80	0.20	5.50	n.d.
RO-PER	0.07%	5.27	0.50	0.27	0.07	0.01	3.23
RO-RET	5.60%	1053.07	11.70	11.20	1.10	12.50	40.10

Table 5
Characterization of the different streams in Line #3. “n.d.” stays for “not determined”.

Line #3	TS (% w/w)	COD (g/kg)	TKN (g/kg)	Ammonium (g/kg)	TP (g/kg)	K_2O (g/kg)	EC (mS/cm)
AGRD	7.76%	718.39	4.08	3.52	1.05	4.10	15.32
PSLS -LF	5.01%	621.34	4.19	3.78	0.38	4.00	15.18
PSLS -SF	11.80%	919.28	3.44	2.92	2.45	4.20	n.d.
CENTR-SUR	2.92%	512.33	4.05	3.97	0.35	4.10	14.91
CENTR-SED	14.43%	1127.12	3.82	2.67	0.50	3.50	n.d.
NF-PER	2.10%	201.00	3.90	3.85	0.20	3.40	14.27
NF-RET	3.01%	554.21	4.05	4.00	0.35	4.20	n.d.
RO-PER	0.09%	25.00	0.70	0.55	0.16	0.65	3.15
RO-RET	7.45%	665.00	13.12	12.90	0.60	10.75	41.01

the monovalent ions and more than 90% of divalent ions. Nevertheless, RO membranes can remove more than 98% of monovalent ions (Ibrahim et al., 2020; Shenvi et al., 2015). Clearly, the failure of Line #3 did not allow to appreciate this difference between mono and divalent ions recovery in the present research work.

Finally, EC values were also measured for the liquid outputs of the three filtration lines (Tables 3–5). EC is a parameter used as an indirect measure of salt concentration. Since salts are soluble compounds, they can pass through the mechanical separation steps as well as the MF and UF membranes. Consequently, the permeates from these membranes exhibited similar EC values to the AGRD. The RO step was the only one capable of retaining salts, showing significantly different EC levels between the permeate and retentate across the three filtration lines.

3.3. Phosphorous compounds recovery from the three filtration lines

With nitrogen and potassium, phosphorus is the other essential macronutrient for the synthesis of fertilizers. But, more than nitrogen and potassium, phosphorous is also considered a strategic element as it derives from phosphate rocks, which are located in few countries, i.e. Marocco and China (Azam et al., 2019; Daneshgar et al., 2018). Then, its recovery is important for the EU energy and food independence and the avoiding of geo-political tensions. The distribution of this element along the outputs from the three filtration lines is shown in Fig. 3.

In contrast to the nitrogen and potassium compounds, phosphorous was already recovered at the first mechanical separation step (PSLS). Specifically, over the 70% w/w of P compounds was retained in the SF generated from the PSLS, consistently with previous research (Mazzini et al., 2020; Van Puffelen et al., 2022). It is important to emphasize that phosphorus separation in the SF can be further improved by the adoption of coagulants and flocculants, which help to bring non-settleable particles together into larger, heavier clumps of solid material that can be easily removed (Nav et al., 2024; Wang et al., 2013). Similarly to nitrogen, total phosphorous (TP) compounds involve organic phosphorous and inorganic one, such as phosphate compounds (PO_4^{3-}). Organic phosphorous has a similar separation trend of organic matter and TS, going in the SF of digestate, while phosphate can be found more in the LF and can be separated through the next filtration steps. With reference to the present work, the pressure driven membranes (MF, UF and NF) assured the recovery of the phosphate. Phosphate content in the AGRD was about 0.20 g kg^{-1}, that means less than 20% w/w of the TP compounds. MF (Line #1) and UF (Lines #1 and #2) were not efficient in their recovery being the dimension of the membranes too large to retain phosphate, which was concentrated in the RO-RET. While NF (Line #3) and RO (Line #2) led to a 15–17% w/w of recovery, assuring almost the complete removal of the TP (Table 2) and, mainly, its separation from the ammonium and potassium compounds. As commented for the ammonium recovery, NF and RO operations were the best for the recovery of ions, with NF demonstrating good removal yields for plus-valent ions, i.e. PO_4^{3-}, and RO both for plus-valent and monovalent ones (Bowen and Jenner, 1995).

Tables 3–5 reported the detailed characteristics of the different streams for Line #1, #2 and 3, respectively.

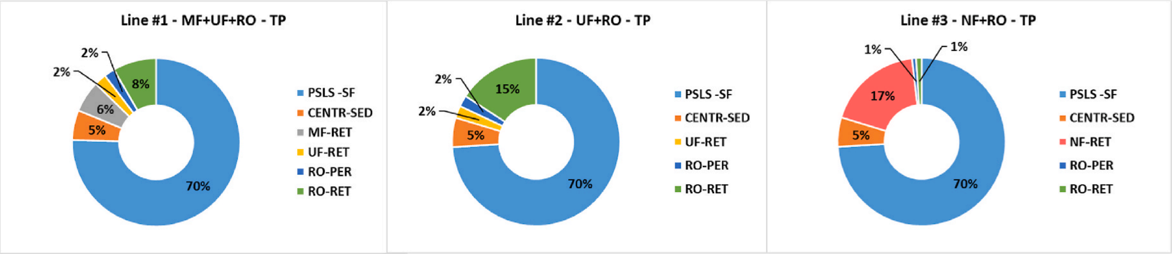

Fig. 3. The distribution of the Phosphorous compounds along the three filtration lines.

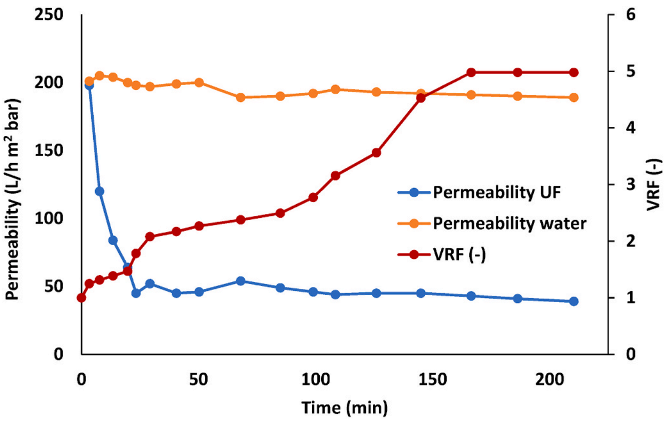

Fig. 4. The trend of permeability and VFR over time for the UF step (Line #2).

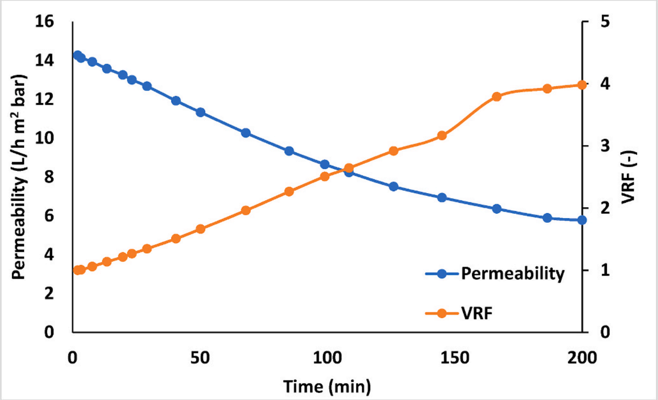

Fig. 5. Permeability and VRF evolution over time for RO step in Line #2.

3.4. Evaluation of the VRF and of permeability for the three filtration lines (Line 2)

VRF quantifies how much the inlet volume has been reduced as a result of the filtration process, often due to the removal of liquid while retaining solids, concentrates, or other components. In pressure driven membranes technologies n filtration processes, the VRF is an important parameter for measuring the degree of concentration achieved. A higher VRF indicates greater concentration of the retained components.

Line #1 had two sequential pressure driven membranes, the MF and the UF followed by RO. They showed a VRF of 3.01, 5.00 and 5.05, respectively, demonstrating the good working of all the separation steps in the reduction of the inlet feeding volumes and in the concentration of the nutrients. Line #2, which used only an UF step followed by RO, achieved a VRF of 5.03 and 3.92 for UF and RO, respectively (Figs. 4 and 5). This outcome is noteworthy, as it not only confirms the UF step effectiveness, but also eliminates the need for the preceding MF step used in Line #1. The UF step provided a good concentration degree, yielding a dual benefit. First, it reduces energy consumption by optimizing the operation of pressure-driven membranes. Second, it prevents the creation of an additional retentate flux (MF-RET), which would otherwise reduce the volume of water recoverable in the RO-PER and increase management costs in a full-scale plant. Finally, Line #3 was characterized by NF and RO. The VFR for NF was very low, 1.12, demonstrating the complete inefficacy of this membrane without a previous filtration step characterized by larger mesh sizes. Finally, the VRF for the RO step was 3.71. Even if it can be considered a good value, it was calculated considering the very low amount of the UF-PER. So, this value demonstrates that the RO was able to operate well and confirmed the inadequacy of the previous NF step.

The permeability parameter over time was plotted for UF step in Line #2 (Fig. 4), which emerged as the best one for water and nutrients recovery. This parameter can be defined as the flux of permeate, passing through a membrane under the action of a force gradient, such as the application of a pressure gradient. The permeability of the UF membrane was tested both using deionized water and CENTR-LP.

The membrane permeability with distilled water was around 200 L m^{-2} h^{-1} bar^{-1}, very close to the value reported in the technical sheet of the UF membrane. It demonstrated the good status of the UF membrane at the beginning of the test. The water permeability remained stable for the entire test, which lasted over 3 h, which demonstrated the good working of the UF process. Instead, the pumping of the CENTR-SUR to the UF membrane (Line #2) led to quick dropping of the membrane permeability which reached a steady state value of about 50 L m^{-2} h^{-1} bar^{-1} after 30 min since the beginning of the test. The permeability reduction was the consequence of the cake formation on the membrane which caused a partial UF membrane fouling. Considering the structure of the lab-scale UF apparatus, it was not possible to manage the membrane in the attempt to improve the UF permeability, by an increasing of the filtration area, which was 35 cm^2, as reported in the Materials and Methods chapter. The permeability decreased under the 10% of the steady state value after 3 h since the starting of the UF operation. The washing of the UF allowed to come back at around 50 L m^{-2} h^{-1} bar^{-1}. It is interesting to observe that permeability and VRF has opposite trends: the latter increased over time as consequence of the increasing of the UF-RET amount, while permeability decreased until the steady state value as consequence of the cake formation on the membrane. Regarding the RO step in Line #2, the initial value of permeability was 14.26 L m^{-2} h^{-1} bar^{-1}. Then it decreased as the system operated in dead-end mode, as reported above and in Fig. 5.

With reference to the permeability of Line #1, MF had a similar trend of the one observed in Line #2 (Fig. 4): it started at 210 L/m^2h bar decreasing until a steady state value of 65–70 L/m^2h bar, slightly higher than UF permeability. However, the configuration in Line #1 was worst in term of nutrient recovery in the RO retentate, as previously commented, as it was coupled to UF which led to the emission of two RET fluxes. It is important to emphasize that the only MF step would not be able to avoid the fouling of following RO. So, Line #1 was not considered convenient for the scale-up of the process. Finally, regarding the Line #3, having the only NF it was observed that after 5 min from the beginning of the filtration, membrane permeability dropped to very low values 1.41 L/m^2h bar, slowly decreasing until 60 min, when the filtration was stopped with a permeability of 1.18 L/m^2h bar. It was a further confirmation of the fouling of NF membrane.

CFV represents another key parameter in filtration processes as it provides information about the fluid dynamics on the cross section area and the choice of the pump in the scale-up of the process. The best filtration line in term of nutrients recovery (Line #2), characterized by the UF membrane, had a CFV of about 2.4 m/s in steady state condition, which is close to the conventional CFV values for pressure driven membranes.

3.5. Comparison of the SMA of AGRD and the UF concentrate

SMA tests were carried out to evaluate the activity of two different potential inoculum: i) the PSLS-LF, conventionally used at this scope and ii) the UF-RET. The test used as substrate both acetic acids, to simulate the degradation of the most biodegradable compounds, and cellulose to reproduce the degradation and conversion into biogas of the most complex organic matter.

Fig. 5 reported the cumulative specific biogas production and the daily specific biogas production rate for all the SMA tests.

PSLS-LP and UF-RET had similar specific biogas production both with acetic acid (Fig. 6a) and cellulose (Fig. 6b). Specifically, the UF-RET and PSLS-LF achieved a biogas production of 630 and 580 mL/gVS, respectively, with acetic acid as substrate. While, with cellulose

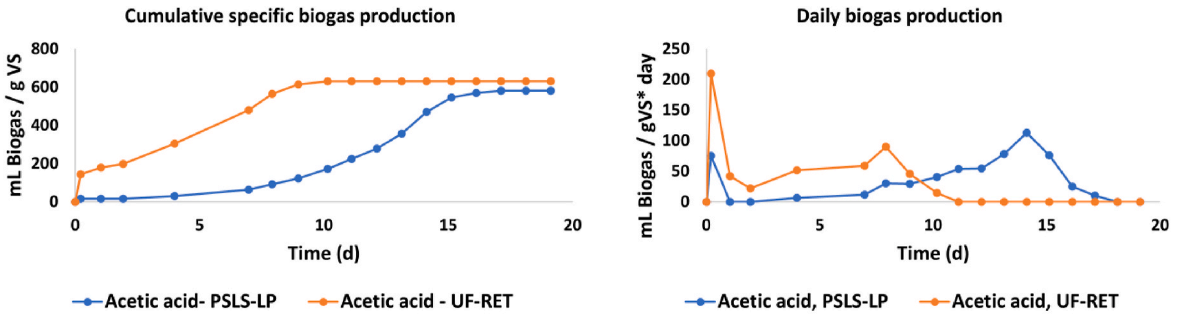

Fig. 6.a _ SMA tests with Acetic acid

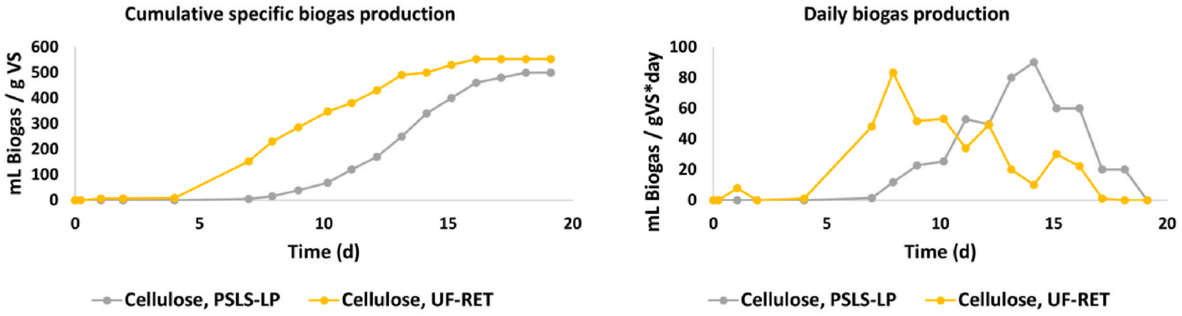

Fig. 6.b _ SMA tests with Cellulose

Fig. 6. SMA test. Fig. 6a SMA tests with acetic acid as inoculum and Fig. 6b SMA tests with cellulose as inoculum.

they were slightly lower at 553 and 550 mL/gVS for UF-RET and PSLS-LF, respectively. These outputs were converted into methane considering its content in the biogas, which was about the 60% v/v for all the tests and divided for the specific methane production for the acetic acid and cellulose of 350 and 380 mL_{CH4}/gVS, respectively (van Loosdrecht et al., 2016). By this way, the SMA values for UF-RET and PSLS-LF were of 0.28 and 0.21 gCOD/gVS, respectively, with acetic acid and of 0.11–0.15 gCOD/gVS, respectively, with cellulose. The SMA test values were higher than 0.1 gCOD/gVS in all the cases, demonstrating the good activity of the two inocula with acetic acid and cellulose (van Loosdrecht et al., 2016). Thus, the main advantage to adopt the UF-RET as inoculum consisted in the reduction time to degrade and convert the organic matter, especially, the simplest ones. It could be associated to the higher microorganisms and nutrients concentrations of the UF-RET than PSLS-LF, which could be the main cause of its highest kinetics.

Regarding the specific biogas production rate, there were bigger differences among the two inocula, especially when acetic acid was adopted as substrate: UF-RET reached a rate of 210 mL/gVS*d in less than one day since the starting of the tests, while PSLS-LF had a biogas rate of only 113 mL/gVS*d which was achieved almost after ten days. With cellulose, the maximum biogas rates were very close: 85 and 90 mL/gVS*d for UF-RET and PSLS-LP, respectively. Moreover, the maximum values were reached later than acetic acid, specifically after 7 and 14 days for UF-RET and PSLS-LP, respectively, demonstrating the most recalcitrant nature of cellulose which required longer time to be converted into biogas than acetic acid.

4. Conclusions and future perspectives

Three different combinations of mechanical separation and pressure driven membranes technologies were tested in order to recover water and nutrients (nitrogen, phosphorous and potassium compounds) from AGRD. The MF did not lead to a complete separation of the nutrients and of the removal of colloids and suspended solids. Consequently, this filtration step can be removed to avoid losing nutrients to be recovered in the RO concentrate. The direct application of NF was neither able to assure good performances as it was characterized by low mesh dimension which led to the rapid fouling of the membrane. Instead UF was able to assure the finest and colloidal particles removal, assuring the passage of the ammonium and potassium compounds in the permeate flux and then in the RO steps, where they were recovered and concentrated. In this study, we focused primarily on evaluating the initial performance and efficiency of the nutrients recovery membranes, given the time constraints and the scope of the research. While this approach allowed us to achieve valuable insights, we acknowledge that fouling behavior and recovery capability are critical factors for determining the durability and operational feasibility of membranes and will need more investigation. Consequentially in our future research, we plan to incorporate extended cyclic testing and assess fouling recovery capabilities using established cleaning protocols to provide a more comprehensive evaluation of membrane performance.

The laboratory results from this research work were used for the design of the scale-up of the process until a TRL of 7. Specifically, three sequential filtration steps composed by a PSLS, UF and RO have been designed for the treating of about 20 ton/d of AGRD derived from an already existing AD plant having a capacity of 1000 kWh and treating bovine manure and lignocellulosic residues from the cultivation of energy crops. The PSLS will be constituted by two rotating disks covered by a 500 μm mesh which will allow the production of a solid and liquid fraction. Then, the UF step will be represented by two columns of ceramic membranes for a total filtration surface of 1.4 m^2, operating at a transmembrane pressure of 4 bars. Finally, the RO, which can work up to 70 bars, will be able to recover about 50% w/w of water from the raw AGRD. The demonstrative scale has been designed in order to assure a high specific filtration area and to operate at different transmembrane pressures. Moreover, the cyclic washing step of the UF membrane will be also set-up to assure a higher and stable permeability of the UF step. Finally, in order to have a better energetic and economic performance of the demonstrative system, the possible installation of solar panels is under evaluation.

CRediT authorship contribution statement

Fabio Rizzioli: Writing – original draft, Investigation, Conceptualization. **Marco Cirilli:** Investigation. **Nicola Frison:** Supervision, Conceptualization. **David Bolzonella:** Supervision. **Federico Battista:** Writing – original draft, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that have not conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work.

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Data availability

No data was used for the research described in the article.

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