Valorization of agricultural digestate by sequential filtration steps for the recovery of nitrogen and phosphorous compounds

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Agricultural residues, and livestock effluents are often treated via anaerobic digestion (AD) with the aim to produce a biogas rich in methane and to recover most of the nutrients from digestate, the main by-product from AD, for bio-fertilizers production. Carbon is recovered obtaining biogas while nitrogen, phosphate and potassium are present in digestate. In 2019 almost 19,000 biogas plants were present in European Union (EU), which over 70% of them used agricultural residues. In 2021 the EU reached 18.1 billion cubic meters (bcm) of combined biogas and biomethane production (EBA, 2022), with over 180 million tonnes of digestate. Moreover, with the introduction of the plan "REPowerEU", the EU plans to boost the biomethane production up to 35 bcm by 2030, increasing consequently the digestate production (European Commission, 2022). The most conventional digestate application consists in its direct application on soil for fertilization purposes or can be treated to recover nutrients that are stable and can be stored. While it is the simplest digestate usage, is also subjected to regulations and limitations due to its high ammonium content, which cause a polluting threat for superficial waters (eutrophication) and atmosphere (nitrogen dioxide emissions). For this reason, EU limited the annual application of nitrogen to 170 kgN/ha in specific areas named "Nitrate Vulnerable Zones" (NVZs), which are often coincident with plains and river drainage basins, where most farms and biogas production plants are located. Consequently, different technologies can be adopted for a proper digestate valorization. Nitrogen is commonly extracted from the digestate through ammonia stripping. The digestate is pretreated with strong bases to volatilize NH3 under negative pressure and high temperature. Then, ammonia is recovered with a sulphuric acid scrubber to obtain ammonium sulphate. This process is done using packed-bed stripping towers and requires high amount of chemicals and electric energy, and thus is not suited for small/medium farms or livestock facility, which instead must transport the excess digestate to a dedicated ammonia stripping plant (Gienau et al., 2018). Alternatively, anaerobic digestate can enter a series of filtration processes, firstly to separate solid and liquid phases by centrifugation and ultrafiltration, and then concentrate the nutrients in the liquid phase by removing water through reverse osmosis. Obtaining as main products a nutrient-rich liquid concentrate and pure water. The liquid concentrate, although does not meet the legal requirements to be considered a proper fertilizer, can be used as a soil conditioner. Moreover, due to the filtration process and the volume reduction, the concentrate is biologically and chemically stable and can be easily stored. This process, compared to ammonia stripping, can be used without any digestate pretreatment and chemicals addition, is less energy demanding and can be scaled based on the biogas plant size, thus allowing small and medium farms or livestock facilities to have a proper digestate treatment plant in loco (Rizzioli et al., 2023). The aim of this work is the optimization of different filtrations steps in order to maximize the nitrogen recovery.

Material and Methods

The agricultural digestate for this work was obtained from the anaerobic digester of a farm in Maaninka (Finland), using cow manure as substrate. The characterization results are shown in Table 1, total and volatile solids were analyzed according to APHA Standards Methods (APHA, 1998). pH and conductibility were measured using CO 3000H portable analyzer by VWR. The ammonium content of the digestate and reverse osmosis effluents was analyzed by a spectrophotometric test supplied by Hach Lange.

Table 1. Digestate characterization

Total Solids (TS)	3.77 %w/w
Volatile Solids (VS)	2.46 %w/w
VS/TS	65 %
pH	8.3
Conductibility	17.4 mS/cm
NH_4^+-N	0.533 g/L

The filtration cascade was composed by three different steps, all performed at laboratory scale: (i) preliminary solid/liquid separation; (ii) ultrafiltration and nanofiltration (UF, NF); (iii) reverse osmosis (RO). In the first step the anaerobic digestate was centrifuged at 4000 rcf, also testing the application of SNF FLOPAM polyacrylamide flocculants (anionic, cationic, and non-ionic; 0.5 g/kgTS) and Kemwater Pix-105 ferric sulphate coagulant (1% w/w). The centrifugation supernatant was then vacuum-filtered testing three different polypropylene filter cloths (Outotec MARO S60, S40, S30) with an air permeability of 12, 7, 3.2 m^3/m^2 respectively. The liquid phase then entered the second step, where it was ultrafiltered in dead-end mode, testing two membranes: Microdyn Nadir® UP150 and Nadir® UP010, 150 and 10 kDa of molecular weight exclusion cut-off and trans-membrane pressure of 2 and 4 bar respectively. Following the UF, the

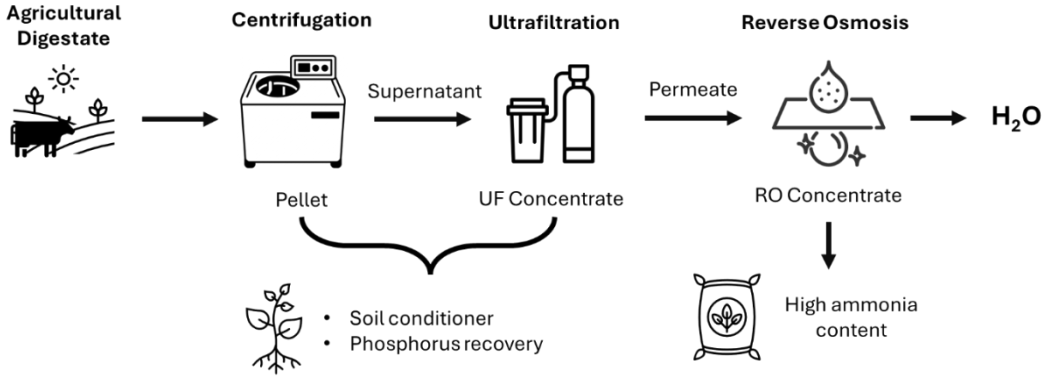
permeate was nano-filtered with FilmTec™ NF270 membrane (~200 Da) at 4.8 bar of trans-membrane pressure. A RO step, to eliminate excess water and thus concentrate salts and nutrients in the retentate, was performed on the NF permeates using FilmTec™ BW30 membrane at 15.5 bar of trans-membrane pressure. For every step, flux ($kg*m^{-2}h^{-1}$), permeability (flux/trans-membrane pressure) and membrane rejection (conductivity-based) were calculated were possible.

Results and Conclusions

In the first step, the centrifugation step let to the sedimentation of all the digestate heavy particles, reducing the TS content to 1.73 ± 0.17 %w/w. The application of flocculation and vacuum-filtration steps after the centrifuge did not significantly reduce the TS content of the supernatant. The application of ferric sulphate coagulant managed to reduce the TS content to 1.51 %. For these reasons, the flocculation and vacuum-filtration steps were discarded, while the coagulant application was carried on to the UF step. The samples tested for UF were: (i) raw digestate, (ii) centrifuged digestate and (iii) centrifuged and coagulated digestate. The UF step reduced the TS content to 1.48 ± 0.09 % and 1.01 ± 0.02 % w/w for UP150 and UP010 respectively. All the UF membranes did not significatively retain salts, with an overall salt rejection of 2 %. The NF step was not able to separate most of the salt, with an average salt rejection of 16.3 % against the expected 95 % of the reference test. The reverse osmosis step achieved an average conductivity rejection of 73 ± 4 % (rejection standard tests: 86 ± 1 %), achieving an average concentration factor of 3.3. The average water recovery was 69 ± 19 % with a mass reduction of 4.21 folds. The ammonium concentration reaches 1.79 ± 0.27 g/L on the retentate, representing an increase in concentration of 3.5 folds.

This preliminary work is focused on the design of a biorefinery cascade for the nutrient recovery and stabilization of AD digestate. Overall, centrifugation, ultrafiltration and reverse osmosis are the main processes for this biorefinery. Flocculant addition, vacuum filtration, and nanofiltration steps are unnecessary for the process and therefore have been excluded from the cascade. Is important to note that the ultrafiltration permeate is biologically sterile. The reduction of the digestate volume after the reverse osmosis step also improves the storability of the concentrate. Furthermore, the RO retentate can be directly used as soil conditioner or can undergo another separation process, for example trough a membrane contactor, to be refined into a proper fertilizer.

Graphical Abstract



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