



Treatment of post-digestion liquors with the application of struvite precipitation and reverse osmosis

Jolanta Bohdziewicz^a, Mariusz Kuglarz^{b,*}

^aSilesian University of Technology, Faculty of Energy and Environmental Engineering, Akademicka 2a, 44-100 Gliwice, Poland

^bUniversity of Bielsko-Biala, Faculty of Materials and Environment Sciences, Willowa 2, 43-309 Bielsko-Biala, Poland

Tel. +48 338279181; Fax: +48 338279101; email: mkuglarz@ath.bielsko.pl

Received 16 March 2012; Accepted 18 July 2012

ABSTRACT

Since the post-digestion liquors exhibited a high content of biogenic substances and organic matter, an attempt was made to develop an effective treatment of their treatment, allowing the treated liquors to be directly released into a natural reservoir. The liquors were treated with the application of reverse osmosis (RO) and chemical precipitation (struvite) as a pre-treatment step. The application of a unit RO process did not ensure an adequate removal of contaminants, mainly due to the excessive concentration of NH_4^+ in the permeate. The treatment of post-digestion liquors with a struvite precipitation and a subsequent RO process turned out to be effective and allowed to decrease contaminants' concentration below discharge limits, allowing direct release of permeate to a natural receiver. However, it was necessary to apply an increased ratio of magnesium and phosphates during struvite precipitation ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.5:1:1.5$), preceding reverse osmosis treatment. As compared to the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, the application of MgO as a Mg^{2+} source allowed to receive an additional removal of COD. Struvite crystals were characterized by regular orthorhombic structure and contained insignificant amounts of heavy metals. Moreover, the struvite precipitation influenced the efficiency of a subsequent membrane process in a positive way.

Keywords: Post-digestion liquors; Struvite; Reverse osmosis; Biogenic substances

1. Introduction

The process of controlled anaerobic digestion for biogas production is one of the most widely-used sewage sludge stabilization method. The main strength of the process is the possibility to generate renewable energy in the form of biogas. Besides, the process generates a digestate, whose quality is mostly determined by characteristics of feedstock used and conditions of the

digestion process performed, such as digestion temperature, organic loading of bioreactors [1–4]. Anaerobic digestion leads to the reduction of organic matter through the biodegradation of macromolecular substances, mainly proteins, fats, carbohydrates as well as their derivative compounds. It is assumed that about 80% of organic matter, which underwent biodegradation, is converted into biogas, while further 10% is converted into complex organic substances, e.g. humic acid. The remaining part passes to the post-digestion

*Corresponding author.

effluent and is responsible for high COD concentration. Sludge digestion results in ammonia-nitrogen and phosphates release. High concentrations of biogenic substances in post-digestion liquids are the results of hydrolytic decomposition of organic nitrogen and phosphorus compounds, and thus in turn cause both ammonia and phosphates release into a post-digestion effluent [5,6]. Besides, the application of polyphosphate-accumulating organisms (PAO), which accumulate phosphorus in quantities exceeding their energetic needs (>2% of TS), increases the contents of phosphorus in the sludge flocs. The enrichment of activated sludge treatment with phosphate accumulating bacteria results in increased content of phosphorus in the sludge, i.e. about 4–7% TS. While, the proportion of phosphorus in the sludge after conventional activated sludge processes usually does not exceed 2% of TS, the final utilization of the digestate is conditioned predominantly by the legal regulations enforced by a given country. Since the digestate contains a significant amount of nutrients, it seems reasonable for the digested sludge to be used in agriculture. However, digestion processes performed in mesophilic conditions do not usually ensure complete hygienization and stabilization of the sludge. The digestate has to be further treated in order to improve its quality. Thus, the digested sludge usually undergoes separation into liquid and solid phases. Solid fraction can be additionally treated, e.g. through composting, which ensures a high degree of hygienization as well as biodegradation of remaining organic matter after digestion [7,8].

The development of effective treatment methods of post-digestion liquors is an urgent issue to be resolved. Nowadays, post-digestion liquors are frequently directed back to the biological treatment facility and treated together with raw wastewater. However, the liquors exhibit an exceptionally unfavourable C/N ratio (0.15–0.20), which has a negative impact on the wastewater treatment processes, especially the denitrification. Their treatment in such a way requires the addition of external carbon source [9,10]. Post-digestion liquors are more and more frequently treated separately with the application of biological as well as physical and chemical methods. Physical and chemical methods in nature include: ions exchange, coagulation, ammonia desorption, advanced oxidation processes, adsorption as well as membrane techniques. While biological methods—except for the traditional method of activated sludge—encompass unconventional systems, e.g. Anammox [11–16], individual unit processes do not ensure a complex removal of contaminants.

Even the application of highly effective reverse osmosis (RO) process does not allow to reduce the level of contaminants so that the treated post-digestion

liquors can be released into a natural reservoir [14,17]. Despite the fact that application of RO membranes ensures a high degree of contaminants removal, in most cases exceeding 90%, the permeate is usually loaded with NH_4^+ concentration exceeding the value allowing direct release into the natural reservoir. The key factors conditioning the degree of ammonia removal through RO process are: initial NH_4^+ content and pH value, which influence the form of ammonia-nitrogen. At high pH values (pH 9), a significant amount of nitrogen-ammonia (>30%) occurs in unionized form, which is not detained by osmotic membranes. While at lower pH values of about 7, ammonia-nitrogen occurs predominantly in ionic form and only less than 1% of ammonia-nitrogen exists in unionized form [12,18,19].

Thus, post-digestion liquors rich in ammonia-nitrogen should undergo pre-treatment oriented towards removing as much of ammonia-nitrogen as possible before applying RO treatment. An interesting solution seems to be the chemical methods of struvite (ammonium magnesium phosphate) precipitation, which allows to bind both ammonia-nitrogen and phosphorus. The aim of the research project presented in the article was to develop an effective treatment method of highly-polluted post-digestion liquors, to a degree allowing the treated liquors to be directly released into a natural reservoir. The post-digestion wastewater underwent high-pressure membrane filtration (RO) and chemical precipitation (struvite) as a pre-treatment step. The study of the struvite precipitation focused on: (1) the selection of the most suitable reagents as Mg^{2+} source, (2) the influence of increased dosages of Mg^{2+} and PO_4^{3-} on the effectiveness of NH_4^+ removal, (3) the possibility of COD removal during precipitation as well as (4) quality analyses of struvite precipitated. In particular, an attempt was made to establish the influence of struvite precipitation as a pre-treatment step on the effectiveness and efficiency of a subsequent reverse osmosis process.

2. Research materials and methods

2.1. Research material

The liquid fraction of the digested sludge, referred further as post-digestion liquors was used as a research material. It originated from a full-scale municipal treatment plant based on Enhanced Biological Nutrients Removal (EBNR). The plant treats domestic as well as industrial wastewater. The industrial fraction constitutes up to the 10% of the total influent and is pre-treated before mixed with domestic wastewater. Table 1 presents the characteristics of the post-digestion liquors.

Table 1
Characteristics of the post-digestion liquors

Parameter	Unit	Post-digestion wastewater
pH	–	7.8 (0.2)*
NH ₄ ⁺	mg/dm ³	1,415 (48)
TN	mg/dm ³	1,520 (41)
PO ₄ ³⁻	mg/dm ³	486 (29)
TP	mg/dm ³	117 (12)
Cl ⁻	mg/dm ³	430 (35)
Mg ²⁺	mg/dm ³	45.5 (7.5)
Ca ²⁺	mg/dm ³	16.5 (4.5)
COD	mg O ₂ /dm ³	1,490 (72)
TS	mg/dm ³	160 (25)

(*)–Standard deviation.

2.2. Analytical methods

The scope of the analyses conducted encompassed: pH value measurement and determinations of total suspension (TS), chemical oxygen demand (COD), ammonia-nitrogen (NH₄⁺) and total-nitrogen (TN, Kjeldahl nitrogen), phosphates (PO₄³⁻), total phosphorus (TP), chlorides (Cl⁻) as well as calcium and magnesium [20,21]. Heavy metals content in the solid fraction after struvite precipitation was determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry, while images of (100×) struvite crystals were taken by means of a Nikon Alphaphot microscope, coupled with a digital camera.

2.3. Ammonium magnesium phosphate precipitation

Struvite precipitation was conducted in a 10-dm³ crystallizer, working in a batch mode. The process was carried out at constant temperature of 20°C and pH value at the level of 9.0–9.5. The applied pH value was in the optimum range for struvite precipitation [22–25]. The retention time of post-digestion liquor in a crystallizer amounted to 2 h. The reactor contents were mixed by means of a magnetic stirrer (100 rpm/min.). In case of the analysed post-digestion liquor, the concentration of NH₄⁺ exceeded significantly the stoichiometric value of struvite, while, the concentration of PO₄³⁻ and Mg²⁺ played the role of limiting factors. The lacking amounts of phosphorus and magnesium were augmented by H₃PO₄ and MgO/MgCl₂·6H₂O, respectively. The process was conducted for the stoichiometric ratio of Mg²⁺:NH₄⁺:PO₄³⁻ as well as 25% and 50% excess amounts of magnesium and phosphorus (Mg²⁺:NH₄⁺:PO₄³⁻ = 1.25:1:1.25; Mg²⁺:NH₄⁺:PO₄³⁻ = 1.5:1:1.5). In order to assess the amounts of NH₄⁺ released into the atmosphere during precipitation,

a parallel trial (blank sample) was conducted without the addition of magnesium and phosphorus. The pH value of post-digestion liquors was adjusted by means of 1 M NaOH.

The effectiveness of struvite precipitation was based on the degree of NH₄⁺ and PO₄³⁻ removal, as compared to their initial concentration in the post-digestion liquors.

2.4. Reverse osmosis (RO) treatment

High-pressure process of reverse osmosis (RO) was conducted in the device type GH-100-400, produced by a US-based company, Osmonics. The device worked in the dead-end mode, on flat membranes with the active volume of 36.3 cm². Polyamide membrane type ADF was applied. The processes were conducted at the trans-membrane pressure of 2 MPa. The rotary velocity of the stirrer was maintained at the level of 200 rpm/min. The pH value of the liquors treated was adjusted to the level of about 6.5 by means of HCl, before the liquor underwent the membrane process. Fig. 1 shows the reverse osmosis unit.

The process of reverse osmosis was conducted with the application of composite polyamide membrane, type ADF, whose characteristics are presented in Table 2.

The efficiency of the reverse osmosis process was determined according to the following formula (1):

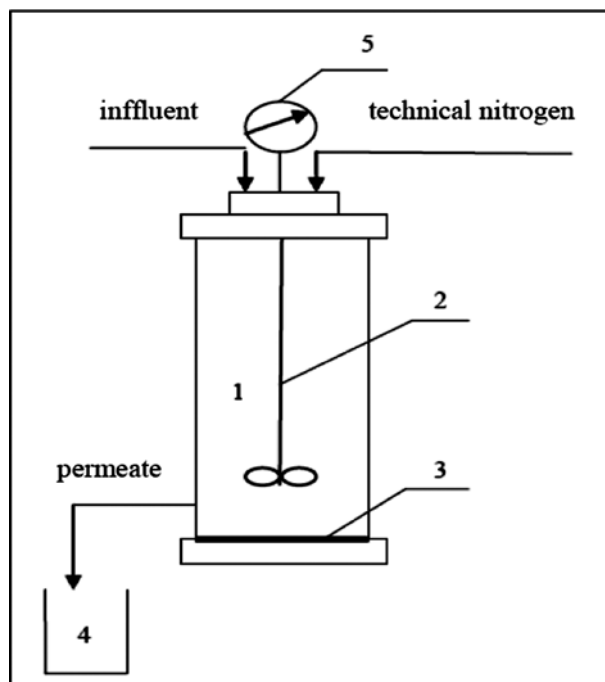


Fig. 1. RO unit for the treatment of post-digestion liquors (1–high pressure container, 2–stirrer, 3–membrane, 4–container for permeate storing, 5–manometer).

Table 2
Characteristics of the ADF membrane

Membrane characteristics	Range of value
pH range	4–11
Max. working temperature (°C)	50
Max. transmembrane pressure (MPa)	5.4
Retention coefficient Cl ⁻ (%) ^a	99.5

^a0.5% NaCl solution.

$$J_v = \frac{V}{F \cdot t}, \text{ m}^3/\text{m}^2\text{s} \quad (1)$$

where J_v is the volumetric permeate flux, $\text{m}^3/\text{m}^2\text{s}$; V is the volume of permeate collected after the particular period of time (t), m^3 ; F is the active surface of membrane, m^2 ; and t is the filtration time, s.

3. Results and discussion

Anaerobic digestion of sewage sludge leads to the release of phosphates, nitrogen-ammonia and organic substances to the liquid phase [26,27]. Since the effluent after anaerobic digestion was loaded with high amounts of such substances, it was attempted to treat the post-digestion wastewater by means of high-pressure membrane treatment (RO) and additionally by chemical precipitation as a pre-treatment step.

3.1. Struvite precipitation

Precipitation of ammonia and phosphate ions in the form of ammonium magnesium phosphate, commonly known as “struvite” is determined to a large extent by the pH value. The most appropriate range of pH value for effective struvite precipitation oscillates between 9 and 10 [22–25,28]. Struvite crystals do not get generated at pH <7. Besides, in the solution containing Mg^{2+} , NH_4^+ , and PO_4^{3-} , other compounds containing phosphorus and magnesium can be precipitated, such as $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$,

and $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. However, all the compounds, except for the struvite, exhibit high solubility at pH between 8 and 10, or are precipitated at a much lower pH value, e.g. $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ crystallizes at a pH value <6 [23,25]. Moreover, phosphates can react with calcium ions in the solution, which inhibits struvite crystallization. According to the literature, however, the ratio of Ca:Mg <1 does not influence the struvite precipitation in a significant way [29]. Since magnesium was added in order to comply with struvite chemical formula, it was assumed that interactions between calcium and phosphorus will not lead to a significant phosphate decrease in the solution. Potassium struvite crystallization for magnesium struvite precipitation was also excluded as a result of high NH_4^+ concentration in analysed post-digestion liquors [30].

3.1.1. Influence of increased molar ratio of Mg^{2+} and PO_4^{3-} on the effectiveness of the NH_4^+ removal

Precipitation of struvite was conducted for the stoichiometric molar ratio of Mg^{2+} , NH_4^+ , and PO_4^{3-} as well as increased molar ratio of phosphates and magnesium ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.25:1:1.25$, $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.5:1:1.5$). In order to assess the amount of ammonia-nitrogen, which might have been released during struvite precipitation, the blank sample without magnesium and phosphorus addition was run. In those conditions, about 5–6% of ammonia was released. Table 3 presents the characteristics of post-digestion liquors after struvite precipitation.

Firstly, the application of stoichiometric ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ ions allowed to receive a high degree of ammonia-nitrogen removal, i.e. 87–92%. In those conditions, the phosphate removal amounted to 81–83%. Slightly lower degrees of removal after application of MgO as a source of Mg^{2+} ions have been ascribed to its slow solubility [31,32]. However, the weight ratio of ($\text{PO}_4^{3-}/\text{NH}_4^+$) reached the value 0.5–0.7, i.e. several times less than the value resulted from struvite formula (5.27). In order to increase the

Table 3
Characteristics of post-digestion liquor after struvite precipitation

Molar ratio $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$	MgO + H ₃ PO ₄			MgCl ₂ ·6H ₂ O + H ₃ PO ₄		
	NH ₄ ⁺ mg/dm ³	PO ₄ ³⁻ mg/dm ³	COD mg/dm ³	NH ₄ ⁺ mg/dm ³	PO ₄ ³⁻ mg/dm ³	COD mg/dm ³
1:1:1	181 (7)	90.7 (3.6)	1222 (98)	118 (10)	84.3 (6.7)	1579 (90)
1.25:1:1.25	72.5 (5.0)	156 (11)	1122 (89)	61.8 (4.5)	142 (9)	1654 (89)
1.5:1:1.5	26.5 (2.5)	189 (11)	956 (60)	18.9 (1.9)	178 (10)	1699 (94)
Blank sample	1330 (85)	484 (21)	1495 (89)	1345 (90)	481 (24)	1530 (94)

(–)–Standard deviation.

effectiveness of the process and thus decrease the residual concentration of NH_4^+ , it was necessary to increase the ratio of phosphates and magnesium.

Secondly, the struvite precipitation was conducted at increased molar ratios of magnesium and phosphates. The degrees of NH_4^+ removal amounted to 95–96% ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.25:1:1.25$) and 98–99% ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.5:1:1.5$). In those conditions, the degree of phosphate removal decreased by about 10% ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.25:1:1.25$) and 20% ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.5:1:1.5$). In case of 50% increased Mg^{2+} and PO_4^{3-} ratio, the weight ratio of ($\text{PO}_4^{3-}/\text{NH}_4^+$) reached the value 7.1–9.4, i.e. above the value resulted from struvite formula (5.27), so further increase of magnesium and phosphate turned out to be unjustifiable. The influence of increased dosages of Mg^{2+} and/or PO_4^{3-} on the effectiveness of ammonia-nitrogen removal was mentioned in previous studies [23,25,32–34]. The authors proved positive effect of Mg^{2+} and/or PO_4^{3-} increased availability on the effectiveness of NH_4^+ removal. To cite an example, the degree of NH_4^+ removal increased from 79% to 86% as result of increased magnesium dosage ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.15:1:1$) [24].

3.1.2. The influence of struvite precipitation on the organic matter removal

On the one hand, struvite precipitation with the application of MgO as a source of Mg^{2+} caused a decrease in COD concentration, which was ascribed to the magnesium oxide properties. It was assumed that a part of organic substances might have been absorbed by generated $\text{Mg}(\text{OH})_2$ and precipitated together with struvite. The higher the dosage of MgO used, the higher the degree of COD removal. The addition of increased ratios of Mg^{2+} in a form of MgO allowed to remove 25–36% of initial COD compounds, as compared to the 18% removed after conducting the process at the stoichiometric ratio. On the other hand, after using magnesium chloride for precipitation, the concentration of COD increased slightly. It might have been an effect of partial release of soluble substances from suspended solids. Fig. 2 presents the influence of both reagents used as a source of Mg^{2+} on the concentration of COD.

3.1.3. Chemical composition, structure and quality of struvite precipitated

The structure of struvite crystals is determined by many factors, such as length of precipitation, intensity of mixing, Mg/P ratio, concentration of ammonia-nitrogen as well as chemical impurities, e.g. heavy metals interfer-

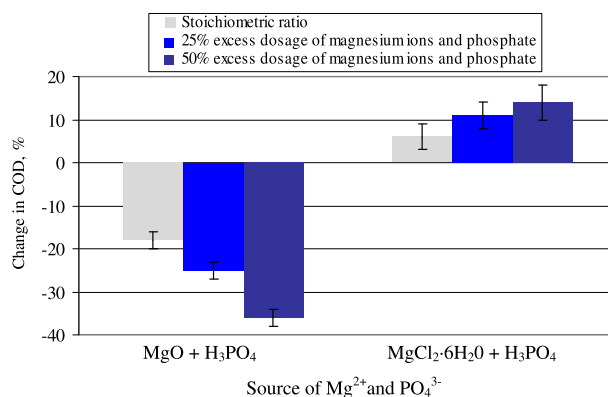


Fig. 2. The influence of struvite precipitation on the changes of soluble organic matter in post-digestion liquors.

ing with the crystallization [35,36]. Based on the performed microscopic pictures, it was established that reagents used as source of Mg^{2+} as well as the application of increased $\text{Mg}^{2+}/\text{NH}_4^+$ ratio did not influence significantly the structure of struvite crystals generated. In all cases, the struvite crystals were characterized mostly by regular orthorhombic structure (Fig. 3). The influence of potential factors determining the structure of struvite precipitated reported in the literature is not clear. However, it may be concluded that one of the most important factors, which has an influence on the structure of generated struvite crystals, is the ammonia-nitrogen content in the solution. In low ammonia-nitrogen conditions, the struvite precipitates in orthorhombic structure, while, high ammonia-nitrogen conditions (above $1500 \text{ mg}/\text{dm}^3$) are privileged for “needle like” structure [35]. It is in agreement with the previous findings [33].

Chemical composition of precipitated struvite did not differ significantly from the theoretical proportion of particular ingredients in the struvite formula. Slightly higher contents of phosphorus and magnesium might have been the result of other compounds precipitated together with struvite. Moreover, the struvite contained insignificant amounts of heavy metals. Table 4 presents chemical composition as well as heavy metal content in precipitated struvite.

3.2. Reverse osmosis post-treatment

Post-treatment with the application of reverse osmosis (RO) underwent the liquor streams directly after anaerobic digestion as well as after initial struvite precipitation conducted with the application of MgO, which was considered as a better source of Mg^{2+} , as compared to $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Despite relatively comparable degrees of NH_4^+ removal, amounting to between 70% and 75%, only in the case of the liquor pre-treated with the application of struvite precipitation based on

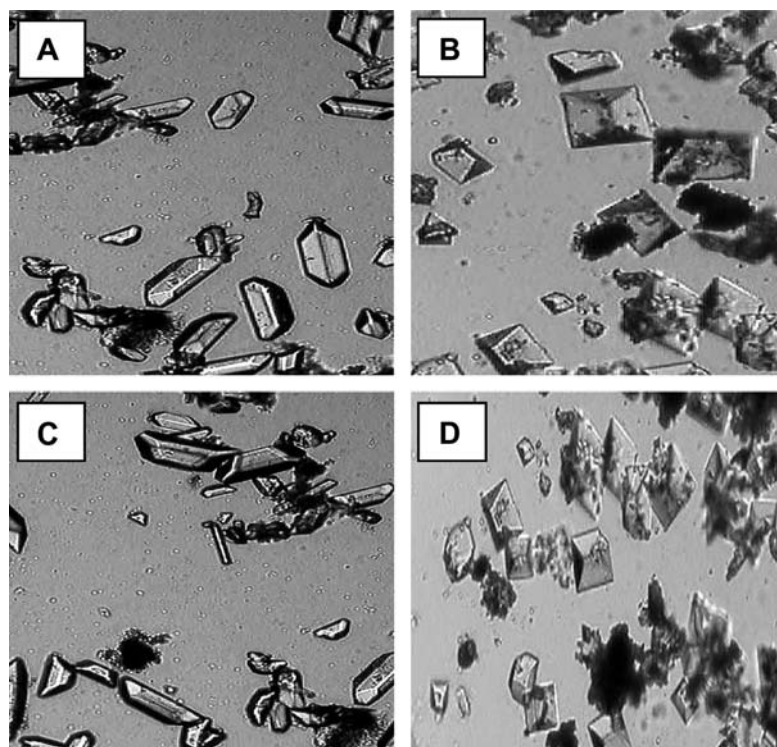


Fig. 3. Microscopic pictures of struvite crystals (A— $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1:1:1$, $\text{MgO} + \text{H}_3\text{PO}_4$; B— $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1:1:1$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{H}_3\text{PO}_4$; C— $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.5:1:1.5$, $\text{MgO} + \text{H}_3\text{PO}_4$; D— $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1.5:1:1.5$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

Table 4
Chemical composition and heavy metals content in precipitated struvite

Parameter	Unit	Precipitated struvite
TP	mg/dm ³	13.48 (0.20)*
TN	mg/dm ³	4.89 (0.51)
Mg	mg/dm ³	11.56 (0.52)
Ca	mg/dm ³	2.17 (0.30)
Cd	mg/dm ³	1.12 (0.20)
Cu	mg/dm ³	16.3 (2.1)
Ni	mg/dm ³	6.15 (0.52)
Pb	mg/dm ³	8.17 (0.40)
Zn	mg/dm ³	35.2 (2.7)
Hg	mg/dm ³	<0.1
Cr	mg/dm ³	19.4 (1.0)

(*)—Standard deviation.

the 50% increased molar ratio of Mg^{2+} and PO_4^{3-} , the concentration of TN exhibited the value (8.4 mg/dm³) allowing direct release of the permeate to the natural reservoir [37]. While, the permeate after membrane treatment without struvite precipitation as well as after dual treatment with struvite precipitation at lower molar ratios of Mg^{2+} and PO_4^{3-} exhibited too high a con-

centration of NH_4^+ , still above discharge limits. Taking into account the above, it was concluded that initial concentration of NH_4^+ plays a crucial role in the residual content of TN after RO treatment. In all conducted trials, the concentration of COD, TS as well as TP decreased below the levels allowing its direct release into the natural reservoir [37]. What is more, the application of RO process eliminated the secondary load of Cl^- , which occurred in treated liquor as a result of pH value adjustment before RO process. Changes in quality indicators characterizing the liquors treated by means of RO are presented in Table 5.

The initial struvite precipitation in all post-digestion liquors influenced the efficiency of the subsequent membrane process in a positive way. The initial value of both volumetric fluxes reached the value of $3.0 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$. In all cases, a greater value of the fluxes occurred in the case of the processes conducted for the liquor after initial struvite precipitation. After about 5 h of conducting the high-pressure process, the flux value of liquor which did not undergo struvite precipitation stabilized at $1.05 \times 10^{-6} \text{ m}^3/\text{m}^2 \cdot \text{s}$. While the value of the flux after initial struvite precipitation conducted for 50% increased molar ratio of Mg^{2+} and PO_4^{3-} stabilized at the level higher of above 30%. The effect was ascribed to the lower organic matter load of the liquor after struvite

Table 5
 Characteristics of post-digestion liquors post-treated with the application of reverse osmosis

Parameter	Unit	Without struvite precipitation	Mg ²⁺ :NH ₄ ⁺ :PO ₄ ³⁻ (1:1:1)	Mg ²⁺ :PO ₄ ⁺ :PO ₄ ³⁻ (1.25:1:1.25)	Mg ²⁺ :NH ₄ ⁺ :PO ₄ ³⁻ (1.5:1:1.5)
pH	–	7.1 (0.1)*	7.1 (0.1)	7.2 (0.1)	7.2 (0.1)
NH ₄ ⁺	mg/dm ³	230 (14)	74.5 (5.4)	25.5 (2.4)	8.0 (0.6)
TN	mgN/dm ³	245 (11)	80.5 (4.5)	28.9 (2.1)	8.4 (0.7)
PO ₄ ³⁻	mg/dm ³	2.1 (0.3)	2.0 (0.1)	1.5 (0.1)	1.3 (0.1)
TP	mgP/dm ³	0.8 (0.1)	0.7 (0.1)	0.6 (0.1)	0.3 (0.1)
Cl ⁻	mg/dm ³	16.9 (2.1)	20.5 (1.5)	28.6 (3.0)	29.6 (2.5)
COD	mgO ₂ /dm ³	11.7 (1.1)	10.5 (1.1)	8.5 (1.0)	9.0 (1.2)
TS	mg/dm ³	1.1 (0.4)	1.4 (0.3)	1.4 (0.4)	1.6 (0.3)

()*—Standard deviation.

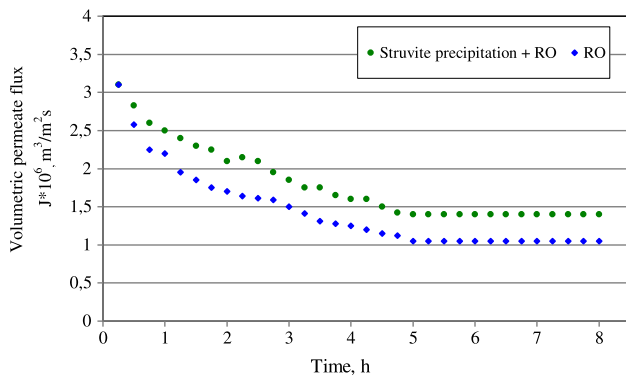


Fig. 4. The influence of struvite precipitation on the efficiency of RO post-treatment.

precipitation. The influence of the initial struvite precipitation (Mg²⁺:NH₄⁺:PO₄³⁻ = 1.5:1:1.5) on the value of volumetric permeate flux is presented in Fig. 4.

4. Conclusions

Post-digestion liquor treatment with the application of struvite precipitation targeted at ammonia-nitrogen binding coupled with reverse osmosis process allowed to decrease the contaminants concentration below values, allowing direct release of treated liquors into natural water bodies. The key role on the TN content after RO treatment was played by the initial concentration of NH₄⁺ in the liquid undergoing membrane treatment. In order to decrease the residual TN content below the level allowing a direct release into the natural receiver, it turned out that it is necessary to use during precipitation an increased molar ratio of Mg²⁺ and PO₄³⁻ (Mg²⁺:NH₄⁺:PO₄³⁻ = 1.5:1:1.5). The source of Mg²⁺ used for the precipitation did not influence significantly the effectiveness of NH₄⁺ removal. As compared to the MgCl₂ · 6H₂O, however, MgO was considered as a

more suitable reagent, mainly due to the possibility of simultaneous COD removal. Precipitated struvite crystals contained insignificant amounts of heavy metals. What is more, the initial struvite precipitation in the analysed liquors influenced the efficiency of a subsequent RO process in a positive way.

Acknowledgement

Authors would like to express their gratitude to the National Science Centre in Krakow for the financial support of the research included in the article (Grant No. 7428/B/T02/2011/40).

References

- [1] M.H. Gerardi, *The Microbiology of Anaerobic Digesters*, Wiley-Interscience, New Jersey, 2003.
- [2] P.F. Stanbury, A. Whitaker, J. Halls, *Principles of Fermentation Technology*, BH, Great Britain, 1995.
- [3] M. Dohányos, J. Zábanská, J. Kutil, P. Jeniček, Improvement of anaerobic digestion of sludge, *Water Sci. Technol.* 49 (2004) 89–96.
- [4] J. Mata-Alvarez, S. Mace, P. Llabres, Anaerobic digestion of solid wastes. An overview of research achievements and perspectives, *Bioresour. Technol.* 74 (2000) 3–16.
- [5] N. Marti, J. Ferrer, A. Bouzas, Optimization of sludge management to enhance phosphorus recovery in WWTP, *Water Res.* 42 (2008) 4609–4618.
- [6] A. Jedrczak, *Wastes Biological Treatment*, PWN, Warszawa, (in Polish) 2007.
- [7] L. Appels, J. Baeyens, J. Degrève, R. Dewil, Principles and potential of the anaerobic digestion of waste-activated sludge, *Prog. Energy Combust. Sci.* 34 (2008) 755–781.
- [8] S. Ponsá, T. Gea, L. Alern, J. Cerezo, A. Sánchez, Comparison of aerobic and anaerobic stability indices through a MSW biological treatment process, *Waste Manag.* 28 (2008) 2735–2742.
- [9] P. Kampas, S.A. Parsons, P. Pearce, S. Ledoux, P. Vale, J. Churchley, E. Cartmell, Mechanical sludge disintegration for the production of carbon source for biological nutrient removal, *Water Res.* 41 (2007) 1734–1742.
- [10] A. Soares, P. Kampas, S. Maillard, E. Wood, J. Brigg, Comparison between disintegrated and fermented sewage sludge for production of a carbon source suitable for biological nutrient removal, *J. Hazard. Mater.* 175 (2010) 733–739.

- [11] A. Bonmati, F. Xavier, Air stripping of ammonia from pig slurry: characterization and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion, *Waste Manag.* 23 (2003) 261–272.
- [12] L. Xiaohui, N. Sugiura, C. Feng, T. Maekawa, Pretreatment of anaerobic digestion effluent with ammonia stripping and biogas purification, *J. Hazard. Mater.* 145 (2007) 391–397.
- [13] D. Karakashev, J.E. Schmidt, I. Angelidaki, Innovative process scheme for removal of organic matter, phosphorus and nitrogen from pig manure, *Water Res.* 42 (2008) 4083–4090.
- [14] L. Masse, D.I. Massé, Y. Pellerin, The effect of pH on the separation of manure nutrients with reverse osmosis membranes, *J. Membr. Sci.* 325 (2008) 914–919.
- [15] B. Wu, Y. An, Y. Li, F.S. Wong, Effect of adsorption/coagulation on membrane fouling in microfiltration process post-treating anaerobic digestion effluent, *Desalination* 242 (2009) 183–192.
- [16] L. Castrillón, Y. Fernandez-Nava, M. Ulmanu, I. Anger, E. Marañón, Physico-chemical and biological treatment of MSW-landfill leachate, *Waste Manag.* 30 (2010) 228–235.
- [17] J. Ćwikła, K. Konieczny, Reduction of the biogenic compounds level in wastewater treatment plant by purification of sludge by means of reverse osmosis, *Proc. Nat. Cong. Environ. Eng. Lublin 1* (2009) 55–62, (in Polish).
- [18] Jr M.C. Sterling, R.E. Lacey, C.R. Engler, S.C. Ricke, Effects of ammonia nitrogen on H₂ and CH₄ production during anaerobic digestion of dairy cattle manure, *Bioresour. Technol.* 77 (2001) 9–18.
- [19] Y. Chen, J.J. Cheng, K.S. Creamer, Inhibition of anaerobic digestion process: A review, *Bioresour. Technol.* 99 (2008) 4044–4064.
- [20] A.D. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg, M.A. Franson, *Standard Methods for the Examination of Water and Wastewater*, APHA, Washington, 2005.
- [21] C.N. Sawyer, P.L. McCarty, G.F. Parkin, *Chemistry for Environmental Engineering and Science*, McGraw-Hill, New York, 2003.
- [22] A. Miles, T.G. Ellis, Struvite precipitation potential for nutrient recovery from anaerobically treated wastes, *Water Sci. Technol.* 43 (2001) 259–266.
- [23] H.D. Ryu, D. Kim, S.I. Lee, Application of struvite precipitation in treating ammonium nitrogen from semiconductor wastewater, *J. Hazard. Mater.* 156 (2008) 163–169.
- [24] T. Zhang, L. Ding, H. Ren, Pretreatment of ammonium removal from landfill leachate by chemical precipitation, *J. Hazard. Mater.* 166 (2009) 911–915.
- [25] A. Uysal, Y.D. Yilmazel, G.N. Demirer, The determination of fertilizer quality of the formed struvite from effluent of a sewage sludge anaerobic digester, *J. Hazard. Mater.* 181 (2010) 248–254.
- [26] S. Uludag-Demirer, G.N. Demirer, S. Chen, Ammonia removal from anaerobically digested dairy manure by struvite precipitation, *Process Biochem.* 40 (2005) 3667–3674.
- [27] N. Marti N., A. Bouzas, A. Seco, J. Ferrer, Struvite precipitation assessment in anaerobic digestion processes, *Chem. Eng. J.* 141 (2008) 67–74.
- [28] Y.-H. Liu, J.-H. Kwag, J.-H. Kim, C. Ra, Recovery of nitrogen and phosphorus by struvite crystallization from swine wastewater, *Desalination* 277 (2011) 364–369.
- [29] Y. Jaffer, T.A. Clark, P. Pearce, S.A. Parsons, Potential phosphorus recovery by struvite formation, *Water Res.* 36 (2002) 1834–1842.
- [30] 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.
- [31] E.V. Münch, K. Barr, Controlled struvite crystallization for removing phosphorus from anaerobic digester sidestreams, *Water Res.* 35 (2001) 151–159.
- [32] N.O. Nelson, R.L. Mikkelsen, D.L. Hesterberg, Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant, *Bioresour. Technol.* 89 (2003) 229–236.
- [33] I. Stratful, M.D. Scrimshaw, J.N. Lester, Conditions influencing the precipitation of magnesium ammonium phosphate, *Water Res.* 35 (2001) 4191–4199.
- [34] K. Yetilmezsoy, Z. Sapci-Zengin, Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer, *J. Hazard. Mater.* 166 (2009) 260–269.
- [35] J. Suschka, E. Kowalski, S. Popławski, Study of the effects of the reactor hydraulics on struvite precipitation at municipal sewage works, Report Commissioned by Centre Européen d'Etudes des Polyphosphate, Bruksela, 2003.
- [36] Y. Song, P. Yuan, B. Zheng, J. Peng, F. Yuan, Y. Gao, Nutrients removal and recovery by crystallization of magnesium ammonium phosphate from synthetic swine wastewater, *Chemosphere* 69 (2007) 319–324.
- [37] EU Council Directive (91/271/EWG) concerning urban wastewater (100 000 inhabitants and above), 21 May 1991.