Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.26199

203 (2020) 1–10
November

Membrane fouling due to concentrating leachate after methane fermentation and nitrification

Magdalena Domańska[a,*], Paweł Wiercik[a], Paweł Mituła[a], Janusz Łomotowski[a], Tomasz Konieczny[b]

[a]Wrocław University of Environmental and Life Sciences, The Faculty of Environmental Engineering and Geodesy, Institute of Environmental Engineering, Grunwaldzki Square 24, 50-363 Wrocław, Poland, Tel. +48 71 320 55 53; email: magdalena.domanska@upwr.edu.pl (M. Domańska); Tel. + 48 71 320 10 38; email: pawel.wiercik@upwr.edu.pl (P. Wiercik), Tel. +48 71 320 55 72; email: pawel.mitula@upwr.edu.pl (P. Mituła), Tel. +48 71 320 10 34; email: janusz.lomotowski@gmail.com (J. Łomotowski)
[b]Municipal Water and Sewage Company Wrocław, 14/16 Na Grobli St., 50-421 Wrocław, Poland, Tel. +48 71 340 95 00; email: tomasz.konieczny@mpwik.wroc.pl (T. Konieczny)

Received 15 November 2019; Accepted 5 June 2020

ABSTRACT

The article presents the results of research on the process of leachate concentration at a nanofiltration installation over the course of six experiments (lasting from 31 to 53 d each), with special emphasis on the process of membrane fouling. The results have shown that organic and mineral sediments, including struvite-type compounds, caused the fouling of nanofiltration membranes even if the concentration of ammonia nitrogen was low. The precipitation of mineral compounds was mostly influenced by the concentration of phosphates in the feed water. Adding magnesium nitrate $Mg(NO_3)_2$ did not speed up the precipitation of crystals on the membrane surface. Studies have shown that the phenomenon of struvite-type compounds precipitation occurs not only on the surface of the membrane but also inside the membrane structure, causing permanent damage to its physical structure.

Keywords: Nanofiltration; Pressure sewage; Recovering nutrients; Scaling; Wastewater Treatment

1. Introduction

Directing leachate after fermentation to the beginning of the wastewater treatment process makes it difficult to remove nitrogen and phosphorus compounds from wastewater. Attempts are being made to find economically-viable methods of removing ammonia nitrogen from leachate after methane fermentation [1]. The leachate subjected to biological processes such as partial or full nitrification becomes a source of nitrates and nitrites. There are many methods of recovering nutrients from effluent [2], including membrane separation.

The main problem connected with membrane filtration is fouling, chiefly caused by particles and colloids (cake level formation), dissolved inorganic matters (concentration polarization), dissolved organic matters (electrostatic repulsion and/or hydrophobic interactions), microbial attachment and growth (biofouling) [3,4]. Despite a large number of publications on membrane fouling, the phenomenon has not been thoroughly understood due to the complexity of interrelated processes, many possible configurations of modules and reactors, the varying composition of wastewater and different operating conditions. Shirazi et al. [5] clearly indicate that there is insufficient

---

* Corresponding author.

information about fouling on the membrane surface in a multi-component system and research in this direction is desirable. It should be noted that laboratory tests are usually conducted on synthetic wastewater and focus on a pre-defined number of factors influencing the process [6]. Laboratory experiments usually involve small quantities of pre-treated solution (often even 1,000 times smaller than in the pilot-scale), whose composition is artificially modified to avoid variation. Such experiments are typically conducted in constant temperatures, with constant hydraulic load and with much higher (even 20-fold) energy inputs. It frequently leads to disregarding the simultaneous influence of various compounds and factors on each other, and for this reason, fouling behavior can be completely different in other scales. It limits the application of lab experiments to full-scale operations because the tests can only be applicable to filtration characterization or fouling rates as long as hydrodynamics and operating conditions while treating fresh precipitate are comparable. The applicability of lab-scale experiments to pilot and full-scale plants is difficult [6].

In the pilot and full-scale research, there is a large variety of foulants in the feed water [3,7]. Some organic impurities can be adsorbed on the membrane surface and thus cause fouling; others may chemically degrade the membrane surface, and yet others are capable of changing their nature during technological processes. Leachate is highly contaminated with organic contaminants measured as chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), ammonia, halogenated hydrocarbons and heavy metals; it also contains high concentrations of inorganic salts (sodium chloride, carbonates) [8]. According to Peters [9], landfill leachate contains 80%–95% inorganic matter, 5%–20% organic matter, and ammonium ion concentration at the level of 0.3–2 g dm^{-3}. Leachate containing a lot of organic substances should be subjected to pre-treatment. In the paper of Simonič [10], where COD exceeded 20,000 mg O_2 dm^{-3}, poly aluminum chloride was chosen in the pre-treatment process. In another study, electrocoagulation before nanofiltration (NF) was used [11].

Due to a large variety of organic substances present in wastewater, their impact on the filtration process is highly complex [12]. According to Aleta et al. [13], organic matter in the form of xylan inhibits phosphorus precipitation. The researchers found that there are few studies on the influence of organic matter on phosphorus precipitation. According to research by Tang et al. [3], when treating secondary effluent on reverse osmosis membranes at a full-scale plant, organic matter constituted as much as 75% of the deposit, with hydrophobic acids and hydrophilic neutrals (produced by microorganisms) accounting for most of its mass. When non-nitrified effluent was treated, adsorption and deposition of organic compounds occurred [7]. Ramaswami et al. [14] emphasize that only a combination of biological and/or physical-chemical technologies together with membrane processes can ensure complete and efficient treatment of landfill leachates.

To prolong the lifespan of reverse osmosis (RO) membranes and achieve higher volume permeate flux, it is recommended to use hybrid systems combining nanofiltration and reverse osmosis [15,16]. Concentrating ammonium and nitrates in wastewater by using NF and RO membranes was tested by Häyrynen et al. [17,18].

Membrane scaling due to the precipitation of inorganic compounds, although seemingly less complex, also carries a number of exploitation problems [19]. Problems in the technological processing of effluent sludge are commonly posed by the precipitation of mineral compounds, mostly phosphate salts such as magnesium phosphate $Mg_3(PO_4)_2{\cdot}8H_2O$ or magnesium ammonium phosphate $MgNH_4PO_4{\cdot}6H_2O$ called struvite. The optimum conditions for the precipitation of struvite are pH > 9 and the Mg:N:P molar ratio of 1:1:1 [20]. When pH drops below 7, struvite does not precipitate [21]. In the case of real wastewater, there usually appear not pure mineral forms, but their mixtures. It is possible for biologically related struvite-type phosphate compounds to precipitate, in which case, for example, ammonium salts could be replaced by potassium and sodium ions $KNaMg_2(PO_4)_2{\cdot}14(H_2O)$, defined as hazenite [22].

Since calcium inhibits the precipitation of struvite when the Mg/Ca ratio is greater than 1:1, or when Ca^{2+} is present at pH > 10, amorphous sodium phosphate forms [23]. The mechanism of the precipitation of mineral phosphate compounds is highly complex. Apatites with the general formula $Ca_5[(PO_4)_3(X)]$, with X being the anion of OH^- (hydroxylapatite), Cl^- (chlorine apatite) or F^- (fluorine apatite), can also precipitate from the effluent.

Tang et al. [3] showed that the scaling contained a lot of iron (although its quantity in the water fed to the RO was low) and calcium, as well as silicon, manganese, magnesium and aluminum. Xu et al. [7] also confirmed that inorganic compounds and scalants (calcium phosphate, magnesium, aluminum, iron) were found to be the chief factors responsible for NF and RO fouling when nitrified/denitrified effluent was treated.

Nanofiltration is used in industries such as textile, clothing, food, paper, chemical for the production of clean water, metal separation or purification landfills agriculture, including purification of landfill leachate [24]. According to the authors' knowledge, there are no publications on using NF membranes to concentrate nitrogen compounds from leachate after methane fermentation and nitrification. Our research was conducted to investigate whether it is possible to produce a leachate concentrate on membranes that could be used to reduce the production of hydrogen sulfide in pressure sewage systems. Currently, biocides and strong oxidants are used for this purpose [25–28]. The aim of this article is to identify problems connected with the fouling of NF membranes during the concentration of this type of leachate.

2. Material and methods

Nitrate and nitrite ions are monovalent, and for this reason they pass through microfiltration, ultrafiltration and nanofiltration membranes. They are only stopped by reverse osmosis membranes. The tests were based on using MF, NF and RO membranes as depicted in Fig. 1, although this article focuses primarily on issues connected with nanofiltration (area marked with red dotted line). The NF membrane used in the experiment is characterized in section 2.1 – filtration unit, membranes and operating conditions.

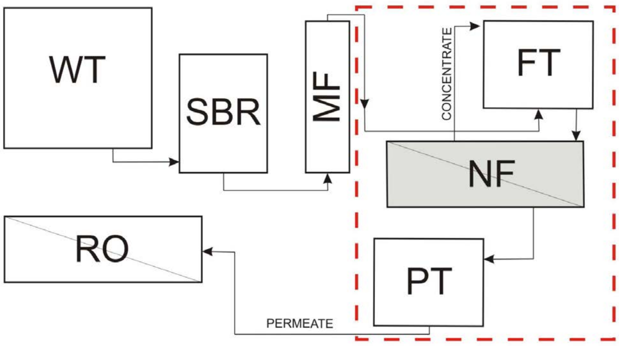

Fig. 1. Schematic diagram of the membrane installation (WT – wastewater tank, SBR – sequencing batch reactor, MF – microfiltration, FT – feed tank, NF – nanofiltration, PT – permeate tank, RO – reverse osmosis, red dotted line – field of interest).

In total, six experimental runs were conducted on real wastewater (leachate after methane fermentation), whose source and composition is described in section 2.2 – source and composition of wastewater. During the concentration of nitrified leachate after MF and NF, continuous measurements of pH, pressure, conductivity, flow and temperature were performed using the supervisory control and data acquisition (SCADA) system (section 2.1 – filtration unit, membranes and operating conditions). The concentration of individual ions (nitrate, nitrite and ammonia nitrogen, orthophosphate, magnesium, calcium, sodium, potassium) in the feed tank (FT) and permeate tank (PT) was regularly analyzed in the laboratory (section 2.3 – physicochemical analysis). Moreover, a sediment analysis was performed by using an X-ray powder diffractometer and scanning electron microscopy (SEM) of the membranes and of the sediment that had formed on their surfaces (section 2.4 – scanning electron microscopy and X-ray powder diffraction (XRD)).

2.1. Filtration unit, membranes and operating conditions

The thin-film membrane produced by General Electric Company (GE) (Boston, Massachusetts, United States) was used in the study. The *D*-series is characterized by an approximate molecular weight cut-off of 150–300 Da for uncharged organic molecules. Other parameters are shown in Table 1.

The cross-flow membrane filtration unit (GE Water & Process Technologies Sepa (Trademark of General Electric Company, United States)– CF II Membrane Cell) system capable of withstanding up to 69 bars was used in the research.

The fouling effect was measured by pressure rise. Preliminary research on clean water did not show a significant fouling effect. The membrane system had sensors measuring pressure, temperature, flow and conductivity. The liquid level in the tank was measured by a pressure transducer (Cerabar PMC131-A11F1D10, Endress+Hauser, Reinach, Switzerland) on the bottom of the tank. The data were automatically recorded using the SCADA system. The working conditions were measured continuously. Due to the amount of data (249 working days), only the most characteristic results are included in the manuscript. The filtration process was based on a cross-flow system with a constant flow of the concentrate. The flow levels varied at 1.5–2 L min^{-1}. At the beginning of the experiment, trans-membrane pressure was kept at the level of 10–15 bar.

The membrane operated at the temperature of the environment, within the range of 20°C–25°C. In the summer the temperatures periodically reached 30°C. When the maximum pressure limit (set at 25 bars) was exceeded, instead of cleaning the membrane, it was removed and replaced with a new one in order to check whether sediment had precipitated. In the first experimental run, the membrane was replaced on the 13th day, in the second run – on the 24th and 44th day, in the third – on the 12th day, in the fourth – on the 7th and 22nd day, in the fifth – on the 22nd and 31st day, and in the sixth – on the 33rd day.

Experiments 5 and 6 were performed to confirm or reject the hypothesis that adding magnesium nitrate $Mg(NO_3)_2$ would increase the concentration of nitrates and accelerate the precipitation of crystals on the membrane surface.

2.2. Source and composition of wastewater

After mechanical pretreatment, raw wastewater at the Janówek Wastewater Treatment Plant in Wrocław flows from primary settling tanks to the biological treatment section, consisting of a denitrification chamber, an anaerobic chamber, an anoxic chamber, two denitrification/nitrification chambers, an oxidation chamber and a secondary settling tank. After concentration and dehydration, raw and waste sludge is directed to closed fermentation chambers where fermentation gas containing methane is produced through mesophilic fermentation.

Leachate after methane fermentation was characterized by a high content of total nitrogen, consisting mainly of ammonium ions. The leachate composition was rather stable and the individual values were characterized by a coefficient of variation of around 20%. Only suspension was subjected to greater fluctuations during individual measurements (Table 2). Wastewater alkalinity, which is a measure of the content of acidic calcium carbonates $Ca(HCO_3)_2$ and magnesium $Mg(HCO_3)_2$, was around 64.3 m val dm^{-3}.

Table 1
Characteristics of the nanofiltration membrane

Model	pH range	Maximum temperature °C	Maximum operating pressure bar	Pure water flux L h^{-1} m^{-2}	Minimum $MgSO_4$ rejection %
DL 2540C	Continuous operation 3–9 Clean in place 2–10.5	50	40°C < 35°C 30°C > 35°C	8–34	96

Table 2
Statistical analysis of physicochemical parameters of leachate after methane fermentation (56 measurements for the period of 4.11.2015–23.02.2017)

Pollutant	Unit	Leachate after methane fermentation		
		Median	SD	Cv (%)
BOD_5	mg O_2 dm^{-3}	156.50	26.35	17.03
COD	mg O_2 dm^{-3}	403.00	107.15	24.97
Suspension	mg dm^{-3}	131.00	76.12	51.54
Total nitrogen	mg dm^{-3}	839.00	154.62	18.69
Total phosphorus	mg dm^{-3}	145.50	32.92	22.32
Alkalinity	m val dm^{-3}	64.30	10.05	15.96

SD = standard deviation, Cv = coefficient of variation.

Over the course of the research, leachate from dehydrated sludge (WT) was directed to sequencing batch reactors that were part of the installation (Fig. 1), in which full or partial nitrification process took place. Nitrified leachate with a volume of about 100 L was subjected to a one-time microfiltration process (MF). After that, wastewater containing trace amounts of ammonium ions and a high concentration of nitrates or nitrites constituted the feed for the membrane processes (FT). Then the effluent was concentrated continuously until the next experiment was completed. Permeate collection took place in the PT tank and was subjected to subsequent processes. The nanofiltration module worked practically continuously, with the exception of technical breaks (membrane replacement, failure). Since the research was conducted at an operating treatment plant, the composition of wastewater varied and it was impossible to repeat the tests on similar leachate. The composition of wastewater at the beginning of the experimental runs is shown in Table 3. A full analysis of leachate after methane fermentation, nitrification, MF and NF in both the concentrate and permeate tanks was performed regularly. Due to the amount of obtained data, not all of them were included in the study.

2.3. Physicochemical analysis

Samples were regularly taken to analyze the physicochemical composition of leachate in the PT and FT. The time of performing the analyses, different in the subsequent experiments, is shown in Figs. 2 and 6–10. Emphasis was put on the analysis of compounds that can potentially influence the precipitation of mineral scaling. Table 3 shows the concentration of various forms of nitrogen (NH_4^+–N, NO^{2-}–N, NO^{3-}–N) as well as PO_4^{3-}, Mg^{2+} and Ca^{2+}. The concentration of nitrogen and phosphate compounds was measured by a colorimetric method using a Cintra 202 spectrophotometer, while the concentration of magnesium and calcium – using atomic absorption spectrometry (AAS).

In order to estimate the potential amount of substances retained by the membrane as sediment, a general equation was used according to which the difference between the amount of ions in the feed and permeate tanks equal to a load of ions retained by the membrane. Knowing the volume of leachate in the tanks, it was possible to convert the concentrations into the amount of individual ions in mg, according to Eq. (1) below.

$$L = C_{\text{FTI}} \cdot V_{\text{FTI}} - C_{\text{FT}} \cdot V_{\text{FT}} - C_{\text{PT}} \cdot V_{\text{PT}} \tag{1}$$

where L is the estimated load in the sediment, mg; C_{FTI} is the initial concentration in the FT, mg dm^{-3}; V_{FTI} is the initial volume in the FT, dm^3; $C_{\text{FT, PT}}$ is the ion concentration in the FT, PT; mg dm^{-3}; $V_{\text{FT, PT}}$ is the volume of the permeate/concentrate, dm^3.

Table 3
Initial conditions in the feed tank (FT)

Experimental runs	pH	NH_4^+–N	NO^{2-}–N	NO^{3-}–N	PO_4^{3-}	Mg^{2+}	Ca^{2+}
	–	mg dm^{-3}					
1	8.38	0.1	43.4	442.0	376.5	15.8	23.9
2	8.75	1.1	0.1	456.0	418.4	9.1	18.9
3	8.45	0.8	162.6	207.8	381.5	9.4	57.5
4	8.50	3.4	106.3	113.1	155.4	12.5	20.4
5/6	8.00	8.3	1,125.8	27.0	185.7	10.7	44.0
5*	8.00	8.3	991.2	108.9	155.4	28.8	26.0
6*	8.50	0.2	983.0	246.6	119.3	45.0	20.5

*Magnesium nitrate in the amount of 20 and 40 mg dm^{-3} respectively in the 5th and 6th experiment.

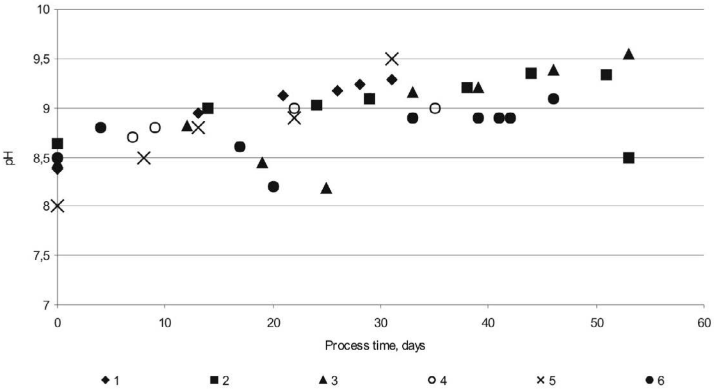

Fig. 2. pH changes in the FT during the 6 experimental runs.

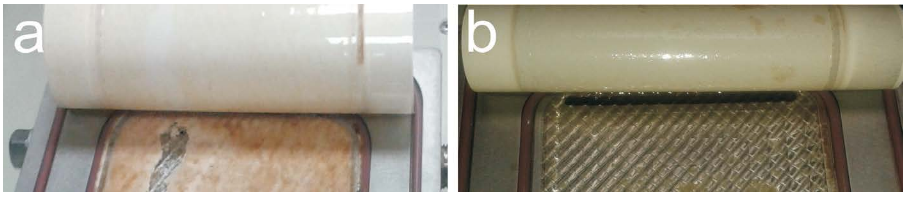

Fig. 3. Pictures of sediment after the end of the first (a) and sixth (b) experiment.

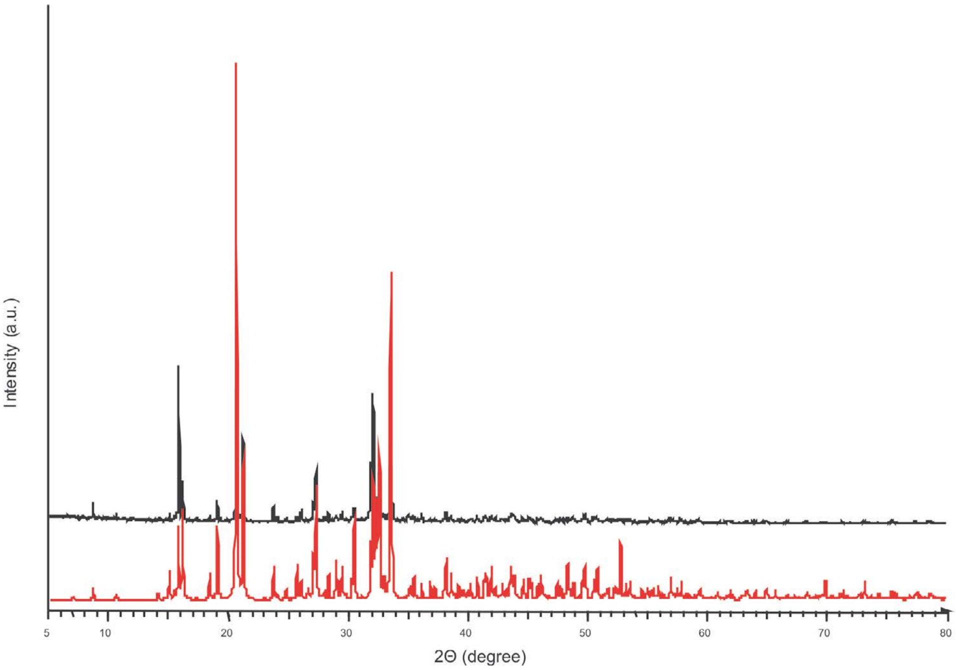

Fig. 4. The experimental (black line) and calculated (red line) XDR patterns. The lower pattern simulated from the crystal structure of $KNaMg_2(PO_4)_2 \cdot 14H_2O$ [32].

The estimated percentage of ions (I%) in the sediment is presented in Figs. 6, 7, and 9 as the estimated load in the sediment compared to the initial amount in the FT, according to Eq. (2).

$$I_{\%} = \frac{(L \cdot 100)}{C_{\text{FTI}} \cdot V_{\text{FTI}}} \tag{2}$$

The uncertainty of the measurement was calculated with maximum accepted relative standard deviation (RSD) at the level of 2% for the concentration ($C_{\text{FTI, FT, PT}}$) measured by AAS and Cintra 202, and 0.5% for volume measured indirectly with a pressure transducer ($V_{\text{FTI, FT, PT}}$). The uncertainty calculated from Eqs. (1) and (2) was 10%.

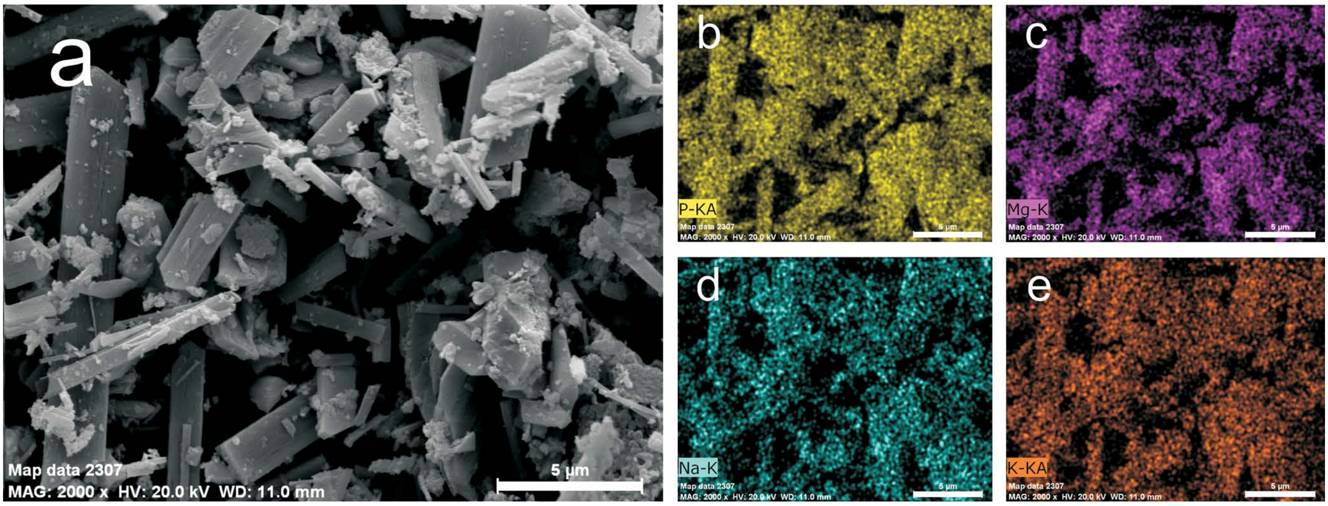

Fig. 5. SEM analysis. Image of prevalent elements (b) phosphorus, (c) magnesium, (d) sodium, (e) potassium in the sediment, and (a) scale

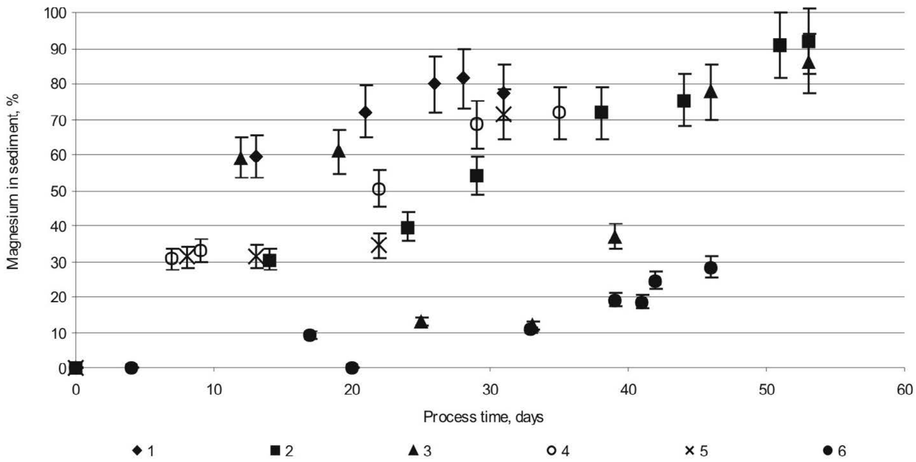

Fig. 6. Magnesium changes in the sediment with process time in the 6 experimental runs. Results with ±10% of measurement uncertainty.

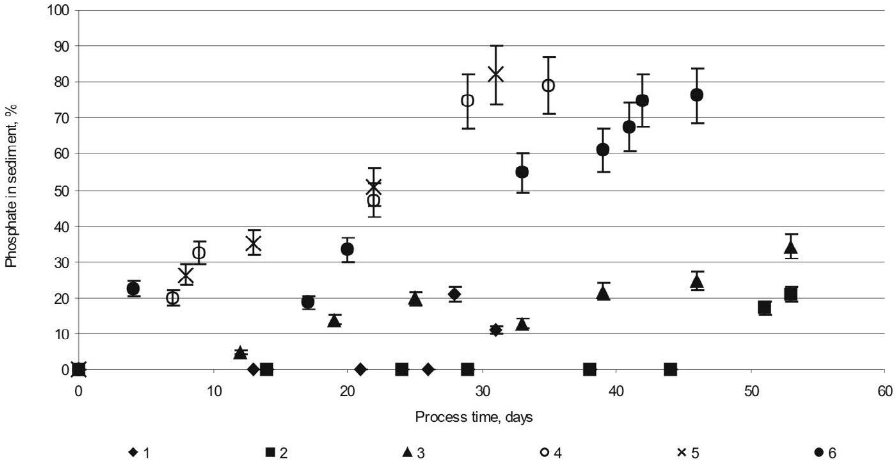

Fig. 7. Phosphates changes in the sediment with process time in the 6 experimental runs. Results with ±10% of measurement uncertainty.

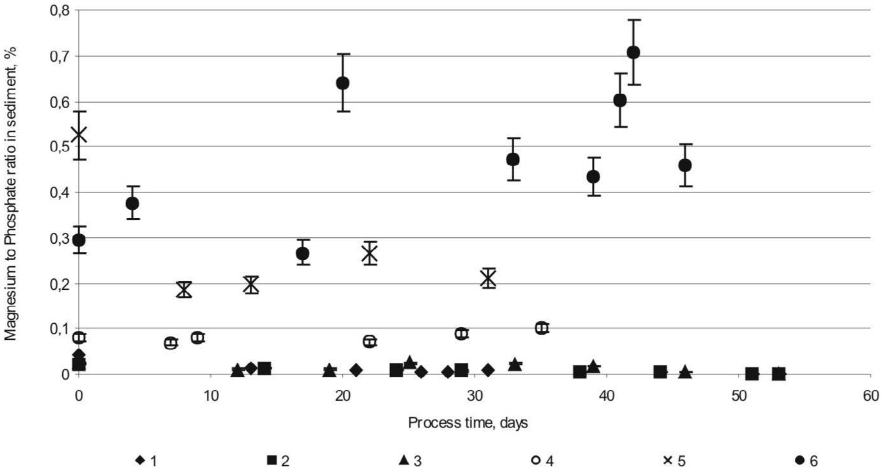

Fig. 8. Magnesium to phosphate ratio changes in the sediment with process time in the 6 experimental runs. Results with ±10% of measurement uncertainty.

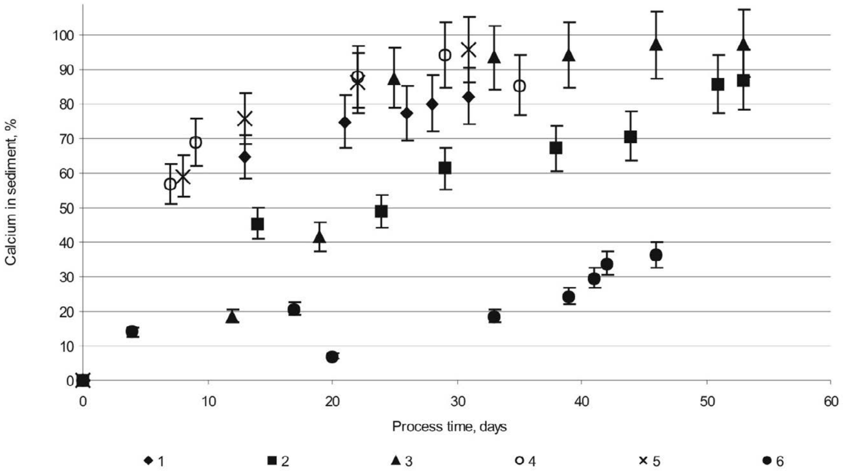

Fig. 9. Calcium changes in the sediment with process time in the 6 experimental runs. Results with ±10% of measurement uncertainty.

2.4. Scanning electron microscopy and XRD

The membrane surface structure and precipitate after the first experiment were analyzed by SEM according to the methodology described by Kaliński et al. [29]. The sediment diffractograms were recorded on a D8 ADVANCE powder diffractometer with nickel-filtered Cu Kα radiation (λ = 1.5418 Å) and a VÅNTEC detector (BRUKER Company, Billerica, Massachusetts, United States). The measurements were performed within a 2θ range of 5°–120°.

3. Results and discussion

The initial composition of leachate in the FT in all the experimental runs was characterized by small amounts of ammonium ions and various amounts of nitrate and nitrite ions. In the first two runs, nitrate ions were predominant, in the fifth and sixth run – nitrite ions, while in the third and fourth trials the concentration of nitrate and nitrite ions was at similar levels (Table 2).

Researchers indicate that reaction contributes greatly to increased fouling of NF membranes [10,30]. Most research is based on negatively charged NF membranes [8]. In Simonič [10], fouled DK and DL nanofiltration membranes were negatively charged above pH 5. Trebouet et al. [8] indicate that greater fouling at low pH values could be explained by electrostatic effects that reduce the repulsion between the negatively charged membrane surface and macromolecules of humic-type substances.

The pH in the FT varied between ca. 8 and 9.5 (Fig. 2), which favored the precipitation of minerals because the solubility of, for example, struvite crystals decreases as pH increases.

According to research by Czajkowska and Siwiec [31], with a pH value of 7.0 struvite did not precipitate in the analyzed conditions, whereas at pH value of 9.0 struvite precipitated irrespective of the concentration levels of ammonium, phosphate and magnesium ions. In our research, in spite of similar pH levels, sediment precipitated mostly in the first three experimental runs (Fig. 3a); in the first two experiments, it had a dense, crystalline, barely soluble structure while in the third one, its structure was more watery. In the subsequent three experiments, only a small amount of watery sediment was observed (Fig. 3b). It could be observed that the chemical composition of the leachate affects the precipitation of struvite-type compounds. The possible reasons for this variability are discussed further in this section.

The composition of sediment in experiments 1 and 2 was analyzed for the identification of ammonium magnesium phosphate (NH_4MgPO_4), struvite ($NH_4MgPO_4 \cdot 6H_2O$) and hazenite $KNaMg_2(PO_4)_2 \cdot 14(H_2O)$. Since the concentration of ammonium ions was negligible, it was more probable that the structure of the mineral contained sodium and potassium ions. An XRD analysis (Fig. 4) confirmed that it was sediment most similar to hazenite $KNaMg_2(PO_4)_2 \cdot 14(H_2O)$ [22,32].

In each experiment, the concentration of sodium and potassium in the FT was at the level of ca. 200 mg dm^{-3} (for sodium it changed between 131 and 236 mg dm^{-3}, and for potassium – between 143 and 272 mg dm^{-3}). During the process of concentration, monovalent ions partly permeated to the PT. It reflects other researchers' findings [8].

The SEM analysis confirmed the crystalline structure of the sediment and revealed that Mg, P, K and Na ions accounted for the largest share – 10.06%, 8.23%, 7.16%, 6.70% atom, respectively (Fig. 5).

Using Eqs. (1) and (2), it was possible to calculate the percentage share of ions forming the structure of the sediment. It was observed that magnesium precipitated on the membrane in each experimental run (Fig. 6). Over the course of the experiments, most magnesium was retained on the membrane surface, although it was not directly connected with the amount of precipitated sediment. The decrease in the percentage of magnesium in the sediment in experiment 3 should not be interpreted as a decrease in magnesium in the sediment. The initial decrease in magnesium concentration in the FT (second and third measurement) was due to the precipitation of magnesium on the membrane while the increase in magnesium concentration in the FT in subsequent measurements was the result of concentrating the leachate. The last two measurements showed again a decrease in magnesium in the FT, observed as a percentage increase of magnesium in the sediment. It follows that the magnesium is not always evenly precipitated.

Experiments 5 and 6 were intended to confirm or reject the hypothesis that adding magnesium nitrate $Mg(NO_3)_2$ would increase the concentration of nitrates and accelerate the precipitation of crystals on the membrane surface. After adding magnesium nitrate (in the amount of 20 and 40 mg dm^{-3}), only a very small amount of sediment precipitated on the membrane. On the basis of estimations given by Eqs. (1) and (2), magnesium should have precipitated in the sediment in experiment 5. When the initial concentration of magnesium was low (experiment 5), it did precipitate as sediment, while with higher initial concentrations (experiment 6), it was identified in the solution. Fig. 6 shows that the precipitation of magnesium in the form of sediment did not influence membrane fouling – it was also confirmed by the observation of the membrane.

Fig. 7 shows that phosphates precipitated as sediment mostly in experiments 4–6, in which very little sediment on the membrane was observed. In the first three experiments, when significant membrane fouling was observed, phosphates precipitated only in the final stage of the experiments, which could be seen after the removal of the membrane. It suggests that if phosphate ions do not precipitate in the first stage of the experiment (e.g. into the tank), they will eventually cause the precipitation of a significant amount of mineral sediment on the membrane. This confirms previous analyses by other researchers, according to which phosphates have a decisive influence on the precipitation of mineral sediments [33].

Fig. 8 presents the ratio of magnesium to phosphates as the estimated load calculated on the basis of Eq. (1). It shows that if the ratio is close to 0, sediment precipitates on the membrane. With initial values >0.08, only small amounts of sediment precipitated.

Research by Jarusutthirak et al. [33] showed that a decrease in the efficiency of the NF membrane was caused by calcium ions rather than magnesium ions. In our research, the initial concentration of calcium did not influence sediment formation on the membrane, as

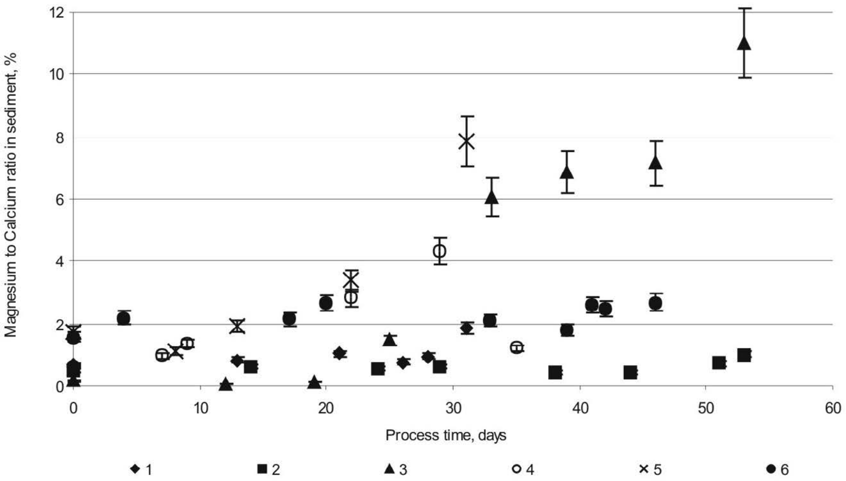

Fig. 10. Magnesium to calcium ratio changes in the sediment with process time in the 6 experimental runs. Results with ±10% of measurement uncertainty.

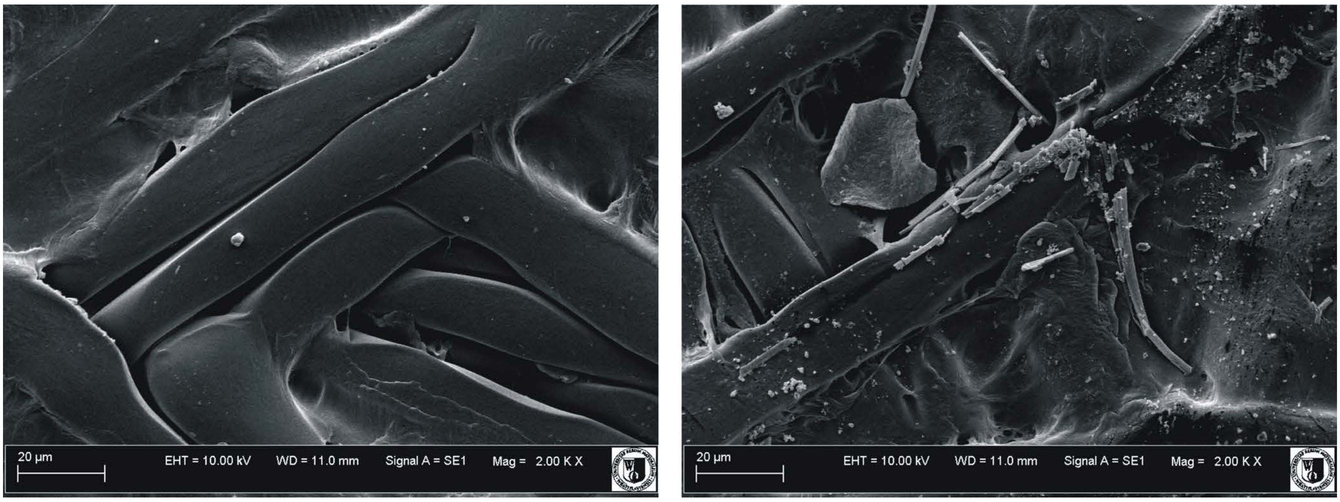

Fig. 11. The bottom surface of the nanofiltration membrane. The new membrane on the left and membrane at the end of the first experiment (damage of the membrane structure) on the right.

demonstrated by close linear trend lines of the Ca % in the sediment in experiments 1 and 5 (Fig. 9). In the first experiment, sediment was visible on the membrane, whereas in the fifth one its quantity was much lower. As this research demonstrated, the initial concentration of calcium did not influence whether sediment precipitated on the membrane or not.

During the experiments, the Mg/Ca ratio exceeded 1 in all runs except experiment 2, in which the Mg/Ca ratio was 1:1 at its end (Fig. 10). It suggests that amorphous calcium phosphate precipitated.

The scanning of the membrane surface after experiment 1 revealed its permanent damage due to the overgrowth of crystals on the other side of the membrane (Fig. 11). Due to the lack of works reporting the struvite-type crystal overgrowth on the other side of the NF membrane, there is a need for research in this direction. Membrane cleaning probably would not have reversed the permanent damage caused by mineral sediment. Thus during treatment, it is necessary to closely monitor the process parameters, especially those regarding phosphates. An alternative form of membrane protection against mineral deposits, which often cause its permanent damage, involves the use of intermediary tanks, in which sediments precipitated on the bottom can be removed much more easily than from the membrane surface.

4. Conclusions

The conducted research confirms the possibility of obtaining nitrate concentrate, although the organic compounds present in the leachate pose a significant problem, especially for membrane systems. While carrying out research on the nanofiltration of leachate after methane fermentation and nitrification, the risk of membrane fouling – not only by organic compounds but also by mineral compounds – should be taken into account.

The results show that despite low concentration of ammonium ions, membrane filtration of leachate after methane fermentation and nitrification can result in the formation of struvite-type mineral compounds. An XRD analysis confirmed that it was sediment most similar to hazenite $KNaMg_2(PO_4)_2 \cdot 14(H_2O)$. In the first three experimental runs, significant membrane fouling was observed; in the subsequent three experiments, only a small layer of highly watery sediment was detected. The results suggest that phosphates had a crucial influence on the precipitation of mineral sediments. The addition of magnesium nitrate $Mg(NO_3)_2$ did not increase the concentration of nitrates in the FT did not speed up the precipitation of crystals on the membrane surface. The precipitation of phosphates in the initial phase of the experiment resulted in very little sediment on the membrane; therefore, the use of intermediary tanks should be taken into consideration to protect the membrane against fouling by mineral compounds. Studies have also shown that the phenomenon of struvite-type compounds precipitation occurs not only on the surface of the membrane, but also inside the membrane structure, which causes permanent damage to its physical structure. To the authors' knowledge, there exists no work reporting the crystal overgrowth on the other side of the membrane during struvite-type crystals formation, therefore research in this direction is desirable.

Acknowledgments

The research described in this paper was financially supported by the National Center for Research and Development in Poland as part of project no. PBS2/B9/25/2014.

Thanks are due to Miłosz Siczek for the X-ray analyses of sediment and Joanna Szczypta and Krystyna Woźniakowska for the physicochemical analyses of leachate.

References

[1] H.M. Huang, J.H. Liu, L. Ding, Recovery of phosphate and ammonia nitrogen from the anaerobic digestion supernatant of activated sludge by chemical precipitation, J. Cleaner Prod., 102 (2015) 437–446.

[2] C.M. Mehta, W.O. Khunjar, V. Nguyen, S. Tait, D.J. Batstone, Technologies to recover nutrients from waste streams: a critical review, Crit. Rev. Env. Sci. Technol., 45 (2015) 385–427.

[3] F. Tang, H.-Y. Hu, L.-J. Sun, Q.-Y. Wu, Y.-M. Jiang, Y.-T. Guan, J.-J. Huang, Fouling of reverse osmosis membrane for municipal wastewater reclamation: autopsy results from a full-scale plant, Desalination, 349 (2014) 73–79.

[4] Y.-R. Chang, Y.-J. Lee, D.-J. Lee, Membrane fouling during water or wastewater treatments: current research updated, J. Taiwan Inst. Chem. Eng., 94 (2019) 88–96.

[5] S. Shirazi, C.-J. Lin, D. Chen, Inorganic fouling of pressure-driven membrane processes — a critical review, Desalination, 250 (2010) 236–248.

[6] M. Kraume, D. Wedi, J. Schaller, V. Iversen, A. Drews, Fouling in MBR: what use are lab investigations for full scale operation?, Desalination, 236 (2009) 94–103.

[7] P. Xu, C. Bellona, J.E. Drewes, Fouling of nanofiltration and reverse osmosis membranes during municipal wastewater reclamation: membrane autopsy results from pilot-scale investigations, J. Membr. Sci., 353 (2010) 111–121.

[8] D. Trebouet, J.P. Schlumpf, P. Jaouen, F. Quemeneur, Stabilized landfill leachate treatment by combined physicochemical–nanofiltration processes, Water Res., 35 (2001) 2935–2942.

[9] T.A. Peters, Purification of landfill leachate with reverse osmosis and nanofiltration, Desalination, 119 (1998) 289–293.

[10] M. Simonič, Compost leachate treatment using polyaluminium chloride and nanofiltration, Open Chem., 15 (2017) 123–128.

[11] T. Mariam, L.D. Nghiem, Landfill leachate treatment using hybrid coagulation-nanofiltration processes, Desalination, 250 (2010) 677–681.

[12] E. Iritani, N. Katagiri, Developments of blocking filtration model in membrane filtration, Kona Powder Part. J., 33 (2016) 179–202.

[13] P. Aleta, S.J. Parikh, A.P. Silchuk, K.M. Scow, M.S. Park, S.P. Kim, The effect of organic matter on the removal of phosphorus through precipitation as struvite and calcium phosphate in synthetic dairy wastewater, Membr. Water Treat., 9 (2018) 163–172.

[14] S. Ramaswami, J. Behrendt, R. Otterpohl, Comparison of NF-RO and RO-NF for the treatment of mature landfill leachates: a guide for landfill operators, Membranes, 8 (2018) 17.

[15] J. Bohdziewicz, M. Bodzek, E. Wąsik, The application of reverse osmosis and nanofiltration to the removal of nitrates from groundwater, Desalination, 121 (1999) 139–147.

[16] K. Linde, A.-S. Jönsson, Nanofiltration of salt solutions and landfill leachate, Desalination, 103 (1995) 223–232.

[17] K. Häyrynen, J. Langwaldt, E. Pongrácz, V. Väisänen, M. Mänttäri, R.L. Keiski, Separation of nutrients from mine water by reverse osmosis for subsequent biological treatment, Miner. Eng., 21 (2008) 2–9.

[18] K. Häyrynen, E. Pongrácz, V. Väisänen, N. Pap, M. Mänttäri, J. Langwaldt, R.L. Keiski, Concentration of ammonium and nitrate from mine water by reverse osmosis and nanofiltration, Desalination, 240 (2009) 280–289.

[19] V. Preuss, C. Riedel, T. Koch, K. Thürmer, M. Domańska, Nanofiltration as an effective tool of reducing sulphate concentration in mine water, Archit. Civ. Eng. Environ., 3 (2012) 127–132.

[20] J.S. Wang, Y.H. Song, P. Yuan, J.F. Peng, M.H. Fan, Modeling the crystallization of magnesium ammonium phosphate for phosphorus recovery, Chemosphere, 65 (2006) 1182–1187.

[21] I. Stratful, M.D. Scrimshaw, J.N. Lester, Conditions influencing the precipitation of magnesium ammonium phosphate, Water Res., 35 (2001) 4191–4199.

[22] H.X. Yang, H.J. Sun, R.T. Downs, Hazenite, $KNaMg_2(PO_4)_2 14H_2O$, a new biologically related phosphate mineral, from Mono Lake, California, U.S.A., Am. Mineral., 96 (2011) 675–681.

[23] J. Wang, J.G. Burken, X. Zhang, R. Surampalli, Engineered struvite precipitation: impacts of component-ion molar ratios and pH, J. Environ. Eng., 131 (2005) 1433–1440.

[24] A.K. Pabby, S. Rizvi, A.M. Sastre Requena, Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications, CRC Press Inc. (Chapman & Hall, Productivity Press, Auerbach Publications), United States of America (USA) (Headquarters Location: Boca Raton, Florida), 2009. Available at: www.routledge.com.

[25] J. García de Lomas, A. Corzo, J.M. Gonzalez, J.A. Andrades, E. Iglesias, M.J. Montero, Nitrate promotes biological oxidation of sulfide in wastewaters: experiment at plant-scale, Biotechnol. Bioeng., 93 (2006) 801–811.

[26] M. Nemati, T.J. Mazutinec, G.E. Jenneman, G. Voordouw, Control of biogenic H_2S production with nitrite and molybdate, J. Ind. Microbiol. Biotechnol., 26 (2001) 350–355.

[27] L. Zhang, P. De Schryver, B. De Gusseme, W. De Muynck, N. Boon, W. Verstraete, Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: a review, Water Res., 42 (2008) 1–12.

[28] G.E. Jenneman, M.J. McInerney, R.M. Knapp, Effect of nitrate on biogenic sulfide production, Appl. Environ. Microbiol., 51 (1986) 1205–1211.

[29] K. Kaliński, K. Marycz, J. Czogała, E. Serwa, W. Janeczek, An application of scanning electron microscopy combined with roentgen microanalysis (SEM–EDS) in canine urolithiasis, J. Electron Microsc., 61 (2011) 47–55.

[30] L.B. Chaudhari, Z.V.P. Murthy, Treatment of landfill leachates by nanofiltration, J. Environ. Manage., 91 (2010) 1209–1217.

[31] J. Czajkowska, T. Siwiec, Crystallization of struvite in variable conditions of the reaction and concentrations of the analyzed components, Infrastruktura i Ekologia Terenów Wiejskich, 7 (2011) 145–154 (in Polish).

[32] H.X. Yang, H.J. Sun, Crystal structure of a new phosphate compound, $Mg_2KNa(PO_4)_2\cdot 14H_2O$, J. Solid State Chem., 177 (2004) 2991–2997.

[33] C. Jarusutthirak, S. Mattaraj, R. Jiraratananon, Influence of inorganic scalants and natural organic matter on nanofiltration membrane fouling, J. Membr. Sci., 287 (2007) 138–145.