Simultaneous Recovery of Struvite and Irrigation Water for Agricultural Purposes Obtained from Dewatering Liquor through Electrodialysis

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Abstract: Wastewater contains resources, which can be recovered for secondary use if treated properly. Besides research in zero liquid discharge solutions, the aim of the study was a simultaneous recovery of products from a wastewater treatment plant’s dewatering liquor. To be specific, we investigated a simultaneous recovery of struvite and irrigation water using electrodialysis (ED) in laboratory experiments. Two products were obtained from ED—concentrate and diluate. The concentrate was precipitated to obtain struvite. On average, 11 g of wet precipitate (including 17.58% of dry solids) were obtained from 1 L of concentrate. Crystal phases were confirmed by powder X-ray diffraction (XRD), with showing 94–97% recovery of struvite, while the remaining 3–6% were identified as hazenite. The average yield of crystal struvite was 1.76 g. Both struvite and hazenite may further be used as a fertilizer. Next, we suggest using the second ED product, the diluate, as irrigation water if it meets the irrigation water requirements. Attention was paid to the concentrations of dissolved solids (DS) in diluate, which decreased by an average of 93% compared to the input values in the dewatering liquor. In line with the observed Czech or EU standards indicators, we can say that the diluate can be used in agriculture, namely as irrigation water (Category I—water suitable for irrigation).

Keywords: dewatering liquor; wastewater treatment plant (WWTP); struvite; irrigation water; electrodialysis; zero liquid discharge (ZLD)

1. Introduction

The world population is growing, and sustainable and responsible food production is important to ensure sufficient food supplies. One of the requirements for proper plant growth is a sufficient amount of phosphorus [1] which is mainly obtained by mining phosphorus rock. As much as 80% of total phosphorus is subsequently used to produce fertilizers for agriculture [2], thus making phosphorus an irreplaceable component of this sector. However, natural phosphorus reserves are depletion, and their quality is falling [3]. The available reserves of phosphorus rock are estimated to last only another 50–300 years [4,5]. Moreover, the availability of phosphorus rock may also be influenced by political, economic, and geographic situations in the site of the rock deposit [4,6]. Already in 2014, the mineral resource of phosphorus was identified as critical by the European Union [7].

However, phosphorus is regarded differently by farmers and wastewater treatment plant operators. Farmers perceive phosphorus as a necessary component for growing crops, while sewage treatment plant operators approach it as a waste substance to dispose of [4]. A solution is seen in the recovery of phosphorus after its primary use, e.g., from wastewater. In addition, increased concentrations of phosphorus in water recipients cause...
eutrophication, which has become a global issue [1]. Overall, the increasing demands for raw materials call for the implementation of circular economy models and the recovery of secondary raw materials from waste products.

In wastewater management it is advisable to proceed as far as zero liquid discharge (ZLD) [6,8]. ZLD is a series of processes aiming to eliminate the aqueous fraction of waste, recover secondary raw materials, and reuse the purified water. Such solutions are particularly suitable for urban environments with well-built networks of sewage treatment plants, leading to the recovery of the substances contained in the wastewater and the water itself [2]. This can also solve the issue of higher amounts of nutrients in water recipients, which causes eutrophication, and a renewable source of phosphorus for agriculture.

The current methods of removing and extracting phosphorus from wastewater include physical, chemical, biological, and physicochemical methods [9–11]. Considering all the available options and factors, a feasible solution lies in the precipitation of magnesium ammonium phosphate (struvite). The solution is based on the combination of physicochemical methods with addition of magnesium [12]. In wastewater treatment plants, struvite naturally forms in wastewater rich in phosphorus and nitrogen under co-occurrence of magnesium and appropriate pH value [13]. For wastewater treatment plant operators, the spontaneous precipitation of struvite in technological devices, such as pumps and pipes, is a big issue because these precipitates are very difficult and expensive to remove [14]. Targeted precipitation of struvite as a white, water-soluble, crystalline substance, suitable for fertilizing agricultural soil is carried out in the molar ratio Mg\(^{2+}\):PO\(_4^{3-}\):NH\(_4^+\) in 1:1:1 [2,15]. This precipitation reaction can be expressed by a simplified Equation (1).

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O}
\]  

(1)

Scientists are looking for new ways of sourcing struvite and governments are optimizing laws to legalize struvite as a fertilizer. For example, the European Union Regulation (EU) 2019/1009 in [16] of the European Parliament and of the Council says that the market demand for struvite as a fertilizer has been identified, and also anticipates the related scientific analyses to be launched to deal with the present requirements in connection with the use of struvite in the EU internal market [16]. For example, Cai et al. in [10] conducted a pilot study of the extraction of phosphorus from synthetic wastewater using electrodialysis (ED) with magnesium anode, where, at optimum pH 8.8 and 200 L/s flow, the phosphate concentration in the diluate was detected as 0.5 mg/L, compared to the 10 mg/L in the input flow. The authors set the price of 1 kg of phosphate obtained by this method at USD 31.27 [10]. Thant Zin and Kim in [17] investigated the extraction of struvite from nutrient-rich wastewater from the food industry and sewage sludge using Mg-Biochar. This biochar, on which magnesium is impregnated, is used as an ingredient necessary for struvite precipitation. Mg-Biochar prepared this way subsequently undergoes physical and chemical adsorption of NH\(_4\)-N and PO\(_4\)-P. The authors state that struvite was the most represented precipitate on the surface of Mg-Biochar and describe this method as promising for commercial use [17].

However, it is also necessary to observe the amount of heavy metals that can transfer into the struvite precipitate. For example, Huang et al. in [18] observed the effect of process parameters on the amount of heavy metals in struvite, namely Zn\(^{2+}\), Cu\(^{2+}\), and Cr\(^{3+}\). The measurements were performed on struvite extracted from synthetic wastewater from pig farming. They found that the increasing pH from 8 to 10.5 leads to a decrease in the content of these heavy metals. The contents of heavy metals were also affected by the molar ratio of total ammonia nitrogen (TAN) to phosphate phosphorus (PO\(_4\)-P). Increasing the TAN:PO\(_4\)-P ratio from 1:1 to 11:1 has a positive effect on reducing the concentrations of heavy metals. On the other hand, Mg:PO\(_4\)-P molar ratio was found as unimportant. In conclusion, the authors state that a consistent setting of parameters, namely TAN concentration and pH, is the way to significantly reduce the heavy metal content during struvite precipitation [18].

Sýkorová et al. in [19] claim that some wastewaters are not suitable for struvite recovery due to low nutrient contents. Not only wastewater treatment operators need to
deal with struvite formation, but researchers have also been looking for ways to reuse treated wastewaters, especially in connection with prolonged periods of drought [20].

Based on the above, the main goal of this study was to concentrate the phosphates in real dewatering liquor from wastewater treatment plant (WWPT) by electrodialysis (ED) and to obtain struvite by precipitation from the concentrate. In addition, the so-called diluate is formed, which can be used, for example, as water for irrigation. Therefore, we can simultaneously obtain struvite and irrigation water from WWPT dewatering liquor.

The aim was also to approach the goals of zero liquid discharge (ZLD). For the full implementation of ZLD it is important to solve the last step, which is dealing with the aqueous waste from struvite precipitation. However, this is still a matter of active research.

2. Materials and Methods

2.1. Dewatering Liquor (DL)—Graphical Representation of the Procedure

Raw DL is a waste product from anaerobic digestion and currently is pumped back into the WWTP inflow because it is still highly polluted and cannot be used or discharged untreated. It has no direct use either. In line with the valid legislation in the Czech Republic (according to ČSN 75 7143 in [21]) it cannot be even used as irrigation water as the value of dissolved solids exceeds the limit set in the Standard three times and places it in the category of water “unsuitable for irrigation”.

Figure 1 below describes the current practice (in black color). Note that standard WWTPs are not equipped with struvite precipitation technology. To better understand our experiments, we added our solution into the current block diagram (in red color), where dewatering occurs in two stages.

![Figure 1](image-url)

**Figure 1.** Contrasting the existing WWTP practice and our proposed solution incorporating ED into municipal WWTPs (where: black color describes the existing practice, and red color represents our solution). Note that DL is dewatering liquor, C is concentrate, and D is diluate.

DL is further concentrated using electrodialysis (ED). Struvite is precipitated from the concentrate (C), and the reject water is discharged into the inflow into the WWTP. At the same time, the diluate (D) can also be used, for example, as water for irrigation.
2.2. DL Samples

Three 20 L samples of dewatering liquor were collected from outlet of sludge decanter of a municipal WWTP with the 88,000-population equivalent (Karviná, Czech Republic) every four weeks during spring of 2020 (from March to May). Normally, this DL is fed as an inflow to the WWTP. The DL was filtered by α-cellulose membrane filter Munktell Ahlstrom 390, Ahlstrom-Munksjö, Helsinki, Finland (particle capture 3–5 µm) and the physicochemical parameters of the treated DL (after filtration) samples are given in Table 1. DL samples treated in this way were the input DL for electrodialysis (ED) to recover struvite from concentrate, and irrigation water from diluate.

Table 1. Physicochemical parameters of input DL.

| Parameter     | Unit          | Sample 1 (March 2020) | Sample 2 (April 2020) | Sample 3 (May 2020) |
|---------------|---------------|-----------------------|-----------------------|---------------------|
| pH            | (-)           | 8.12                  | 8.23                  | 8.01                |
| Conductivity  | (mS/cm)       | 8.02                  | 7.94                  | 8.10                |
| Temperature   | (°C)          | 20.60                 | 20                    | 20.10               |
| Turbidity     | (NTU)         | 255                   | 260                   | 250                 |
| N<sub>total</sub> | (mg/L)       | 1540                  | 1380                  | 1700                |
| NH<sub>4</sub><sup>+</sup> | (mg/L)       | 1112                  | 1118                  | 1106                |
| PO<sub>4</sub><sup>3-</sup> | (mg/L)       | 420                   | 423                   | 417                 |
| Mg<sup>2+</sup> | (mg/L)       | 21                    | 19                    | 25                  |
| COD<sub>Cr</sub> | (mg/L)       | 319                   | 323                   | 315                 |
| DS<sub>105</sub> | (mg/L)       | 2595                  | 2417                  | 2803                |

Note: Power of hydrogen, conductivity, and temperature were measured by WTW GmBH Multi340i, WTW, Prague, Czech Republic; turbidity was measured according Standard ČSN EN ISO 7027-1 [22]; N<sub>total</sub> was measured according Standard ČSN EN ISO 11905-1 [23]; PO<sub>4</sub><sup>3-</sup> was measured according Standard ČSN EN ISO 6878 [24]; Mg<sup>2+</sup> was measured spectrometrically according to Standard ČSN EN ISO 15587-2 [25]; COD was measured according to Standard ČSN ISO 6060 [26]; DS<sub>105</sub> was measured gravimetrically according to Standard ČSN 75 7346 [27]. Note: measurement uncertainty—pH up to 3%, other indicators up to 5%.

2.3. Electrodialysis (ED)

Electrodialysis (ED) is an electrochemical membrane process. Electrodialysis transfers ions by using direct current as a driving force. Cation- and anion-exchange membranes are arranged alternately between electrode cells at both ends, and desalination and concentration are carried out utilizing the selectivity that these membranes can provide [28].

ED laboratory unit type EDR-Z (MEGA, Stráž pod Ralskem, Czech Republic) of P series with automatic voltage regulation was used to concentrate phosphorus in batch process. The ED module of EDR-Z/10-0.8 consists of two titan electrodes with a platinum layer and polarity reversal. The important ED module specifications and operating working parameters are summarized in Table 2. As mentioned above, two products were obtained during ED from the input DL: diluate and concentrate. For the struvite recovery experiments we needed 8 L of concentrate from each sample. Desalination (concentration) was performed in batch mode in a ratio of diluate to concentrate 1:1. The voltage on the module was 14 V. A 2% Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrode solution. From each sample of input DL there were 4 batch desalination tests adding up to 8 L of composite diluate and 8 L of composite concentrate obtained from each sample of input DL (the pH and concentrations of the observed metals are summarized in Section 3.3). A salt test with 2% Na<sub>2</sub>SO<sub>4</sub> was performed before and after DL ED to control ED module assembly and membrane fouling. Then, the ED module was cleaned and regenerated according to the recommendations of the ED manufacturer.
Table 2. ED module specifications and operating working parameters.

| Parameter                                      | Value           |
|------------------------------------------------|-----------------|
| Effective area of ED module                    | 1344 cm$^2$     |
| Effective area of one membrane                 | 64 cm$^2$       |
| Number of membrane pairs in ED module          | 10 pcs          |
| Anion-exchange membrane RALEX® AM(H)-PES       | 10 pcs          |
| Cation-exchange membrane RALEX® CM(H)-PES      | 11 pcs          |
| PP spacer (thickness)                          | 20 pcs (0.8 mm) |
| Electrodes (anode, cathode) Ti+Pt              | 2 pcs           |
| Hydraulic connection inner/outer               | Ø 6/8 mm        |
| ED module dimension (l × w × h)                | 128 mm × 90 mm × 250 mm |
| ED module weight                               | 1.5 kg          |
| Operating voltage (on membrane pair)           | 1–1.2 V         |
| Max. voltage                                   | 30 V            |
| Max. electrical current                        | 3 A             |
| Operating flow rate of diluate, concentrate    | 45–65 L/h       |
| Operating flow rate of electrode solution      | 50–60 L/h       |
| Operating temperature                          | 20–30 °C        |

Note: Capacity (batch process): 95% desalination of 1 L of 20 g/L Na$_2$SO$_4$ takes about 45 min at the temperature of 25 °C.

2.4. Struvite Recovery

Precipitation tests were realized in a jar stirrer (Lovibod ET 750, GmBH, Dortmund, Germany) in laboratory conditions. Phosphorus was precipitated from the ED concentrate into the form of struvite—MgNH$_4$PO$_4$ × 6H$_2$O, having added magnesium in the form of granulated MgSO$_4$ × 7H$_2$O. The addition of two quantities of magnesium sulphate was tested; the first molar ratio was PO$_4^{3-}$:Mg$^{2+}$ 1:1, and the second molar ratio was PO$_4^{3-}$:Mg$^{2+}$ 1:1.3. Next, the pH value of the solution was modified to 9 by 10% NaOH. The solutions were stirred at mixing column 50 rpm for 60 min and filtered. The obtained precipitate was left to dry in open air in laboratory conditions for 24 h before it was subjected to powder X-ray diffraction (XRD) analyses to identify the crystal phases of the precipitate (measurement uncertainty to 5%). XRD analyses were carried out using a Bruker-AXS D8 Advance instrument (Bruker, Mannheim, Germany) with a 2θ/θ measurement geometry and the positionally sensitive detector LynxEye under the following conditions: radiation CuKα/Ni filter, current 40 kV, 40 mA voltage, step mode with a step of 0.014° 2θ, and a total time of 15 s per step. Analysis of diffraction patterns was performed using the EVA software (Bruker-AXS, Mannheim, Germany) and the database PDF-2, release 2011 (International Centre for Diffraction Data, https://www.icdd.com/pdf-2/ (accessed 18 November 2021). The Rietveld method using the TOPAS software, version 4.2 (Bruker, Mannheim, Germany) was applied to verify the qualitative analyses and for its quantification. The final percentages of the precipitated struvite obtained under two different doses of magnesium sulphate are given in Section 3.2.

2.5. Heavy Metal and Dissolved Solids (DS) Analysis

We assumed that the diluate stream may be applied for irrigation purposes in agriculture. However, because supernatant liquor may contain heavy metals, the diluate was analyzed using two methods. The first was atomic absorption spectrometry (AAS) using a device Varian AA280FS (Agilent, Santa Clara, CA, USA). The second method to trace heavy metals was inductively coupled plasma mass spectrometry (ICP-MS), and a device
Analytik Jena GmbH PlasmaQuant MS Elite (Jena, Germany). The samples decomposition proceeded according to the Standard ČSN EN ISO 15587-2 [25].

3. Results and Discussion

3.1. Electrodialysis (ED)

The desalination of 2 L of the DL feed took 90 min on average. The resulting conductivity of the composite diluates and composite concentrates are shown in Table 3. The effect of membrane fouling was manifested by the prolongation of the time between individual batch tests by approximately 3 min, i.e., the 4th batch test lasted 99 min.

Table 3. Conductivity of input DL and ED products.

| Sample 1 | Conductivity (mS/cm) | Sample 2 | Conductivity (mS/cm) | Sample 3 | Conductivity (mS/cm) |
|----------|----------------------|----------|----------------------|----------|----------------------|
| Input DL | 8.02                 | Input DL | 7.94                 | Input DL | 8.10                 |
| Concentrate | 15.23              | Concentrate | 15.08               | Concentrate | 15.60              |
| Diluate | 0.33                 | Diluate | 0.30                 | Diluate | 0.38                 |

Note: Conductivity was measured by WTW GmBH Multi340i, WTW, Prague, Czech Republic. Measurement uncertainty up to 5%.

3.2. Struvite Recovery

The final percentages of the precipitated struvite obtained under two different doses of magnesium sulphate of individual samples are given in Table 4 below. Figures 2 and 3 show the XRD patterns of Sample 1 precipitate (enlarged the hazenite curves peaks).

Table 4. Percentages of phase values obtained from precipitates identified using XRD method.

| Molar Ratio Phase (%) | PO₄³⁻:Mg²⁺ 1:1 Struvite | PO₄³⁻:Mg²⁺ 1:1.3 Struvite |
|-----------------------|--------------------------|---------------------------|
| Sample 1              | 95                       | 97                        |
| Sample 2              | 93                       | 97                        |
| Sample 3              | 94                       | 98                        |

Note: Measurement uncertainty up to 5%.

Rietveld reliable factors are Rp 16.32, Rp 12.38 in molar ratio 1:1, and Rp 14.89, Rp 11.26 in molar ratio 1:1.3. The peaks may be asymmetrical due to the occurrence of several struvite modifications, see studies by Meira et al. in [29] and Heraldy et al. in [30], where the peaks are also asymmetrical.

The results imply that the supernatant concentrate from ED may be used to precipitate phosphorus in the form of struvite. The obtained precipitate contained at least 93% of struvite, while the remaining percentage was represented by hazenite (KNaMg₂(PO₄)₂·×14H₂O).

During the experiments we compared two molar ratios of PO₄³⁻:Mg²⁺ as the ratios represent an important part of phosphorus precipitation into the form of struvite [31]. In comparison with Sýkorová et al. in [19] when at best, they obtained a precipitate in the amount of 0.54 g/L of “raw” dewatering liquor (without concentration), of which 40% were struvite crystals. In our proposed procedure, i.e., concentration of DL and precipitation of struvite in concentrate, the average yield of precipitate per 1 L of concentrate was 10 g of wet precipitate from 1 L of concentrate (molar ratio 1:1). The 10 g of wet precipitate included 19.25% of dry solids. Using the molar ratio 1:1.3 we obtained 12 g of wet precipitate (including 15.91% of dry solids). This way, 1 L of concentrate produced 1.83 g of crystalline phase with 94% struvite content, i.e., 1.72 g of crystal struvite (molar ratio 1:1) and 1.85 g of crystalline phase with 97% struvite content, i.e., 1.79 g of crystal struvite (molar ratio 1:1.3).
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| Sample   | Conductivity (mS/cm) |
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| Concentrate | 15.23             |
| Diluate  | 0.33                 |
| Sample 2 | 7.94                 |
| Concentrate | 15.08             |
| Diluate  | 0.30                 |
| Sample 3 | 8.10                 |
| Concentrate | 15.60             |
| Diluate  | 0.38                 |

Note: Conductivity was measured by WTW GmBH Multi340i, WTW, Prague, Czech Republic. Measurement uncertainty up to 5%.

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The final percentages of the precipitated struvite obtained under two different doses of magnesium sulphate of individual samples are given in Table 4 below. Figures 2 and 3 show the XRD patterns of Sample 1 precipitate (enlarged the hazenite curves peaks).

Figure 2. XRD pattern of precipitate Sample 1—molar ratio PO$_4^{3-}$:Mg$^{2+}$ 1:1.

Figure 3. XRD pattern of precipitate Sample 1—molar ratio PO$_4^{3-}$:Mg$^{2+}$ 1:1.3.

Table 4. Percentages of phase values obtained from precipitates identified using XRD method.

| Molar Ratio | PO$_4^{3-}$:Mg$^{2+}$ 1:1 | PO$_4^{3-}$:Mg$^{2+}$ 1:1.3 |
|-------------|---------------------------|-----------------------------|
| Phase (%)   | Struvite                  | Hazenite                    |
| Sample 1    | 95                        | 5                           |
| Sample 2    | 93                        | 7                           |
| Sample 3    | 94                        | 6                           |

Note: Measurement uncertainty up to 5%.

Rietveld reliable factors are R$_{wp}$ 16.32, R$p$ 12.38 in molar ratio 1:1, and R$_{wp}$ 14.89, R$p$ 11.26 in molar ratio 1:1.3. The peaks may be asymmetrical due to the occurrence of several struvite modifications, see studies by Meira et al. in [29] and Heraldy et al. in [30], where the peaks are also asymmetrical.

The results imply that the supernatant concentrate from ED may be used to precipitate phosphorus in the form of struvite. The obtained precipitate contained at least 93% of struvite, while the remaining percentage was represented by hazenite (KNaMg$_2$(PO$_4$)$_2$·14H$_2$O).

During the experiments we compare two molar ratios of PO$_4^{3-}$:Mg$^{2+}$ as the ratios represent an important part of phosphorus precipitation into the form of struvite [31]. In comparison with Sýkorová et al. in [19] when at best, they obtained a precipitate in the amount of 0.54 g/L of “raw” dewatering liquor (without concentration), of which 40% were struvite crystals. In our proposed procedure, i.e., concentration of DL and precipitation of struvite in concentrate, the average yield of precipitate per 1 L of concentrate was 10 g of wet precipitate from 1 L of concentrate (molar ratio 1:1). The 10 g of wet precipitate included 19.25% of dry solids. Using the molar ratio 1:1.3 we obtained 12 g of wet precipitate (including 15.91% of dry solids). This way, 1 L of concentrate produced 1.83 g of crystalline phase with 94% struvite content, i.e., 1.72 g of crystal struvite (molar ratio 1:1).
3.3. Heavy Metal, Phosphate, and Dissolved Solids (DS) Analysis

Using AAS and ICP-MS we identified the concentrations of selected heavy metals in the input wastewater, the obtained diluate, and the concentrate. The values were compared with those stated in Standard ČSN 75 7143 [21], which is a document regulating conditions for water irrigation purposes. The concentrations of the measured heavy metals are stated in Table 5. The effect of ED on the concentration of heavy metals was not significant. This phenomenon is related to the permeability of the membranes and the degree of dissociation of individual metals and their ionic size, when in the ED process they pass between the diluate and the concentrate.

Table 5. Values of heavy metals in ED products of samples 1–3.

| Sample 1 | pH (-) | t (°C) | Cd (mg/L) | Co (mg/L) | Crtotal(mg/L) | Cu (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) | Fe (mg/L) |
|----------|------|-------|----------|-----------|---------------|--------|--------|--------|--------|--------|
| Input DL | 8.12 | 20.60 | <0.01    | <0.01     | <0.01         | 0.042  | 0.029  | 0.003  | 0.109  | 1.570  |
| Concentrate | 7.98 | 20.00 | <0.01    | <0.01     | <0.01         | 0.032  | 0.029  | 0.008  | 0.198  | 2.160  |
| Diluate | 5.46 | 20.00 | <0.01    | <0.01     | <0.01         | 0.027  | 0.022  | 0.002  | 0.109  | 1.460  |

| Sample 2 | pH (-) | t (°C) | Cd (mg/L) | Co (mg/L) | Crtotal(mg/L) | Cu (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) | Fe (mg/L) |
|----------|------|-------|----------|-----------|---------------|--------|--------|--------|--------|--------|
| Input DL | 8.23 | 20.00 | <0.01    | <0.01     | <0.01         | 0.039  | 0.034  | 0.003  | 0.112  | 1.548  |
| Concentrate | 8.01 | 20.00 | <0.01    | <0.01     | <0.01         | 0.033  | 0.031  | 0.008  | 0.195  | 2.165  |
| Diluate | 5.84 | 20.00 | <0.01    | <0.01     | <0.01         | 0.025  | 0.025  | 0.002  | 0.111  | 1.488  |

| Sample 3 | pH (-) | t (°C) | Cd (mg/L) | Co (mg/L) | Crtotal(mg/L) | Cu (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) | Fe (mg/L) |
|----------|------|-------|----------|-----------|---------------|--------|--------|--------|--------|--------|
| Input DL | 8.01 | 20.10 | <0.01    | <0.01     | <0.01         | 0.045  | 0.024  | 0.003  | 0.106  | 1.556  |
| Concentrate | 7.95 | 20.10 | <0.01    | <0.01     | <0.01         | 0.031  | 0.027  | 0.008  | 0.201  | 2.155  |
| Diluate | 5.08 | 20.10 | <0.01    | <0.01     | <0.01         | 0.029  | 0.019  | 0.002  | 0.107  | 1.432  |

Note: Measurement uncertainty—pH and t up to 3%, metals up to 20%.

Phosphate content in input and output streams is captured in Table 6. It is clear from the table that the phosphate concentration was doubled by ED. The results of the analysis of the filtrate show that phosphates precipitated with 99% efficiency.

Table 6. Phosphate content in input and output streams.

| Sample | Input DL (mg/L) | Concentrate (mg/L) | Diluate (mg/L) | Filtrate After Precipitation Molar Ratio 1:1 (mg/L) | Filtrate After Precipitation Molar Ratio 1:1.3 (mg/L) |
|--------|----------------|-------------------|----------------|-----------------------------------------------|-----------------------------------------------|
| 1      | 420            | 270               | 30             | 3.12                                         | 6.08                                         |
| 2      | 423            | 725               | 31             | 3.54                                         | 6.71                                         |
| 3      | 417            | 710               | 25             | 2.75                                         | 6.25                                         |

Note: Measurement uncertainty up to 5%.

Due to its composition, dewatering liquor (DL) falls into the category of water “unsuitable for irrigation” (see Table 1). This can be evaluated, for example, on the indicator “DS”, when the value measured in DL is in the range of 2500–2800 mg/L, while according to Czech Standard ČSN 75 7143 [21] is the limit for suitable resp. conditionally suitable less than 800 resp. 1200 mg/L. For this reason, DL is not suitable for irrigation.

The diluate parameters (see Table 7) may be classified as Category I water—i.e., water suitable for irrigation. The greatest decrease was manifested in DS or in the conductivity of
the diluate when the DS decreased on average by 93% compared to the input values. The monitored heavy metals also meet the requirements for irrigation—Category I.

Table 7. Classification of the different sample parameters into water quality classes according to Standard ČSN 75 7143.

| Parameter | Unit | Diluate 1 | Diluate 2 | Diluate 3 | Category I * | Category II ** | Category III *** |
|-----------|------|-----------|-----------|-----------|---------------|----------------|-----------------|
| pH        | (-)  | 5.46      | 5.84      | 5.08      | 5 to 8.5      | 4.5 to 9       | <4.5 to >9      |
| t         | (°C) | 20.00     | 20.00     | 20.10     | 35            | 40             | >40             |
| DS105     | (mg/L) | 176.00   | 182.25    | 150.84    | 800           | 1,200          | >1,200          |
| Cd        | (mg/L) | <0.01     | <0.01     | <0.01     | 0.01          | 0.02           | >0.02           |
| Co        | (mg/L) | <0.01     | <0.01     | <0.01     | 0.5           | 1              | >1              |
| Cr_{total} | (mg/L) | <0.01     | <0.01     | <0.01     | 0.2           | 0.5            | >0.5            |
| Cu        | (mg/L) | 0.027     | 0.025     | 0.029     | 0.5           | 2              | >2              |
| Ni        | (mg/L) | 0.022     | 0.025     | 0.019     | 0.1           | 0.2            | >0.2            |
| Pb        | (mg/L) | 0.002     | 0.002     | 0.002     | 0.05          | 0.1            | >0.1            |
| Zn        | (mg/L) | 0.109     | 0.111     | 0.107     | 1             | 2              | >2              |
| Fe        | (mg/L) | 1.460     | 1.488     | 1.432     | 10            | 100            | >100            |

Note: Measurement uncertainty—pH and t up to 3%, metals up to 20%. Note: Category I * water suitable for irrigation; Category II ** water conditionally suitable for irrigation; Category III *** water unsuitable for irrigation.

However, more detailed research is needed before such water can be used for irrigation purposes, especially various biological indicators must be tested.

Nowadays, there are numerous countries facing the problem of clean water supply shortage. In [32,33] the authors summarize the pros and cons of using treated wastewater for irrigation purposes. They conclude that there are more advantages to the approach. The drawbacks lie in the likelihood of high heavy metals concentrations in irrigation water, which shall transfer into the soil and crops, and related health risks. However, the advantages are seen in dealing with water shortages, especially in dry regions, or areas with minimum sources of drinking water. Another benefit is nutrients for crops and soil through irrigation, and thus high crop yields [33].

The main contribution of our research lies in the usage of the ED products of diluate and concentrate from DL. The concentrate contains the ions required for the chemical precipitation of phosphorus under the formation of struvite precipitate. This way, phosphorus gets recycled in the form of fertilizer, which has been known for its low solubility and good fertilizing properties. The second product is the diluate stream, which we classified into Category I—water suitable for irrigation according to Standard ČSN 75 7143 in [21], thus rendering the diluate stream a potential irrigation water resource, especially for areas with limited access to water. All the residual liquid wastes may be recycled, i.e., incorporated into sludge management or re-fed as the inflow of municipal WWTP.

4. Conclusions

In view of the fact that phosphorus is one of the critical raw materials of the 21st century, it can be expected that the recovery of phosphorus will become part of wastewater treatment sludge management. In addition, we face more frequent occurrences of drought, so we need to look for alternative sources of water. On the other hand, the incorporation of a struvite recovery technology will undoubtedly be a costly investment.

The aim of this research was to reuse ED products obtained from DL treatment. The measured data show that both products can be reused in agriculture. From a concentrated stream of ED concentrate, MgNH₄PO₄·6H₂O—struvite, can be obtained by precipitation with the addition of MgSO₄·7H₂O and NaOH, which can be used as a fertilizer in agriculture.
The yield of crystal struvite per 1 L of concentrate is 1.72 g (in molar ratio 1:1) and 1.79 g (in molar ratio 1:1.3). Based on our findings, the molar ratio 1:1 shows as effective and sufficient. In comparison with Šykorová et al. in [19], where the authors obtained 0.21 g of crystal struvite in the best result, we obtained an eightfold amount of crystal struvite.

A more desalted ED stream—diluate can be used as irrigation water. The detected concentrations of heavy metals and DS in the diluate were compared with the standard ČSN 75 7143 in [21], which in the Czech Republic sets conditions for water suitable for irrigation. By comparing the determined values of heavy metal and DS concentrations with the values given in the relevant standard, it was found that the analyzed samples of diluate belong to Category I, i.e., water suitable for irrigation. To close the ZLD cycle, the remaining liquid waste can be recycled within sludge management of municipal WWTP. In further research, attention should be paid to the hygienic security of the resulting products and to the possibilities of alkali recovery by electrodialysis with bipolar membranes (EDBM).

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