

Nutrient recovery from deammonification effluent in a pilot study using two-step reject water treatment technology

Agnieszka Tuszynska, Krzysztof Czerwionka*

Gdansk University of Technology, Faculty of Civil and Environmental Engineering, Narutowicza 11/12, 80-233, Gdansk, Poland

ARTICLE INFO

Keywords:

Liquid fraction of digestates
Nitrogen and phosphorus removal and recovery
Deammonification
Struvite production

ABSTRACT

The aim of this study was to assess the possibility of phosphorus and nitrogen recovery from the liquid fraction of digestates (reject water) pilot study using a two-step technology, where the precipitation of biogenic compounds in the form of magnesium ammonium phosphate (struvite) will be preceded by a deammonification process.

The tests confirmed the possibility of nutrient recovery from deammonification effluent. A removal efficiency from 85.0 to 92.0% of PO_4^{3-} ions and from 13.0 to 21.0% of NH_4^+ ions in the form of magnesium salt was achieved, at a pH in the range of 8.7–9.0. However, when the pH value was from 9.1 to 9.3, phosphate ions were precipitated not only as magnesium salts, but also as calcium salts. The maximum struvite crystal sizes ranged from 0.72 to 1.65 mm, and was determined by the concentration of the suspended solids in the reject water, whose presence was a factor limiting the crystallization of struvite.

1. Introduction

Wastewater treatment plants (WWTPs) are currently subjected to a gradual paradigm shift. Initially, the emphasis was on the basic goal of wastewater treatment and increasing the requirements for the quality of treated wastewater discharged to receivers. In recent years, the concept of changing traditional WWTPs into plants recovering raw materials from wastewater has emerged. With this new outlook, wastewater is not so much waste but a source of raw materials that can potentially be recovered. The interconnected chain “biogenic compounds - energy - water” is part of the greater idea of circular economy and sustainable resource management [1,2].

In the case of municipal WWTPs, using a conventional approach, digested sludge is separated into two fractions - solid and liquid (reject water) before their final management. After sludge dewatering, the reject water is most often directed to the beginning of the wastewater treatment line. However, side stream nitrogen removal lines are used more often in WWTPs. On a technical scale, innovative methods for removing nitrogen compounds from the liquid fraction of digestates have been developed, e.g. in the CANON (Completely Autotrophic Nitrogen Removal Over Nitrite), OLAND (Oxygen-Limited Autotrophic Nitrification – Denitrification), SHARON (Single reactor system for High activity Ammonium Removal Over Nitrite), Anammox, or SNAP (Single-Stage Nitrogen Removal) a process using Anammox and Partial Nitritation [3,4]. While the latest trend adopts the use of technology not only intended for increased nitrogen removal from reject water, but also for nutrient recovery through their precipitation in the process of struvite crystallization [5,6]. The development and proven economic efficiency of solutions used in the Netherlands, Germany, Switzerland, Japan and Austria, currently set the principles of phosphorus compound management for municipal facilities and the need to adapt to

* Corresponding author.

E-mail address: kczer@pg.edu.pl (K. Czerwionka).

<https://doi.org/10.1016/j.wri.2021.100148>

Received 14 October 2020; Received in revised form 2 April 2021; Accepted 6 April 2021

Available online 15 April 2021

2212-3717/© 2021 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

the requirements of EU Directive 91/271 (The Urban Wastewater Treatment) justifies development of phosphorus recovery technology. Looking to the future, the recovery of nutrients from waste products generated in wastewater treatment plants is likely to become effective in other European countries, especially that agricultural use of sewage sludge is no longer allowed in the Netherlands, Denmark and some Austrian states. Rodriguez-Garcia et al. [7] based on the life-cycle assessment (LCA) analysis assessed that the combination of CANON processes and controlled struvite precipitation proved to be the best technology, in economic and environmental terms for the treatment of the liquid fraction of digestates. The measurable benefits of such solutions include reduction of nutrient loads in the reject water recycled to biological treatment; minimization of the use of chemicals for phosphorus precipitation contributes to cost reduction and reduction of struvite formation in fermentation chambers by up to 90.0%.

This work proposes an innovative approach to the treatment of the liquid fraction of digestates, i.e. an integrated two-stage technology for the removal and recovery of biogenic compounds using the processes of biological deammonification and chemical precipitation of ammonium and phosphate ions in the form of magnesium ammonium phosphate. The liquid fraction of digestates redirected to the main biological line of WWTP can constitute up to 30% of the total nitrogen (TN) load flowing into bioreactors, which increases the energy demand (for aeration) for its removal. Deammonification can enable effective removal of up to 100% of the ammonium nitrogen contained in the reject water [8]. While the search for alternative sources of phosphorus, and in particular the possibilities of its recovery in sewage sludge treatment processes, is one of the most important issues in the world for the phosphorus industry it stands to say that the technologies used for recovery of phosphorus from the liquid fraction of digestates are still the subject of research [6,9–14].

The literature presents the researcher's results for simultaneous removal and recovery of biogenic compounds in integrated reject water treatment technologies. The most frequently presented technology is in the following configuration: chemical phosphorus precipitation in reject water (as the first stage of integrated technology) and biological removal of nitrogen compounds (as the second stage of integrated technology) [15,16]. However, the subject of continuous and intensive research is technology using an inverted configuration (biological nitrogen removal process as the 1st step and struvite precipitation process as the 2nd step). This configuration was adopted for research in the presented paper in order to determine whether it is possible and justified from the operational point of view. For the chemical precipitation of struvite the anhydrous magnesium sulfate was used as an external magnesium source. The nitrogen removal was carried out in a deammonification reactor. The aim of this study was not only to determine the highest P/N elimination rates, but also the greatest efficiency in the formation of struvite salts and the avoidance of problems with crystal growth because of ion competition due to excessively high Ca^{2+} contents. The upstream deammonification process location, which leads to an increase in the pH and temperature values, allows one to reach the determined optimal pH and temperature value environment (8.7–9.0 and 23–28 °C, respectively) in a resource-efficient manner. This lowers the operating costs of such a configuration, including costs related to the purchase of alkaline compounds dosed to the MAP reactor and the costs of electricity related to possible aeration of

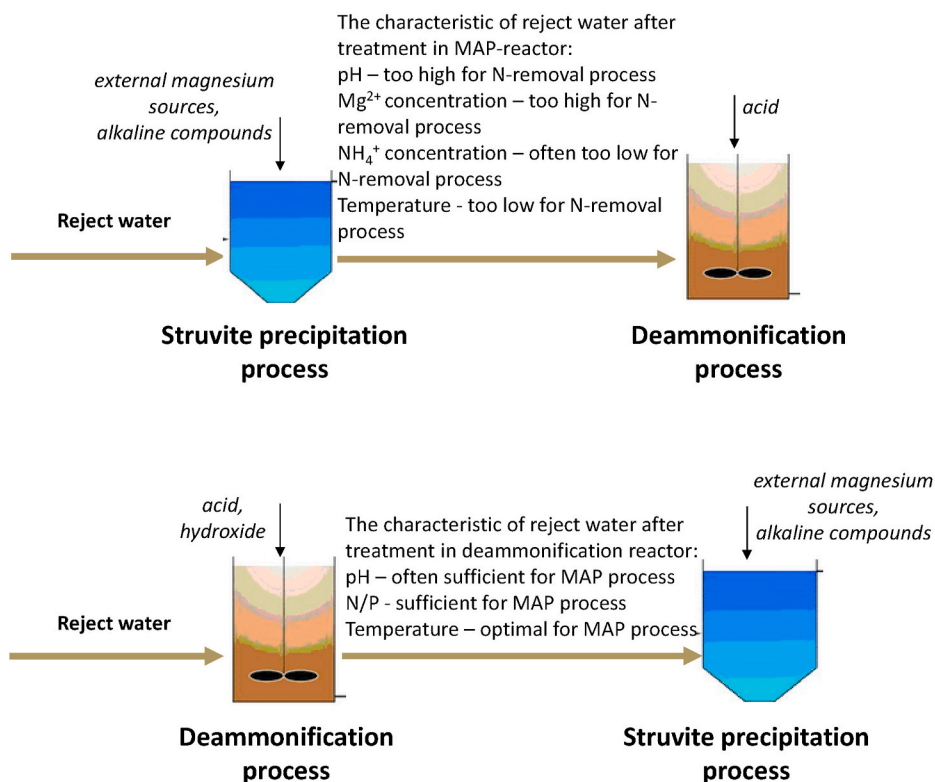


Fig. 1. Different two-step reject water treatment technology.

the reactor. In this configuration, the risk from alkalinity and ammonia stand availability is limited, which, as in the case of the MAP-production/deammonification configuration, could take place (Fig. 1). The research was conducted under the assumption that the deammonification process can be configured with phosphorus recovery technology.

2. Materials and methodology

2.1. Description of integrated two-step treatment technology

The integrated technology scheme for the removal and recovery of biogenic compounds from the liquid fraction of digestates (originating from the municipal WWTP) is shown in Fig. 2. Fig. 3 shows the reactors that were part of the integrated technology. The reject water samples were taken before and after subsequent purification stages, i.e. at the outflow from reactors in which the processes of biological ammonium ion removal (deammonification) and chemical precipitation of struvite took place.

The research was carried out at municipal WWTP in Swarzewo, located in northern Poland (Europe). It is the largest facility in the Polish coastal zone, with sizes of 130,000 or 50,000 population equivalent (PE), which treats on average 15,000 to 5000 m³/d of wastewater in the SBR system, at summer time and remaining period of the year, respectively. The mixed sludge produced in the treatment plant (primary and excessive activated sludge) together with the external organic cosubstrate (waste from the food industry) are directed to the methane fermentation process in closed fermentation chambers. The digestate is dehydrated in two centrifuges: Gea Westfalia (capacity 600 kg TS/h) and Alfa-Laval (capacity 400 kg TS/h). Ekoline PFC9000S flocculant (cationic polyacrylamide) is dosed to the digestate before centrifuged with a dose of approx. 6.9 kg/Mg TS. The dehydration process aims to obtain a dry matter content in the solid fraction at the level of 20–21%, which is a condition of the optimization of the final composting process. Typical suspended solids concentrations in the centrifuge effluents are 200 mg/L, however, during the start-up phase and during digestate overload, this concentration can increase significantly, even above 2000 mg/L. The liquid fraction of the digestate (reject water) in an amount corresponding to 2–6% of the daily wastewater flow recycled to SBR reactors.

The research system was set up in the centrifuge hall building and was fed with real reject water flowing from the centrifuge.

2.2. Parameters of the deammonification process

The investigations were carried out in a pilot-scale SBR reactor with a working capacity of 250 L (total capacity 500 L) (Fig. 3a). A deammonification biomass from the WWTP in Duisburg-Kasslerfeld (Germany) was used. Previously, for 6 months, the biomass was multiplied in laboratory conditions using synthetic reject water used in previous studies (e.g. Ref. [8]). After transporting the pilot SBR reactor to the WWTP Swarzewo, the sludge was acclimated to the rejected water for a period of 21 days. The one-stage deammonification process was carried out at a temperature of 30 ± 1 °C. The 24 h cycle of operation included: 5 min of reject water filling, 23.5 h working period, 15 min of sedimentation and 10 min of effluent discharge. Intermittent aeration was used in the working period using the option of 10 min mixing and 5 min aeration at the assumed dissolved oxygen concentration of 0.5 mg O₂/L. The ammonium nitrogen load of the reactor was maintained in the stable working phase at 0.4 kgN/m³.d. The sludge age approx. 7 d was used in order to increase the leaching of nitrite oxidizing bacteria (NOB) (mainly in the form of flocs). This strategy was also intended to increase the efficiency of removing suspended solids occurring in reject water. It is also indicated that this strategy promotes increasing the load of anammox bacteria with free ammonia, which inhibits the second phase of nitrification [17]. The parameters of the deammonification process were adopted based on previous results of tests on a laboratory scale (Table 1).

2.3. Precipitation of biogenic compounds from the liquid fraction of digestates

The procedure of P and N precipitation in insoluble salt forms was decided based on reviewing the literature and the conditions of chemical precipitation most often suggested in the literature were adopted (Table 2). The magnesium ion deficit was a factor limiting struvite precipitation from digestates. Therefore, to obtain the maximum efficiency of phosphorus and nitrogen precipitation from the

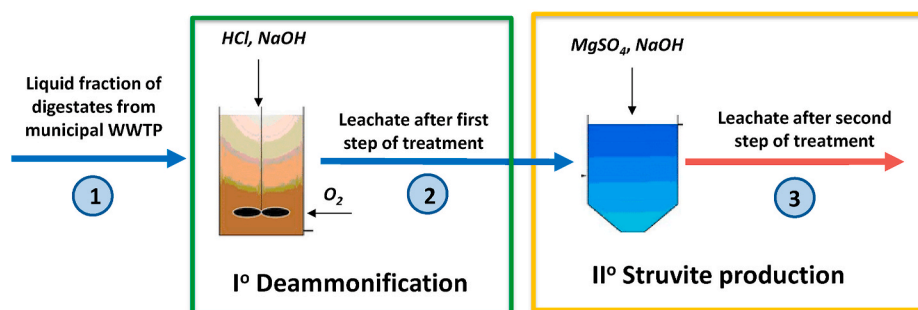
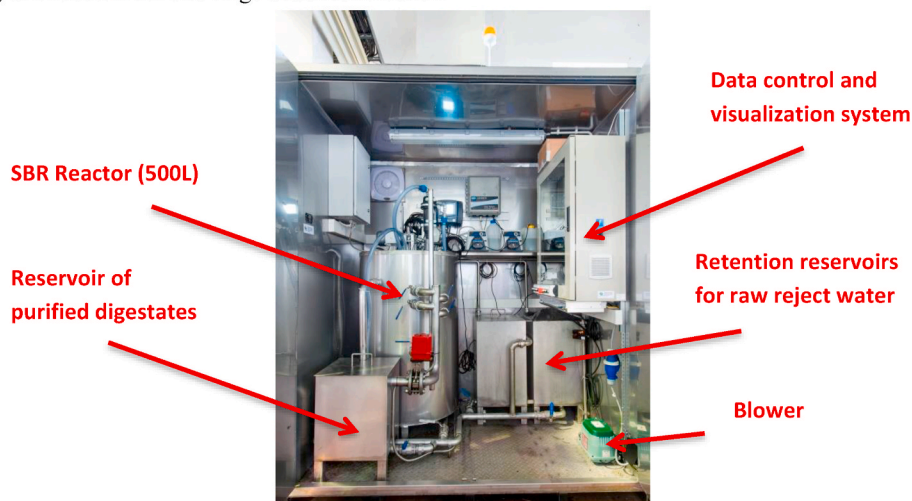


Fig. 2. The scheme of the integrated two-stage technology for the removal and recovery of biogenic compounds from the liquid fraction of digestates, 1–3 - The sampling sites of reject water.

a) SBR reactor for one-stage deammonification



b) Struvite precipitation reactor

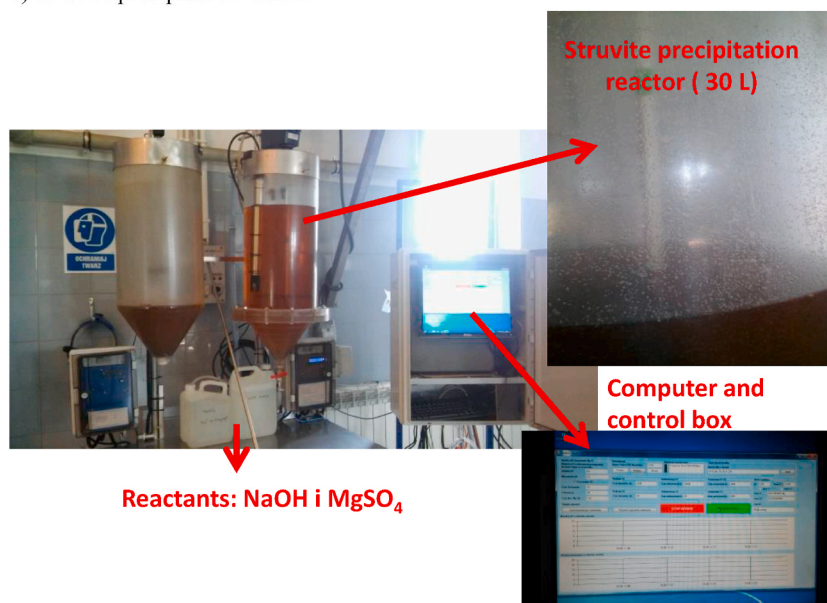


Fig. 3. Elements of the integrated technology for nutrients removal and recovery from the liquid fraction of digestates: a) deammonification reactor, b) struvite precipitation reactor.

Table 1

The conditions of the deammonification process in presented studies and literature review.

Parameter		Aeration mode		Ammonium nitrogen load [kg N/m ³ ·d]
Temperature [°C]	Sludge age [d]	Mixing/Aeration time [min]	Oxygen concentration [mg O ₂ /L]	
<i>The conditions of deammonification process in presented studies</i>				
30 ± 1	7	10/5	0.5	0.4
<i>The optimal parameters of deammonification process - summary based on literature review</i>				
25–35	5–80	3/3–30/30	0.08–3.0	0.03–1.1

Akaboci et al. [18]; Al-Hazmi et al. [8]; Cema et al. [19]; De Clippeleir et al. [20]; Miao et al. [21]; Lackner et al. [22]; Regmi et al. [23]; Wang et al. [24]; Zhao et al. [25]; Zubrowska-Sudol et al. [26].

effluent in the form of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, external dosing of magnesium salts was necessary to achieve more favorable conditions for controlling struvite precipitation. According to literature recommendations (Table 2), the doses of magnesium salts were selected so that at the same time the values of the molar ratio of magnesium to PO_4^{3-} ions were from 1.2:1 to 2:1, and the value of the molar ratio of Ca:Mg were below 1.

Anhydrous magnesium sulfate (minimum content 94.5%, Chempur) was used as a magnesium supplement in pilot studies due to its alkalinity (pH 7.9) - to apply lower doses of alkaline compounds to correct the pH value of the reject water a solution of magnesium salt (1 mL of the solution contained 10 mg Mg) with a constant dose, i.e. 250 mL for one 6 h operation cycle was added to the reactor, filled with reject water (30 L volume). The duration of the mixing phase was 90 min, with a mixing intensity of 240 rpm. After a certain period of mixing, a 180 min sedimentation phase was foreseen. After the sedimentation phase, a drain phase of "purified" reject water was adopted, which lasted 60 min. In this study, a pH of 8.7–9.3 was used for struvite precipitation, therefore it was necessary to increase the pH of reject water using sodium hydroxide (a 4 M NaOH solution was used). The NaOH solution was dosed until the set pH value was obtained and its doses were added to the reactor automatically by means of a pump installed in the system, cooperating with the pH meter.

Recovery of biogenic compounds that precipitated in insoluble salts forms and the percentage of removal of the remaining analyzed impurities (total suspended solids - TSS, Ca^{2+} and Mg^{2+} ions) were calculated as the quotient of the difference in concentration before (C_0) and after the process of struvite precipitation (C_e) to the initial concentration (C_0), $\eta = (C_0 - C_e)/C_0$.

2.4. Analytical methods

Physicochemical determinations were carried out in the analyzed reject water: TSS, ammonium nitrogen (N-NH_4^+), phosphorus compounds (P-PO_4^{3-} , total phosphorus - TP), magnesium ions, calcium ions, pH and temperature. The analytical methodology was based on the Standard Methods for Examination of Water and Wastewater [39]. The granulometric analysis of the precipitated struvite was also carried out using a Mastersizer 2000 diffraction analyzer with a Hydro 2000MU unit from Malvern Instruments Ltd. The Mastersizer software enabled the reading of the struvite crystal size.

3. Results and discussion

The physicochemical properties of digestates before and after the subsequent stages of treatment, i.e. in the liquid fraction of digestates flowing into integrated technology, and at the outflow from reactors, in which the processes of biological ammonium ion removal (deammonification) and chemical precipitation of struvite, respectively, took place, are given in Table 3.

The liquid fraction of digestates flowing into the integrated two-stage technology was characterized by variable concentrations of phosphate phosphorus and ammonium nitrogen. The concentration range varied from 18.5 to 35.8 mg/L for P-PO_4^{3-} and from 392.7 to 1007.0 mg/L for N-NH_4^+ . Large variations in P-PO_4^{3-} and N-NH_4^+ concentration values are also reported in the literature. Their concentration ranges (depending on the batch components used and digestate separation technology) were: 30–235 mg/L for P-PO_4^{3-} and 460 to 3580 mg/L for N-NH_4^+ [40–42]. Concentrations of other analyzed parameters varied: from 476.3 to 2165.0 mg/L for TSS, 62.7–85.5 mg/L for calcium and 25.5–46.5 mg/L for magnesium ions. Similar concentration for magnesium and calcium in the liquid fraction of digestates were obtained by Bachmann et al. [43] and Kolecka et al. [44].

After a period of sludge adaptation to the real reject water from WWTP Swarzewo (21 d), the efficiency of ammonium nitrogen removal in the deammonification process varied from 50 to 75%. A significant problem during the operation of the deammonification reactor was the periodic inflow of leachate with very high concentrations of TSS (over 2000 mg/L), which caused a significant decrease in ammonium nitrogen removal (to 10%), and in the sedimentation properties of the sludge and its outflow from the reactor. Attempts, made by the operator of the Swarzewo WWTP, to increase the efficiency of suspension separation during digestates dewatering on centrifuges by increasing the dose of polyelectrolytes, contributed to the decrease in the TSS concentration in liquid phases of digestates. However, a negative effect on the formation of "sticking" deammonification sludge granules was observed. This contributed to the further higher outflow of sludge from the deammonification reactor and its inflow to the second stage of integrated technology. Due to the problems described above, the average efficiency of the deammonification process for the entire study period was only 30%.

The efficiency of ammonium ion removal in the second stage of integrated technology, i.e. in the pilot reactor for struvite,

Table 2

The conditions of chemical precipitation of P and N in insoluble salts forms in presented studies and literature review.

Parameter	pH [–]	Temperature [°C]	Mixing speed [rpm]	Reaction time [min]	Ions molar ratio [–]		
					Mg:P	N:P	Ca:Mg
<i>The conditions of chemical precipitation of P and N in presented studies</i>							
	8.7–9.3	23–28	240	180	1.2:1–2:1	1.9:1–4.2:1	below 1
<i>The optimal parameters for struvite formation - summary based on literature review</i>							
	8.0–10.5	20.0–30.0	100–250	60–360	1.1:1–2:1	1.1–3.1	below 1

Battistioni et al. [27]; Munch and Barr [28]; Stratful et al. [29]; Le Corre et al. [30–32]; Zhang et al. [33]; Pastor et al. [34]; Hao et al. [35]; Hutnik et al. [9]; Rahman et al. [5]; Ye et al. [36]; Fang et al. [37]; Yan and Shih [11]; Shih et al. [13]; Cieřlik and Konieczka [38]; Moulessehouli [12]; Tansel et al. [14].

Table 3

Selected physicochemical properties of reject water before and after subsequent stages of treatment in integrated two-step technology (n = 11).

TSS mg/L	TP mg/L	P-PO ₄ ³⁻ mg/L	Mg ²⁺ mg/L	Ca ²⁺ mg/L	N-NH ₄ ⁺ mg/L	pH	Temp. °C
min. - max.							
<i>The liquid fraction of digestates flowing into integrated technology</i>							
476.3–2165	23.2–39.9	18.5–35.8	25.5–46.5	62.7–85.5	392.7–1007	7.7–8.0	20–26
<i>Reject water after I^o integrated technology</i>							
275.2–3923	21.8–37.3	16.6–33.7	26.7–43.7	60.1–76.8	301.8–695.7	7.9–8.4	23–28
<i>Reject water after II^o integrated technology</i>							
194.7–2575	2.8–7.7	0.7–2.2	33.2–97.1	55.2–69.1	257.8–558.9	8.7–9.3	20–25

where: n – the number of tests.

precipitation varied from 13.0 to 27.0% (Fig. 4). The obtained results do not clearly indicate a specific numerical effect of NH₄⁺ recovery potential. The differences in the recovery of ammonium ions were probably due to the qualitative characteristics of the reject water. In the analyzed liquid fraction of digestates the ammonium ion concentration was much higher than the magnesium and phosphate ions concentrations (Table 3), therefore the efficiency of ammonia removal was relatively small. It was also found that by increasing reject water alkalinity/pH values, the efficiency of ammonium ion removal also increased (Fig. 4). The pH value is important in converting NH₄⁺ ions to gaseous NH₃ in the process of stripping ammonia during the struvite precipitation reaction. Celen and Turker [45], and Stratful et al. [29] studied the effect of pH value on the efficiency of nitrogen and phosphorus removal. Studies have shown greater nitrogen removal as pH increases.

With the increase of the reject water pH value, the efficiency of calcium ion removal also increased. The highest efficiency of Ca²⁺ removal (14.0–26.0%) was found when the liquid fraction of digestates pH value ranged from 9.1 to 9.3 (Fig. 4). When the pH values ranged from 8.7 to 9.0, the concentration of calcium ions decreased to a maximum of 11.0% in relation to the concentrations in the initial samples (Fig. 4). Therefore, it can be assumed that despite maintaining the Mg²⁺:Ca²⁺ < 1 M ratio, phosphate ions at pH 9.1 to 9.3 could be precipitated not only in the form of struvite but also as other calcium salts (e.g. Ca₃(PO₄)₂ and CaHPO₄). Yigit and Mazlum [46], and Rahman et al. [5] found that the presence of Ca²⁺ in a solution with a pH above 9.0 contributes to an increase in the number of impurities such as Ca₃(PO₄)₂ and CaHPO₄. Jaffer et al. [47] showed that phosphorus precipitated in struvite only when the Ca²⁺:Mg²⁺ molar ratio was below 1. Le Corre et al. [31] observed precipitation of pure struvite only when the Ca²⁺:Mg²⁺ molar ratio ranged from 0.5 to 1.0. Hao et al. [35], cited by Rahman et al. [5], found that XRD data misled the researchers into believing that the harvested crystals were struvite, but in fact, it was amorphous phosphorus. Struvite precipitation is a pH-dependent reaction and pure struvite is formed at a near neutral pH. From the elemental analysis of the crystals, they confirmed that the highly purified (99.7%) struvite was formed at pH 7.0–7.5. They also found that the struvite content decreased to around 30–70% at pH 8.0–9.0 and with a pH over 9.5 the content decreased sharply to <30%. Higher pH levels (>10.5) resulted in the complete disappearance of struvite in the precipitates. According to Hermassi et al. [48], the optimum pH to achieve the formation of struvite and bobierite is approximately 9.5 and the optimum pH conditions to achieve the maximum recovery of ammonium is in the range between 4 and 8.5, as the total ammonium concentration is present in a higher concentration of NH₄⁺.

However, irrespective of the value of the molar quotient of Mg:P and pH, high efficiency of phosphate removal in reject water was observed (which varied from 85.0 to 93.0%) (Fig. 4). Similar phosphate removal efficiency was obtained by Munch and Barr [28], Yan and Shih [11], Moulessehouli et al. [12], Kim et al. [49], Kim et al. [50] and Quintana et al. [51].

The analyzed liquid fraction of digestates had a temperature of 23–28 °C, and according to literature reports, the optimal temperature range in which struvite crystals were more effectively precipitated was in the range of 20–30 °C (Table 2). Thus, it can be assumed that the observed temperature of the reject water could favor the precipitation of struvite crystals.

The particle size of the precipitated struvite suspension is of great importance to the struvite recovery technology design. On this basis, the method of separating struvite from liquids can be determined. Based on the granulometric analysis, information on the size of the precipitated struvite particles was obtained. It was observed that the crystals were of different sizes and their maximum sizes ranged from 0.72 to 1.65 mm (Table 4).

During the research, a certain trend was also observed. With increasing concentration of the TSS in the inflow to the second stage reactor, the size of the struvite crystals decreased. The largest crystal size was from 0.72 to 0.89 mm when the TSS concentration was from 2.3 to 3.9 g/L. However, when the TSS concentration was more than ten times lower, struvite crystal sizes were almost twice as large (up to 1.65 mm). The obtained test results confirmed the assumption that the presence of interfering factors (suspensions) may affect the dynamics of struvite precipitation and crystallization. Also, Ariyanto et al. [52] are of the opinion that the presence of impurities in solution can inhibit the precipitation of struvite as well as affect the size of its crystals. Taddeo et al. [53] determined how the presence of a suspension in the liquid fraction of digestates affects the process of struvite formation. The crystallization efficiency and the presence of struvite in the precipitate were inversely proportional to the concentration of the suspension. If the TSS concentration in the liquid fraction of digestates was 0.8 g/L, the crystallization efficiency and the struvite content in the sediment were 94% and 76%, respectively. However, when the concentration of TSS in the reject water was seven times higher, crystallization and the presence of struvite in the precipitate decreased (they were 61% and 48%, respectively).

Despite the similar parameters of struvite precipitation (values of Mg:P molar ratio, temperature, reaction time and mixing intensity), researchers who tested only on synthetic wastewater observed lower sizes of struvite crystals (Table 4), which confirms that synthetic reject water does not reflect the quality of real reject water, and the dynamics of struvite precipitation and crystallization in

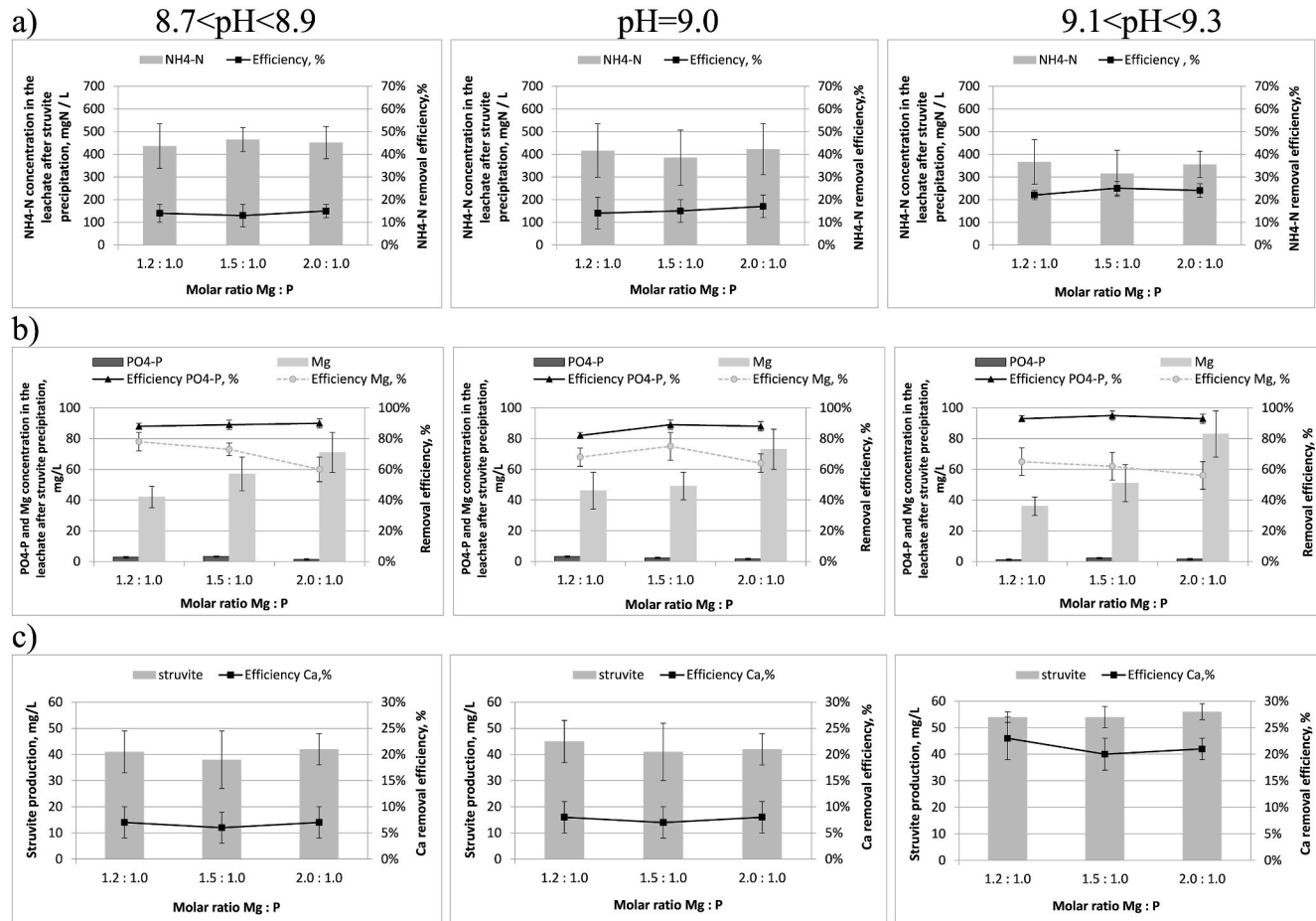


Fig. 4. Concentration and efficiency of recovery/removal of ammonium nitrogen (a), phosphate phosphorus and magnesium (b) in the process of crystallization of struvite and its production (c) at variable molar proportions of Mg: P and pH.

Table 4

Impact of selected parameters (Mg:P molar ratio, temperature, stirring intensity, reaction time and suspension concentration) on the size of precipitated struvite crystals.

Origin of liquid fraction of digestates	Mg:P molar ratio	Temperature	Reaction time	Stirring intensity	TSS	Maximum size of struvite crystals	Literature
	[–]	[°C]	[min]	[rpm]	[g/L]	[mm]	
Liquid fraction of digestates	1.2 : 1.0	23–28	240	240	0.32–1.52	0.82–1.65	Results obtained in these studies
	1.5 : 1.0				0.27–3.91	0.72–1.14	
	2.0 : 1.0				0.65–2.33	0.89–1.22	
Syntenic wastewater	1.0 : 1.0	20–25	80	400	–	0.29	Ye et al. [36]
Syntenic wastewater	2.0 : 1.0	21	–	30	–	0.01	Barbosa et al. [54]
Syntenic wastewater	1.2 : 1.0	20	60	–	–	0.08	Kozik et al. [55]
Syntenic wastewater	2.0 : 1.0	25	360	–	–	0.41	Moulessehouli et al. [12]

the analyzed real reject water may differ significantly from the results of tests with synthetic reject water.

High concentrations of nitrogen and phosphorus compounds in the liquid fraction of digestate from agricultural biogas plants is reported in the literature, which are a valuable product from the point of view of the recovery of these elements. The by-products of fermentation (e.g. liquid fraction of digestate) may contain, depending on feedstock and digestate separation technology, 0.03 to 1.50 gP_{tot}/L and 0.01 to 0.70 gPO₄³⁻/L [41,53,56]. The liquid fraction of digestate from agricultural biogas plants is characterized by concentrations of biogenic compounds similar to reject water from municipal wastewater treatment plants. This is important because if it will be necessary to remove or recover nutrients from the liquid fraction of digestate, the use of a two-stage technology (deammonification process/struvite production process) could be considered. While there are many publications about phosphorus recovery from raw animal excrements or dairy industry waste, only a few works concern the recovery of phosphorus from the liquid fraction of digestates.

4. Conclusions

In the pilot study, the possibility of the nutrient recovery in a two-step technology for reject water treatment (I^o Deammonification/II^o Struvite production) was conducted. The deammonification process (I^o integrated technology) did not interfere with the struvite precipitation course (II^o), because the reject water after I^o was characterized by N:P molar ratios from 1.7 to 4.5 (the necessary molar ratio of these elements for struvite precipitation is 1.0:1.0). The interferences concerned the leaching of biomass from the first reactor (in which the deammonification process was carried out) to the second reactor (in which struvite was precipitated) resulting in an increase in the concentration of the suspension in the digestates. The obtained results indicate the great importance of a proper digestate dewatering process with the practical possibility of struvite crystals precipitation.

CRedit authorship contribution statement

Agnieszka Tuszynska: Conceptualization, Methodology, Investigation, Writing – original draft. **Krzysztof Czerwionka:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The project was financially supported by Provincial Fund for Environmental Protection and Water Management in Gdansk/Poland (WFOŚiGW) in the “Pomeranian R & D projects” competition (2017 edition), contract No. WFOŚ/D/201/3/2018.

References

- [1] W. Mo, Q. Zhang, Energy–nutrients–water nexus: integrated resource recovery in municipal wastewater treatment plants, *J. Environ. Manag.* 127 (2013) 255–267.
- [2] J.P. van der Hoek, H. de Fooij, A. Struiker, Wastewater as a resource: strategies to recover resources from Amsterdam’s wastewater, *Resour. Conserv. Recycl.* 113 (2016) 53–64.
- [3] G. Bowden, H.D. Stensel, R. Tsuchihashi, Technologies for Sidestream Nitrogen Removal, Water Environment Research Foundation, 2015.
- [4] A. Magrí, F. Béline, P. Dabert, Feasibility and interest of the anammox process as treatment alternative for anaerobic digester supernatants in manure processing—an overview, *J. Environ. Manag.* 131 (2013) 170–184.
- [5] M.M. Rahman, M.A.M. Salleh, U. Rashid, A. Ahsan, M.M. Hossain, C.S. Ra, Production of slow release crystal fertilizer from wastewaters through struvite crystallization: a review, *Arabian J. Chem* 7 (2014) 139–155.
- [6] K. Zhou, M. Barjenbruch, Ch Kabbe, G. Inial, Ch Remy, Phosphorus recovery from municipal and fertilizer wastewater: China’s potential and perspective, *J. Environ. Sci.* 52 (2017) 151–159.



- [7] G. Rodriguez-Garcia, N. Frison, J.R. Vázquez-Padín, et al., Life cycle assessment of nutrient removal technologies for the treatment of anaerobic digestion supernatant and its integration in a wastewater treatment plant, *Sci. Total Environ.* 490 (2014) 871–879.
- [8] H. Al-Hazmi, D. Grubba, J. Majtacz, P. Kowal, J. Makinia, Evaluation of partial nitrification/anammox (PN/A) process performance and microorganisms community composition under different C/N ratio, *Water* 11 (2270) (2019) 1–17.
- [9] N. Hutnik, A. Kozik, A. Mazieniczuk, K. Piotrowski, B. Wierzbowska, A. Matynia, Phosphates (V) recovery from phosphorus mineral fertilizers industry wastewater by continuous struvite reaction crystallization process, *Water Res.* 47 (2013) 3635–3643.
- [10] O. Krüger, K.P. Fattah, Ch Adam, Phosphorus recovery from the wastewater stream - necessity and possibilities, *Desalin. Water Treat.* 57 (2016) 15619–15627.
- [11] H. Yan, K. Shih, Effects of calcium and ferric ions on struvite precipitation: a new assessment based on quantitative X-ray diffraction analysis, *Water Res.* 95 (2016) 310–318.
- [12] A. Moulessehoul, D. Gallart-Mateu, D. Harrache, S. Djaroud, M. de la Guardia, M. Kameche, Conductimetric study of struvite crystallization in water as a function of pH, *J. Cryst. Growth* 471 (2017) 42–52.
- [13] Y.J. Shih, R.R.M. Abarca, M.D.G. de Luna, Y.H. Huang, M.C. Lu, Recovery of phosphorus from synthetic wastewaters by struvite crystallization in a fluidized-bed reactor: effects of pH, phosphate concentration and coexisting ions, *Chemosphere* 173 (2017) 466–473.
- [14] B. Tansel, G. Lunn, O. Monje, Struvite formation and decomposition characteristics for ammonia and phosphorus recovery: a review of magnesium-ammonia phosphate interactions, *Chemosphere* 194 (2018) 504–514.
- [15] W.R. Abma, W. Driessen, R. Haarhuis, M. van Loosdrecht, Upgrading of sewage treatment plant by sustainable and cost-effective separate treatment of industrial wastewater, *Water Sci. Technol.* 61 (7) (2010) 1715–1722.
- [16] O.F. Schoumans, P. Ehlert, I. Regelink, I. Nelemans, W. Rulkens, Chemical Phosphorus Recovery from Animal Manure and Digestate. Laboratory and Pilot Experiments, Wageningen University, 2017, pp. 1566–7197.
- [17] Y. Feng, X. Lu, H. Al-Hazmi, J. Makinia, An overview of the strategies for the deammonification process start-up and recovery after accidental operational failures, *Rev. Environ. Sci. Biotechnol.* 16 (2017) 541–568.
- [18] T. Akabaci, F. Gich, M. Rusalleda, M. Dolors Balaguera, J. Colprima, Effects of extremely low bulk liquid DO on autotrophic nitrogen removal performance and NOB suppression in side- and mainstream one-stage PNA, *J. Chem. Technol. Biotechnol.* 93 (2018) 2931–2941.
- [19] G. Cema, E. Plaza, J. Trela, J. Surmacz-Górska, Dissolved oxygen as a factor influencing nitrogen removal rates in a one-stage system with partial nitrification and anammox process, *Water Sci. Technol.* 64 (2011) 1009–1015.
- [20] H. De Clippeleir, S.E. Vlaeminck, M. Carballa, W.A. Verstraete, Low volumetric exchange ratio allows high autotrophic nitrogen removal in a sequencing batch reactor, *Bioresour. Technol.* 100 (2009) 5010–5015.
- [21] Y. Miao, Y. Peng, L. Zhang, et al, Partial nitrification-anammox (PNA) treating sewage with intermittent aeration mode: effect of influent C/N ratios, *Chem. Eng. J.* 334 (2018) 664–672.
- [22] S. Lackner, K. Thoma, E.M. Gilbert, W. Gander, D. Schreff, H. Horn, Start-up of a fullscale deammonification SBR-treating effluent from digested sludge dewatering, *Water Sci. Technol.* 71 (2015) 553–559.
- [23] P. Regmi, R. Bunce, M.W. Miller, et al., Ammonia-based intermittent aeration control optimized for efficient nitrogen removal, *Biotechnol. Bioeng.* 112 (2015) 2060–2067.
- [24] Y. Wang, Y. Wang, Y. Wei, M. Chen, In-situ restoring nitrogen removal for the combined partial nitrification-anammox process deteriorated by nitrate build-up, *Biochem. Eng. J.* 98 (2015) 127–136.
- [25] J. Zhao, J. Zuo, J. Lin, P. Li, The performance of a combined nitrification-anammox reactor treating anaerobic digestion supernatant under various C/N ratios, *J. Environ. Sci.* 30 (2015) 207–214.
- [26] M. Zubrowska-Sudol, J. Yang, J. Trela, E. Plaza, Evaluation of deammonification process performance at different aeration strategies, *Water Sci. Technol.* 63 (2011) 1168–1176.
- [27] P. Battistoni, A. De Angelis, P. Pavan, M. Prisciandaro, F. Cecchi, Phosphorus removal from a real anaerobic supernatant by struvite crystallization, *Water Res.* 35 (2001) 2167–2178.
- [28] E.V. Munch, K. Barr, Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams, *Water Res.* 35 (2001) 151–159.
- [29] I. Stratful, M. Scrimshaw, J. Lester, Conditions influencing the precipitation of magnesium ammonium phosphate, *Water Res.* 35 (2001) 4191–4199.
- [30] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Impact of calcium on struvite crystals size, shape and purity, *J. Cryst. Growth* 283 (2005) 514–522.
- [31] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, B. Jefferson, S.A. Parsons, Agglomeration of struvite crystals, *Water Res.* 41 (2007) 419–425.
- [32] K.S. Le Corre, E.V. Jones, P. Hobbs, S.A. Parsons, Phosphorus recovery from wastewater by struvite crystallization: a review, *Crit. Rev. Environ. Sci. Technol.* 39 (2009) 433–477.
- [33] T. Zhang, L. Ding, H. Ren, Pretreatment of ammonium removal from landfill leachate by chemical precipitation, *J. Hazard Mater.* 166 (2009) 911–915.
- [34] L. Pastor, D. Mangin, J. Ferrer, A. Seco, Struvite formation from the supernatants of an anaerobic digestion pilot plant, *Bioresour. Technol.* 101 (2010) 118–125.
- [35] X. Hao, C. Wang, M.C.M. van Loosdrecht, Y. Hu, Looking beyond struvite for P-recovery, *Environ. Sci. Technol.* 47 (2013) 4965–4966.
- [36] Z. Ye, Y. Shen, X. Ye, Z. Zhang, S. Chen, J. Shi, Phosphorus recovery from wastewater by struvite crystallization: property of aggregates, *J. Environ. Sci.* 26 (2014) 991–1000.
- [37] C. Fang, T. Zhang, R. Jiang, H. Ohtake, Phosphate enhance recovery from wastewater by mechanism analysis and optimization of struvite settleability in fluidized bed reactor, *Sci. Rep.* 6 (2016) 1–12.
- [38] B. Ciešlik, P. Konieczka, A review of phosphorus recovery methods at various steps of wastewater treatment and sewage sludge management. The concept of “no solid waste generation” and analytical methods, *J. Clean. Prod.* 142 (2017) 1728–1740.
- [39] Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, DC, USA, 2005.
- [40] M. Gajewska, H. Obarska-Pempkowiak, Multistage treatment wetland for treatment of reject waters from digested sludge dewatering, *Water Sci. Technol.* 68 (2013) 1223–1232.
- [41] F. Tambone, V. Orzi, G. D’Imporzano, F. Adani, Solid and liquid fractionation of digestate: mass balance, chemical characterization, and agronomic and environmental value, *Bioresour. Technol.* 243 (2017) 1251–1256.
- [42] W. Dabrowski, B. Karolinaczek, P. Malinowski, D. Boruszko, Modeling of pollutants removal in subsurface vertical flow and horizontal flow constructed Wetlands, *Water* 180 (2019) 1–17.
- [43] S. Bachmann, R. Uptmoor, B. Eichler-Löbermann, Phosphorus distribution and availability in untreated and mechanically separated biogas digestates, *Sci. Agric.* 73 (2016) 9–17.
- [44] K. Kolecka, M. Gajewska, P. Stepnowski, M. Caban, Spatial distribution of pharmaceuticals in conventional wastewater treatment plant with Sludge Treatment Reed Beds technology, *Sci. Total Environ.* 647 (2019) 149–157.
- [45] I. Celen, M. Türker, Recovery of ammonia from anaerobic digester effluents, *Environ. Technol.* 22 (2001) 1263–1272.
- [46] N. Yigit, S. Mazlum, Phosphate recovery potential from wastewater by chemical precipitation at batch conditions, *Environ. Technol.* 28 (2007) 83–93.
- [47] Y. Jaffer, T.A. Clark, P. Pearce, S.A. Parsons, Potential phosphorus recovery by struvite formation, *Water Res.* 36 (2002) 1834–1842.
- [48] M. Hermassi, J. Dosta, C. Valderrama, et al., Simultaneous ammonium and phosphate recovery and stabilization from urban sewage sludge anaerobic digestates using reactive sorbents, *Sci. Total Environ.* 630 (2018) 781–789.
- [49] D. Kim, H.D. Ryu, M.S. Kim, J. Kim, S.I. Lee, Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate, *J. Hazard Mater.* 146 (2007) 81–85.
- [50] D. Kim, K. Min, K. Lee, M. Yu, K. Park, Effect of pH, molar ratios and pre-treatment on phosphorus recovery through struvite crystallization from effluent of anaerobically digested swine wastewater, *Environ Eng Res* 22 (2017) 12–18.
- [51] M. Quintana, M.F. Colmenarejo, J. Barrera, et al., Removal of phosphorus through struvite precipitation using a by-product of magnesium oxide production (BMP): effect of the mode of BMP preparation, *Chem. Eng. J.* 136 (2008) 204–209.

- [52] E. Ariyanto, T.K. Sen, H.M. Ang, The influence of various physico-chemical process parameters on kinetics and growth mechanism of struvite crystallization, *Adv. Powder Technol.* 25 (2014) 682–694.
- [53] R. Taddeo, M. Honkanen, K. Kolppo, R. Lepisto, Nutrient management via struvite precipitation and recovery from various agroindustrial wastewaters: process feasibility and struvite quality, *J. Environ. Manag.* 212 (2018) 433–439.
- [54] S.G. Barbosa, L. Peixoto, B. Meulman, M.M. Alves, M.A. Pereira, A design of experiments to assess phosphorous removal and crystal properties in struvite precipitation of source separated urine using different Mg sources, *Chem. Eng. J.* 298 (2016) 146–153.
- [55] A. Kozik, N. Hutnik, A. Matynia, J. Gluzinska, K. Piotrowski, Recovery of phosphate (V) ions from liquid waste solutions containing organic impurities, *Chemik* 65 (2011) 675–686.
- [56] A. Tuszynska, K. Czerwionka, H. Obarska-Pempkowiak, Phosphorus concentration and availability in raw organic waste and post fermentation products, *J. Environ. Manag.* (2) (2021) 278, <https://doi.org/10.1016/j.jenvman.2020.111468>.