



## Article

# Influence of Phosphorus Speciation on Its Chemical Removal from Reject Water from Dewatering of Municipal Sewage Sludge

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**Abstract:** The aim of the presented research was the assessment of phosphorus speciation impact on the precipitation of phosphorus in reject water using  $\text{Ca}(\text{OH})_2$ . To achieve this, phosphorus speciation (organic and inorganic phosphorus in suspension and in dissolved form) in reject water that is produced during sludge dewatering, after methane digestion in wastewater treatment plants (WWTPs), was determined. This study covered the materials from four WWTPs with different compositions of feedstock for anaerobic digestion (AnD). In one, the AnD process of primary and secondary sludge was carried out without co-substrate, while in three others, co-substrate (waste from the agri-food industry and external waste-activated sludge and fats from industrial plants) was examined. The investigation was conducted in batch reactors using doses of  $\text{Ca}(\text{OH})_2$  ranging from 2500 to 5500 mg Ca/dm<sup>3</sup>. The percentage of phosphorus forms determined in the raw reject water was similar, with the dominant form being soluble reactive phosphorus (SPR) (percentage from 87 to 96%). The small differences observed were dependent on the composition of the AnD feedstock. The results showed that, in all analysed wastewater, very high (exceeding 99.9%) phosphate phosphorus removal efficiencies were obtained using  $\text{Ca}(\text{OH})_2$  for short reaction times ( $t = 1$  h). The efficiency of phosphate removal depended on pH but not on the forms of phosphorus in the analysed reject water.

**Keywords:** phosphorus speciation; phosphorus precipitation; reject water; municipal wastewater treatment plant



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## 1. Introduction

The last two decades have seen intensive development of wastewater collection and treatment systems in Poland, involving the construction and modernisation of wastewater treatment plants and the expansion of water and sewage networks. The result of these developments has been an increase in the volume of wastewater treated. In addition, between 2000 and 2021, there has been more than doubling the amount of wastewater treated in treatment plants with enhanced biological removal of nutrients, which now accounts for more than 83% of total treated wastewater [1]. Highly efficient wastewater treatment systems generate significant amounts of sewage sludge, of which a total of 1025.8 thousand tonnes of (dry mass) d.m. was generated in Poland in 2021 [1]. As a result of wastewater treatment processes, phosphorus, whose concentrations in raw municipal wastewater range from 5–20 mg/dm<sup>3</sup>, is bound in sewage sludge. Significant amounts of it then find their way into reject water generated during sludge dewatering, including sludge after methane fermentation. According to research [2,3], as a result of sludge digestion, up to 60% of phosphate phosphorus can be re-released into reject water through polyphosphate hydrolysis. The amount of supernatant is even 20% of the volume of wastewater flowing into the treatment plant [4,5]. This makes reject water a valuable material from which phosphorus can be recovered. In the context of the dwindling reserves of this element and the ever-increasing demand for phosphorus in agriculture, its recovery is now becoming a necessity and a key element of a circular economy [6]. It is estimated

that agricultural production must increase by nearly 50% by 2050, compared with 2012 to meet the growing demand for food, fibre and biofuels. According to the World Bank, the necessary increase could be as high as 70% [7,8]. Consumption of phosphate fertilisers in 2020 in Poland already amounted to 358.8 thousand tonnes in terms of pure components, and this represents an increase of 3% compared with 2010. At the same time, there was also a more than twofold increase in the consumption of lime fertilisers, whose consumption in 2020 amounted to 1,340,000 tonnes of Ca [1]. Instead, current and future trends indicate that the extraction of natural phosphorus resources occurs faster than natural geological replenishment. The supply of phosphorus as an agricultural fertiliser depends on a limited reserve of phosphate minerals, but inefficient use means that this resource is not being used in a sustainable manner. In addition, the loss of phosphorus from historically accumulated soil reserves can cause significant environmental damage. The risk of soil erosion and loss of this element also increases as the share of heavy rainfall in total precipitation increases, which is observed in many regions of the world [9–11]. The development of sustainable phosphorus management will require optimising the efficiency of its use, as well as its recovery from secondary sources, such as municipal wastewater [12].

Precipitation of phosphorus from municipal wastewater or reject water from sludge dewatering can be carried out to obtain struvite [13–15] or various forms of calcium phosphate, such as hydroxyapatite [16]. Struvite is a product that contains phosphorus in a form that is difficult for plants to access, which severely limits its use as a fertiliser, while calcium phosphates can be a valuable agriculturally slow-release fertiliser [16]. Using  $\text{Ca}(\text{OH})_2$  to precipitate phosphorus compounds can be advantageous compared with other reactants—it is a low-cost formulation, and ions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  are not introduced into the wastewater. In addition, as a result of the alkalisation that occurs as a result of dosing  $\text{Ca}(\text{OH})_2$ , the correct pH for the process is ensured, and there is no need to add NaOH, which is often a necessary procedure during struvite digestion [16–18].

Sewage sludge is also a valuable raw material for biogas production through methane fermentation. Furthermore, through the production of electricity in cogeneration systems, they contribute to improving the energy balance of wastewater treatment plants. A significant increase in biogas production can be achieved by co-digesting sewage sludge with waste from the agri-food industry, but this can affect the quality of the reject water and thus the potential for biogen recovery [19,20].

The composition of feedstock is crucial for nitrogen and phosphorus content and the forms in which they occur in digestates from agricultural biogas plants. A high content of inorganic phosphorus has been observed in sewage sludge and animal manure AnD, while the use of fruit and vegetable waste is characterised by the lowest values [21,22]. Moreover, the fermentation process affects the mobility of phosphorus forms in post-fermentation fractions (solid and liquid) [23,24]. It was found that P speciation in digestates depends on the temperature and composition of the feedstock [25]. This has been observed in the highest concentrations of organic phosphorus in the liquid fraction of digestates from the fermentation of distillery brew and livestock manure and the lowest in the fermentation of fruit and vegetable waste. Although there are publications concerning the effect of the composition of feedstock on the characteristics of the digestate from agricultural biogas plants, there is still a lack of research into co-digestion in WWTPs (e.g., wastewater sludge and agricultural wastes) and its effect on post-digestion product quality. The novelty of this work is the assessment of the impact of co-digestion on phosphorus forms in reject water and subsequent removal efficiency. The purpose of this study was to determine the occurrence of phosphorus fraction in reject water from AnD in municipal WWTPs varying feedstock composition (only sewage sludge and their co-digestion with waste from the agro-food industry), and the effect of this speciation on the efficiency of its precipitation using  $\text{Ca}(\text{OH})_2$ . The study was conducted for different doses of  $\text{Ca}(\text{OH})_2$ , determining the optimal dose for phosphate removal.

## 2. Materials and Methods

### 2.1. Research Material

The study of the phosphate precipitation process was performed for samples of reject water from digestate dewatering taken from four municipal wastewater treatment plants located in northern Poland. All treatment plants are classified as large facilities with a population equivalent (PE) of more than 100,000. The wastewater treatment system for all these plants includes the biological removal of nitrogen and phosphorus for various configurations of the activated sludge method. The primary sludge and excess primary sludge produced in these treatment plants are subjected to methane digestion. The produced biogas is burned in cogeneration systems with the generation of heat and electricity. Three of the four WWTPs surveyed conduct co-digestion of sewage sludge with waste from the agro-food industry. Basic information on these treatment plants is summarised in Table 1.

**Table 1.** Basic characteristics of the studied WWTPs.

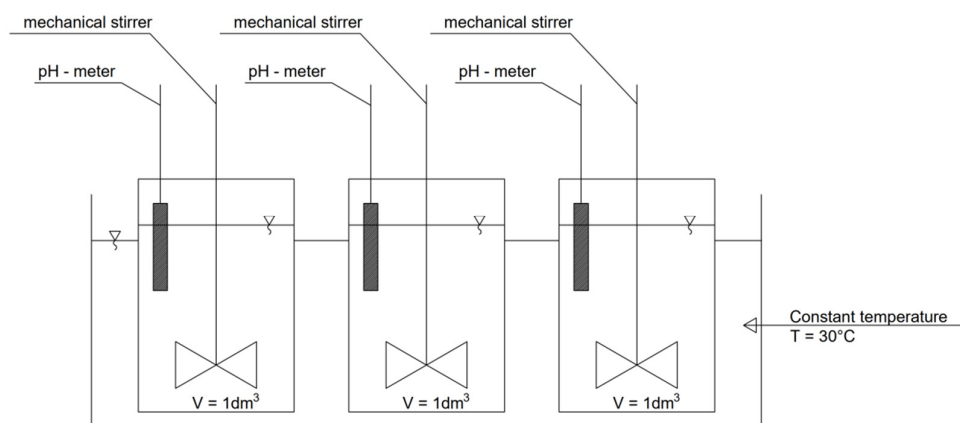
WWTP Size	Flow Rate	Configuration of Bioreactor	Sludge Handling
PE	m <sup>3</sup> /d	-	-
Debogorze 515,500	56,000	A2/O with final simultanic denitrification	AnD * of primary and secondary sludge without the use of co-substrates
Poznan 1,200,000	102,200	JHB	AnD of primary and secondary sludge with use of co-substrates (waste from the agri-food industry and external waste activated sludge)
Slupsk 200,000	20,000	JHB modified to 5-stage reactor	AnD of primary and secondary sludge with use of co-substrates (fats from industrial plants)
Swarzewo 150,000	14,000	SBR with final sedimentation in settling tanks	AnD of primary and secondary sludge with use of co-substrates (waste from the agri-food industry and external waste activated sludge)

The composite samples of reject water were collected in an eight-hour working time sludge dewatering devices.  
\* AnD—anaerobic digestion.

### 2.2. Research Methodology

In samples of raw reject water, the following parameters were determined: ammonia nitrogen, total phosphorus (TP), orthophosphate (PO<sub>4</sub>-P), chemical oxygen demand (COD), calcium and magnesium. Additionally, phosphorus speciation (organic and inorganic phosphorus in suspension and in dissolved form) was determined.

Phosphorus precipitation studies were conducted in a laboratory model consisting of three 1 dm<sup>3</sup> reactors placed in a water bath (Figure 1). Each reactor was equipped with a mechanical stirrer and a pH probe. Precipitation of phosphorus from reject water was carried out using various doses of Ca(OH)<sub>2</sub>, ranging from 2500 to 5500 mg Ca/dm<sup>3</sup> administered in the form of milk of lime, which allowed the reject water to become alkaline enough for the process. The doses of calcium hydroxide used are shown in Table 2. Experiments were conducted at 30 °C. Samples were stirred using mechanical stirrers for the first 5 min at 400 rpm and then at 130 rpm. The pH was measured continuously, and in addition, samples were taken after 1 h, 2 h, 3 h, 12 h and 24 h of the study, except for experiments in which more than 99% phosphorus precipitation efficiency was achieved after just 1 h. Total phosphorus and phosphate phosphorus concentrations were determined in the samples.



**Figure 1.** Measuring the effectiveness of phosphorus precipitation in laboratory model—overview diagram.

**Table 2.** Doses of  $\text{Ca}(\text{OH})_2$  used in the study.

WWTP	Dose of $\text{Ca}(\text{OH})_2$ [ $\text{mg}/\text{dm}^3$ ]								
	2250	2500	2750	3000	3250	3500	3750	4000	5500
Debogorze	+	+	+	+	+	+	−	−	−
Poznan	+	+	+	+	+	+	+	+	−
Slupsk	+	−	+	+	+	+	+	+	+
Swarzewo	+	+	+	+	+	+	−	−	−

\* doses used only for WWTP Slupsk: 4250; 4500; 4750.

### 2.3. Analytical Methods

The ammonia nitrogen ( $\text{NH}_4\text{-N}$ ), total phosphorus (TP), orthophosphate ( $\text{PO}_4\text{-P}$ ), chemical oxygen demand (COD), calcium and magnesium were measured using a DR20000 spectrophotometer (Hach Company, Loveland, CO, USA). The pH was measured using a portable multi-parameter meter (WTW InoLab pH 720). All chemical parameters were determined in the samples filtered through a  $1.6 \mu\text{m}$  glass membrane filter Millipore (Billerica, MA, USA).

### 2.4. Procedure for the Determination of Phosphorus Speciation

Phosphorus forms were determined in the analysed reject water using the generally accepted vanadomolybdic acid method of phosphorus determination. This method is used for the determination of phosphorus fractions in wastewater and water samples to assess the potential bioavailability of phosphorus and the risk of eutrophication [26–28]. With this analytical method, total phosphorus (TP), total dissolved phosphorus (TDP), and reactive and non-reactive molybdate phosphorus in dissolved and suspended forms (SRP and SNRP and PRP and PNRP fractions, respectively) were distinguished (Figure 2). Reactive molybdate phosphorus in dissolved form is often identified with orthophosphate ions. In contrast, organic and most condensed phosphorus compounds are classified as non-reactive molybdate phosphorus (both in dissolved and suspended form). The determination of phosphorus fractions in the digestion reject water was performed according to the test methodology proposed [27–30] [31]. Total phosphorus and dissolved phosphorus were determined according to the spectrophotometric method using vanadomolybdic acid after digestion with potassium peroxydisulfate in non-filtered and filtered samples, respectively, through a  $0.45 \mu\text{m}$  pore diameter filter [32]. Total reactive phosphorus (TRP) and dissolved reactive phosphorus (SRP) were determined according to the spectrophotometric method using vanadomolybdic acid. The fraction of PNRP was calculated as the difference between TP, SP and PRP. The SNRP fraction was calculated as the difference between SP and SRP.

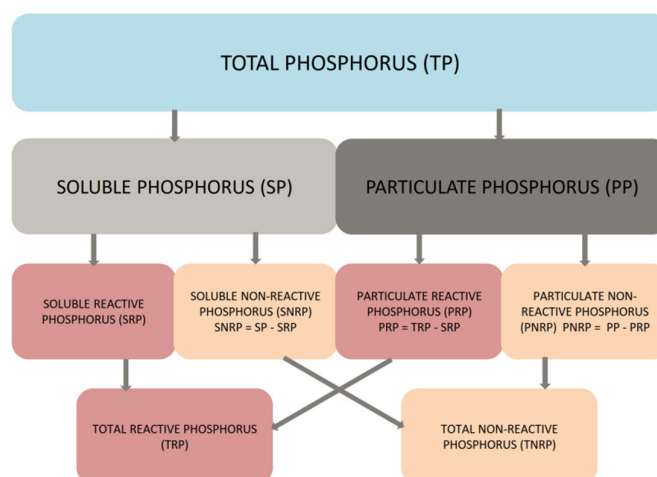


Figure 2. Scheme of phosphorus fractionation.

### 3. Results and Discussion

#### 3.1. Characteristics of Reject Water

The characteristics of raw reject water from digestate dewatering for the four wastewater treatment plants analysed are shown in Table 3. The total phosphorus concentrations for three of the four treatment plants ranged from 192.8 to 278.0 mg P/dm<sup>3</sup>, with the highest values observed for reject water from WWTP Slupsk. Significantly lower values were recorded for WWTP Swarzewo (39.0 mg P/dm<sup>3</sup>), which is probably due to the high dose of iron salts used for the chemical precipitation of phosphorus in SBR reactors. Phosphate phosphorus accounted for 96.4% and 99.3% of the total phosphorus (for WWTP Swarzewo and Slupsk, respectively). The reject water was characterised by a high concentration of phosphorus: over 122 mg P-PO<sub>4</sub>/dm<sup>3</sup> [33], 125 mg P-PO<sub>4</sub>/dm<sup>3</sup> [34] 60–130 mg P/dm<sup>3</sup> [35], and 208 mg P-PO<sub>4</sub>/dm<sup>3</sup> [36]. Malinowski [37] estimated these values (thermophilic aerobic stabilisation) at around 128.5 mg P/dm<sup>3</sup> for TP. Ammonium nitrogen concentrations ranged from 504 mg N-NH<sub>4</sub>/dm<sup>3</sup>, in reject waters from WWTP Debogorze to 1524 mg N-NH<sub>4</sub>/dm<sup>3</sup> in reject water from WWTP Slupsk, and COD from 378 mg O<sub>2</sub>/dm<sup>3</sup> (WWTP Debogorze) to 519 mg O<sub>2</sub>/dm<sup>3</sup> (WWTP Poznan). The reject water pH varied in a narrow range from 7.24 (WWTP Debogorze) to 7.88 (WWTP Poznan). The high concentrations of ammonium nitrogen in reject water from sludge dewatering are due to the hydrolysis and ammonification of organic nitrogen compounds that occur during anaerobic digestion [38]. Similarly, high values, more than 1700 mg N-NH<sub>4</sub>/dm<sup>3</sup>, have also been reported [33]; values of 891 mgTKN/dm<sup>3</sup> and COD 592 mgO<sub>2</sub>/dm<sup>3</sup> have also been observed [34].

Table 3. Characteristics of raw reject water, average values, n = 3.

WWTP	pH	TP	P-PO <sub>4</sub>	N-NH <sub>4</sub>	COD	Ca	Mg
	-	mg/dm <sup>3</sup>	mg/dm <sup>3</sup>	mg/dm <sup>3</sup>	mg O <sub>2</sub> /dm <sup>3</sup>	mg/dm <sup>3</sup>	mg/dm <sup>3</sup>
Debogorze	7.24	232	228	504	378	52.1	26.7
Poznan	7.48	196.2	192.8	926	519	55.3	23.4
Slupsk	7.88	278	276	1524	494	64.5	32.8
Swarzewo	7.80	39	37.6	724	437	72.1	58.4

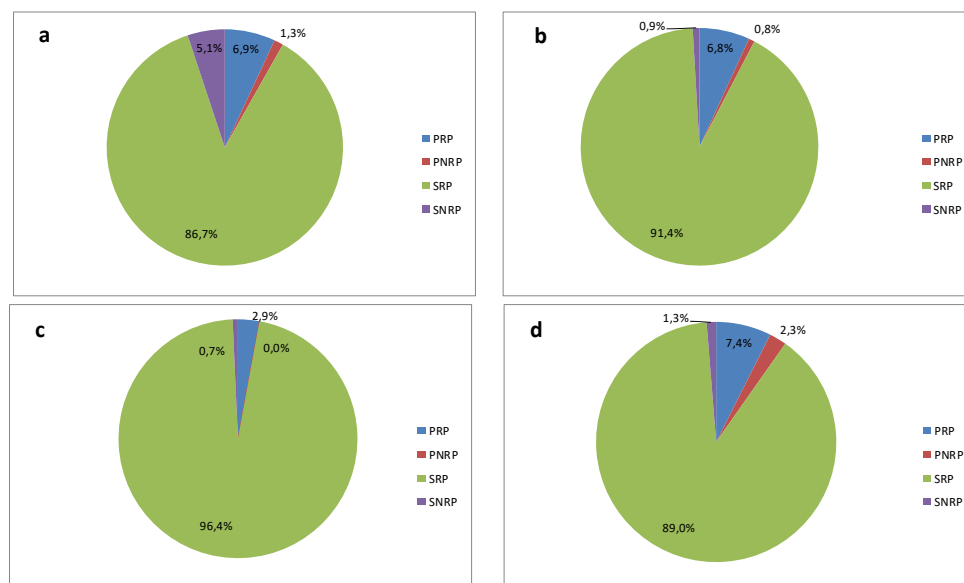
#### 3.2. Phosphorus Speciation

Based on the results, phosphorus in reject water was also in the form of suspension (PP fraction = PRP fraction + PNRP fraction) and dissolved (SP fraction = SRP fraction + SNRP fraction), with the dissolved fraction clearly predominating. The phosphorus for the analysed reject waters was characterised by a similar fractional distribution, regardless of

the composition of the inputs directed to the digesters. For 3 of 4 WWTPs, the distributions of P (mean values) were as follows:

SRP fraction > PRP fraction > SNRP fraction > PNRP fraction

Only for reject water from the Swarzewo WWTP was the order of the last two fractions reversed (PNRP fraction > SNRP fraction), probably due to the coagulant phosphorus precipitation used at this WWTP. The percentage of SRP fraction varied from 86.7% to 96.4% and the percentage of PRP fraction varied from 2.9% to 7.4% (Figure 3). The concentrations of phosphorus forms are reported in Table 4.



**Figure 3.** The percentage of phosphorus fraction in reject water from 4 WWTP: (a) Debogorze, (b) Poznan, (c) Slupsk, and (d) Swarzewo.

**Table 4.** The concentrations of phosphorus forms in reject water from 4 WWTP, mg P-PO<sub>4</sub>/dm<sup>3</sup> average values, n = 4.

WWTP	TP	PRP	PNRP	SRP	SNRP	SP
Debogorze	232	16	2.9	201.3	11.8	213
Poznan	196.2	13.4	1.6	179.4	1.8	181.2
Slupsk	278	8	0	268	2	270
Swarzewo	39	2.9	0.9	34.7	0.5	35.2

TP, total phosphorus; PRP, particulate reactive phosphorus; PNRP, particulate non-reactive phosphorus; SRP, soluble reactive phosphorus; SNRP (OP), soluble non-reactive phosphorus (organic phosphorus); SP = SRP + SNRP—soluble phosphorus, n, number of tests.

The mean values of the concentration of phosphorus in suspension (PP fraction) and phosphorus present in dissolved form (SP fraction) in the analysed reject water changed from 3.8 to 19 mg PO<sub>4</sub><sup>3-</sup>/dm<sup>3</sup> and from 35.2 to 270 mg PO<sub>4</sub><sup>3-</sup>/dm<sup>3</sup>, respectively.

A similar percentage of phosphorus fraction was observed in the liquid fraction of digestates from agricultural biogas plants, obtained from the fermentation of three different waste groups: agricultural lignocellulosic waste, food waste and animal manure [25]. The predominant share of the SRP fraction is probably related to the hydrolysis of phosphorus-containing organic compounds that occur during sludge digestion processes. The research lacks comprehensive data on the speciation of phosphorus in reject water from the dewatering of sewage sludge, which was co-fermented with the use of agricultural waste in WWTPs. However, according to a researcher [24], the authors expected that the composition of feedstock may be an important factor that affects phosphorus forms of reject water and

the phosphorus precipitation process. In the case of reject water from WWTP Dębogórze, the only one where anaerobic digestion was provided without the use of co-substrates, a higher proportion of the SNRP fraction was observed (Figure 3). The influence of batch composition on phosphorus speciation is also indicated by the very similar percentage fraction of phosphorus in the reject water from the Swarzewo and Poznan WWTPs, where co-digestion was carried out using comparable materials (primary and secondary sludge with waste from the agro-food industry and waste-activated sludge externally) (Figure 3). It is worth noting that the distribution of phosphorus fractions is very similar despite the large difference in phosphorus concentrations in wastewater (WWTP Swarzewo: 39 mgP/dm<sup>3</sup> and WWTP Poznan 196.2 mgP/dm<sup>3</sup>).

### 3.3. Precipitation of Phosphorus

#### 3.3.1. Reject Water from Debogorze WWTP

Phosphorus precipitation was carried out for 6 increasing doses of Ca(OH)<sub>2</sub>. In the case of the effluent from this treatment plant, at the lowest applied dose of 2250 mg Ca/dm<sup>3</sup> and pH = 11.7, phosphorus removal occurred with an efficiency of more than 99.4%, and at a dose of 2500 mg Ca/dm<sup>3</sup> and pH = 11.8 with an efficiency of more than 99.9%, after 1 h of the experiment. At the same time, a reduction in the concentration of ammonium nitrogen was observed to a value of 178 mg N-NH<sub>4</sub> (a reduction of 64.7%) for a maximum dose of 3500 mg Ca/dm<sup>3</sup> and pH = 12.1. This is associated with its transformation into gaseous form and diffusion into the atmosphere from the surface of the liquid.

#### 3.3.2. Reject Water from Poznan WWTP

A range of 8 doses of 2250–4000 mg Ca/dm<sup>3</sup> was tested for reject water from this treatment plant. A 99.3% reduction in phosphate phosphorus was recorded for a dose of 3000 mg Ca/dm<sup>3</sup> and pH = 10.4 after 1 h of the experiment. For higher doses (from 3250 to 4000 mg Ca/dm<sup>3</sup>), the efficiency of P-PO<sub>4</sub> removal was more than 99.9% at a pH ranging from 11.3 to 12.2 (experiment time of 1 h). The highest decrease in ammonium nitrogen concentration occurred after 24 h for the highest dose (4000 mg Ca/dm<sup>3</sup>) and was 82%.

#### 3.3.3. Reject Water from Slupsk WWTP

Achieving more than 99% phosphate phosphorus removal efficiency required a dose of 4500 mg Ca/dm<sup>3</sup> (pH = 10.4). A dose of 5000 mg Ca/dm<sup>3</sup> (pH = 11.9) and higher resulted in a P-PO<sub>4</sub> reduction of more than 99.9%. On the other hand, for ammonium nitrogen removal, the best results were obtained after 24 h (75% reduction for the dose of 4500 mg Ca/dm<sup>3</sup>, pH = 10.3 and 84.8% for the dose of 5500 mg Ca/dm<sup>3</sup>, pH = 11.9).

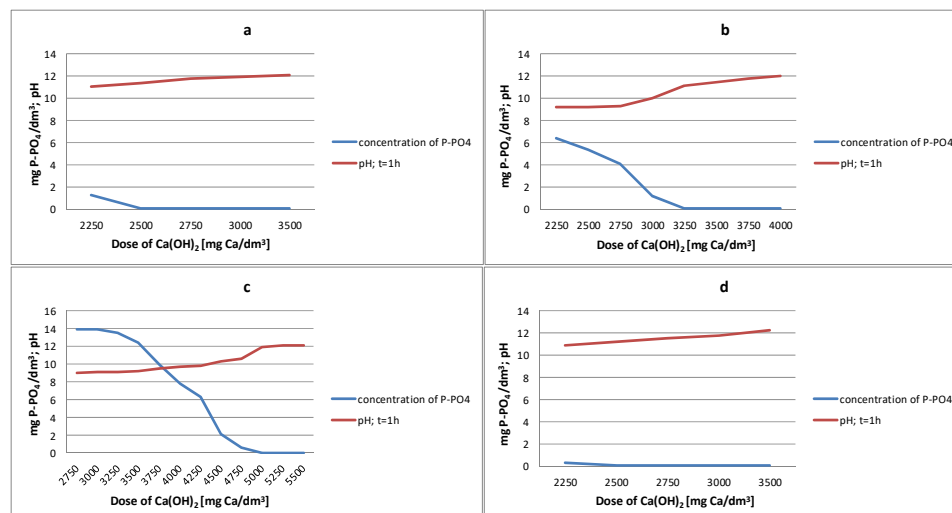
#### 3.3.4. Reject Water from Swarzewo WWTP

The effluent from this facility was characterised by a significantly lower range of phosphate phosphorus concentrations (37.6 mg P-PO<sub>4</sub>/dm<sup>3</sup> on average) due to phosphorus precipitation with iron coagulants used at the treatment plant. At a precipitation rate of 2250 mg Ca/dm<sup>3</sup> and pH = 10.7, a phosphate phosphorus removal efficiency of more than 99.3% was achieved, and at a rate of 2500 mg Ca/dm<sup>3</sup>–99.9% (pH = 11.1). Ammonium nitrogen removal efficiency of 71% was achieved for the highest applied dose of 3500 mg Ca/dm<sup>3</sup> after 24 h (pH = 12.2).

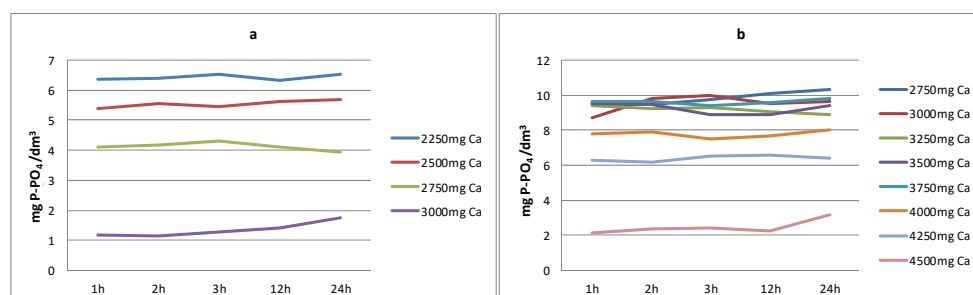
The results of phosphorus precipitation tests using Ca(OH)<sub>2</sub> conducted for reject water from 4 wastewater treatment plants are shown in Figure 4a–d. They clearly show that very high phosphate phosphorus removal efficiency was achieved for reject water from each facility, in each case for different doses of reactant and at different pH. The process was rapid, with a reduction of more than 99.9% achieved after just 1 h of the experiment. At the same time, the analyses indicate that for lower doses (for WWTP Poznan and Slupsk), increasing the precipitation time has no effect on the efficiency of phosphate phosphorus removal (Figure 5a,b). It was observed that the values of phosphate phosphorus concentrations obtained after 1 h did not decrease any further, showing only



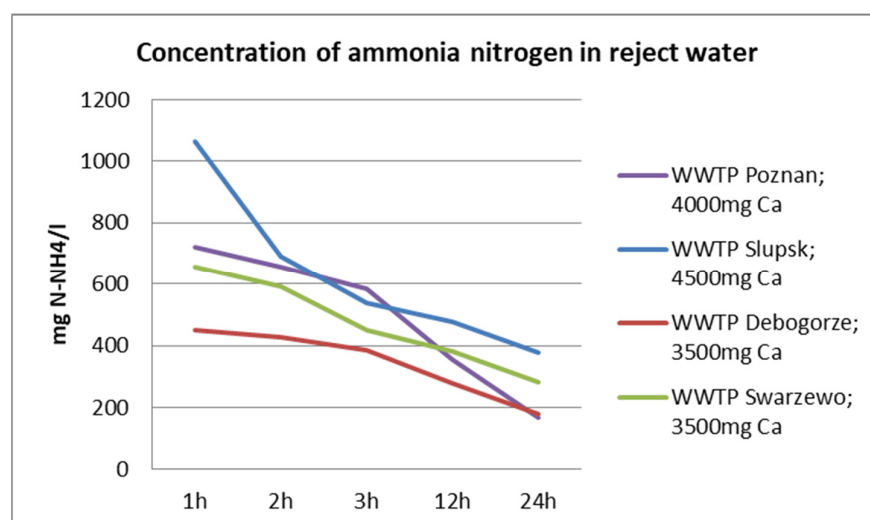
slight fluctuations. The process of ammonium nitrogen removal was different, in which the highest efficiencies were achieved for a time of 24 h (Figure 6). However, in this case, the removal of ammonia took place from the surface of the mechanically stirred reactors without assisting the process by blowing with air.



**Figure 4.** Changes in reject water P-PO<sub>4</sub> concentrations and pH changes for increasing doses of Ca(OH)<sub>2</sub> in the 4 analysed WWTP (a) Debogorze (b) Poznan (c) Slupsk (d) Swarzewo.



**Figure 5.** Changes in P-PO<sub>4</sub> concentrations in reject water over time for different doses Ca(OH)<sub>2</sub> for (a) WWTP Poznan and (b) WWTP Slupsk.



**Figure 6.** Changes in N-NH<sub>4</sub> concentrations in reject water during a series of 24-h tests for 4 WWTPs.

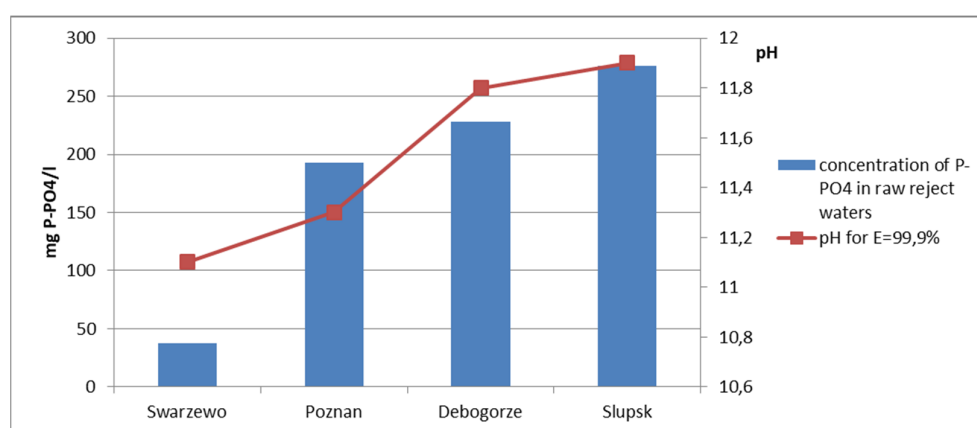


It is noteworthy that a very high phosphorus removal efficiency of 99.9% was obtained for all tested reject water. This indicates that, despite the observed differences in the percentage of phosphorus fractions in the four WWTPs, phosphorus speciation did not affect phosphorus precipitation. In fact, all forms of phosphorus were precipitated.

The minimum doses at which the highest phosphate phosphorus removal efficiencies (99.9%) were obtained were as follows:

- WWTP Debogorze: 2500 mg Ca/dm<sup>3</sup> and pH = 11.8
- WWTP Poznan 3250 mg Ca/dm<sup>3</sup> and pH = 11.3
- WWTP Slupsk 5000 mg Ca/dm<sup>3</sup> and pH = 11.9
- WWTP Swarzewo 2500 mg Ca/dm<sup>3</sup> and pH = 11.1

Analysing the above data, the pH range at which the phosphorus precipitation process proceeded most effectively was from 11.1 to 11.9, with the highest pH values determined for the highest initial concentrations of phosphate phosphorus (Figure 7).



**Figure 7.** Relationship between phosphate concentration values in raw wastewater and pH achieved during phosphate precipitation (Efficiency E = 99.9%).

The pH of solutions and mixtures affects the solubility of phosphorus compounds, and raising the pH shifts the chemical equilibrium towards the formation of dissociated phosphate ions, which facilitates their precipitation as insoluble Ca and Mg phosphates. According to the research, the optimal pH values for the calcium phosphate precipitation process should be in the range of 10–12.5 [17,39–41]. The pH values obtained in the study in question to achieve 99.9% phosphate reduction confirm these observations. A high phosphate removal efficiency of more than 85% was obtained in several locations [39,42,43]. According to one example [16], the key parameter determining the efficiency of calcium phosphate precipitation is the Ca:P molar ratio, as well as the Ca/P molar ratio and the initial pH are dependent parameters. The authors reported that for Ca/P equal to 2.07, 98% of phosphorus was removed. The molar ratio calculated in this paper ranged from 8.5 (WWTP Debogorze) to 51.5 (WWTP Swarzewo), but the efficiency was E = 99.9%. Thus, it appears that a significant portion of calcium hydroxide is consumed to raise the pH. A further study also observed a greater than 99% efficiency of phosphate removal using Ca(OH)<sub>2</sub> as a pH adjustment reagent [42].

The observed increasing values of ammonium nitrogen removal efficiency with increasing pH obtained in the analysed studies are related to the characteristics of the conversion of ammonium ions to gaseous NH<sub>3</sub> in the ammonia removal process. Analogous relationships were found in further studies [44,45], which examined the effect of pH values on the removal efficiency of nitrogen and phosphorus.

Further research directions should address the fertiliser values of precipitated sludge, which is a potentially rich and valuable source of phosphorus and calcium for agriculture. Taking into consideration the increasing recognition of pre-fermentation disintegration

technologies prior to co-digestion [46,47], it may also be very important to analyse their impact on post-digestion products and their ability to process and recover nutrients.

#### 4. Conclusions

1. The concentration of phosphate phosphorus and ammonium nitrogen in reject waters from the dewatering of digested sewage sludge (with or without co-substrates) varies over a relatively wide range and depends on the wastewater treatment technology adopted at the plant, the co-substrate used for the digestion process and the efficiency of sludge dewatering.
2. In all analysed reject waters, very high (exceeding 99.9%) phosphate phosphorus removal efficiencies were obtained using  $\text{Ca}(\text{OH})_2$  for short reaction times ( $t = 1$  h).
3. The efficiency of phosphate phosphorus removal depends on the pH value of the reaction obtained during the precipitation process.
4. The percentage of phosphorus forms determined in the raw reject water was similar for the four analysed treatment plants. Phosphorus in reject water was mainly bound in the SPR (soluble reactive phosphorus) fraction. However, slight differences were observed due to the composition of the feedstock.
5. The forms of phosphorus in the analysed reject water did not affect the efficiency of the phosphorus precipitation process with calcium hydroxide. This means that the phosphorus precipitation method used in this work is very effective for both mono- and co-digestion processes, regardless of the composition of the feedstock.

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