



# Article Treatment of Liquid Fraction of Digestate by Integrated Process Struvite Precipitation—Forward Osmosis

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Abstract: The research undertaken in this paper was aimed at determining the effect of struvite precipitation, one of the potential products that can be obtained during digestate management, on the performance of the non-pressurized membrane process-forward osmosis (FO). The effect of using an integrated struvite precipitation-forward osmosis process to treat the digestate liquid on the changes in the properties of organic substances present in the treated solution (particle size distribution,  $\zeta$ -potential) was analysed as well. The study was conducted for the liquid fraction of municipal waste biogas plant digestate. The obtained results demonstrate the suitability of this process for recovering water from liquid digestate. It was found that forward osmosis conducted for a digestate pre-treated by chemical struvite precipitation leads to higher water flux values and increased salt concentration in the receiving solution (from 0.5 to  $3 \text{ mol/dm}^3$  NaCl). There is practically no concomitant infiltration of organic substances into the receiving solution. Therefore, the use of 3 mol/dm<sup>3</sup> NaCl as a draw solution results in the recovery of the highest volume of water per unit of time. An analysis of the particle size distribution shows that the removal of the macromolecular fraction of organic compounds from the digestate mainly takes place simultaneously with the chemical precipitation of struvite. It was found that an increase in the concentration of the draw solution, which allows for greater water recovery, resulted in the aggregation of the concentrated organic molecules.

**Keywords:** digestate; municipal waste biogas plant; struvite precipitation; forward osmosis; size distribution; zeta potential

### 1. Introduction

The operation of a biogas plant, regardless of type, is associated with the formation of both biogas and a large amount of digestate as one of the products of organic substance processing. Management of the resulting digestate is troublesome, which is why the technology of waste processing in biogas plants needs to be improved, along with both existing and developing methods of digestate management [1]. Because digestate is a fertilizer and a source of water, it is extremely important to choose the right method of purification to ensure that all valuable components can be recovered from the substance previously treated as a troublesome waste. This is very important from the point of view of implementing the circular economy.

Forward osmosis (FO), i.e., the diffusion of a solvent through a semi-permeable membrane separating two solutions of different concentrations, may be an alternative method of purifying the liquid fraction of the digestate to the processes currently in use. At atmospheric pressure, water passes through a synthetic membrane from the solution being treated to a concentrated receiving solution (the draw solution). The driving force of the process is produced naturally, and is the result of the difference in the osmotic pressure of the solutions on both sides of the membrane. The flow of water is spontaneous [2].



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). This process does not require external energy other than the energy associated with the circulation of solutions on both sides of the membrane, and continues until the osmotic pressures of the solutions on both sides of the membrane equalize. The efficiency of FO is highly dependent upon, among other things, the properties of the receiving solution. This solution should be characterized by high osmotic pressure at the lowest possible concentration, low viscosity, ease of recovery, and low purchase/production cost, and must not exhibit toxicity. The most common receiving solutions are [3]:

- gases dissolved in water (SO<sub>2</sub> or a mixture of NH<sub>3</sub> and CO<sub>2</sub>)
- sugars (glucose, fructose, sucrose)
- inorganic salts (NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>)
- organic salts (Na<sup>+</sup> and Mg<sup>2+</sup> salts of formic, acetic or propionic acid)
- hydrophilic magnetic nanoparticles.

FO uses non-porous asymmetric membranes manufactured from hydrophilic polymers. The most common are membranes made of cellulose triacetate or composite membranes containing a polyamide active layer [3]. Because the transport of water through the membrane does not require hydrostatic pressure, the membranes used in FO can be thinner than those used in reverse osmosis. To reduce flow resistance, the pores in the support layer should be low in tortuosity [4]. FO is increasingly used in many fields of environmental engineering, including those related to water and wastewater treatment [5-15]. While there are many reports on the subject in the literature, at present there is relatively little information on the direct use of this process to treat the liquid fraction of the digestate. As an example, only the research presented by Wu et al. [10] shows that it is possible to use FO for water recovery and struvite precipitation from agricultural digestate. In the experiments described therein, more than 50% of water recovery was achieved, along with a 99% removal of phosphate and 93% removal of ammonium nitrogen. In addition, the studies by Camilleri-Rumbau et al. [16] indicate the high potential of this process for purifying the liquid fraction of agricultural digestate. Regardless of the process conditions used, ammonium nitrogen removal was at the 95.5% level. These authors suggest that FO can be extremely useful for purifying the digestate, thus rendering it useful in agriculture. Similar conclusions can be found in other publications [5,7,8,17]. In the case of treating the liquid fraction of digestate from a biogas plant, the receiving solution can be a concentrate of fertilizer substances [18–20]. The water from the digestate permeating the membrane can be used to dilute this concentrate, as its original concentration may be too high for it to be used directly in agriculture. Another example might be seawater or groundwater with increased salinity, which might be made suitable for watering plants after dilution with water extracted from the digest [21,22].

While many studies have been conducted on the agricultural biogas plant digestate liquid fraction (e.g., [23–25]), there are few reports on the treatment of liquid municipal waste biogas plant digestate. Furthermore, despite the examples of various applications of the FO process cited earlier in the literature, to our knowledge there are no reports on the application of the integrated struvite precipitation—forced osmosis process for treatment of the digestate liquid fraction. The digestate liquid fraction is a mixture of many organic and inorganic components; most of these can be utilized, however, they may negatively affect the FO water recovery process. Thus, we decided to conduct a study to determine the effect of struvite precipitation (as one of the potential products obtainable during digestate management) on the performance of the membrane process. The effect of the struvite precipitation–FO integrated process on the changes in the organic matter properties present in the treated solution (particle size distribution,  $\zeta$ -potential) was investigated, as was its suitability for treatment of the liquid fraction of digestate from municipal waste biogas plants.

#### 2. Materials and Methods

The study was conducted for the liquid fraction of digestate from a biogas plant processing the organic fraction of municipal waste. This fraction was from one of the Polish waste management plants located in the Lower Silesia province  $(50^{\circ}53'15.5'' \text{ N} 17^{\circ}23'28.0'' \text{ E})$ . It was separated from digestate pulp with sedimentation centrifuges. The characteristics of the test solution are shown in Table 1. Physico-chemical analysis of the solution was carried out according to the Standard Methods for the Examination of Water and Wastewater, 23rd Edition [26].

 Table 1. Properties of the liquid fraction of municipal digestate.

Index	Value
рН	7.23
Temperature, °C	21
Conductivity, mS/cm	20.3
Dry residue, mg/dm <sup>3</sup>	55,820
Alkalinity, mmol/dm <sup>3</sup>	150
Total hardness, mval/dm <sup>3</sup>	753
Chemical oxygen demand (COD), mg $O_2/dm^3$	11,450
5-days biochemical oxygen demand (BOD <sub>5</sub> ), mg $O_2/dm^3$	3600
Dissolved organic carbon (DOC), mg C/dm <sup>3</sup>	4210
$N-NH_4^+$ , mg/dm <sup>3</sup>	776
$N-NO_2^-$ , mg/dm <sup>3</sup>	5.9
$N-NO_3^-$ , mg/dm <sup>3</sup>	below level of detection
$PO_4^{3-}$ , mg/dm <sup>3</sup>	21.2
Mg, mg/dm <sup>3</sup>	235
$Ca, mg/dm^3$	420
$K, mg/dm^3$	3220
Li, mg/dm <sup>3</sup>	7
$P, mg/dm^3$	21.4

The molar ratio of N:Mg:P in the test solution was 40.1:14.2:1; hence, there was a need to dose the Mg and P compounds in order to ensure the optimal proportion of these components for struvite precipitation. In the tests conducted, two chemical reactants were added to the digestate solution:  $MgCl_2$  as magnesium supplement, and  $NaH_2PO_4$  as phosphorus supplement. Their characteristics are shown in Table 2.

Table 2. Characte	rization of the cl	nemical reagents	used in struvi	te precipitation	[27,28]
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	Magnesium Chloride	Monosodium Phosphate
manufacturer	Chempur	
chemical formula	MgCl <sub>2</sub>	NaH <sub>2</sub> PO <sub>4</sub>
molar mass, g/mol	95.211	119.98
form	solid	solid
color	colorless to white	white to colorless
odour	odourless	n.a.
рН	5–6.5 (5%, 20 °C)	4–4.5 (5%, 20 °C)
density, g/cm <sup>3</sup>	1.57 (20 °C)	1.91 (20 °C)
solubility in water, g/dm <sup>3</sup>	2430 (20 °C)	n.a.

The FTS H<sub>2</sub>O membrane from Sterlitech Corporation made of cellulose triacetate with 140 cm<sup>2</sup> of effective filtration area was used to carry out FO. The manufacturer provides that the membrane can operate in temperatures up to 50 °C and within a pH range of 3–7 [29]. According to our own measurements, its wetting angle is  $32.2^{\circ}$ .

The integrated process involved a combination of struvite precipitation and FO. Experiments related to the precipitation of struvite from the liquid fraction of the digestate were carried out with parameters determined as being the most effective in earlier studies [30]. The process was carried out at pH 9.0. The sample of the digestate, with a volume of 500 cm<sup>3</sup>, was set on a Velp Scientifica FC6S mechanical stirrer. MgCl<sub>2</sub> and NaH<sub>2</sub>PO<sub>4</sub> were then dosed into the sample at 1.318 g/dm<sup>3</sup> and 2.084 g/dm<sup>3</sup>, respectively. The doses of the

reactants were set such that after taking into account the concentrations of  $Mg^{2+}$ , N-NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> in the test solution, the molar ratio of N:Mg:P reached 5.13:1:1. The temperature of the solution was 21 °C. After adding in the appropriate amount of reagents, the pH was adjusted to 9.0 with 0.1 mol/dm<sup>3</sup> NaOH. According to the literature, these properties (temperature and pH) promote struvite precipitation [31]. The samples were then stirred for 5 min at a rate of 160 rpm, followed by 30 min of sedimentation. The properties of the solution obtained after struvite precipitation are shown in Table 3.

Index	Value
Conductivity, mS/cm	19.7
pH	9.0
$COD, mg O_2/dm^3$	10,360
$BOD_5$ , mg $O_2/dm^3$	3510
DOC, mg C/dm <sup>3</sup>	3990
$N-NH_4^+$ , mg/dm <sup>3</sup>	772
Mg, mg/dm <sup>3</sup>	23.1
Ca, mg/dm <sup>3</sup>	42.3
K, mg/dm <sup>3</sup>	2970
Li, mg/dm <sup>3</sup>	6.9
$P, mg/dm^3$	1.9

Table 3. Properties of the liquid fraction of municipal digestate after struvite precipitation.

The pretreated liquid (indicated in the text as solution A) was then subjected to FO for 180 min. Experiments were performed using a laboratory SEPA FO CELL plant from Sterlitech Corporation (Figure 1), with a 0.014 m<sup>2</sup> membrane with an active layer facing the feed solution. The installation allows for cross-flow separation tests, with a flow rate in the range of 10–100 dm<sup>3</sup>/d and a maximum operating pressure of 6.9 MPa. Its main elements include a SEPA FO cell (active surface dimensions: 0.97 mm × 14.7 cm × 9.53 cm), a feed solution tank, a draw solution tank, two peristaltic pumps (Gear Pump Drive by Masterflex) with variable flow rate and a pressure of 7.6 MPa that allows fluid circulation in the system, and two digital balances (Isolab by Archem) for monitoring weight changes of the feed and draw solution. The minimum volume of each tank was equal to 3.7 dm<sup>3</sup>. The cross-flow velocity of fluid in the system was 0.2 m/s. In the experiments, NaCl solutions of 0.5, 1, and 3 mol/dm<sup>3</sup> were used as receiving (draw) solutions. During the process, chloride concentration, conductivity, and DOC concentration were measured in the feed solution and in the receiving solution.

All treatment experiments were duplicated.

Particle size distribution was measured by a Mastersizer 2000 laser diffractometer (Malvern Panalytical Ltd., Malvern, UK) equipped with a HydroMu dispersion device (Malvern Panalytical Ltd., Malvern, UK) with a particle size measurement range of 0.1–2000  $\mu$ m. During measurement, depending on the concentration of solid particles, about 3 cm<sup>3</sup> of the solution was added into a 700 cm<sup>3</sup> beaker filled with water circulating in the measuring cell. Particle size distribution was measured without ultrasound (the suspension was circulated through the measuring cell, with no ultrasound generated), followed by ultrasound sonication of the suspension (this took place in a beaker from which the suspension was pumped and circulated through the measuring cell) until the particle size distribution stabilized (i.e., until the disintegration of any agglomerates). Particle size distributions were determined by a Nicomp 380 DLS apparatus (Nicomp Particle Sizing Systems, Santa Barbara, CA, USA), in which the dynamic light scattering (DLS) method is used to study particle size distributions in samples with particle sizes of  $1 \text{ nm}-5 \mu \text{m}$  [32]. The measurement was carried out in about 3.5 cm<sup>3</sup> of diluted suspension placed in a chamber. Using the Nicomp analysis algorithm, complex multimodal distributions were analyzed with the highest resolution and repeatability.



**Figure 1.** Diagram of the SEPA FO CELL installation (1—feed solution tank, 2—feed solution pump, 3—draw solution tank, 4—draw solution pump, 5—concentrate control valve, 6—draw solution control valve, 7—concentrate pressure gauge, 8—draw solution pressure gauge, 9—concentrate flow meter, 10—draw solution flow meter, 11—SEPA FO cell).

The  $\zeta$ -potential was measured at 25 °C with a  $\zeta$ -potential analyzer (Zetasizer 2000, Malvern Panalytical Ltd., Malvern, UK). The diluted test solution was conditioned in a beaker for 10 min at the specified pH. The pH was adjusted with sodium hydroxide or hydrochloric acid. Then, the test solution was placed in an electrophoretic chamber by means of a syringe. The value of the  $\zeta$ -potential was determined as the average of five successive measurements.

#### 3. Results

The preliminary studies were aimed at determining the feasibility of precipitating struvite from the liquid fraction of municipal-derived digestate. The research was intended to find a way to both improve the final quality of the test solution and reduce the fouling of membranes applied in the subsequent purification step. Figure 2 shows the removal efficiency of selected components from samples of the liquid fraction of the digestate in which struvite was precipitated by employing MgCl<sub>2</sub> salt (which is an external source of magnesium) and NaH<sub>2</sub>PO<sub>4</sub> (which is an internal source of phosphorus). The adopted molar ratio of N:Mg:P of 5.13:1:1 brought about a low degree of organic compound removal. COD, BOD<sub>5</sub>, and DOC concentrations in the pretreated digestated (supernatant) decreased by a maximum of 13% compared to the concentrations in the initial sample. The removal efficiency of N-NH<sub>4</sub><sup>+</sup> was 48%. The resulting effect may be partly due to the desorption of gaseous  $NH_3$ , which at pH 9 can account for about 30% of the ammonium nitrogen in solution. The efficiency of magnesium and calcium ion precipitation from the digestate was about 91%, while that of potassium was about 14% as compared to the concentration in the initial sample. Negligible removal of Li occurred, along with an increase in the concentration of Na ions, which is completely understandable due to the application of a phosphorus source in the form of NaH<sub>2</sub>PO<sub>4</sub> to the treated digestate. On the other hand, the concentrations of phosphorus ions in the treated sample of digestate (84%) decreased significantly. The adopted conditions are likely to have favored the precipitation of this element in the crystalline form of potassium struvite (MgKPO<sub>4</sub>  $\cdot$  6 H<sub>2</sub>O).



Figure 2. Removal efficiency of selected contaminants in the analyzed sample during struvite precipitation.

An analysis of the precipitates performed with a scanning electron microscope (Figure 3) confirmed that crystalline forms of struvite were separated from the solution of the liquid fraction of the digestate as a result of chemical precipitation. The pictures show a large amount of organic matter and a large number of microorganisms.



**Figure 3.** SEM images of sediment after struvite precipitation at a molar ratio of 5.13:1:1 from municipal liquid digestate.

Studies on the purification of the liquid fraction of digestate by the integrated process of struvite precipitation—FO were begun by determining the effect of the duration of the process and the draw solution osmotic pressure (Table 4) on the flux of water permeating the membrane from the solution of liquid digestate after struvite precipitation.

NaCl Concentration	Osmotic Pressure	
[mol/dm <sup>3</sup> ]	[MPa]	[atm]
0.5	2.478	24.46
1	4.985	48.93
3	14.87	146.8

Table 4. Properties of draw solutions.

Figures 4-6 present the results of experiments conducted with redistilled water as a feed solution. Redistilled water can serve as a reference point for the results, as it has negligibly low osmotic pressure and does not show the presence of any contaminants. It was observed (Figure 4) that as the concentration of NaCl in the draw solution decreased, the water flux declined. This was a result of the decreasing value of the driving force of the process. In the case of FO of liquid digestate, similar trends were observed as for redistilled water, with the flux values, however, being much lower than those measured for water. This was due to the fact that the difference in osmotic pressures on both sides of the membrane was smaller for the digestate solution/receiving solution combination than for the redistilled water/receiving solution system. Analyzing the effect of process duration on the change in water flux, it was noted that it successively decreases. This is due to the decreasing osmotic pressure of the receiving solution and the progressive blockage of the membrane. This effect was found regardless of the concentration of NaCl in the receiving solution. In this respect, the results are consistent with the literature reports [33–35]. This was due to the fact that the water diffused through the membrane, the receiving solution diluted, and the water flux decreased as a result of the decreasing value of the driving force of the process, which is the difference in osmotic pressures between the solutions on either side of the membrane.



**Figure 4.** Water flux time dependence of FO for different concentrations of NaCl in the receiving solution for redistilled water and solution of the digestate after struvite precipitation.



**Figure 5.** Changes of the conductivity in: (**a**) the draw solution and (**b**) the feed solution with the FO process duration.

Figures 5 and 6 show the changes in conductivity and chloride concentration in the feed and receiving solutions, respectively, as a function of time. The conductivity in the feed solution increased slightly with process time, from 28.9 mS/cm to 34.2 mS/cm on average (in the case of digestate solution after struvite precipitation) and from 0 to 1.9 mS/cm (in the case of redistilled water) due to the reverse permeation of salts through the membrane. The literature [36] indicates that the membrane used in FO with an average pore radius of 0.37 nm can retain most multivalent ions and organic pollutants. However, salt ions (a Na<sup>+</sup> ion with a hydration radius of 0.36 nm and a Cl<sup>-</sup> ion of 0.33 nm) [37] were able to penetrate the FO membrane, a phenomenon known as reverse salt transport. In the draw solution, on the other hand, the conductivity decreased slightly over time as a result of dilution. Similar trends were observed when analyzing chloride concentrations in both solutions. Over time, the flow of water through the membrane caused dilution of the receiving solution.

Concurrently, a small amount of salt permeated through the membrane in the opposite direction (from the draw solution to the feed solution) due to diffusion (for the redistilled water) and concentration (for the digestion fluid), causing the salt concentration in the feed solution to increase on average down to  $625 \text{ g/m}^3$  and from  $4850 \text{ g/m}^3$  to  $6820 \text{ g/m}^3$ , respectively. Similar conclusions can be found in other works [38–41].



**Figure 6.** Changes of chloride concentration in: (**a**) the draw solution and (**b**) the feed solution with the FO process duration.

Due to the nature of FO processes, it was reasonable to check whether pollutants present in the liquid fraction of the digestate after struvite precipitation, which is the feed solution in the ongoing process, can permeate through the membrane into the receiving solution (NaCl solution). This could negatively affect the subsequent regeneration of the receiving solution and water recovery. The results presented in Figure 7 clearly show low penetration of organic substances (<0.1%). The amount of organic matter as determined by DOC concentration and colour increased to a non-significant degree with the duration of FO and as the initial concentration of NaCl in the draw solution increased. For example, after 180 min of the process with a brine solution of 3 mol/dm<sup>3</sup> NaCl as the receiving solution, the DOC concentration was 2.3 g C/m<sup>3</sup> due to the permeation of organic compounds and the colour intensity was 5 g Pt/m<sup>3</sup>. COD and BOD<sub>5</sub> were determined in the draw solution; however, because the values were at a very low level they are not presented in the figure. The results show that the FO membrane is an effective barrier to the transport of organic compounds in the feed solution–receiving solution direction.



**Figure 7.** Changes in DOC concentration and colour intensity in the draw solution with the FO process duration.

Because the liquid fraction of the digestate in which struvite precipitation had previously been carried out was subjected to FO as a protection against excessive membrane fouling, and samples of the purified liquid (FO feed) were analyzed for particle size distribution and changes in  $\zeta$ -potential. The visual effect of the purification of municipal digestion liquid at various stages, including by FO after struvite precipitation, can be observed in Figure 8. As can be seen, the precipitation of struvite, with which part of the organic matter (including compounds responsible for colour intensity), was separated from the digestate solution, resulting in a decrease in colour intensity. FO used in the next step to recover water affected the colour changes of the feed solution. The solution obtained by applying 3 mol/dm<sup>3</sup> NaCl as a receiving solution had the highest colour intensity after FO. As shown in Figure 4, the use of 3 mol/dm<sup>3</sup> NaCl as the draw solution produces the highest flux of water and retrieves the largest amount of water, which results in the greatest concentration of coloured substances in the feed solution. The lower colour intensity as compared to the solution of the digestate treated with struvite precipitation of the liquid after FO carried out with 0.5 and 1 mol/dm<sup>3</sup> NaCl as the draw solution could be the result, among other things, of a change in the chromophoric properties of the organic matter due to the penetration of salt into the feed solution.



**Figure 8.** Visual changes in the quality of the liquid fraction of the digestate after successive stages of purification (a—liquid raw digestate; b—solution A (after struvite precipitation); c—solution A after FO with 0.5 mol/dm<sup>3</sup> NaCl; d—solution A after FO with 1 mol/dm<sup>3</sup> NaCl; e—solution A after FO with 3 mol/dm<sup>3</sup> NaCl).

In addition, particle size changes were analyzed during integrated struvite precipitation/FO. As shown in Figure 9, pretreatment of the digest by chemical precipitation of struvite resulted in a significant reduction in the mean diameter of the particles present in the tested solution. This confirms early observations that macromolecules and colloids of the largest size are separated from the solution along with struvite. Measurements of particle size distribution taken by means of the DLS method show that the finest particles (about 675 nm) are present in the sample after FO, when a 0.5 mol/dm<sup>3</sup> NaCl solution was applied as the receiving solution. The increase in the driving force of the process (higher concentration of NaCl in the receiving solution) resulted in an increase in the particle size in the feed solution after FO (to about 807 nm and 1113 nm for 1 and 3 mol/dm<sup>3</sup> NaCl, respectively). This could have been a result of the concentration of the feed solution indicated earlier and the formation of larger particles due to their bridging by salts permeating from the feed solution.



Figure 9. Average particle diameter in the tested solutions after struvite precipitation and FO.

The results of particle size distribution analyses based on the laser diffraction method are shown in Figures 10 and 11. This method is employed under conditions of continuous mixing and pumping of the dilute dispersion through the measuring cell. In this case, there is no possibility of sedimentation of larger particles, which is otherwise common in dynamic light scattering measurements, where the sample is placed in a cuvette and larger particles settle on the bottom. For the raw digestate, lower and upper deciles of about 1  $\mu$ m and 34  $\mu$ m were obtained, respectively, and half of the particle population had diameters of up to about 7.7  $\mu$ m. Sonication of the sample during measurement of the particle size distribution of the raw digestate allowed the individual diameters  $(d_{10}, d_{50} \text{ and } d_{90})$  to be reduced to 0.8, 4.6 and 23  $\mu$ m, respectively (Figure 10). The analysis of particle size distribution in solution A (Figure 11) revealed that the diameters of  $d_{50}$  and  $d_{90}$  decreased to 2  $\mu$ m and 19  $\mu$ m, respectively, compared to the values obtained for the raw digestate. In contrast, the lower decile remained virtually unchanged (about  $0.9 \mu m$ ). The use of an integrated process combining struvite precipitation with FO did not practically change the particle size distribution in terms of the finest and medium fractions. The only noticeable differences were in the share of the largest particles. The results confirm that the digestate particles form agglomerates that can be easily broken up.



**Figure 10.** Raw digestate liquid fraction particle size distribution (red line—without sonication, green line—with sample sonication).



**Figure 11.** Particle size distribution for the liquid raw digestate, solution A (digestate after struvite precipitation) and the feed solution (solution A after FO).

In the course of the study, the isoelectric point values of the particles were determined in the liquid fraction of digestate, in the digestate after struvite precipitation, and in the samples after integrated struvite precipitation/FO. This may be important from the point of view of conducting the integrated process, as at the isoelectric point (pH<sub>IEP</sub>) the particles have the lowest solubility, the smallest viscosity, and the smallest osmotic pressure. Measurements of the  $\zeta$  potential in the pH range from 1.2 to 12.7 allowed the pH<sub>IEP</sub> to be determined. For all samples tested, the value was about 1.9 (Figure 12). Above pH<sub>IEP</sub>, the value of the  $\zeta$  potential was negative, reaching the lowest value of -33 mV for samples of the digestate solution subjected to struvite precipitation and FO using NaCl solutions of 1 mol/dm<sup>3</sup> and 3 mol/dm<sup>3</sup>. In general, the course of the correlation of  $\zeta$  potential with pH did not differ significantly between samples; only the raw digestate and the sample after struvite precipitation showed lower values of  $\zeta$  potential at the same pH. This may indicate that despite the higher ionic strength in the samples after FO with electrolyte (NaCl), the potential at the slip boundary is higher. 10

5

0

-5

-10

-15

-20

-25

-30

-35

ζ potential, mV





The results obtained with the struvite precipitation—FO integrated process indicate that it can be effectively used to treat the municipal digestate liquid fraction. The water recovered from the digestate (after removal of excess salt or dilution) can be used agriculturally, e.g., for crop watering or fertiliser preparation. However, it should be kept in mind that the efficiency of water recovery from the liquid fraction of the digestate preceded by struvite precipitation is determined by the difference in electrochemical potential between the feed solution and the receiving solution. As shown earlier, an increase in the salt concentrated, which adversely affects the properties of the liquid via increased salinity. This may be undesirable, for example, when trying to use the concentrated digestate as an organic fertilizer.

The proposed technological solution for the management of digestate, i.e., preceding the water recovery stage using forward osmosis with struvite precipitation, fits the trend of research aimed at promoting a closed-loop economy in the waste management sector. Such an approach to the management of digestate has been presented, for example, by Jurgutis et al. [42], who showed that digestate used as biofertilizer can affect soil properties and plant growth. However, the work carried out thus far on incorporating the management of digestate into the idea of a circular economy [43] has been limited mainly to the use of its fertilizing properties (source of organic matter and certain elements needed for plant growth). The proposed approach to processing the liquid fraction of the digestate makes it possible to take advantage of the properties of this waste stream and allows for the recovery of water, which is an extremely valuable and limited resource these days. Another advantage of the proposed technology is that it requires much less energy consumption than alternative processes used to produce fertilizers (i.e., thermal or vacuum processes [44]) or treat the liquid fraction of the digestate (i.e., pressure-driven membrane processes [45]. It should be borne in mind that in previous work, in an effort to close the circularity of matter, the precipitation of struvite, for use as a mineral fertilizer was carried out during the management/treatment of wastewater [46,47], while in our study [30] this fertilizer was obtained from the liquid fraction of digestate, which shows the potential of this liquid in terms of promoting a circular economy.

## 4. Conclusions

The present study showed that the liquid fraction of the digestate generated during the treatment of the organic fraction of municipal waste, when further processed using an integrated process involving struvite precipitation and forward osmosis, can allow for the obtaining of very valuable products such as struvite, concentrated organic matter, and water. Any of these products can be used in agriculture; with natural, mineral and organic materials in decline, as well as limited water resources, all sectors of the economy, including waste management, are seeking to introduce the concept of a circular economy, in which that existing waste products becomes a source of valuable raw materials. The precipitated struvite and concentrated organic matter can be used as fertilizers, while the water can be utilized to irrigate plant crops.

Studies on the effectiveness of digestate purification carried out by struvite precipitation and FO have demonstrated the usefulness of this process for recovering water and valuable components from digestate obtained from municipal waste processing. The research presented in this thesis leads to the following conclusions:

- Struvite precipitation allowed for organic compounds removal of 2.5–9.5% and removal of Mg/Ca/P up to ca. 90%.
- A novel concept of struvite precipitation from liquid digestate applied at the solution pretreatment stage before FO allowed us to obtain a final solution of significant quality (DOC removed by 99.9%) and protected the membranes from excessive blockage.
- FO performed on a stream of digestate pretreated by chemical precipitation of struvite yielded higher values of water flux, as the concentration of salt in the receiving solution increased and there was practically no infiltration of organic substances into the draw solution.
- The removal of the macromolecular fraction of organic compounds from the digestate took place mainly simultaneously with the chemical precipitation of struvite.
- An increase in the salt concentration of the draw solution, which allowed for a greater water recovery, resulted in the aggregation of the concentrated organic molecules in the feed solution.
- The correlation of the ζ potential with pH did not change when comparing raw digestate and concentrated samples (after process performance); pH<sub>IEP</sub> was about 1.9.

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