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Research article

Nutrient recovery from digestate: Pilot test experiments

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ABSTRACT

A series of technologies have been employed in pilot-scale to process digestate, i.e. the byproduct remaining after the anaerobic digestion of agricultural and other wastes, with the aim of recovering nutrients and reducing the load of solids and organics from it, hence improving the quality of digestate for potential subsequent reuse. In this case the digestate originated from a mixture of dairy and animal wastes and a small amount of agricultural wastes. It was processed by the application of several treatments, applied in series, i.e. microfiltration, ultrafiltration, reverse osmosis, selective electrodialysis and combined UV/ozonation. The initially applied membrane filtration methods (micro- and ultra-filtration) removed most of the suspended solids and macromolecules with a combined efficiency of more than 80%, while the reverse osmosis (at the end) removed almost all the remaining solutes (85–100%), producing sufficiently clarified water, appropriate for potential reuse. In the selective electrodialysis unit over 95% of ammonium and potassium were recovered from the feed, along with 55% of the phosphates. Of the latter, 75% was retrieved in the form of struvite.

1. Introduction

The manufacture of synthetic (inorganic) fertilizers has been crucial in sustaining global population over the last century, increasing substantially the agricultural productivity; however, it also presents a high environmental footprint, both in terms of GHG emissions and in terms of depleting the respective mineral resources (Kyriakou et al., 2017; Calabi-Floody et al., 2018). Digestate is the residue after the application of anaerobic digestion, i.e. when agricultural, animal, sludge etc. wastes of high organic load are treated for biogas/energy production. It is rich in nutrients required for plant growth and has been considered as a possible alternative to common mineral fertilizers (Chojnacka et al., 2020; European Biogas Association and Gas).

However, the nutrient content of digestates can vary considerably, not only between the different biogas plants, but even from day to day within the same plant (Li et al., 2018; Rehl and Müller, 2011; Drosg et al., 2015; Fouda et al., 2013; Proskynitopoulou et al., 2022). This means that the direct application of digestate to an agricultural field will not always confer the same benefits to the crop, with some nutrients being in excess and others deficient. At the same time, the overuse of digestate can lead to the same undesirable impacts on soil and surface waters, as those documented from the overuse of synthetic fertilizers (Huang et al., 2017; Gurmessa et al., 2020; Logan and Visvanathan, 2019). Moreover, management difficulties arise from the high water content and efforts to comply with the ever-stricter environmental and other regulations for the disposal/use of digestate (Proskynitopoulou et al., 2022; Dahlin et al., 2015).

Under these conditions, the only widely employed current treatment of digestate in the biogas plants is a preliminary liquid-solid separation by using (mostly) screw presses, or centrifuges and filter presses (Gurmessa et al., 2020; Barampouti et al., 2020; Wang et al., 2021). These processes can produce a solid fraction, which is relatively lower in weight and can be used as a nutrient rich soil amender directly or after proper composting (Peng and Pivato, 2019; Lu and Xu, 2021; Wang et al., 2013). On the other hand, the liquid fraction is considerably larger in volume and mass and its transportation (for reuse or disposal) can be rather energy intensive (Proskynitopoulou et al., 2022; Britz and Delzeit, 2013; Vondra et al., 2019).

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Among others, membrane processes are intensively studied for digestate processing to reduce volume and recover nutrients for land application (Kedwell et al., 2021; Shi et al., 2020; Vaneeckhaute et al., 2017). The main challenges faced while treating digestate with membranes are low nutrient selectivity and high concentrate volumes produced containing heavy metals and other contaminants (Xie et al., 2016; Li et al., 2022). Zacharof et al. (2019) studied the fractionation of digestate originating from agricultural and animal waste via a series of membrane processes. In their study, they separated ammonium and phosphate anions with ultrafiltration and nanofiltration membranes retaining the phosphate anions in the concentrate and the ammonium cations in the permeate. Other studies, used ultrafiltration alone or combined with other membranes producing nutrient rich liquid fractions (Świątczak et al., 2019; Salud Camilleri-Rumbau et al., 2019; Waeger et al., 2010; Gienau et al., 2018; Gerardo et al., 2015).

The present work explores, for the first time to our knowledge, a combination of five digestate processing methods i.e. microfiltration, ultrafiltration, selective electrodialysis, advanced oxidation process (UVOX) and reverse osmosis applied in series and at pilot-scale, being of relatively high technological readiness, in order to recover the nutrients as solid fertilizers and water from the liquid fraction of digestate. The biogas plant from which the digestate was obtained, used as feed animal (poultry and cattle) manure and dairy waste mixture. The methods studied herein led to the recovery of nutrients in the form of precipitates, as well as of water, leading to a reduction in the volume of digestate to be finally disposed of or used and could be easily further scaled-up to improve the economics of biogas plants, while minimizing their overall environmental impacts. The detailed characterization of nutrients' precipitates by several spectroscopic and other methods was also conducted.

2. Experimental

Fig. 1 depicts schematically the implemented treatment processes, along with the initial anaerobic digester and the preliminary screw press, which form parts of the biogas-producing plant. The process train includes the application of microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), selective electrodialysis (SED), for the separation of ionic (nutrient) content, and the UV/ozonation combined unit for the supplementary oxidative removal of dissolved organics (UVOX), located before the application of RO.

2.1. Biogas plant digestate

The experiments were carried out on the anaerobic digestate liquid fraction from a biogas production and combustion plant with 0.999 MWe nominal energy output production and annual feedstock treatment capacity of about 66,000 t (food industry, animal and agricultural wastes), located outside of Thessaloniki, Greece. The feedstock composition of the anaerobic digester consists of a mixture of animal waste (15%), agricultural waste (5%) and food industry waste (80%) and the digester operated in the mesophilic range (39–40 °C). The produced digestate is separated (screw press) and pasteurized (70 °C for 1h) and then stored in a lagoon until the farming season, where it can be reutilized as soil amender.

2.2. Digestate processing Equipment

The MF unit consisted of four bag filters (made from polyester) in cascade arrangement, contained in 20" big blue filter housings. The bag filters used in this set of experiments had openings of 800, 100, 50 and 1 μm and were fed by a centrifugal pump at flowrates up to 1200 L/h and pressures that did not exceed 2 bar.

The UF system (SolarSpring GmbH, Germany) consisted of two dead-end tubes, containing hollow polymer (PESM) fiber membranes with 0.9 mm bore, 20 nm pore size and an effective area of 6 m^2 each. The UF feed was pumped to the membranes at pressures increasing from 0.9 up to 4.5 bars, as fouling progressively increased.

The RO system (SPECTRUM, UK) employed four spiral-wound polyamide membranes (SRO-4040-2500-LE) with a total active area of 8.36 m^2 (90 ft^2), capable of withstanding pressures up to about 12 bars, or feed with dissolved solids concentration up to 2000 mg/L.

The SED unit (PCCell GmbH, Germany) was employed for the recovery of nutrients through the separation of ions from the initial feed and is described more comprehensively in previous communications (Proskynitopoulou et al., 2022); Ye et al., 2019a). The unit is centered around a 25 × 25 cm^2 cell (ED Q380), containing twenty "cell pairs", each consisting of standard anionic and cationic membranes, as well as monovalent anionic and cationic ones, arranged so as to divide the ions into three streams; multivalent anionic, multivalent cationic and monovalent (schematic in Fig. 2). The feed tank (tank A) was typically filled with 20 L of filtered digestate, while tanks B, C and D that receive the separated ion streams, anionic, monovalent and cationic products,

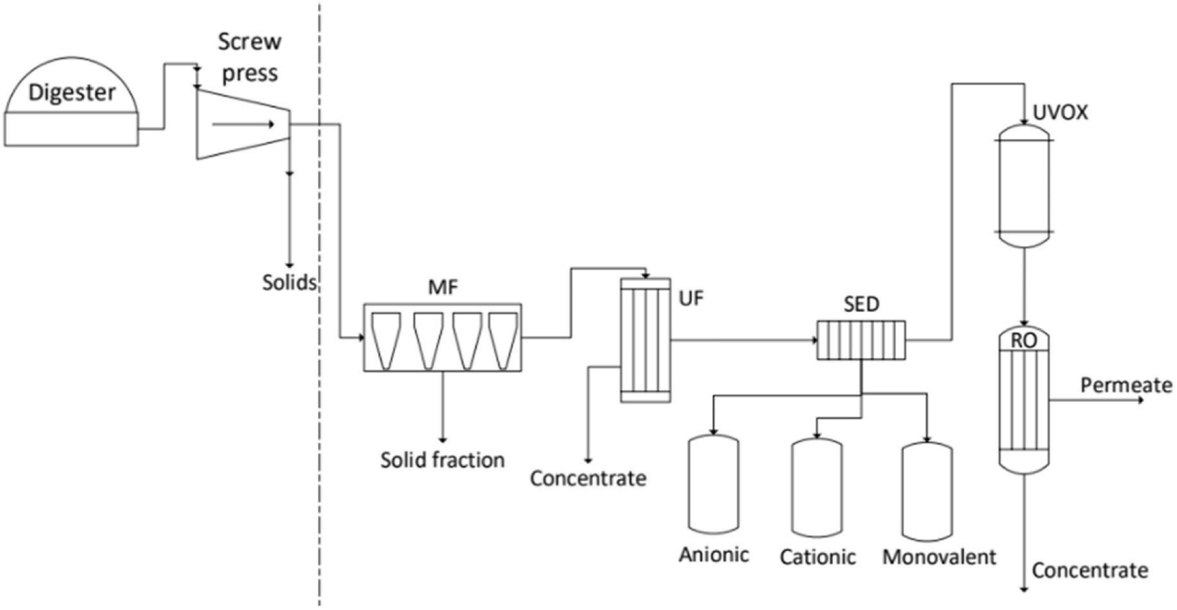


Fig. 1. Flow diagram of the overall digestate treatment pilot-scale processes.

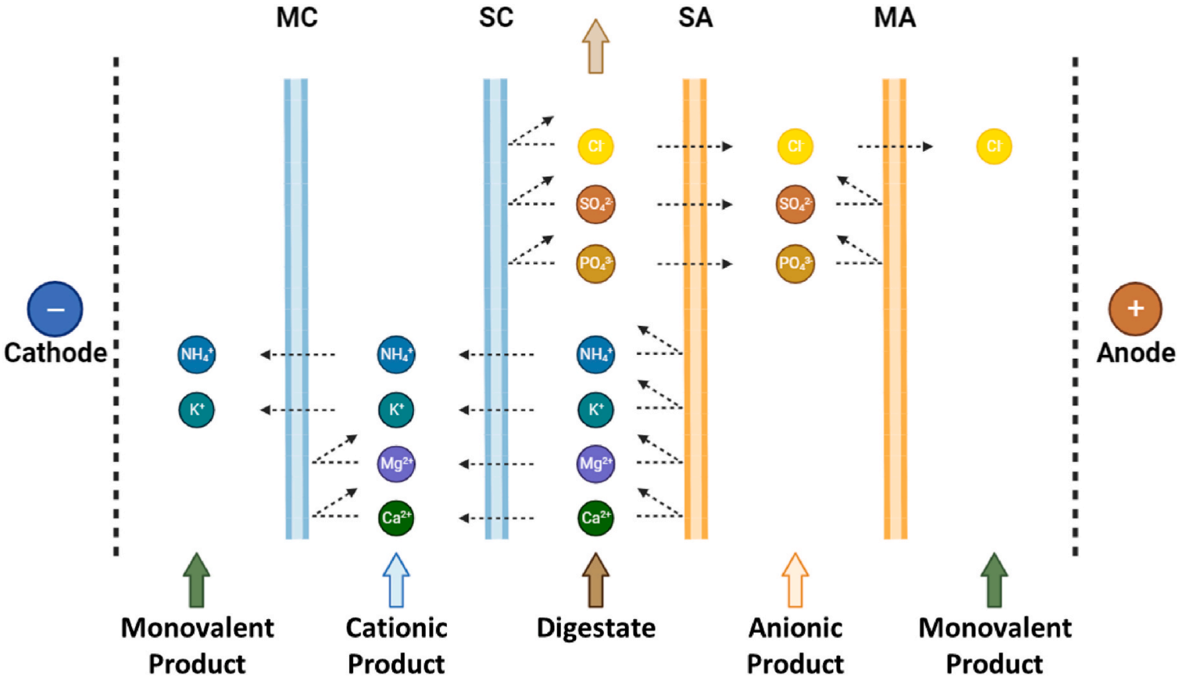


Fig. 2. Schematic diagram of an SED single cell. The stack used was made up of twenty such cells. MC: monovalent cation membrane, SC: standard cation membrane, SA: standard anion membrane, MA: monovalent anion membrane.

respectively, were filled with 10 L of a 1% NaCl solution, which is necessary for the increase of initial conductivity of the product streams, expediting the transfer of ions from the digestate, as well as balancing the electrical charges in the tanks. The cell operating voltage was kept at 35 V, while the liquid streams were fed through the cell at 250 L/h. The duration of each SED run was determined by the conductivity of the digestate; runs were terminated, once the measured value in the feed dropped below 1 mS/cm.

The UVOX unit consists of a UV ozonator (WAPURE International GmbH, Germany), a holding tank and a recirculation pump. The ozonator was equipped with four 200 W UV lamps, each capable of producing up to 0.9 kg/h of ozone, and a venturi pump for air intake. The air coming in the venturi passes around the lamps, where O_2 is converted to O_3, and is then mixed with the liquid to be processed. The aerated liquid is then cycled past the lamps where UV radiation helps convert O_3 (and water) to ·OH radicals to increase the oxidizing potential. The unit was fed with ion-depleted digestate, from the previously described SED unit, and cycled through the ozonator at a rate of 125 L/min to reduce its dissolved organic load.

2.3. Precipitation experiments

After nutrients' fractionation into three different products, further treatment is required to obtain solid fertilizers. Mixing all three separate products, in the proper stoichiometric ratio could produce fertilizers such as struvite or phosphate precipitates such as hydroxyapatite. In this study, to adjust the ratio of Mg/PO_4 the appropriate solution of $MgCl_2$ was added.

2.4. Analytical methods

To perform a complete characterization and evaluation of the process, as well as of the products, the regular sampling of input and output streams was performed, as well as the monitoring of the several stream flows of this treatment system. The sampling of digestate took place several times during 3 months of pilot-plant operation. The samples were stored in 1 L bottles at 4 °C and then analyzed within a week.

Several analytical determinations were used to evaluate various parameters before and after the processing by each treatment unit. Total Solids (TS) and Total Suspended Solids (TSS) were measured according to Standard Methods for the Examination of Water and Wastewater, i.e., 2540C and APHA 2540-D, respectively. Total nitrogen (TN) was determined by the photometric method after digesting the samples with Merck Tests (DIN 38405-9). Phosphorus was analyzed as PO_4^{3-} by using the vanado-molybdo-phosphoric acid colorimetric method and the absorption monitored by using a spectrophotometer (Spectroquant Pharo 300) at 470 nm, according to Standard Methods. The determination of Total Organic Carbon (TOC) was performed according to APHA 5310 B method with the TOC-L Analyzer (Shimadzu, Japan). The measurement of COD in the digestate samples was performed, according to APHA 5220 D.

Ion chromatography for the analytical determination of ions (K^+, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-} and NH_4^+) employed a Prominence ion chromatograph (Shimadzu, Japan). For the anions, an anion column IC SI-52 4E (Shodex, Japan) and sodium carbonate 3.6 mM as mobile phase at a constant flow of 0.8 mL/min applied, whereas for the case of cations an IC YS-50 (Shodex, Japan) column and methanesulfonic acid 4.0 mM as mobile phase at a constant flow 1 mL/min used.

Elemental/ion rejection (R_i) was calculated according to Equation (1), where C is concentration and f and p indicate feed and permeate, respectively.

$$R_i = \left(1 - \frac{C_p}{C_F}\right) \times 100 \tag{1}$$

Transmission electron microscopy (TEM) using the JEOL 2011 High Resolution Transmission Electron Microscope was used for the morphological characterization of solids precipitated during the nutrient recovery process. Before microscopy the samples were immersed in absolute ethanol and ultrasonically de-agglomerated for 30 min in order to disintegrate the large clusters. Micro-Raman spectroscopy (using the Qontor in Via Renishaw device), equipped with a microscope and a CCD detector was also applied to identify the characteristic spectrum of the produced material from the precipitation of nutrients. As the source of excitation, a diode laser with a radiant emission wavelength of $\lambda = 785$ nm was used and objective lenses 100×

0.85 NA.

3. Results and discussion

3.1. Digestate characterization

The digestate, although from the same source, varied regarding the nutrient and organic content. The total solids in the digestate ranged from 17.9 to 46.2 g/L (about 45% of which were suspended solids), while the TOC varied from 0.59 to 2.58 g/L. Table 1 shows the average values of the main characteristics of interest, as measured in several different digestate batches with minimum and maximum values included. The main nutrient ions monitored throughout these experimental runs are ammonium, phosphates and potassium, while magnesium and calcium are also important, due to their involvement in numerous physiological and metabolic processes in plants (Maathuis et al., 2011), as well as for their usefulness in precipitating phosphates. This table also depicts the values for sodium and chloride ions, whose concentrations must be below certain limits for application on agricultural land. The largest variation in terms of concentrations was observed for ammonium ions, which ranged, approximately, from 1800 to 3400 mg/L, with similarly large variations for the cases of potassium and calcium. On the other hand, the phosphate, chloride, sodium and magnesium ion concentrations did not vary substantially, as the respective ranges were narrower than 200 mg/L. These values are in general agreement with those reported for digestates derived from other animal and dairy wastes (Gienau et al., 2018).

3.2. Removal of solids and organics

The MF/bag filtration unit produces a liquid stream (permeate) almost free of large (i.e., >1 μm) solids, which are retained by the bag filters. Subsequently, the UF produces a stream largely free of suspended solids (filtrate or permeate) and a concentrate stream that is heavy with solids, split about 70-30 by volume. What the UF does to suspended solids the RO does to solutes, both organic and inorganic, producing a permeate stream of sufficiently clean water that ranges from deionized to grey water quality, depending (largely) on the specific feed of the treatment process.

The percentage of the total and suspended solids in the liquid fraction after the application of various membrane processes are illustrated in Fig. 3. The total solids (diagonal lines) are shown as the percentage of the solids exiting the unit in comparison with those entering, i.e., the solids in the UF permeate (nominally <20 nm) are 48% of those in the UF feed (MF permeate). There is a progressive increase of solids removal as the processed digestate passes through finer membranes. The suspended solids (mesh) are presented as the percentage of total solids in the same sample. As expected, the percentage of solids that are suspended successively decreases with the increase in filtration efficiency of the filtration systems regarding lower particle diameters. Thus, in the raw digestate 43% of solids content are suspended, in the UF permeate this drops below 20% and the final refinement through the RO produces a particle-free liquid fraction. Zacharof et al. (2019) used dilution and settling prior to ultrafiltration treatment of agriculture and food waste originated digestate achieving 56% of TS reduction. Ceramic membranes' performance has also been investigated for particle removal of anaerobic digestion effluents (Waeger et al., 2010). The authors highlighted the influence of particle size distribution on the filtration process and used chemicals to shift it. Addition of 0.5 % v/v ferric chloride led to an increase of 16.5% of TS removal compared to ultrafiltration without chemicals addition. Camilleri-Rumbau et al.(Salud Camilleri-Rumbau et al., 2019) also used chemical addition as a pretreatment enhancing the retention of larger particles and improving the membrane fouling.

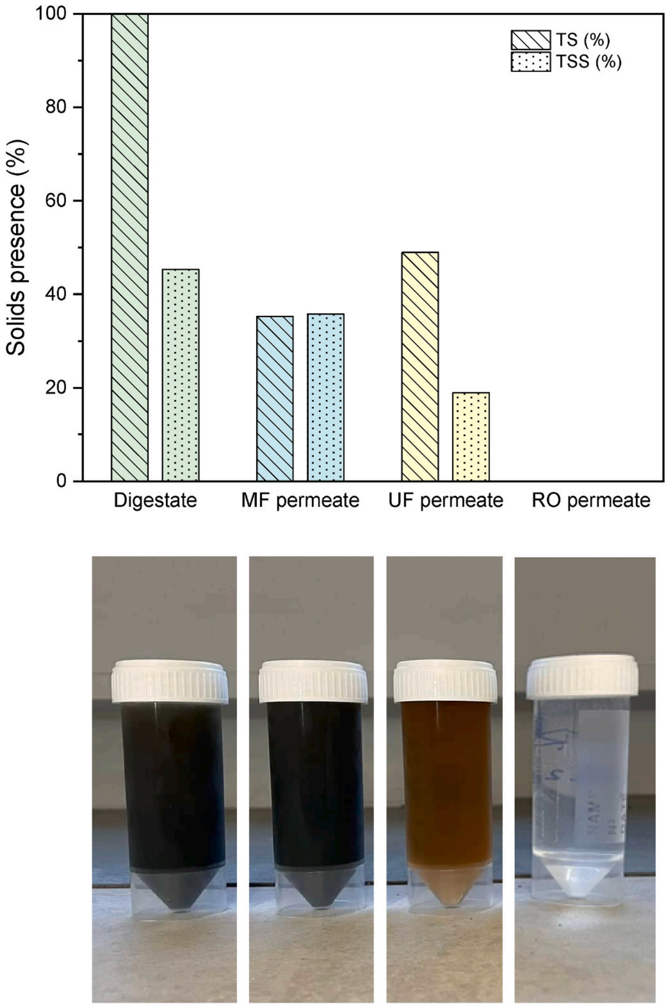


Fig. 3. Top: Total and suspended solids at various stages of applied filtration processes. Total solids are the percentage of inlet solids at each unit that pass through the membrane, suspended solids are given as the percentage of total solids in the same stream. Bottom: Samples of the streams analyzed in top (from left to right: digestate, MF permeate, UF permeate, RO permeate).

Table 1
Measured characteristics of digestate.

Parameter (units)	Average value	Minimum value	Maximum value
pH	8.18	7.99	8.35
EC (mS/cm)	23.1	21.5	24.3
Turbidity (NTU)	133.7	73.3	194
TS (g/L)	28.43	17.95	46.21
TSS (g/L)	12.88	1.90	31.17
FSS (g/L)	4.67	0.49	11.93
TOC (mg/L)	1699.7	586	2578
COD (mg/L)	4533.3	2600	5600
Na^+ (mg/L)	1399.1	1268.4	1505
NH_4^+ (mg/L)	2556.5	1787.1	3409.2
K^+ (mg/L)	1981.2	1494.4	2337.4
Mg^{2+} (mg/L)	54.4	21.8	105.2
Ca^{2+} (mg/L)	297.7	41.4	697.4
Cl^- (mg/L)	2273.7	2218.2	2353.8
NO_3^- (mg/L)	123.4	31.2	193.6
$PO_4{}^{3-}$ (mg/L)	450.3	270.9	549.1
$SO_4{}^{2-}$ (mg/L)	170.5	26.0	315.0

This gradual removal of solids can be seen in the bottom panel of Fig. 3, which displays samples taken from the aforementioned streams, i.e., the digestate and the permeates of the MF, UF and RO units, with the respective opacity decreasing in that order. The solids thus removed could be used as soil amenders after drying and/or composting (Zhang et al., 2020). In the case of the organics' gradual removal from the process liquid (Fig. 4), nearly 43% of feed organics are retained by the MF and nearly 80% by the UF, while almost 10% remains in the SED, contributing to the gradual fouling of the membranes in this process. About 6% of the initial organic carbon is decomposed and mineralized to CO_2 in the UVOX unit and a final 7% ends-up in the RO concentrate, leaving the RO permeate free of organics and ready to be reused either for irrigation purposes or covering the water needs of biogas plant. Table 2 shows criteria set by the EU for water reuse in the irrigation of food crops consumed raw where the edible part is in direct contact with reclaimed water (The European Parliament and the Council, 2020), the strictest category in this regulation, and the corresponding values measured in the RO permeate well within these limits. Due to the origin of the digestate being largely food waste, the concentrations of heavy metals were very low in the received material (<10% of limits for fertilizers (The European Parliament and the Council of the European Union, 2019)). The highest concentrations, measured in the UF concentrate (0.01, 0.03, 0.05, 0.08, 0.31, 0.34, 2.31 and 15.2 mg/kg for Cd, Hg, As, Pb, Cr, Ni, Cu and Zn respectively), are still safely below the limits for fertilizer applications (The European Parliament and the Council of the European Union, 2019), with negligible concentrations in the UF permeate and below detection in all subsequent process streams.

The liquid fraction after the SED unit was introduced in the UVOX unit and circulated through it for 202 h. The ion-depleted liquid from SED was used to mitigate any potential interference of inorganic compounds ın the removal of organics. As can be observed in Fig. 5(left), the TOC concentration decreased approximately linearly with the treatment time in the UNOX unit. However, the removal of organics was limited to about 50% of the starting value. The ammonium concentration in the starting and in the final liquid samples was unchanged, indicating that there was no competing reaction of oxidizing agents with the inorganics' content that could reduce the effectiveness of UVOX.

The relatively low performance of the UVOX unit could be attributed to the dark color of the starting liquid, which decreases the UV permeability through the ozonated liquid. However, if this was the problem, it could be expected that the TOC degradation rate will increase with time, especially towards the end of treatment run, where the liquid is quite clear in appearance (Fig. 5 right), which was not observed. Therefore, it is more likely that the high organic content (250–500 mg/L) interferes with the UV radiation, rather than the initial color. The insufficient UV permeability in the liquid to be treated after the addition of ozone is expected to limit the conversion of ozone towards the production of more effective oxidative agents (i.e., hydroxyl radicals), presenting much higher oxidation capacity, and whose presence can expedite the oxidation process, enhancing further the removal of organics.

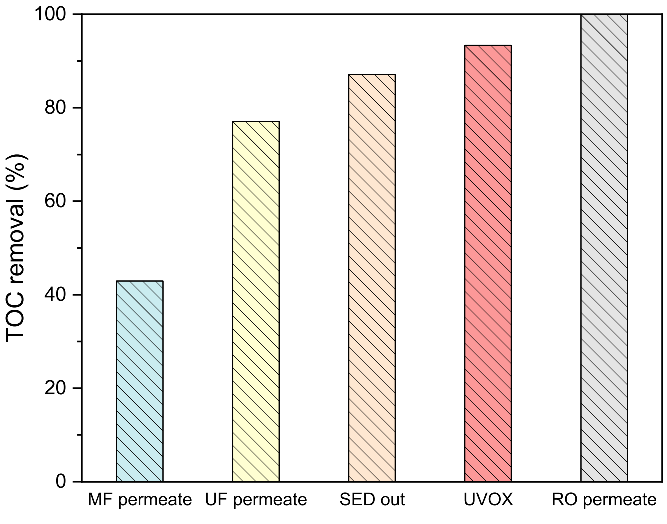


Fig. 4. TOC removal in the various examined treatment units, given as the percentage of TOC in the raw digestate.

Table 2
Quality criteria for water reuse and values measured in RO permeate.

	BOD_5 (mg/l	TSS (mg/l)	Turbidity (NTU)
EU Regulation 2020/741	≤10	≤10	≤5
RO permeate	5.11	0	2

An overview of the solids removal and water (volume) distribution through the overall process can be seen in Fig. 6. This schematic gives the volume and total solids concentration of the digestate at each stage of the process as it is split into permeates and concentrates in the filtration processes (in the SED it is split into the ion-depleted diluate and the concentrated product). The MF retentate is not depicted because neither its volume nor its solids concentration could be reliably measured. The UVOX unit is also not depicted because the reduction in solids was very minor and no volume was lost. As can be expected, the concentrates in each unit have higher solids loads than both the respective feeds and permeates, while their volume is below 30% of the feed volume.

3.3. Recovery of nutrients

3.3.1. Ion separation and filtration units

The main nutrients that are monitored during these treatment processes are ammonium, phosphates and potassium. As the liquid feed passes through the filtration units the nutrients are divided, not necessarily evenly, between the permeate stream and the retentate (or concentrate) stream of each unit. The portion of nutrients, or other measured constituents, which does not pass through the membranes of filtration units is usually referred to as rejection. Fig. 7 depicts the three main nutrients' rejection in the MF, UF and RO units. Approximately 20% is found for the case of the MF, with the exception of potassium, which is rejected by less than 15%. In the UF the rejection is higher for all examined ions, because the membrane has finer pores, leading to a larger mass/volume of UF concentrate, than of MF retentate. However, the phosphate rejection is disproportionately higher (i.e., around 60% vs. <30% for the other two nutrients). This might be partially explained by the difference in ionic radius of the respective constituents (Marcus, 2012), but may also occur because the phosphates tend to adhere with the finer solids, which are rejected by the UF (Gienau et al., 2018), while ammonium and potassium do not. Finally, the RO unit is fed with the ion-depleted digestate, which facilitates high rejection values. For all three of these ions the rejection rate is above 85%, which is desirable for an RO unit, reaching 100% for the case of phosphate ions.

3.3.2. Selective electrodialysis (SED)

3.3.2.1. Ion separation. As described earlier, the selective electordialysis unit employed for the recovery of nutirents from the pre-filtered digestate, includes a tank that contains the feed (tank A) and three tanks that receive the separated ions (tanks B, C and D), i.e. anion, monovalent and cation products, respectively. The distribution of the main nutrients, as detected in the initial SED feed and the resulting liquid at the end of the average experimental run, are shown in Fig. 8.

In the beginning, almost all examined ions are detected in the feed (tank A). Small quantities of potassium, calcium and phosphates are also detected in the rest of the tanks and can be attributed to impurities, either from the sodium chloride used to prepare the starting solutions, or from residues of previous runs, since phosphates are especially persistent and tend to adsorb on plastic surfaces, such as the tanks used in the SED unit.

At the end of the experiment, the feed tank contains very low concentrations of ammonium, potassium and phosphates and practically no magnesium, calcium or sulphates. Of these ions remaining, the first two are in the highest concentrations at the beginning and the complete removal of them would greatly prolong treatment time. The latter are

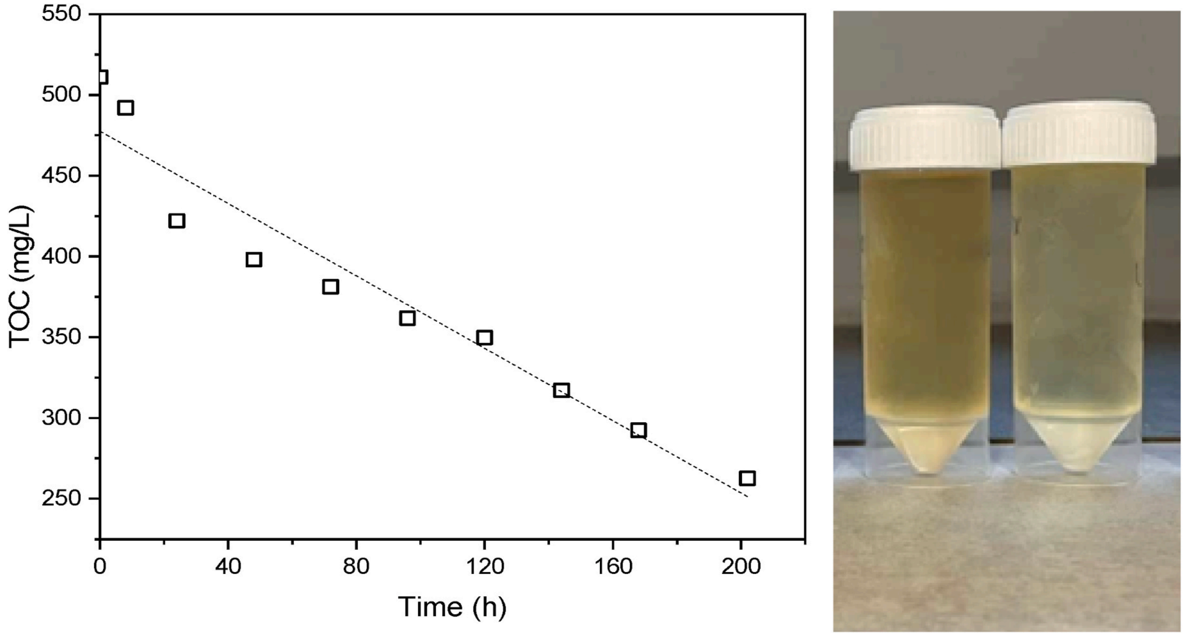


Fig. 5. TOC reduction during UVOX operation (left) and samples taken from the UVOX after 146 and 202 h treatment time (right).

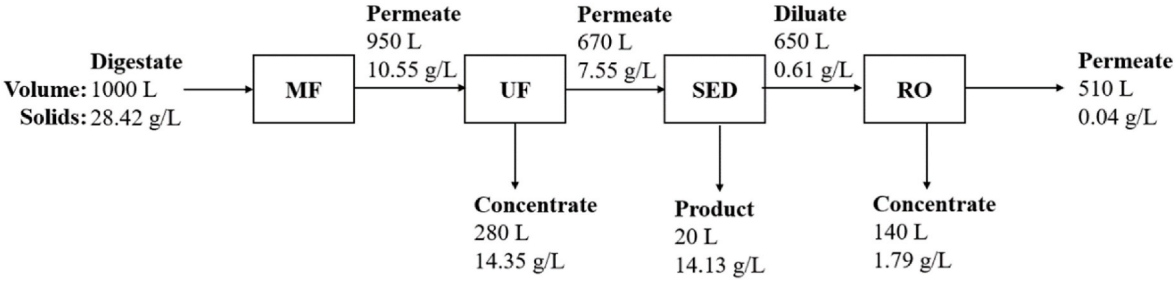


Fig. 6. Solids and water balances around each unit in the process.

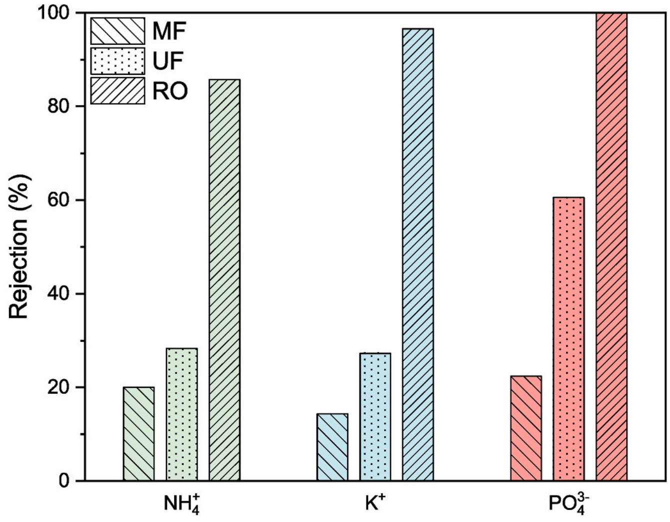


Fig. 7. Nutrient rejection in the MF (diagonals), UF (mesh) and RO (reverse diagonals) units.

among the largest in size of the examined nutrients, and consequently, present relatively lower mobility through the treatment cell, rendering their complete removal also rather time-consuming. Ye et al. (2019b) studied the profiles of migration rate of the aforementioned ions in a similar selective electrodialysis system. Their study revealed that the mobility of various anions is determined by their charge and hydrated radius relative to those of coexisting anions.

On the other hand, the three product tanks (tank B, C and D) accumulate significant concentrations of nutrient ions. Tank B, the anionic product tank, contains considerably more phosphates and sulphates than at the beginning. Tank C, that receives mainly the monovalent products, contains almost all the ammonium and potassium cations from the initial feed (tank A), while tank D, the cationic product tank, has concentrated mainly the magnesium and calcium content, along with some ammonium and potassium, which did not separate with the monovalent stream. The higher concentrations observed in the product tanks, when compared to the initial ones of tank A, notably for ammonium, are due to the smaller volumes collected in these tanks than in the feed tank.

In terms of nutrient recovery, Fig. 9 shows the typical percentages of the main nutrients that are recovered by an SED run. For all the examined nutrient ions, except phosphates, the recovery is above 90%. This discrepancy, although at odds with some of the literature (Wang et al., 2013; Kedwell et al., 2021; Shi et al., 2020; Gao et al., 2020; Shi et al., 2018), could be in part explained by the larger hydrated radius of phosphate ions (295 p.m. (Li et al., 2022; Marcus, 2012)), as compared to the other ions. This is likely compounded by the large co-presence of the other more mobile ions, such as ammonium and potassium, as well as with the similar amounts of sodium and chloride ions (Table 1), which

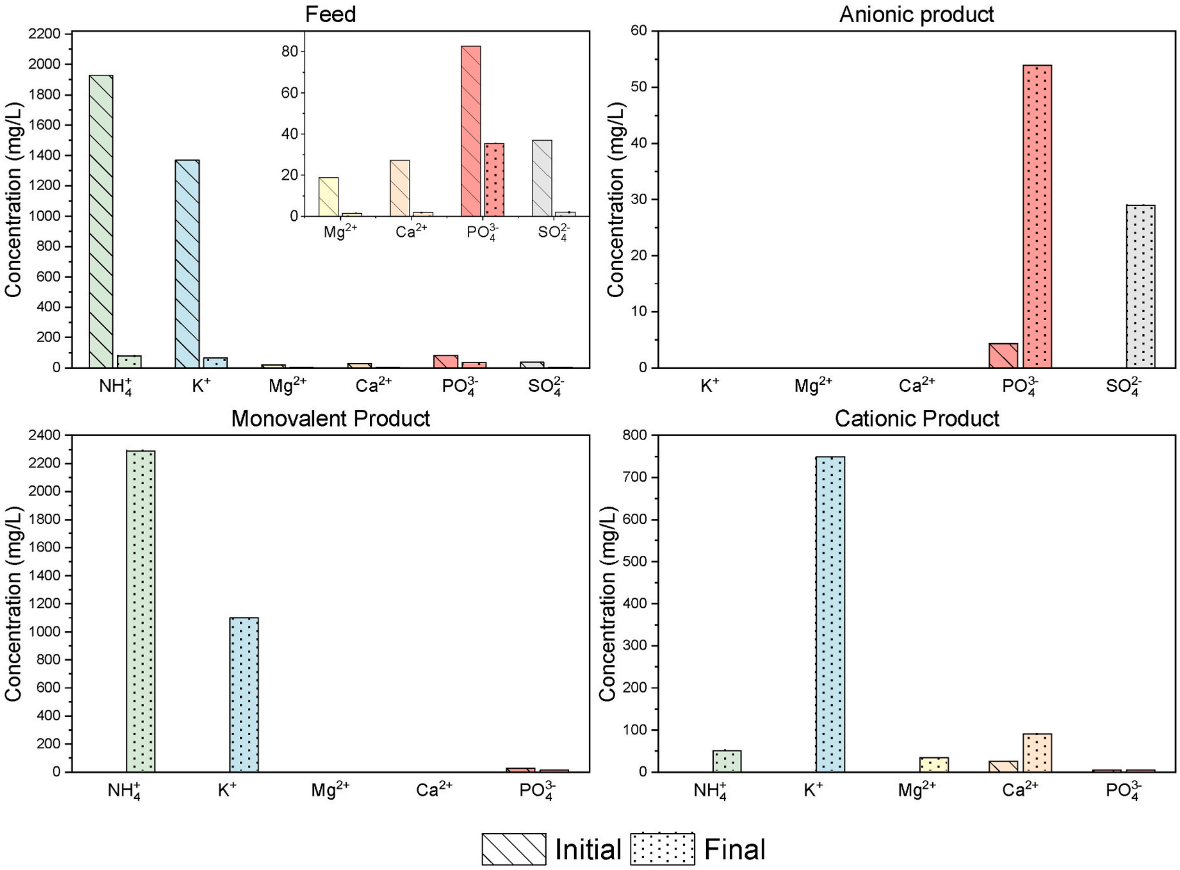


Fig. 8. Concentrations of nutrient ions in the four process tanks of the SED unit: (a) tank A (feed), (b) tank B (anionic product), (c) tank C (monovalent product), and (d) tank D (cationic product), at the beginning (diagonal lines) and the end (mesh) of a typical experimental run.

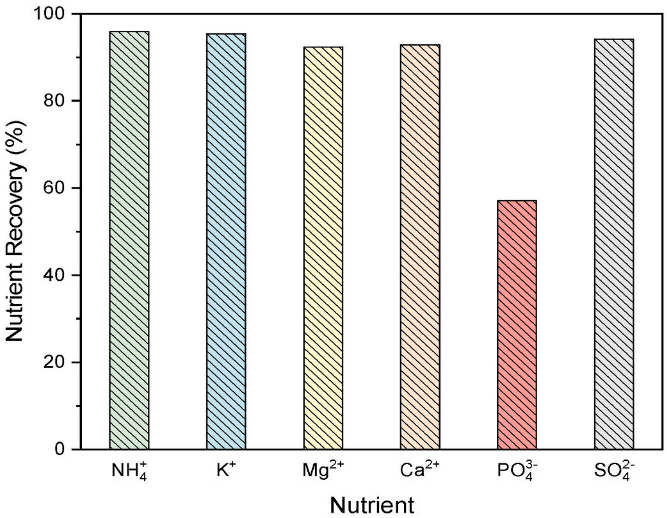


Fig. 9. Percentage of nutrients typically recovered from the feed in a typical SED run.

can more easily carry the electric current through the cell. Furthermore, when a trivalent phosphate anion moves from the feed stream to the anionic collection compartment, the demand for electroneutrality dictates that an equal charge move out of that stream, i.e., three chloride ions must leave tank B for every phosphate ion entering it. Studies with synthetic solutions show higher phosphate recoveries (up to 89.6% (Ye et al., 2019b)), however, in the cases of real wastewaters lower phosphate recovery is a common bottleneck in electrodialysis processes, with reports in the range of 19–56% (Li et al., 2022; Wang et al., 2022; An et al., 2023), likely due to fouling. Kedwell et al. (2021) proposed a diverse membrane set up achieving phosphate recovery up to 70% by treating the supernatant of centrifuged digestate.

3.3.2.2. Membrane fouling. The particular digestate used here seems to have had a relatively light load of larger solids, which made the work of the MF/bag filtration unit easier. Thus, the bag filters only needed to be cleaned, simply washed with water, after processing an entire 1000 L batch of digestate. The UF unit had a significant solids load to handle (TS ~9.5 g/L), but by increasing the frequency of back-flushing to once per every 10 L of treated permeate it was also able to process a whole batch of 1000 L without the need for chemical cleaning. It was however found that if this cleaning was omitted at the end of a run, it would become necessary early in the next one, i.e., less than 200 L of a second batch could be processed before intensive cleaning is required again. On the other hand, the RO unit faced the lightest load (TSS: 6.7 μg/L, TDS: 463 mg/L), since it was the last treatment unit in the overall process. Specifically, most of the suspended solids were removed by the UF unit and most of dissolved solids by the SED unit. Furthermore, a certain amount of organics was removed/oxidized by the UVOX unit before this stream was fed to the RO. Nevertheless, the RO unit was chemically cleaned between uses in the different experimental runs, due to the quite large intervals between successive uses.

Thus, the only unit which displayed long-term fouling problems was the SED. In spite of the filtration technologies employed for the preliminary removal of solids, a considerable amount of organics still remain in the filtered solution, as well as some suspended solids. When this liquid is processed by the SED unit some of these molecules, especially those with ionic functional groups, adhere to the membranes, causing fouling (Gurreri et al., 2020; Lindstrand et al., 2000). This fouling interferes both with the flow/flux of digestate across the membrane surface and with the transfer of ions through (or towards) the membranes. Both these degradations of membrane can lead to the decrease of electric current that passes through the cell (Mondor et al., 2009). Fig. 10 shows the measured current versus the respective experimental runtime (i.e., the time that is required for the minimization of conductivity in the feed solution of tank A), regarding the 1st, 10th and 20th run. It can be observed that the current is decreasing, but also that the time required to achieve the desired ion removal can be more than double over the examined period. Lindstrand et al. (2000) examined the fouling of ion exchange Membranes (IEMs) in the electrodialysis (ED) process, when treating solutions of octanoic acid, sodium octanoate and sodium dodecylbenzene sulphonate, as well as an alkaline bleach plant filtrate from a sulphate pulp mill, and found that the anionic IEMs were affected much more than the cationic ones. An et al. (2023) also report a somewhat higher fouling of anion exchange membranes, when treating the liquid stream produced from the dewatering of digested sewage sludge (TSS, 2060 mg/L, COD 1784.2 mg/L) filtered down to 5 μm. This behavior might also contribute to the lower phosphate recovery, as observed in this work (Fig. 9).

3.3.2.3. Nutrient recovery. The separated anionic and cationic solutions produced by the application of SED (i.e., the concentrated solutions of ions in the product tanks B, C and D) are not readily applicable as fertilizers, due to the co-presence of NaCl, which was added in the starting solution (Ward et al., 2018). One approach for recovering the targeted ions for potential reuse is through the synthesis of phosphates from the SED concentrate product in the form of struvite precipitate ($NH_4MgPO_4 \cdot 6H_2O$). Since the phosphates are mostly located in tank B, the ammonium in tank C and the magnesium in tank D this would require mixing all three separate products, but in the proper stoichiometric ratio. However, the concentrations of magnesium and phosphates in the respective tanks are lower than the necessary values, and therefore, it is not possible to create an overconcentrated solution by simply mixing them together. Since phosphorus is the most important (and possibly rarest) of these three nutrient constituents, especially with respect to demand, experiments were focused on the anionic product (tank B). To adjust the ratio of Mg/PO_4 the appropriate addition of $MgCl_2$ is necessary. A 45 wt% solution of $MgCl_2$ was formed by dilution of the precursor in deionized water and was added dropwise to the anionic product. By adding 1 mL of the monovalent product/L of anionic product and then 0.6 mL of the aforementioned $MgCl_2$ solution (per liter of product liquid), under stirring at room temperature, whitish crystals formed. The precipitated solid was recovered by vacuum filtration and air dried at room temperature. Characterization with TEM revealed the morphology of the precipitated particles, being mainly aggregates of nm sized particles (Fig. 11, left). The measured d-spacings (Fig. 11, right) belong to the (101), (201), (221) and (202) crystal planes of struvite (magnesium ammonium phosphate hexahydrate). Analyses of phosphates in the SED anionic product before and after precipitation showed that it was possible to retrieve 75% of its phosphorus content in the form of struvite precipitate.

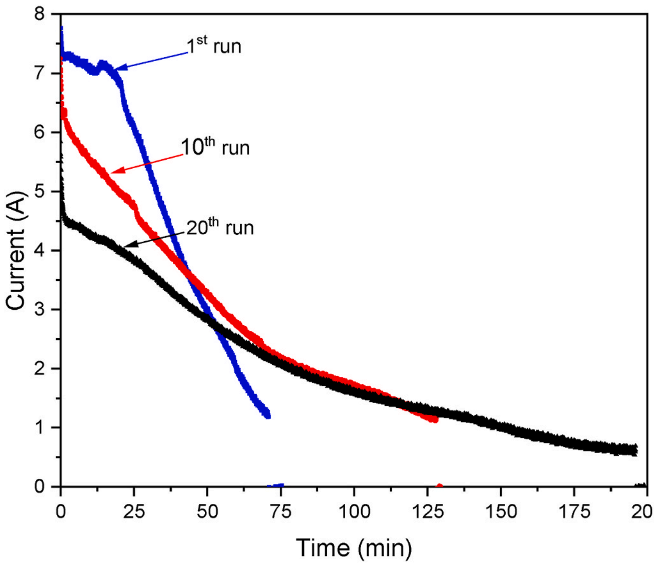


Fig. 10. Effect of fouling on SED current and experimental runtime.

The struvite presence in the recovered solid particles was also confirmed by Raman spectroscopy ((Prywer et al., 2016) Fig. 12). Two main peaks were observed at 945 cm^{-1} and at 560 cm^{-1}, which are characteristic of the phosphate vibrations ($–PO_4$) (Capdevielle et al., 2013; Frost et al., 2005; Prywer et al., 2016). There is also a very broad peak from 1300 to 1700 cm^{-1} that could be attributed to ammonium vibrations. Other smaller peaks at lower wavenumbers are also characteristic of struvite.

4. Conclusions

An advanced oxidation and different membrane technologies have been employed for the processing of digestate from an anaerobic digestion biogas plant that uses as feed animal waste (15%), agricultural waste (5%) and food industry waste products (80%), targeting the removal of solids and organics and the recovery of nutrients.

Micro- and ultra-filtration gradually minimized the solids' content of liquid digestate, while the application of reverse osmosis produced almost deionized water, with quality varying with the solid content of the feed. The solids retained by the filtration units can be dried and/or composted for further use as soil amenders. Application of a UV-ozonation unit for the supplementary decomposition of organic compounds of the pre-filtered by membranes digestate resulted in the reduction of organic content by around half of the initial input load, even after long-term operation, indicating that this method needs further optimization for handling such liquids with low UV permeation, e.g. dilution.

The filtered liquid digestate fraction was further treated by the application of selective electrodialysis to produce anionic and cationic solutions that could be recombined for the synthesis of alternative fertilizers through the production of an appropriate solid precipitate, such as struvite. In the current work, successful precipitation of struvite was achieved with the addition of $MgCl_2$ solution, which was required for the adjustment of the proper Mg/PO_4 ratio.

In general, it can be concluded that although the solid separation technologies can effectively remove the solids and result in the recovery of good quality water from digestate for potential agricultural reuse, the recovery of nutrients from the liquid fraction of the digestate is still a challenging procedure. Acidification of digestate for phosphorous release, and thus higher availability in SED feed, could result in a more concentrated anionic product and higher recovery efficiencies.

CRediT authorship contribution statement

Vera Proskynitopoulou: Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Ioannis Garagounis:** Data curation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Anastasios Vourros:** Data curation, Formal analysis, Visualization. **Panagiotis Dimopoulos Toursidis:** Formal analysis. **Souzana Lorentzou:** Methodology, Supervision, Writing – review & editing. **Anastasios Zouboulis:** Supervision, Writing – review & editing. **Kyriakos Panopoulos:** Conceptualization, Methodology, Project administration, Supervision, Writing – review & editing.

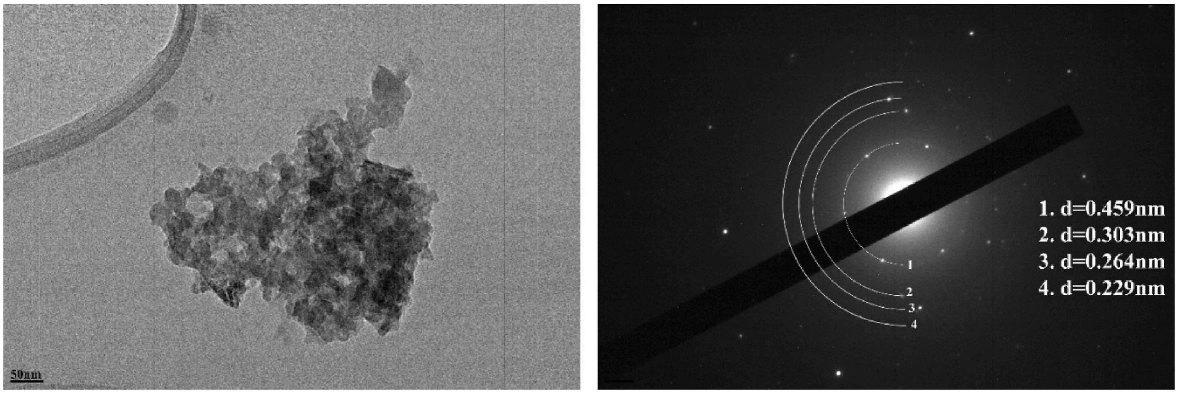
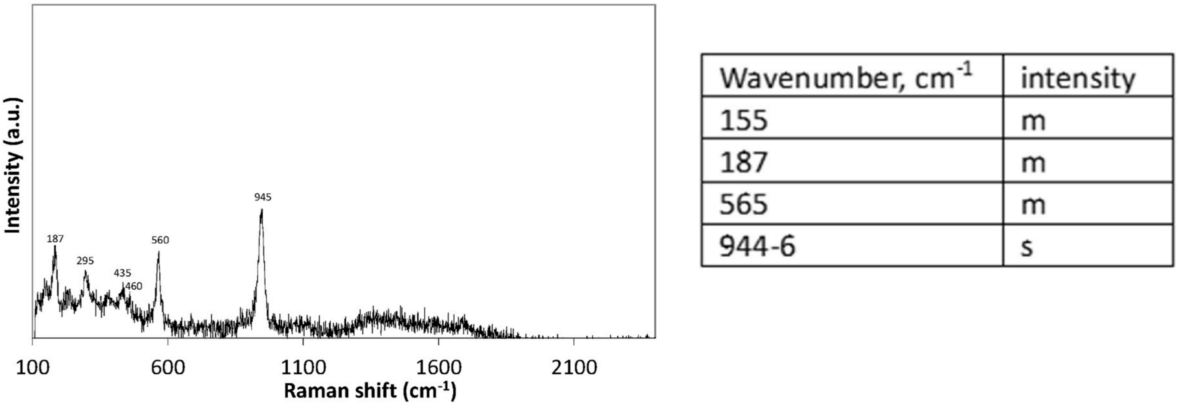


Fig. 11. TEM image (left) and diffraction pattern (right) of the recovered solid particles derived from the SED liquid products. The d-spacing (given in the righthand image) corresponds to struvite.



Wavenumber, cm^{-1}	intensity
155	m
187	m
565	m
944-6	s

Fig. 12. Raman shift spectrum of the recovered solid particles precipitated from the SED product with the characteristic peaks of struvite present in the spectrum (left). The strong and medium peaks presented by the Raman shift spectrum, corresponds to struvite (Prywer et al. (Prywer et al., 2016)) (right).

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.

Data availability

Data will be made available on request.

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