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POST-DIGESTION LIQUOR TREATMENT
IN THE METHOD COMBINING CHEMICAL PRECIPITATION
WITH REVERSE OSMOSIS

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Abstract: The aim of the study was to develop an effective treatment of post-digestion liquors highly-loaded with biogenic and organic substances. The scope of the research project encompassed: mesophilic anaerobic digestion of waste activated sludge (WAS) as well as the treatment of post-digestion liquors, coming from the most appropriate HRT value of 25 days, in the process of ammonium magnesium phosphate (struvite) precipitation targeted at ammonia nitrogen binding and a subsequent reverse osmosis (RO) process. It was established that the method combining chemical precipitation and high-pressure filtration ensures a high degree of contaminants removal allowing for a direct release of treated liquors into the natural reservoir. However, in order to decrease the residual NH_4^+ concentration (6.1 mg NH_4^+/dm^3) in the purified post-digestion liquors below the level allowing for a direct release to the natural reservoir, it turned out to be necessary to apply increased molar ratio of magnesium and phosphates ($Mg:NH_4^+ : PO_4^{3-} = 1.5:1:1.5$).

INTRODUCTION

Ever stricter regulations concerning biogenic substances content in treated wastewater require the application of advanced chemical and biological treatment, which has an impact on the amount and quality of sludge generated. One of the most widely-used methods of wastewater treatment is the activated sludge method, which allows for the concomitant removal of both biogenic and organic substances. Excess sludge generated in those processes is periodically removed from the bioreactor's chambers [3, 32]. One of the methods constitutes a controlled anaerobic digestion for biogas production. The main strength of the process is the possibility to generate renewable energy in the form of biogas. Besides, the process generates a digestate [2, 13, 16, 25, 36]. The final utilization of the latter 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, mesophilic digestion does not

ensure complete hygienization and stabilization of the substrates undergoing digestion. The digestate has to be further treated if its quality is to be improved. Thus the digested sludge usually undergoes separation into liquid and solid phase. Solid fraction can be additionally treated, e.g. through composting, which ensures a high degree of hygienization and further decomposition of remaining organic matter after anaerobic digestion [2, 31].

After the digested sludge has been dewatered, the generated liquor has to be utilized. It is usually recirculated to the biological treatment facility and treated together with raw wastewater. However, post-digestion liquors exhibit an exceptionally unfavorable C/N ratio (BOD_5/N in the range of 0.15–0.20), which has a negative impact on the wastewater treatment process, especially on the denitrification. Their treatment in such way requires the addition of external carbon source [19, 35].

The development of effective treatment methods of post-digestion liquors is an urgent issue to be resolved. They can be treated with the application of biological as well as combinations of physical and chemical methods. Physical and chemical methods in nature include: ions exchange, coagulation, ammonia desorption, degassing, adsorption on activated carbon, advanced oxidation processes as well as membrane techniques. Whilst biological methods – except for the traditional method of activated sludge – encompass unconventional systems, e.g. ANAMMOX [1, 7, 9, 20, 24, 42, 43]. However, individual unit processes do not ensure a complex removal of contaminants. Even the application of highly effective reverse osmosis (RO) process does not allow reducing the level of contaminants so that the treated post-digestion liquor can be released to a natural reservoir [12, 24, 39]. Despite of the fact that the application of RO membranes ensures a high degree of contaminants removal, in most cases exceeding 90%, the effluent is usually loaded with NH_4 concentration exceeding the norm allowing for direct release to the natural reservoir. The key factors conditioning the degree of ammonia removal through RO process are initial ammonia content and pH value, which influence the form of ammonia-nitrogen. Thus, post-digestion liquors rich in ammonia-nitrogen should undergo pre-treatment oriented towards removing as much as possible of ammonia--nitrogen before applying RO treatment. An interesting solution seems to be chemical method of ammonium magnesium phosphate (struvite) precipitation, which allows to bind both ammonia-nitrogen and phosphorus.

The aim of the study was to develop an effective treatment method of post-digestion liquors generated after dewatering of digested sludge. In contrary to our previous studies involving the digestate taken from municipal treatment plants [5–6], our present study encompasses the continuous mesophilic digestion (HRT = 10–30 days) and the treatment of generated post-digestion liquors in the process of reverse osmosis (RO) coupled with a subsequent ammonium magnesium phosphate (struvite) precipitation – targeted at ammonia-nitrogen binding. Taking into account our previous results, MgO was used during struvite precipitation as a source of Mg^{2+}, mainly due to the possibility of simultaneous organic matter removal from post-digestion liquors as well as lack of secondary contamination, e.g. Cl^- after addition of $MgCl_2$ [6, 21]. The following criteria were adopted to establish the most appropriate hydraulic retention time (HRT) of WAS in a bioreactor: degree of organic matter decomposition, quantity and quality of the biogas produced as well as indices of process stability (VFA, VFA/TA). In the case of struvite precipitation, stoichiometric molar ratio of Mg^{2+}, NH_4^+ and PO_4^{3-} ions as well as increased molar ratio, i.e. $Mg^{2+}:NH_4^+:PO_4^{3-}$ (1,5:1:1,5) were tested. It was assumed that the method combining chemical precipitation

and high-pressure filtration ensures a high degree of contaminants removal allowing for a direct release of the treated liquors into the natural reservoir.

RESEARCH MATERIALS AND METHODS

The waste activated sludge (WAS) taken after thickening from a full scale municipal treatment plant based on Enhanced Biological Nutrients Removal (EBNR) was used as research material. The facility operates on activated sludge method and 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 physical and chemical properties of the waste activated sludge.

Table 1. Characteristics of the waste activated sludge

Indicator	Unit	Waste activated sludge (WAS)	
		Range of values	Average value
pH	–	5.9÷6.6	6.3 (0.3)
Total solids	%	5.17÷5.41	5.27 (0.17)
Volatile solids	%	3.63÷3.83	3.71 (0.16)
COD	mg O_2/dm³	102.0÷430.0	247.0 (122.0)
Ammonia-nitrogen	mg NH_4^+/dm³	11.4÷19.8	15.8 (5.9)
Phosphates	mg PO_4^{3-}/dm³	103.2÷200.8	145.5 (32.6)
Calcium	mg Ca^{2+}/dm³	42.5÷54.5	48.5 (9.5)
Magnesium	mg Mg^{2+}/dm³	20.6÷32.4	26.5 (5.5)
VFA	mg CH_3COOH/dm³	60.0÷124.0	83.0 (20.0)
TA	mg $CaCO_3$/dm³	1035.0÷1260.0	1192.0 (181.0)

() – standard deviation

Anaerobic digestion tests

The digestion process was conducted under mesophilic conditions at a constant temperature of 36°C (±0.5) in a bioreactor with a working volume of 3 dm³. The process was carried out at the following hydraulic retention times (HRT): 10, 12, 15, 17, 20, 25 and 30 days. The applied range of HRT corresponds to the organic loading rate (OLR) value of between 1.23 and 3.71 kg VS/(m³·d). The digesters contents were mixed periodically – 5 minutes in every 3 hours. The scope of the analyses conducted encompassed: pH value measurement and determinations of total solids (TS), volatile solids (VS), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), total volatile fatty acids (VFA), total alkalinity (TA), ammonia nitrogen (NH_4^+), phosphates (PO_4^{3-}), total phosphorus (TP), calcium (Ca^{2+}) and magnesium (Mg^{2+}), chlorides (Cl^-). The susceptibility of the digested sludge to separation into solid and liquid phase was based on the capillary suction time (CST) measurement. Both quantitative and qualitative analyses of the biogas produced were carried out during the experiment. The biogas was stored in a plexus tube containing 5% NaOH solution. The recorded amounts of biogas were adjusted to the volume at standard temperature (0°C) and pressure (1 atm). The biogas was periodically analyzed for CH_4 content (% vol.) [14, 34].

Ammonium magnesium phosphate (struvite) precipitation tests

Struvite precipitation was conducted in a 1 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 9.0–9.2. The applied pH value was included within the optimum range for struvite precipitation [26, 33, 41, 45]. The retention time of post-digestion liquor amounted to 24 hours. The reactor contents were mixed by means of a magnetic stirrer (100 rpm/min). In the case of the analysed post-digestion liquor, the concentration of NH_4^+ exceeded significantly the stoichiometric value of struvite, while, the concentration of PO_4^{3-} and Mg^{2+} played the role of limiting factors. The lacking amounts of phosphorus and magnesium were augmented by H_3PO_4 and MgO respectively. The process was conducted for the stoichiometric ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$ as well as 150% of stoichiometric dosage of magnesium and phosphorus ($Mg^{2+}:NH_4^+:PO_4^{3-} = 1.5:1:1.5$). A parallel trial (blank sample) was conducted without the addition of magnesium and phosphorus in order to assess the amounts of NH_4^+ released to the atmosphere during precipitation.

Reverse osmosis (RO) process

High-pressure process of reverse osmosis (RO) was conducted in the device type GH-100-400, produced by a US-based company Osmonics. Its capacity amounted to 400 cm³. The device worked in the dead-end mode, on flat membranes (ADF) with the active volume of 36.3 cm². The process was 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 digestion liquor after struvite precipitation was adjusted to the level of about 7 by means of 1M HCl before the liquor underwent the membrane process. Figure 1 shows the flow chart of the experiment.
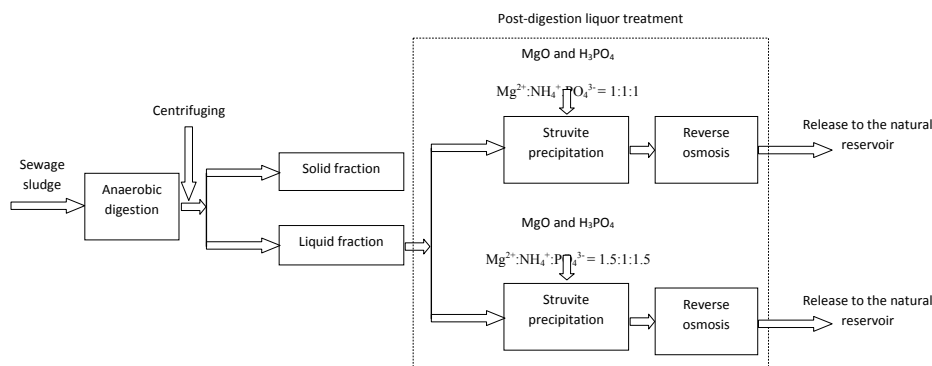

Fig. 1. Flow chart of the experiment concept

RESULTS AND DISCUSSION

As the sludge was undergoing the methane fermentation, the value of hydraulic retention time (HRT) was successfully increased in the range of between 10 and 30 days. The influence of particular HRT values on the degree of organic matter reduction, biogas

production and process stability was discussed. Physical and chemical characteristics of the digested sludge are presented in Table 2.

Table 2. Characteristics of the digested sludge

HRT [days]	pH –	TS g/dm³	VS g/dm³	COD mg O₂/dm³	VFA mg/dm³	TA mg CaCO₃/dm³	NH₄⁺ mg/dm³	PO₄³⁻ mg/dm³	Ca²⁺ mg/dm³	Mg²⁺ mg/dm³
10	7.4	48.48	27.24	2250	1908	4511	1679	625.3	59.9	31.0
12	7.5	46.39	25.17	2398	733	5020	1677	609.8	62.5	38.0
15	7.5	46.16	25.01	1779	695	5080	1623	560.7	66.7	40.5
17	7.6	45.07	24.24	1717	780	4949	1510	517.0	74.5	39.0
20	7.8	44.57	23.27	1807	894	5571	1553	579.7	76.5	42.5
25	7.8	43.44	22.52	1920	870	5647	1586	575.7	77.0	39.0
30	7.8	43.25	22.43	1684	945	5843	1607	545.9	70.0	35.4

The process of anaerobic digestion for biogas production was initially adopted by the application of the shortest HRT value, i.e. 10 days, which was tantamount to 3.71 kg VS/(m³·d) of bioreactor organic loading rate (OLR). Under those conditions, low organic matter reduction was achieved, i.e. 24.9%. As the value of HRT was subsequently extended from 12 days to 20 days, reduction degrees of VS increased and amounted to between 30.7% and 35.9%. The highest value of VS reduction, i.e. 38.9–39.1% was achieved when the HRT was extended to 25–30 days, which was associated with an OLR value of 1.48–1.85 kg s.m.o./(m³·d). Taking into account the concept of technical stabilization boundary established for mesophilic conditions at the level of 38–40% [38] of volatile solids removal, it was stipulated that the above condition was met for HRT value above 20 days. Figure 2 shows the influence of HRT value on the degree of organic matter (volatile solids) removal.
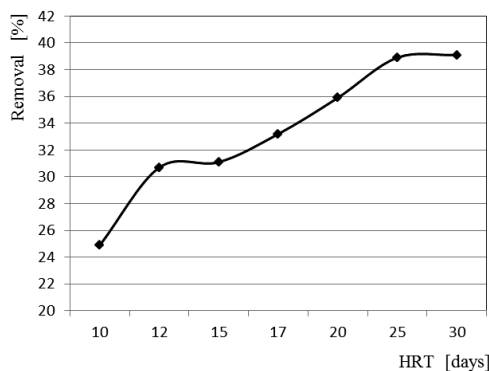

Fig. 2. The influence of HRT value on the degree of organic matter removal

During the experiment, the biogas production as well as methane content in the biogas generated was recorded. Figure 3 shows the amount of biogas produced for various HRT, expressed in terms of daily production and biogas yield. A significant decrease in daily biogas production was observed as the HRT values were extended. For the HRT value in the range of 10–12 days, the daily biogas production was twice, as compared to the amount of biogas generated for the HRT in the range 20–25 days (Figure 3). When the biogas production was recalculated and presented per unit of organic matter fed into the bioreactor, significant differences in values of the biogas yield were not to be seen. The highest value of the parameter (0.379 m^3/kg VS_{added}) was achieved for the HRT value of 15 days. Further extending the HRT value caused a slight decrease of the biogas yield value. The value of biogas yield for the HRT value in the range of 20–30 days, oscillated in the range of 0.312–0.326 m^3/kg VS_{added} (Figure 3).

On the one hand, the daily biogas production depends primarily on the amount of biodegraded organic matter added to the bioreactor. On the other hand, the composition of the biogas produced is conditioned by the feedstock composition, i.e. the content of proteins, fats and carbohydrates. Accordingly, the study was not focused exclusively on the amount of biogas generated but also on its methane content. The lowest methane content measured in stable state of the process amounted to 50–52% vol. and was recorded for the HRT in the range of 10–12 days. When the HRT value was exceeded above 12 days, the CH_4 in the biogas produced reached the level of 57–59% vol. A lower content of CH_4 recorded for the HRT value lower than 15 days was ascribed to a low range of HRT, which did not ensure a complete course of the methanogenesis. It was also reflected in lower levels of volatile solids removal.
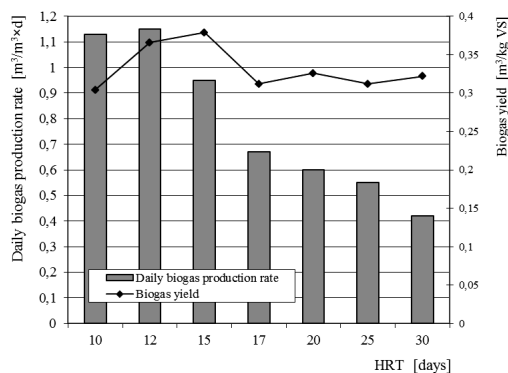

Fig. 3. The relationship between HRT values and the amount of biogas produced

Discussing the overall stability of the anaerobic digestion, a primary indicator which influences the biological conversion is pH value. The use of the pH as a process indicator is based on the fact that the pH decrease is commonly related to the accumulation of VFAs, which consumes buffer capacity [4, 17]. However, a significant decrease of pH value does not take place until the process collapses and the acidic phase dominates. Taking into account the above facts, a more reliable stability indicator seems to be a volatile fatty acids to total alkalinity (VFA/TA) ratio. If the latter exceeds the threshold of 0.3–0.4, it is

believed to have an inhibitive effect on biogas production or can even lead to the collapse of the process in a short term [8, 11]. It can be pointed out that the process exhibited stable properties for the HRT value above 12 days. For the lowest value of HRT (10 days), both significant accumulation of VFA (1908 mg CH_3COOH/dm^3) as well as increased value of the VFA/TA ratio (0.42) were recorded (Figure 4).
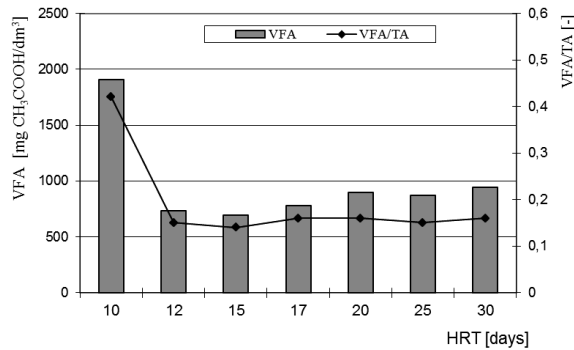

Fig. 4. The influence of HRTs on the concentration of VFAs and VFA/TA ratio

Digested sludge usually undergoes dewatering in order to separate it into solid and liquid phase. Susceptibility of the sludge to dewatering has a significant impact on further treatment as well as capacity of containers used for digested sludge storage [27, 44]. Considering the above, the research encompassed the analysis of the influence of various HRT values on the separation properties of the digested sludge. Figure 5 shows the results of CST test recorded for both raw and digested sludge. The highest value, i.e. 156 s was measured for the shortest value of the hydraulic retention time (HRT). A gradual decrease in CST was observed as the HRT value increased. The most favorable value, i.e. 67–68 s was achieved for the HRT in the range of between 17 and 20 days. Furthermore, a slight deterioration of susceptibility of the sludge to dewatering was observed for longer HRT values.
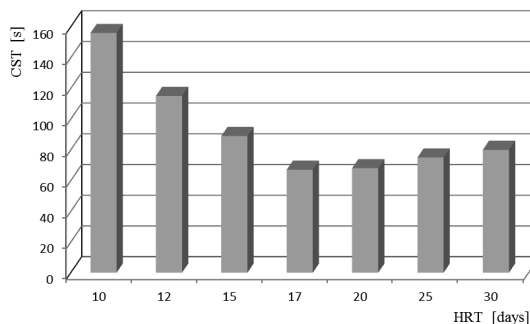

Fig. 5. The influence of HRTs on the susceptibility of the digested sludge to dewaterability

Assuming that the main aim of sewage sludge anaerobic digestion is its stabilization, the degree of organic matter reduction was adopted as the most important parameter. Taking into account the concept of "technical stabilization boundary", the HRT value of 25–30 days was selected as adequate to ensure a sufficient degree of organic matter removal. In such conditions the process exhibited stable conditions. Since, within the specified range of HRT (25–30 days), the highest biogas production was generated at 25 days, the value was selected as the most favorable and further experiments were conducted at it.

Post-digestion liquor treatment

Anaerobic digestion of sewage sludge leads to the release of phosphates, nitrogen--ammonia and organic substances to the liquid phase of digestate [22–23, 40]. Since the effluent after anaerobic digestion was loaded with high amounts of such substances (Table 2), it was attempted to treat the post-digestion liquors by means of chemical precipitation and a high-pressure filtration (RO). Since, the experiment was conducted for the post-digestion liquor originated from sewage sludge stabilization conducted at HRT of 25 days, the value assumed to be the most appropriate.

Struvite crystallization in the post-digestion liquor

Key factors conditioning the precipitation of ammonia and phosphate ions in the form of ammonium magnesium phosphate, commonly known as "struvite" are determined to a large extent by the pH value. The optimum range of pH value for effective struvite precipitation oscillates around 9 [18, 26, 33, 41, 45]. Struvite crystals do not get generated at pH <7. Besides, in the solution containing Mg^{2+}, NH_4^+ oraz PO_4^{3-}, other compounds containing phosphorus and magnesium, such as $MgHPO_4 \cdot 3H_2O$, $Mg_3(PO_4)_2 \cdot 8H_2O$, $Mg_3(PO_4)_2 \cdot 22H_2O$, $Mg_3(PO_4)_2 \cdot 4H_2O$ can be precipitated, However, all the compounds, except for the struvite, exhibit high solubility at pH between 8 and 10, are precipitated at a much lower pH value, e.g. $MgHPO_4 \cdot 3H_2O$ crystallizes at pH value <6 [33, 41]. Moreover, phosphates can react with Ca^{2+}, 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 [18]. Since magnesium was added in order to comply with struvite chemical formula, it was assumed that the interactions between calcium and phosphorus will not lead to a significant phosphates decrease in the solution. Potassium struvite crystallization for magnesium struvite precipitation was also excluded as a result of high NH_4^+ concentration [30].

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 ($Mg^{2+}:NH_4^+:PO_4^{3-}$ =1.5:1:1.5). As mentioned above, MgO was used as a source of magnesium. The MgO properties allow for a pH value to increase up to the level needed for effective course of struvite precipitation. The main weakness of MgO is its slow solubility and thus reaction time, which is longer than in the case of $MgCl_2$ or $MgSO_4$ [28–29]. Lack of post-reaction chlorides or sulphates in the solution after precipitation makes MgO an attractive Mg^{2+} source. Table 3 presents the characteristics of the sludge liquor after struvite precipitation.

The application of stoichiometric molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$ allowed receiving a high degree of ammonia-nitrogen and phosphates, i.e. 93.6% and 85.0% respectively.

Table 3. Characteristics of the post-digestion liquor after struvite precipitation

Molar ratio $Mg^{2+}: NH_4^+: PO_4^{3-}$	Concentration (mg/dm³):					
	NH_4^+	TKN	PO_4^{3-}	TP	Mg^{2+}	COD
1:1:1	100.9	128.6	86.6	29.2	8.5	1354
1:1.5:1.5	29.5	38.2	243	80.9	45.0	895
Blank sample	1480	1517	537	177	35.0	1855

Moreover, struvite precipitation played a positive way on the organic matter removal. About 30% of COD was removed together with the precipitated struvite. However, the weight ratio of (PO_4^{3-}/NH_4^+) reached the value of 0.86, i.e. several times less than the value resulted from struvite formula. In order to increase the effectiveness of the process and thus decrease the residual concentration of ammonia, it was necessary to apply the increased doses of phosphates and magnesium. A 50% excess of PO_4^{3-} and Mg^{2+} ions, as related to ammonia content, was tested.

An excess of phosphates and magnesium ($Mg^{2+}:NH_4^+:PO_4^{3-} = 1.5:1:1.5$) influenced the effectiveness of ammonia removal, which rose from 93.6% ($Mg^{2+}:NH_4^+:PO_4^{3-} = 1:1:1$) to the level of 98.1%. Accordingly, the addition of excess amounts of Mg^{2+} and PO_4^{3-} ions allowed receiving a significant decrease in residual NH_4^+ concentration. A residual NH_4^+ content in the liquor after struvite precipitation with stoichiometric amounts of Mg^{2+} and PO_4^{3-} amounted to 100.9 mg NH_4^+/dm^3, while, the same liquor after struvite precipitation with the application of excess amounts of reagents was loaded with more than three times less residual NH_4^+. The NH_4^+ concentration in a blank sample decreased by about 6.7%, which corresponds to the removal of 106.0 mg NH_4^+/dm^3. Accordingly, it can be stated that a part of ammonia-nitrogen in the process of chemical precipitation was in fact released to the atmosphere ($NH_3\uparrow$). The above mechanism of ammonia volatilization accompanying the struvite precipitation was mention in previous reports [40–41].

The addition of increased molar ratio of magnesium influenced the degree of organic matter in a positive way. As compared to the stoichiometric ratio, the degree of COD removal increased from 30% to 53%. Considering the excessive amounts of magnesium, organic substances might have been removed from the solution and precipitated together with struvite crystals. A similar relationship between the amount of magnesium added and the degree of organic matter removal was mentioned in other papers. For example, during struvite precipitation in liquors after sewage sludge anaerobic digestion the degree of COD removal increased from 27% ($Mg^{2+}:NH_4^+:PO_4^{3-} = 1:1:1$) to about 40% at molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$ ions amounting to 1.5:1:1.5 [41]. Figure 6 presents degrees of NH_4^+, PO_4^{3-} and COD removal achieved during the process of struvite precipitation.

Post-digestion liquor treatment with the application of reverse-osmosis process
In order to fulfill the norms allowing for a direct release of the treated post-digestion liquor to the natural reservoir, the liquor streams after struvite precipitation were treated in reverse osmosis (RO) process. Since the post-digestion liquors exhibited a high value of pH (9.0–9.2), the pH value was adjusted to the level of about 7 by means of HCl. At high pH values (pH>9), a significant amount of nitrogen-ammonia (>30%) occurs
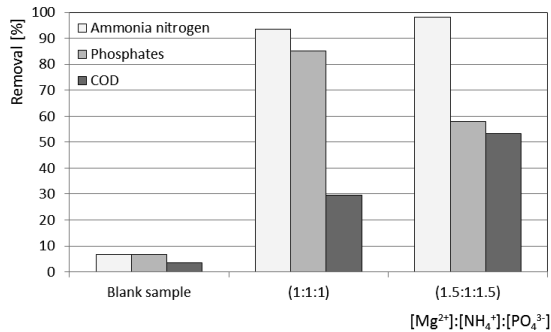
Fig. 6. Degrees of NH_4^+, PO_4^{3-} and COD removal during struvite precipitation process

in unionized form, which is not detained by osmotic membranes. While at lower pH values of about 7, ammonia-nitrogen occurs predominantly in an ionic form and only less than 1% of ammonia-nitrogen exists in unionized form. To cite an example, the effluent after anaerobic digestion exhibiting the pH value of about 9.0 and the temperature of 20°C, the fraction of unionized form amounts to as much as 30% of total ammonia ($NH_4^+ + NH_3$). While the same effluent exhibiting the pH value of 7 contains only about 0.4% of unionized form of ammonia [10, 37, 43]. The relationship between volumetric permeate fluxes and the length of the process is depicted in Figure 7. The initial value of both volumetric fluxes reached the value of $2.0 \cdot 10^{-6}$ m^3/m^2s. As expected, a greater value of the flux occurred in the case of the process conducted for the liquor after struvite precipitation, during which an excessive amounts of reagents were applied. The waters were loaded with about 30% less of COD in comparison to the liquor after struvite precipitation, during which stoichiometric doses of reagents were applied. After about 4 hours of conducting the high-pressure process, the flux permeate value of liquor after precipitation for stoichiometric decreased significantly and stabilized at $0.55 \cdot 10^{-6}$ $m^3/m^2 \cdot s$. While the value of the other permeate flux exhibited higher values during the whole process and stabilized at $0.8 \cdot 10^{-6}$ $m^3/m^2 \cdot s$ after 6 hours of the experiment.
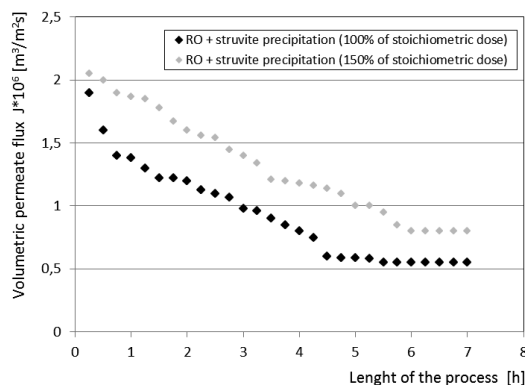

Fig. 7. The relationship between volumetric permeate fluxes and the length of the RO process

Despite a comparable degrees of ammonia removal recorded for both streams of treated liquors (78.9–80.3%), only in the case of the liquor pre-treated with the application of struvite precipitation based on excessive amounts of reagents, the NH_4^+ concentration in the effluent exhibited the value (6.1 mg NH_4^+/dm^3) allowing for direct release to the natural reservoir [15]. However, the key role in the concentration of ammonia after RO treatment was played by its initial concentration in the liquors undergoing treatment. The concentration of NH_4^+ in the liquor after struvite precipitation for stoichiometric ratio of $NH_4^+:PO_4^{3-}:Mg^{2+}$ was more than three times higher (109.0 mg NH_4^+/dm^3), as compared to the concentration of ammonia (29.5 mg NH_4^+/dm^3) recorded for liquor after struvite precipitation conducted for excessive amounts of reagents, i.e. $NH_4^+:PO_4^{3-}:Mg^{2+}$ = 1:1.5:1.5. In both cases of conducted RO processes, COD concentration and total phosphorus decreased below the levels allowing for its direct release to the natural reservoir [15]. What is more, the application of RO process eliminated the secondary load of Cl^-, which occurred in treated waters as a result of pH values adjustment before the RO process. Changes in quality indicators characterizing the liquors before and after membrane treatment are presented in Table 4.

Table 4. Characteristics of liquors treated with the application of reverse osmosis

Indicator	Post-digestion liquors after struvite precipitation						Permissible limits*
	$Mg^{2+}:NH_4^+:PO_4^{3-}$ =1:1:1			$Mg^{2+}:NH_4^+:PO_4^{3-}$ =1.5:1:1.5			
	Post-digestion liquor after struvite precipitation and pH adjustment	Value after reverse osmosis	Removal [%]	Post-digestion liquor after struvite precipitation and pH adjustment	Value after reverse osmosis	Removal [%]	
pH [-]	7.0	7.7	–	7.0	7.8	–	6.5–9.0
TP [mg P/dm³]	31.5	0.21	99.3	86.9	0.52	99.4	1.0
Ammonia-nitrogen [mg NH_4^+/dm^3]	113.0	23.8	78.9	31.0	6.1	80.3	10.0
TKN [mg N/dm³]	130.5	25.5	80.5	39.0	8.2	79.0	
Chlorides [mg Cl^-/dm^3]	6200.0	93.0	98.5	8455.0	112	98.7	500.0
COD [mg O_2/dm^3]	1422.0	12.5	99.1	935.0	10.7	98.9	125.0

* EU Council Directive of 21 May 1991 (91/271/EWG) concerning urban wastewater: 100 000 inhabitants and above.

CONCLUSIONS

1. Since the post-digestion liquor exhibited a high content of nutrients and organic substances, an attempt was made to treat the liquor – originated from optimum HRT value of 25 days – with the application of controlled precipitation of

ammonium magnesium phosphate (struvite) and high-pressure filtration – reverse osmosis (RO).

2. Post-digestion liquor treatment with the application of struvite precipitation targeted at ammonia binding coupled with reverse osmosis method allowed to achieve a high degree of contaminants removal. In terms of COD and total phosphorus (TP) removal, the process of reverse osmosis combined with a subsequent struvite precipitation ensures an adequate treatment and allowed for a direct release of post-digestion liquor to the natural reservoir. However, in order to decrease the residual NH_4^+ concentration (6.1 mg NH_4^+/dm^3) in the purified liquor below the level allowing for a direct release to the natural reservoir, it turned out to be necessary to apply an increased molar ratio of phosphates and magnesium ($Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1.5:1:1.5). In fact, the key role in the concentration of ammonia after RO treatment was played by its initial concentration in the liquors undergoing treatment.

3. About 29–53% of organic matter loaded with post-digestion liquors was removed simultaneously during the process of struvite precipitation. The degree of COD removal rose almost twice as the molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$ ions increased from 1:1:1 to 1.5:1:1.5. Taking into account excessive amounts of magnesium added as well as coagulative properties of magnesium compounds, organic substances might have been removed from the solution and precipitated together with struvite crystals.

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Celem badań przedstawionych w artykule było opracowanie efektywnej metody oczyszczania wysoko obciążonych wód pofermentacyjnych, związkami biogennymi oraz organicznymi. Zakres przeprowadzonych badań obejmował mezofilową fermentację nadmiernych osadów czynnych oraz oczyszczanie powstałych wód pofermentacyjnych. Wody pochodzące z fermentacji osadów prowadzonej w warunkach uznanych za najkorzystniejsze (HRT = 25 dni) poddano oczyszczeniu z zastosowaniem procesu strącania fosforanu amonowo-magnezowego (struwitu) oraz wysokociśnieniowej filtracji membranowej (RO). Na podstawie przeprowadzonych badań ustalono, że oczyszczanie wód pofermentacyjnych w procesie łączącym strącanie fosforanu amonowo-magnezowego z membranową filtracją wysokociśnieniową jest metodą efektywną, zapewniającą wysoki stopień usunięcia ładunku zanieczyszczeń. Jakkolwiek, zastosowanie 50% nadmiaru jonów magnezowych i fosforanowych (Mg:NH_4^+:PO_4^{3-} =1.5:1:1.5) podczas strącania struwitu okazało się niezbędne w celu obniżenia stężenia azotu amonowego (6.1 mg NH_4^+/dm^3) poniżej poziomu pozwalającego na bezpośrednie odprowadzenie oczyszczonych wód do odbiornika naturalnego.