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Pre-treatment of co-digestion effluents before reverse osmosis (RO) application

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ABSTRACT

Effective treatment method of highly polluted post-digestion effluents, allowing the treated waters to be directly released into a natural reservoir, was developed. The co-digestion effluents containing varied ammonia-nitrogen content (1,400–5,445 mg NH₄⁺/dm³) underwent chemical precipitation (struvite) as a pre-treatment step and subsequent membrane filtration (RO or NF+RO). The application of dual treatment by means of struvite precipitation and subsequent RO turned out to be effective in case of all analysed post-digestion effluents (1,400–5,445 mg NH₄⁺/dm³), and allowed to decrease contaminants concentrations below discharge levels. However, it was necessary to apply an increased molar ratio of reagents during precipitation and RO allowed to decrease the dosage of reagents used for struvite precipitation (pre-treatment). Thus, waters containing initially up to 2980 mg NH₄⁺/dm³ fulfilled discharge standards after struvite precipitation was conducted at molar ratio of reagents (Mg²⁺:NH₄⁺:PO₄³⁻ = 1:1:1) and subsequent two-step membrane filtration (NF+RO).

Keywords: Reverse osmosis; Nanofiltration; Struvite; Ammonia-nitrogen removal; Co-digestion effluents

1. Introduction

The process of anaerobic digestion (AD) has been used for sewage sludge stabilization for many years. Nowadays, better understanding of the mechanisms occurring during biodegradation results in wider range of substrates, which can be used as a feedstock. Thus,

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besides facilities operating at wastewater treatment plants and municipal landfills, more and more frequently plants taking advantage of the co-digestion concept are built. It offers several advantages over single substrate digestion, such as: more optimal nutrient content, enhanced biodegradation of the treated substrates, increased biogas production, improved buffer capacity as well as dilution of inhibitive

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compounds. The range of valuable substrates used in co-digestion of plants includes: animal excretes, agricultural leftovers, municipal biowaste, green wastes, energy crops as well as wastes after food manufacturing [1-4] Co-digestion technologies are currently developing in two directions-digestion of two substrates, in which the sewage sludge or animal faeces are the main substrates or feedstock comprising of several ingredients. The application of sewage sludge or animal wastes as main feedstock components is associated with certain benefits. They provide the appropriate content of macro- and micro-nutrients as well as high buffer capacity, which enables the processing of acid in nature wastes, such as kitchen bio-wastes or fruit and vegetable wastes [5]. However, besides above mentioned advantages of the co-digestion processes, they also exhibit some disadvantages. Due to the more varied feedstock composition and higher organic loading of bioreactors, they usually require a greater amount of energy to mix digesters. As compared to liquors after digestion of one substrate (e.g. sewage sludge), generated post-digestion effluents which contain higher concentrations of organic compounds (COD) and nutrients, which influence their treatment in a negative way [4,5].

Post-digestion liquors are frequently directed back to the biological treatment facility and treated together with raw wastewater. Due to the exceptionally unfavourable C/N ratio (0.15-0.20), which has a negative impact on the wastewater treatment processes, their treatment in this way requires the addition of external carbon source. Nowadays, post-digestion liquors are more and more frequently treated separately with the application of biological as well as physical and chemical processes (e.g. exchange, coagulation, ammonia desorption, advanced oxidation processes, adsorption as well as membrane techniques) [6-10]. However, individual unit processes do not ensure a complex removal of contaminants. Due to the fact that such effluents contain high concentration of NH₄⁺, even the application of highly effective reverse osmosis (RO) process does not allow to reduce the level of contaminants so that the treated liquors can be released directly to a natural reservoir [9,11]. Post-digestion liquors rich in ammonianitrogen should undergo pre-treatment oriented towards removing as much as possible the ammonia-nitrogen before applying membrane techniques. An interesting solution seems to be the chemical methods of struvite (ammonium magnesium phosphate) precipitation.

The aim of this research project presented in the paper is to develop an effective treatment method of highly polluted post-digestion effluents, to a degree allowing the treated waters to be directly released into a natural reservoir. The post-digestion effluents characterized by varied ammonia-nitrogen content (1,400–5,445 mg NH₄⁺/dm³) underwent high-pressure membrane filtration (NF or/and RO) and chemical precipitation (struvite) as a pre-treatment step. The study of the struvite precipitation (pre-treatment) before applying membrane processes focused on: (1) the influence of increased dosages of Mg²⁺ and PO₄³⁻ on the effectiveness of NH₄⁺ removal as well as and (2) quality analyses of struvite precipitated. In particular an attempt was made to establish the influence of initial NH₄⁺ loading of post-digestion effluents on the effectiveness of final treatment by means of nanofiltration (NF) and/or reverse osmosis (RO).

2. Research material and methods

2.1. Co-digestion effluents

The liquors after co-digestion of: (1) waste glycerine and secondary sludge-referred below as waters containing low NH_4^+ content, (2) kitchen biowaste or rapeseed cake and secondary sludge-referred below as waters containing medium NH⁺₄ content as well as (3) kitchen biowaste and animal manure-referred below as effluents containing high amount of NH_4^+ , were used as research material. All post-digestion waters taken into account were coming from digestion processes performed in laboratory conditions. Secondary sludge used as feedstock during anaerobic digestion originated form a full-scale municipal treatment plant-based on Enhanced Biological Nutrients Removal (EBNR). By-products after biodiesel production (waste glycerol and rapeseed cake) were taken from a local biorefinery. Kitchen biowaste was collected selectively from households as well as institutions (restaurants, school canteens etc.). Whilst, animal manure was taken from a non-straw bedded rearing pig farm. Effluents after co-digestion processes were dewatered mechanically in order to remove the solid particles remaining after AD processes. Table 1 presents characteristics of the post-digestion liquors used during experiments.

2.2. Ammonium magnesium phosphate (struvite) precipitation

Struvite precipitation was conducted in a 10 dm^3 tank, working in a batch mode. The process was carried out at constant temperature of 20° C and pH of 9.0–9.5. The applied pH value was in the optimum range for struvite precipitation [12–14]. Retention time of post-digestion liquors in a crystallizer amounted to 24 h. In case of all post-digestion liquor, the concentration of NH⁴₄ exceeded significantly the stoichiometric

characteristics of the post algestion endents							
Parameter	Unit	Post-digestion w	Post-digestion waters				
		Waste glycerol + sludge	Kitchen biowaste + sludge	Rapeseed cake + sludge	Kitchen biowaste + animal manure		
pН	-	7.2 ± 0.1	7.3 ± 0.1	7.3 ± 0.1	7.8 ± 0.1		
NH_4^+	mg/dm ³	$1,400 \pm 95$	$2,450 \pm 75$	$2,980 \pm 90$	$5,445 \pm 180$		
TN	mg/dm^3	$1,556 \pm 96$	$2,650 \pm 78$	$3,115 \pm 95$	$5,525 \pm 176$		
PO_4^{3-}	mg/dm ³	333 ± 25	568 ± 45	456 ± 34	817 ± 35		
TP	mg/dm ³	129 ± 10	211 ± 11	168 ± 12	295 ± 17		
Mg ²⁺	mg/dm ³	41.5 ± 6.5	55.5 ± 7.5	47.5 ± 4.9	75.5 ± 6.5		
Ca ²⁺	mg/dm^3	14.5 ± 3.5	16.6 ± 3.6	15.8 ± 4.2	27.5 ± 4.9		
COD	mgO_2/dm^3	$2,656 \pm 201$	$3,226 \pm 401$	$2,745 \pm 165$	$14,000 \pm 585$		
BZT ₅	mgO_2/dm^3	$1,594 \pm 125$	1871 ± 179	$1,\!674 \pm 148$	$6,890 \pm 456$		
TS	mg/dm ³	115 ± 10	125 ± 17	132 ± 15	452 ± 27		

Table 1 Characteristics of the post-digestion effluents

± standard deviation

value of struvite, whilst 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^+ and PO_4^{3-} as well as 25 and 50% excess amounts of magnesium and phosphorus ($Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1.25:1:1.25; $Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1.5:1:1.5). 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 NH_4^+ removal, as compared to its initial content in the post-digestion liquors. The technological scheme of the experimental unit used for struvite precipitation is presented in Fig. 1.

2.3. Membrane filtration

Membrane filtration (NF and RO) were conducted in the device (type GH-100–400) produced by a USbased company Osmonics. The device worked in the dead-end mode, on flat sheet membranes with the active volume of 36.3 cm². The processes were conducted under 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 liquors underwent membrane processes. Fig. 2 shows experimental unit used for membrane treatment.



Fig. 1. Experimental unit used for struvite precipitation.



Fig. 2. Experimental unit used for membrane filtration (1 – container used for collecting permeate, 2 – flowmeter, 3 – "Osmonics" apparatus, 4 – pressure gauge, 5 – pump). Detailed description of the membrane apparatus used during experiments is presented in [15].

Process (membrane applied)			
NF (cellulose type SF)	RO (polyamide type ADF)		
150–300	_		
6.9	5.4		
>85	99.5		
95	98.0		
-	Process (membrane applied) NF (cellulose type SF) 150–300 6.9 >85 95		

Table 2 Characteristics of the membranes applied

^aEstablished experimentally for deionized water containing 1 g/dm3 NaCl or MgSO₄, under working pressure of 2 MPa.

The RO and NF processes were conducted with the application of composite polyamide membrane (type ADF) and cellulose membrane (type SF 10), respectively. Characteristics of the membranes used is presented in Table 2.

2.4. 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), as well as calcium and magnesium [16,17]. Heavy metals content in the solid fraction after struvite precipitation was determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry. Whilst images of struvite crystals were taken by means of a Nikon Alphaphot microscope (×100), coupled with a digital camera. All analyses were conducted in three replicates.

3. Results and discussion

Since the effluents after co-digestion processes exhibited high amounts of organic and biogenic substances, an attempt was made to treat them by means of membrane techniques as well as dual methods, involving chemical precipitation as a pre-treatment step.

3.1.	Treatment of	co-digestion	effluents	by	means	of
men	nbrane techniq	jues				

Firstly, co-digestion effluents were treated with the application of high-pressure RO process, which ensured a high level of organic substances (COD, BZT₅) removal (>99%) as well as phosphorus (>99%) and decreased their concentration below discharge standards [18]. However, despite a relatively high removal of nitrogen compounds, amounting to between 84 and 89%, the permeate still contained too high, i.e. high above permissible limits, concentration of total nitrogen (215–847 mg/dm³), mainly NH_4^+ (96– 97% of TN). The higher the initial concentration of NH_4^+ in treated post-digestion liquors, the higher residual NH₄⁺ concentration in the permeate. Concentration of NH₄⁺ in the permeate above discharge limits was not unexpected, as the initial NH₄⁺ content was very high $(1,400-5,445 \text{ mg/dm}^3)$. What is more, a part of total-nitrogen in post-digestion liquors occur in unionized form, which is not detained by osmotic membranes. The key factors conditioning the degree of ammonia removal through RO process are: initial NH₄⁺ content and pH value, which influence the form of ammonia-nitrogen [7,19].

Secondly, the post-digestion effluents were treated by dual method, i.e. NF and subsequent RO. As compared to the treatment by means of RO, a significantly lower concentrations of nitrogen compounds were

	1 0 1			
Parameter	Unit	RO	NF+RO	Discharge limits [18]
рН	_	7.2–7.4	7.1–7.2	6.5–9.0
$\rm NH_4^+$	mg/dm ³	210-817	74–286	$10^{\rm a}$ - $15^{\rm b}$
TN	mg/dm ³	215-845	79–299	
ТР	mg/dm ³	1.12-1.98	<0.1	1 ^a -2 ^b
COD	mgO_2/dm^3	19–110	8.5–56	125
BZT ₅	mgO_2/dm^3	5.5-13.5	4.5-8.5	15
TS	mg/dm ³	1.1-1.6	<1.0	35

Table 3

Characteristics of the post-digestion liquors after membrane treatment

^a100,000 inhabitants and above; ^b10,000 –100,000 inhabitants.

recorded (TN: 79–299 mg/dm³). However, they were still above standards allowing direct release of treated waters into natural reservoir [18]. The application of NF before RO ensured almost complete removal of phosphorus ($<0.1 \text{ mg} \text{ P/dm}^3$). Characteristics of the permeate after RO filtration and dual method (NF + RO) is presented in Table 3.

3.2. Struvite precipitation as a pre-treatment before membrane filtration

Precipitation of struvite was conducted under stoichiometric as well as increased molar ratio of phosphates and magnesium (Mg²⁺:NH₄⁺:PO₄³⁻ = 1.25: 1:1.25, $Mg^{2+}:NH_4^+:PO_4^{3-} = 1.5:1:1.5$). Before struvite precipitation, post-digestion liquors underwent pH adjustment to about 9.5, i.e. the range ensuring effective precipitation and preventing the generation of other compound, containing Mg^{2+} and PO_4^{3-} [13,14,20]. 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 [21]. Due to the fact that Mg^{2+} ions were added in order to comply with struvite chemical formula, and thus caused an increase of Ca:Mg ratio ≪1, it was assumed that 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 in all tested post-digestion liquors [22].

3.2.1. Effectiveness of NH₄⁺ removal

Under stoichiometric molar ratio of Mg²⁺, NH₄⁺ and PO_4^{3-} the degree of NH_4^+ removal fluctuated between 86% (lower NH_4^+ initial content) and 92%(higher NH₄⁺ initial content). Taking into account the fact that the weight ratio of (PO_4^{3-}/NH_4^+) reached the value of 0.7-0.9, i.e. several times less than the value resulted from struvite formula (5.27), further treatment was carried out with the application of increased PO_4^{3-} and Mg^{2+} dosages. As the ratio was increased to 125 and 150% of the stoichiometric value, the degree of NH₄⁺ increased to 95-96 and 98-99%, respectively. Whilst, the residual NH₄⁺ concentration amounted to 72-260 mg/dm³ (Mg²⁺:NH₄⁺:PO₄³⁻ = 1.25:1:1.25) and 26–54 mg/dm³ (Mg²⁺:NH₄⁺:PO₄³⁻) = 1.5:1:1.5). In case of 50% increased Mg²⁺ and PO₄³⁻ ratio, the weight ratio of (PO_4^{3-}/NH_4^+) reached the value of 7.1-9.4, i.e. above the value resulted from struvite formula (5.27), so further increase of magnesium and



Fig. 3. Influence of precipitation conditions on the residual NH_4^+ concentration.



Fig. 4. Influence of Mg²⁺ dosage on COD removal during struvite precipitation.

phosphate turned out to be unjustifiable. Positive influence of increased Mg^{2+} and/or PO_4^{3-} dosages on NH_4^+ removal was mentioned in other studies [13,23,24]. Fig. 3 shows residual NH_4^+ concentration in



Fig. 5. Structure of the struvite precipitated.

Parameter	Unit	Heavy metals content	Struvite precipitated
Cd	mg/dm ³	0.9–1.2	
Cu	mg/dm^3	9–14	
Ni	mg/dm^3	3–6	
Pb	mg/dm^3	6-8	
Zn	mg/dm^3	15–35	
Hg	mg/dm^3	<0.1	
Cr	mg/dm ³	12–19	

Table 4 Ouality of the struvite precipitated

treated liquors as well as achieved values of $\rm NH_4^+$ removal.

Struvite precipitation caused an additional decrease in COD concentration, which was ascribed to MgO coagulative properties. It was assumed that a part of organic substances might have been absorbed by generated Mg(OH)₂ and precipitated together with struvite. The higher the dosage of MgO used, the higher the degree of COD removal. Conducting the process at stoichiometric ratio of ions allowed to remove 19–22% soluble organic compounds, expressed as COD. Whilst, application of increased dosages of Mg²⁺ allowed to bind from 31 to 34% ($Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1.25:1:1.25) to 43–46% ($Mg^{2+}:NH_4^+:PO_4^{3-}$ = 1.5:1:1.5) of COD. Fig. 4 depicts degrees of COD removal, as regards to different precipitation conditions.

3.2.2. Chemical composition, structure and quality of struvite precipitated

The influence of precipitation conditions on the structure of struvite crystals was also taken into account. Main factors influencing struvite structure include: reaction time, Mg/P ratio as well as initial

Table 5

Characteristics of co-digestion liquors treated with the application of chemical precipitation (pre-treatment) and RO

Parameter	Unit	Initial NH_4^+ content		Discharge			
		Low range 1,400 mg/dm ³	Medium range 2,450–2,980 mg/dm ³	High range 5,445 mg/dm ³	limits [18]		
Pre-treatme	ent: struvite precipitatio	on $(Mg^{2+}:NH_4^+:PO_4^{3-}=1:$	1:1)				
pН	-	7.2	7.1–7.2	7.3	6.5–9.0		
NH_4^+	mg/dm ³	27	30–37	61	10 ^a -15 ^b		
TN	mg/dm^3	29	32–38	63			
TP	mg/dm^3	0.6	0.6–0.7	0.9	1 ^a -2 ^b		
COD	mgO_2/dm^3	18	42–47	102	125		
BZT ₅	mgO_2/dm^3	5.2	9.5–10.9	12.0	15		
TS	mg/dm ³	1.5	1.9–2.3	2.1	35		
Pre-treatment: struvite precipitation (Mg ²⁺ :NH ⁺ ₄ :PO ³⁻ ₄ = 1.5:1:1.5)							
pН	-	7.2	7.2–7.3	7.4	6.5–9.0		
NH_4^+	mg/dm ³	3.4	4.8–5.4	8.0	10 ^a -15 ^b		
TN	mg/dm ³	4.4	6.5–7.0	8.5			
TP	mg/dm ³	0.4	0.5–0.6	0.7	1 ^a -2 ^b		
COD	mgO_2/dm^3	12	34–42	95	125		
BZT ₅	mgO_2/dm^3	4.5	8.0-10.5	11	15		
TS	mg/dm ³	1.8	2.2–2.5	2.5	35		

^a100,000 inhabitants and above; ^b10,000–100,000 inhabitants.

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 $\rm NH_4^+$ content in treated liquors [25,26]. In our study, the molar ratio of reagents ($\rm Mg^{2+}$ and $\rm PO_4^{3-}$) did not influence the structure of the struvite precipitated. However, we observed the relationship between initial $\rm NH_4^+$ content in treated liquors and the form of struvite generated. In case of initial $\rm NH_4^+$ content up to 2,980 mg/dm³, orthorhombic structure of crystals were generated. In case of the highest $\rm NH_4^+$ content (5,445 mg/dm³, liquors after kitchen biowaste and animal faeces co-digestion), the struvite precipitated mostly in "needle like" structure. It is in consistent with our previous results concerning struvite precipitation in liquors after sewage sludge digestion (initial $\rm NH_4^+$ content: 1,415 mg/dm³) [27] as well as previous findings described [28] (Fig. 5).

Chemical composition of struvite precipitated (P: 13.1–13.5% of dry mtter, N: 4.7–5.3% of dry matter, Mg: 11.4–12.6% of dry matter, Ca: 1.9–2.1% of dry matter) did not differ significantly from the theoretical proportion of particular ingredients (% of dry matter) in the struvite formula (P: 12.69, N: 5.73, Mg: 9.950). Slightly higher contents of P and Mg might have been the result for other compounds precipitated together with struvite, whilst, the presence of Ca reflects small amounts of this component in MgO powder, used as Mg^{2+} source. In case of all post-digestion liquors, the

struvite precipitated contained insignificant amounts of heavy metals (Table 4).

3.3. Post-treatment of co-digestion effluent by membrane techniques

Post-treatment with the application of RO and dual method combining NF (I step) and subsequent RO process—underwent the liquor streams after struvite precipitation, conducted at stoichiometric molar ratio (Mg²⁺:NH₄⁺:PO₄³⁻ = 1:1:1). as well as in conditions of 50% increased dosages of Mg²⁺ and PO₄³⁻ (Mg²⁺:NH₄⁺:PO₄³⁻ = 1.5:1:1.5).

Firstly, effluents after pre-treatment were treated by the application of RO process. Despite a relative comparable degrees of NH_4^+ removal, amounting to between 84 and 87%, only in case of the liquor pre-treated with application of struvite precipitation based on the 50% increased molar ratio of Mg^{2+} and PO_4^{3-} , the concentration of TN exhibited the value (4.4–8.5 mg/dm³) allowing direct release of the permeate to the natural reservoir. Whilst, the permeate after RO treatment of liquors pre-treated at molar ratio of ions exhibited too high concentration of NH_4^+ (29–63 mg/dm³), i.e. still above discharge standards. Taking into account the above, it was

Table 6

 $Characteristics \ of \ co-digestion \ liquors \ purified \ with \ the \ application \ of \ dual \ membrane \ filtration \ (NF+RO) \ after \ struvite \ precipitation \ as \ a \ pre-treatment$

Parameter	Unit	Initial NH ₄ ⁺ content			Discharge limits [18]
		Low range 1,400 mg/dm ³	Medium range 2,450–2,980 mg/dm ³	High range 5,445 mg/dm ³	
Pre-treatme	nt: struvite pro	ecipitation (Mg ²⁺ :NH ₄ ⁺ :P	$PO_4^{3-} = 1:1:1)$		
pН	-	7.2	7.1–7.2	7.3	6.5–9.0
NH_4^+	mg/dm ³	7.4	8.5-8.9	32	10 ^a -15 ^b
TN	mg/dm ³	8.1	9.1–9.6	37	
TP	mg/dm ³	<0.1	0.1–0.2	0.3	1 ^a -2 ^b
COD	mgO_2/dm^3	6.5	7.5–8.5	47	125
BZT ₅	mgO_2/dm^3	3.0	5.5–6.0	8.0	15
TS	mg/dm ³	<1.0	<1.0	<1.0	35
Pre-treatme	nt: struvite pro	ecipitation (Mg ²⁺ :NH ₄ ⁺ :P	$PO_4^{3-} = 1.5:1:1.5)$		
pН	-	7.2	7.2–7.3	7.4	6.5–9.0
NH_4^+	mg/dm ³	2.5	2.8–3.4	4.0	10 ^a -15 ^b
TN	mg/dm^3	3.0	3.1–3.5	4.6	
ТР	mg/dm ³	< 0.1	<0.1	0.5	1 ^a -2 ^b
COD	mgO_2/dm^3	5.5	6.5–7.5	42	125
BZT ₅	mgO_2/dm^3	2.5	4.5–5.0	7.5	15
TS	mg/dm ³	<1.0	<1.0	<1.0	35

^a100,000 inhabitants and above; ^b10,000–100,000 inhabitants.

concluded that initial concentration of NH_4^+ plays the crucial role on the residual content of nitrogen compounds after RO treatment. In all conducted trials, the concentration of COD, BOD₅, TP decreased below the levels allowing its direct release to the natural water bodies [18]. Characteristics of co-digestion liquors treated with the application of chemical precipitation (pre-treatment) and RO are presented in Table 5.

The application of struvite precipitation as a pre-treatment step and subsequent two-step membrane filtration (NF+RO) ensured a high degree of contaminants removal. Chemical pre-treatment conducted at stoichiometric ratio of Mg^{2+} , NH_4^+ and PO_4^{3-} allowed to decrease nitrogen content below discharge levels, but only in case of co-digestion effluents containing initially up to 2,980 mg NH₄⁺/dm³. In case of the liquor containing the highest ammonia-nitrogen content, i.e. 5,445 mg/dm³ (effluent after co-digestion of kitchen biowaste and animal faeces), the permeate still exhibited TN concentration (37 mg/dm^3) highly above the permissible values. In this case, similar to the method based on one-step membrane filtration (RO), it was necessary to apply increased molar ratio of Mg^{2+} and PO_4^{3-} in order to decrease nitrogen content below permissible standards. As in the method based on one-step RO filtration, the dual method (NF +RO) allowed to decrease all other contaminants (COD, BOD₅, TP, TS) below discharge limits. What is more, the application of membrane processes in both of the analysed cases (RO or NF+RO) eliminated the secondary load of Cl⁻, which occurred in treated liquors as a result of pH value adjustment before applying membrane filtration. Characteristics of the permeate after dual filtration method (NF+RO) is presented in Table 6.

4. Conclusions

Struvite precipitation targeted at ammonia-nitrogen binding coupled with membrane processes (RO and NF+RO) turned out to be an effective treatment method of highly contaminated effluents after co-digestion processes. The treatment of all analysed postdigestion liquors by means of struvite precipitation and subsequent RO process allowed to achieve permeate quality allowing its direct release to the natural receiver. In order to achieve this, it was necessary to apply an increased molar ratio of Mg²⁺ and PO₄³⁻ (Mg² ⁺:NH₄⁺:PO₄³⁻ = 1.5:1:1.5) during precipitation (pre-treatment). Whilst, the liquors after RO filtration and pretreatment at stoichiometric ratio of reagents still contained excessive amounts of NH₄⁴ (above permissible values). However, their reuse in biogas facilities as a technological water (e.g. for cleaning purposes or feedstock dilution) should be taken into consideration. In case of post-digestion effluents containing up to 2,980 mg NH_4^+/dm^3 , introducing NF between struvite precipitation and RO influenced positively the amount of reagents used during precipitation (pre-treatment). Thus, discharge standards were met after conducting the struvite precipitation under molar ratio of Mg^{2+} , NH_4^+ and PO_4^{3-} . What is more, the application of NF before subsequent RO process will likely lengthen life cycle of membrane used in RO processes.

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