



Application of Eco-innovative Technologies of Nutrients Removal in Wastewater – Case Study BARITECH Project

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1. Introduction

Eco-innovative technologies in wastewater treatment should provide not only stringent standards for the quality of treated wastewater but also ensure maximum recovery of energy and raw materials from wastewater. One of the ways to improve the removal efficiency of nitrogen and phosphorus compounds in existing conventional wastewater treatment plants is pretreatment of reject water generated during the mechanical dewatering of the digested sewage sludge.

In conventional wastewater treatment plants, where sludge treatment process is stabilized by fermentation, the most common way of handling return flow of reject water is recirculation to the mechanical part, resulting in small hydraulic load (not exceeding 1.5%) with high amount of nutrients in between 10 and 20% of raw wastewater load (Fux et al., 2003, 2006; Gajewska and Obarska-Pempkowiak, 2011a). Reject water (RW) generated during mechanical dewatering of digested sewage sludge is not only characterized by uneven formation in time but also irregular composition. Characteristic for RW are high concentrations of: organic matter in the form difficult to biodegradation (COD: 800-2850 mg O₂/dm³), total nitrogen, primarily in the form of ammonium nitrogen (N-NH₄⁺: 450-1710 mg/dm³) and total phosphorus (up to 400 mg/dm³) (Fux et al., 2003, Wett and Alex, 2003, Fux et al. 2006,

Gajewska and Obarska-Pempkowiak, 2008). Phosphorus compounds are usually removed in process of precipitation with aluminum or iron salts and are constantly lost by becoming difficult manageable chemical sludge which in the end causes losing the possibility of recovering phosphorus. The removal of nitrogen compounds is causing difficulties, due to their high concentration and adverse composition. For several years, to remove nitrogen compounds from RW the unconventional technologies with shorten removal path have been used. These processes allow to remove nitrogen compounds with limited oxygen access (energy) and easily accessible source of carbon. Unfortunately, according to literature reports, these processes in full scale are characterized by high sensitivity and instability, which in consequence do not provide proper quality of treated effluent. On the basis of studies and available literature data, it has been shown that the quality of effluent discharged after the SBR reactor in the nitrification/anammox process is variable in time. Particularly noticeable are changes in concentration of total nitrogen from 120 up to 500 mg N/dm³. At the same time the process of nitrification/anammox does not provide the removal of phosphorus compounds.

According to the concept of circular economy adopted on December 2nd 2015, treatment technology should support the reuse of water, including the secondary use of water produced from treated wastewater. The approach applied in this circular economy assumes the closure of the product life cycle in the following sequence: production – usage – waste utilization. The essence of this approach is the use of waste generated during applied processes while at the same time limiting raw material consumption, reducing the amount of waste deposited and increasing the waste stream used for recovery and recycling.

The aim of this research is to select the technological parameters of processes to ensure effective removal of nutrient elements (N, P) from RW treated in a SBR reactor in the nitrification/anammox process. In project „Integrated technology for improved energy balance and reduced greenhouse gas emissions at municipal wastewater treatment plants” (BARITECH 2013-2017) among others the following goals have been established: stable treatment and quality of RW which does not interfere with main stream treatment of recirculation and treatment processes with minimal use of energy and raw materials consumption and possibilities to phosphorus recovery, in natural ecological process.



2. Methodology of research

The study was divided into two stages. The first stage was carried out to optimize nitrogen removal and parallelly in the second stage the optimization of phosphates removal was carried out.

The idea of these innovative assumptions is in accordance with the principles of circular economy. There are many benefits of applying previously stated technical solutions, e.g. resulting in reduction of generated secondary and chemical sludge during nutrient removal from the reject water. In case of a phosphorus compounds removal method, the product might be easily recirculated and used as natural fertilizer. These proposed methods are characterized by having low influence for environment (Gajewska M. and Obarska-Pempkowiak, H., 2011b, Nastawny et al., 2015, Pempkowiak J. and Obarska-Pempkowiak, H., 2002).

2.1. Methodology of research, experimental design – nitrogen removal

Material and experimental design

The installation consists of four single vertical subsurface flow (VSSF) beds located in stainless steel containers (LxWxH: 40 cm x 40 cm x 80 cm) working parallel marked as BED control “0”, “I”, “II” and “III”. Each bed consists of a filtration layer (45 cm), a thin geotextile and a 10 cm drainage layer made of 16-32 mm gravel. The substrate for each filter is: I – 0.5-1.2 mm sand; “0”, II and III – 2-8 mm gravel. Control bed remains unplanted, other three beds are planted with common reed. Each bed is equipped with a manual ball valve and a flexible ending pipe which are necessary in case of need to prolong the contact time for removal both forms of nitrogen ($\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$). The ending pipes are mounted to sampling tanks, which have a sealed lid to ensure minimum contact with atmospheric air. The effluent is discharged to the sewage system.

A main distribution stainless steel tank (LxWxH: 20 cm x 20 cm x 60 cm) is divided into five sections: 5, 10, 15, 20 and 24 dm³. It is equipped with stainless steel pipes, solenoid valves and sprinkler heads for automatic feeding and even distribution of influent on each filter. All valves are controlled by electronic timers. A HDPE tank (IBC – Intermediate Bulk Container) of volume 1000 dm³ for preparation of synthetic wastewater is equipped with a pump to supply the distribution tank.

Common reed plants, around 1.8 m height with 50 cm root length, were excavated from a natural wetland and planted in the filter beds. Prior main investigation, the filter beds were washed through for one week to avoid future clogging. Start of laboratory research with synthetic sewage was on the 21st August 2016.

Due to limited light conditions (indoor), two CFL 85W light bulbs were placed above the beds to ensure photosynthesis and better growth.

Sampling and chemical analysis

During the investigation, each day a new batch of synthetic wastewater was prepared with assumed concentrations of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and 6 mg/dm^3 of carbon source (glucose). The compounds used in this research are NH_4Cl , KNO_3 and simple carbohydrates $\text{C}_6\text{H}_{12}\text{O}_6$.

The system was set for 4 feeds of $24 \text{ dm}^3/\text{d}$ resulting in 96 dm^3 per each bed per day with assumed hydraulic load of $600 \text{ mm/m}^2/\text{d}$. The filtration through the system lasts 1.5-2 hours depending on the bed. After the daily cycle samples were taken from each tank. Afterwards each tank was emptied to provide next day sampling. The temperature in the laboratory fluctuated from 19 to 21°C .

The concentration of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ was measured with a spectrophotometer by using cuvette tests HACH Lange LCK 303 for ammonium ($2.0\text{-}47.0 \text{ mg/dm}^3 \text{ NH}_4^+\text{-N}$), LCK 340 for nitrate ($5\text{-}35 \text{ mg/dm}^3 \text{ NO}_3^-\text{-N}$) and LCK 341 for nitrite ($0.015\text{-}0.6 \text{ mg/dm}^3 \text{ NO}_2^-\text{-N}$).

2.2. Methodology of research, experimental design – phosphorus removal

Material and experimental design

Phoslock® is an adsorbent based on lanthanum-modified bentonite clay, characterized by high capacity of phosphate binding. Removal of phosphorus compounds is based on their adsorption on the surface of the material, where they form an insoluble complex of adsorbed ions of orthophosphorus ion: PO_4^{3-} sediment (Phoslock General Brochure).

Lanthanum is a chemical element that binds phosphate ions in a 1:1 ratio. The product of this reaction is rhabdophane. Rhabdophane, a stable mineral of low solubility, is the only product of this process, and the lack of by-products is a very important benefit during the wastewater treatment (Haghseresht et al., 2009, Zamparas et al., 2015). The relative-



ly small size of adsorbent particles, with high specific surface area and pore volume, still allow to use maximum of adsorption area. According to Haghseresht et al. (2009), the adsorption capacity of phosphorus cannot be higher than 10.6 mg per 1 gram of adsorbent.

Phoslock® is able to operate in pH values from 4 to 11 (Ross & Haghseresht, 2008). The optimal range of pH is 5.0-9.0, but the maximum efficiency for phosphorus removal using Phoslock® is achieved at pH of 5.0-7.0, (PWS Report Number: IR 019/12, 2012).

To determine the sorption capacity of Phoslock®, the model solution was prepared with distilled water and potassium dihydrogen phosphate KH_2PO_4 . Four beakers, each with a capacity of 2 dm^3 , were filled with 1.5 dm^3 of the model solution. The concentration of $\text{PO}_4^{3-}\text{-P}$ was approx. 15 mg/dm^3 . Five series (repetitions) have been performed (Table 1).

Table 1. Initial concentration of $\text{PO}_4^{3-}\text{-P}$ in control samples ("0") in each series
Tabela 1. Początkowe stężenia $\text{PO}_4^{3-}\text{-P}$ w kontrolnych próbach ("0") w poszczególnych seriach

Series	1 st (0 hour)	2 nd (24 hours)	3 rd (72 hours)	4 th (96 hours)	5 th (120 hours)
Initial concentration [mg/dm^3]	15.2	15.0	16.1	15.1	15.6

Before the addition of Phoslock®, the following parameters of the synthetic wastewater were determined: concentration of $\text{PO}_4^{3-}\text{-P}$, temperature, total suspended solids (TSS), conductivity, pH, turbidity and color. To each beaker 100 g of adsorbent was added. Stirring was provided by a magnetic stirrer (1000 rpm) in each beaker batches 5, 10, 20 and 30 minutes of mixing times followed by sedimentation. The sampling was made after 0.5, 1, 2, 3, 4, and 24 hours of sedimentation from each beaker. When reduction of the entire $\text{PO}_4^{3-}\text{-P}$ from model solution was observed, the whole process was repeated five times until reaching the exhaustion of sorption capacity of Phoslock®. All tests were conducted at room temperature approx. 20°C. In total there were 5 series of investigation resulting in 7.5 dm^3 synthetic wastewater treated per each batch reactor. 28 samples were taken from every beaker giving in total 112 samples.



Physical and chemical analysis

Prior to the designation of the parameters of synthetic wastewater, the samples were filtrated to define total suspended solids (TSS). The concentration of TSS was calculated by gravimetric method. The concentration of $\text{PO}_4^{3-}\text{-P}$ was marked by using cuvette tests HACH Lange LCK 049 (1.6-30 mg/dm^3 $\text{PO}_4\text{-P}$), LCK 348 (0.5-5.0 mg/dm^3 $\text{PO}_4\text{-P}$) and LCK 349 (0.05-1.5 mg/dm^3 $\text{PO}_4\text{-P}$). Conductivity was defined by conductivity meter HACH Lange HQ40D Multi. Turbidity and color were measured by using a spectrophotometer HACH Lange DR3900. The temperature and pH were performed with a pH meter: WTW inoLab pH 720. Sorption capacity of Phoslock® was defined according to the following equation (Nastawny et al., 2015):

$$q = \frac{(C_0 - C)}{m} * V \quad (1)$$

where:

q – the value of sorption [mg/g],

C_0 – initial concentration of $\text{PO}_4^{3-}\text{-P}$ [mg/dm^3],

C – final concentration of $\text{PO}_4^{3-}\text{-P}$ [mg/dm^3],

m – mass of the adsorbent [g],

V – volume of solution [dm^3],

$(C_0 - C) * V$ – load of absorbed phosphates [mg].

3. Results and discussion

3.1. Nitrogen removal

Influent concentration and working conditions

Based on literature information (Fux et al., 2003; van Loosdrecht & Salem, 2005; van Hulle et al., 2010; van Kempen et al., 2001) about anammox, reject water (RW) a hydraulic load of 600 $\text{mm}/\text{m}^2\text{d}$ was assumed (Table 2). Additional source of carbon was used to enhance possible denitrification. After a few vegetation seasons decaying plant tissue will become a good source of. In this investigation a higher concentration of $\text{NH}_4^+\text{-N}$ was assumed due to enhance nitrification process. The aim of the research was to define the influence and treatment efficiency of high concentrated anammox reject water on VSSFs with high hydraulic load.



Table 2. Parameters of synthetic reject water after SBR with ANAMMOX
Tabela 2. Parametry ścieków syntetycznych po reaktorze SBR z ANAMMOX

Parameter	Inflow [mg/dm ³]			MEAN load of TN [g/m ² d]	Synthetic influent load	
	Min.-Max.	MEAN	SD		Feed volume [dm ³ /bed per day]	Hydraulic load [mm/m ² d]
NH ₄ ⁺ -N	60.4-65.4	63.0	±1.51	37.8	96	600
NO ₃ ⁻ -N	23.8-28.2	26.0	±1.07	15.6		
NO ₂ ⁻ -N	–	0.00	–	0.0		
TN	86.2-92.5	89.0	±1.81	53.4		

Comparison of nitrogen compounds concentrations during treatment

The variation of influent and effluent concentrations of nitrogen compounds in each bed are presented in Table 3, 4, 5.

Table 3. Average characteristic of nitrogen form in outflow with efficiency removal

Tabela 3. Charakterystyka frakcji azotu w odpływie wraz ze skutecznością usuwania

Bed	Parameter	Outflow [mg/dm ³]			Efficiency of removal
		Min.- Max.	MEAN	SD	Mean ± SD
‘0’	NH ₄ ⁺ -N	21.3-63.0	43.0	±16.6	32.9±16.2
	NO ₃ ⁻ -N	5.0-26.0	14.4	±7.6	45.1±27.9
	NO ₂ ⁻ -N	0-2.5	1.3	±1.0	production
	TN	43.3- 89.0	57.5	± 11.8	34.3±17.8
‘I’	NH ₄ ⁺ -N	23.3-63.0	38.5	±13.9	40±21.4
	NO ₃ ⁻ -N	13-35,1	25.2	±8.7	2.3 ±35
	NO ₂ ⁻ -N	0-4.6	1.8	±1.3	production
	TN	41.9-89.0	63.7	±13.1	26.9 ±23.2
‘II’	NH ₄ ⁺ -N	25.4-63.0	35.7	±12.0	44.4±18.6
	NO ₃ ⁻ -N	7.0-39.1	21.6	±7.8	16.4 ±33.3
	NO ₂ ⁻ -N	0-3.6	1.7	±1.0	production
	TN	37.5-89.0	57.3	±14.7	33.8±15.6

In case of bed “I”, with the smallest substrate, since 21st August 2016 until the first sampling no treatment was observed, a decrease of 2.2 mg/dm³ of NH₄⁺-N was indicated. Significant decrease of NH₄⁺-N in the effluent was noticed in 2nd sample on 28th August resulting in a treatment



efficiency of 48.6% NH_4^+ -N indicating that nitrification is occurring due to significant increase of NO_2^- -N. In samples 2-10, there was a "stable" treatment efficiency from 48.6% up to 63.0%. A visual changes in plants was observed on 7th December 2016. A significant increase of NH_4^+ -N in last sample from 15th December indicate end of any treatment processes. Those observation prove that the plants have finally finished their biological cycle and changed into winter sleep.

Table 4. Concentration of NH_4^+ -N in effluent from analyzed beds "0" – control, "I" and "II"

Tabela 4. Stężenie NH_4^+ -N w analizowanych złożach "0" – kontrola, "I" i "II"

Sampling date	NH_4^+ -N [mg/dm ³]		
	Bed 0	Bed I	Bed II
23.08	60.8	54.6	34.8
28.08	32.4	37.8	39.7
30.08	28.9	30.5	46.3
01.09	24.0	25.5	38.9
03.09	29.5	31.3	46.8
07.09	23.0	25.4	41.7
09.09	31.6	26.5	45.7
15.09	23.3	28.1	43.5
01.11	28.7	20.3	21.3
04.11	31.2	29.3	35.5
07.11	44.3	34.0	32.8
09.11	44.0	33.7	35.8
17.11	45.1	38.7	50.5
07.12	44.4	37.6	52.3
15.12	62.0	55.1	60.7

For bed "II", with core sand as a substrate, similar pattern of NH_4^+ -N changes has been noticed, but the removal efficiency was higher than in bed "I" with a minimum 46.0% on the 7th November and maximum 67.8% on 1st November. What is surprising, the second highest removal efficiency of NH_4^+ -N was observed for the bed "0". On 1st November it reached 21.3 mg/dm³ which gives a 66.2% efficiency. This high effectiveness of NH_4^+ -N removal in the first period of VSSF bed exploitation could be explained by sorption process described by other researchers (Saeed & Sun, 2012; Wojciechowska et al., 2017). Important



is, that when the sorption capacity has been exhausted, other removal processes become more importance Table 4, 5.

Table 5. Concentration of NO_3^- -N in effluent from analyzed beds “0” – control, “I” and “II”

Tabela 5. Stężenie NO_3^- -N w analizowanych złożach “0” – kontrola, “I” i “II”

Sampling date	NO_3^- -N [mg/dm^3]		
	Bed 0	Bed I	Bed II
23.08	60.8	54.6	34.8
28.08	32.4	37.8	39.7
30.08	28.9	30.5	46.3
01.09	24.0	25.5	38.9
03.09	29.5	31.3	46.8
07.09	23.0	25.4	41.7
09.09	31.6	26.5	45.7
15.09	23.3	28.1	43.5
01.11	28.7	20.3	21.3
04.11	31.2	29.3	35.5
07.11	44.3	34.0	32.8
09.11	44.0	33.7	35.8
17.11	45.1	38.7	50.5
07.12	44.4	37.6	52.3
15.12	62.0	55.1	60.7

Significant decrease of NO_3^- -N in the effluent at the beginning of the process indicates either that sorption was occurring or assimilation by plants, more likely even both. The amount of NO_3^- -N was rising till 7th August and staying stable up to 15th August indicating that production of NO_3^- was higher than the concentration assimilated by sorption and plants, possibly sorption capacity has been exhausted.

In general it has been already proven that faster and more effective nitrification occurs in beds with fine substrate – bed “I” (Kadlec & Wallace, 2009). In this research for the beginning of nitrification process the 1st November could be assumed since the concentration of NO_3^- -N started to increase above the discharged concentration indicating the transformation of NH_4^+ into NO_3^- in nitrification process.



The NO_2^- -N presence in the effluent could be explained only by occurrence of partial nitrification process. It is important to notice that in the first two weeks of investigation the concentration of NO_2^- -N was very low and in the third week rapid growth appeared in beds inhabited by reed indicating the initiation of nitrification process. Since then concentration of NO_2^- -N has been significantly various indicating that the transformation process was unstable. Concentration of NO_2^- -N in bed "II" effluent between 28th August and 1st September indicates that the ammonia oxidizing bacteria (AOB) were in their highest function. AOB are the first group of nitrifiers in nitrification and are responsible for oxidizing ammonia to nitrite (Ward, 2013).

The input concentration of nitrogen is only present in the form of NH_4^+ -N and NO_3^- -N due to treatment in VSSF bed models show different pattern of processes responsible for their transformation and removal, depending on the bed substrate and vegetation cycle.

3.2. Results and discussion for phosphates removal

Effect of Phoslock® on phosphates reduction

This investigation showed a significant sorption capacity of Phoslock®. The total amount of adsorbed PO_4^{3-} -P and sorption value defined according to (Nastawny et al., 2015) are presented in Table 6.

The 1st series have shown that the concentration of phosphates ions rapidly decreased after 30 minutes of sedimentation with the effectiveness over 99%. During each mixing the concentration of PO_4^{3-} -P has been reduced from the initial quantity to a value of 0.1-0.2 mg/dm³. In 4th series, a smaller decrease in concentration of PO_4^{3-} -P was observed, but the reduction rate oscillated around 90%. After 5th series, the phosphorus level decreased by only 80% to approx. 3 mg/dm³, indicating the moment of exhaustion of Phoslock® sorption capacity. For each mixing time similar results were achieved.

During the field study presented by Haghseresht (2009), 95% reduction of phosphorus compounds were achieved. The research of Van Oosterhout and Luring (2013) shows binding of phosphates by Phoslock® with effectiveness close to 100%. According to Ross (2008), in the optimal pH range, sorption capacity reached 4.37 mg/g, therefore this investigation demonstrated a higher efficiency of Phoslock® (Table 6).



Table 6. The value of sorption capacity of Phoslock® material for each time of mixing

Tabela 6. Pojemność sorpcyjna preparatu Phoslock® dla poszczególnych czasów mieszania

Time of mixing	Summary load of $\text{PO}_4^{3-}\text{-P}$ L_0 [mg]	Final load of $\text{PO}_4^{3-}\text{-P}$ L [mg]	Quantity of adsorbed $\text{PO}_4^{3-}\text{-P}$ [mg]	Sorption q [mg/g]	Removal efficiency [%]
5 min	77.00	2.41	74.59	5.59	96.9
10 min		2.39	74.61	5.60	96.9
20 min		3.33	73.67	5.53	95.7
30 min		2.70	74.30	5.57	96.5

Effect of Phoslock® on total suspended solids (TSS)

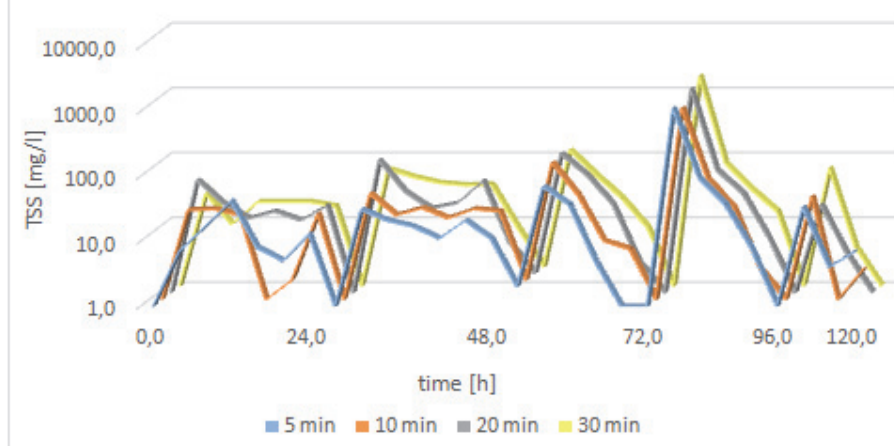


Fig. 1. Characteristic of total suspended solids (TSS) during the investigation (logarithmic scale)

Rys. 1. Charakterystyka zmian zawiesiny podczas trwania doświadczenia (skala logarytmiczna)

Figure 1 shows the variability in TSS concentration during the research. The initial value was 0-1 mg/dm³ and was very low due to the use of model solution. Phoslock® caused the release of suspension after use. The increase in TSS concentration followed along with the course of the investigation.

The highest TSS concentration was noticed after 20 and 30 minutes of mixing time. In the 4th series (72 h) after 30 minutes of sedi-



mentation TSS reached approx. 1000 mg/dm^3 (for 5 and 10 minutes mixing time) and 1398 mg/dm^3 and 1740 mg/dm^3 for 20 and 30 minutes of mixing respectively. In 5th series, samples were not collected after 30 minutes of sedimentation, due to high concentration of solids. In each series TSS decreased to average value of 10 mg/dm^3 after 3 hours of sedimentation for 5 and 10 minutes mixing time, while for 20 and 30 minutes mixing time after 24 hours of sedimentation.

From the values of TSS, we can concluded, that the multiple use of the same deposits (resuspension) and extended mixing time have unfavorable influence to a solution with Phoslock®.

Effect of Phoslock® on conductivity

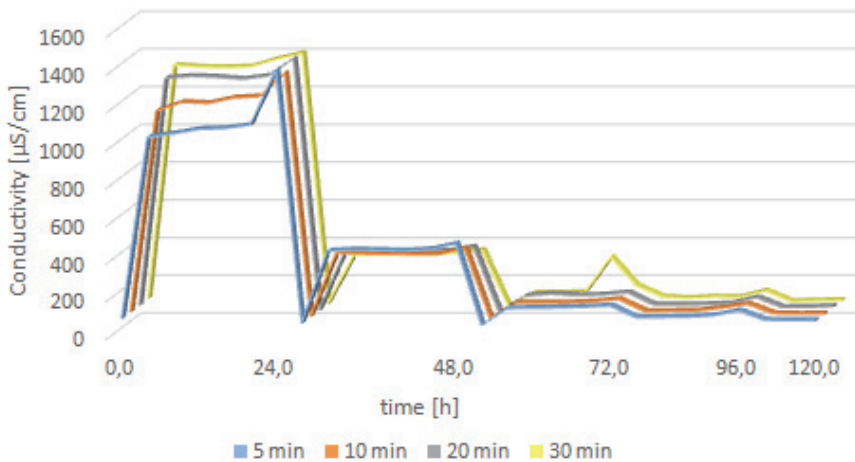


Fig. 2. Characteristic of the conductivity during the investigation

Rys. 2. Charakterystyka przewodności podczas trwania doświadczenia

The conductivity of the control samples was fluctuating significantly (Fig. 2). Over 1st series the conductivity has increased to values $1000\text{--}1400 \text{ }\mu\text{S/cm}$ (longer time of mixing gave higher conductivity). In each next series conductivity decreased gradually to average values: after 2nd series to $400 \text{ }\mu\text{S/cm}$, after 3rd series to $150 \text{ }\mu\text{S/cm}$, after 4th series – $100 \text{ }\mu\text{S/cm}$. After 5th series dropped to approx. $90 \text{ }\mu\text{S/cm}$, so the value of conductivity was close to the control sample. Investigation has not shown

correlation between conductivity and time of mixing. The conclusion might be stated that Phoslock® material, releases dissolved substances in the early stage of process. After resuspension ensue resorption of dissolved compounds and conductivity values decrease again.

Effect of Phoslock® on pH

During the experiment no significant changes in the value of pH have been observed. Investigation has proceeded in pH from 6.45 to 7.50. Only in 3rd series, after 24 hours of sedimentation for 30 minutes mixing time an increase of pH to 8.74 was noticed. To achieve the highest effectiveness in reduction of phosphorus compounds the optimal pH values were from 6.0 to 9.0 (PWS Report Number: IR 019/12, 2012).

Effect of Phoslock® on color and turbidity

This research has shown a significant influence of Phoslock® on color and turbidity of the model solution. Results for control samples "0" for color and turbidity were 2-5 mg Pt/dm³ and 0.1-1.0 mg/dm³ respectively. After 1st series, color and turbidity fluctuated slightly, but over time of subsequent series, both color and turbidity increased notably. In 2nd series, color was changing between 400-500 mg Pt/dm³ and turbidity value reached 143.7 mg/dm³ for 20 minutes mixing time. For 30 minutes mixing time did not present any readings on the spectrophotometer (absorbance>3.5). After 24 hours of sedimentation, lower values were noticed: color 278 mg Pt/dm³, turbidity 75.1 mg/dm³. In every next series higher values were observed. Many samples values were impossible to be analyzed. In 4th series measurements have been made for control samples and after 24 hours of sedimentation time, which shows values of 300-400 mg Pt/dm³ for color and 80-100 mg/dm³ for turbidity. For 30 minutes mixing time content of color and turbidity could not be analyzed due to high values. In 5th series, only for 20 minutes mixing time and 24 hours of sedimentation readings were made and reached values for color – 372 mg Pt/dm³ and for turbidity – 95.9 mg/dm³.

Investigation described by Van Oosterhout and Luring (2013) either indicates a significant increase in turbidity after using Phoslock® from 0.15 mg/dm³ to 218 mg/dm³ and it decreases along with period of sedimentation. After 6 h turbidity values were about 13 mg/dm³ and after 24 hours reached 6.5 mg/dm³.



4. Conclusions

Applied technologies: removal of total nitrogen (TN) in VSSF beds connected with removal of $\text{PO}_4^{3-}\text{-P}$ in batch reactors (beakers) using Phoslock® secured the assumptions of circular economy. Based on the carried out investigations following statements could be concluded:

1. The investigation has shown different pattern of processes responsible for nitrogen compounds transformation and removal efficiency, depending on the bed substrate and vegetation.
2. The initial high removal of ammonia nitrogen in the "0" bed can be attributed only to the sorption process in the substrate. After exhausting the sorption capacity (after four months) no further ammonium nitrogen removal was observed in this process
3. In VSSF reed beds ("I" and "II") $\text{NH}_4^+\text{-N}$ concentration decreased in wastewater and $\text{NO}_2\text{-N}$ production with simultaneous $\text{NO}_3\text{-N}$ changes were observed, what indicated the nitrification process
4. VSSF reed beds("I" and "II") provide a better environment for the conversion of nitrogen compounds and in consequence they provide better removal of the N compounds.
5. Investigation has shown high sorption capacity of Phoslock® – 5.60 mg/g. The sorption of removed $\text{PO}_4^{3-}\text{-P}$ was in average 5.5 mg/g and over 95.0% of phosphorus removal efficiency from model solution.
6. The optimal condition for adsorption in steady condition is: (1) mixing time should not exceeded 10 min and (2) sedimentation time is 3 h.
7. Conductivity of the solution was subjected to significant changes. It was noticed that resuspension of Phoslock® reduces its ability to increase the conductivity. The conductivity oscillation changes were not connected with mixing time.
8. Phoslock® material causes a slight fluctuation in pH, where the mixing time did not affect the changes.
9. Further investigation by using different loads and additional air input to recognized the processes responsible for N removal as well as working conditions of VSSF beds applied for treatment of effluent after the SBR with anammox need to be performed. In case of phosphorus removal there is necessity to lower the color and turbidity due to application of Phoslock®.



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References

- Fux, Ch., Lange, K., Faessler, A., Huber, P., Grueniger, B., Siegrist, H. (2003). Nitrogen removal from digester supernatant via nitrite-SBR or SHARON? *Water Science and Technology*, 48(8), 9-18.
- Fux, Ch., Valten, S., Carozzi, V., Solley, D., Keller, J., (2006). Efficient and stable nitrification and denitrification of ammonium-rich sludge dewatering liquor using SBR with continuous loading. *Water Research*, 40(14), 2765-2775.
- Gajewska M., Obarska-Pempkowiak H. (2008). Wpływ zawracania odcieków z odwadniania osadów ściekowych na pracę oczyszczalni ścieków. *Przemysł Chemiczny*, 87(5), 448-452
- Gajewska M., Obarska-Pempkowiak, H. (2011b). Efficiency of pollutant removal by five multistage constructed wetlands in a temperate climate. *Environment Protection Engineering*, 37(3), 27-36.
- Gajewska, M., Obarska-Pempkowiak, H. (2011a). The role of SSVF and SSHF beds in concentrated wastewater treatment, design recommendation. *Water Science and Technology*, 64(2), 431-439.
- Haghseresht, F., Wang, S., Do D.D., (2009). A novel lanthanum-modified bentonite, Phoslock, for phosphate removal from wastewaters. *Applied Clay Science*, 46, 369-375.
- Kadlec, R. H., Wallace, S. D. (2009). *Treatment Wetlands*, Second Edition. CRC Press Taylor & Francis Group.
- Nastawny, M., Jucherski, A., Walczowski, A., Józwiakowski, K., Pytka, A., Gizińska-Górna, M., Marzec, M., Gajewska, M., Marczuk, A., Zarajczyk, J. (2015). Preliminary evaluation of selected mineral adsorbents used to remove phosphorus from domestic wastewater (in Polish). *Przemysł Chemiczny*, 94(10), 1001-1004.
- Pempkowiak, J., Obarska-Pempkowiak, H. (2002). Long-term changes in sewage sludge stored in a reed bed. *Science of The Total Environment*, 297(1-3), 59-65.
- Phoslock General Brochure: <http://www.phoslock.com.au/irm/content/scientific-report/genbrochureSara.pdf> [cited 18 March 2017]



- PWS (Phoslock Water Solutions Limited) Report Number: IR 019/12, (2012): <http://www.phoslock.com.au/irm/content/scientificreport/AlumvsPhoslock-March2012.pdf> [cited 18 March 2017]
- Ross, G., Haghseresht, F., Cloete, T.E., (2008). The effect of pH and anoxia on the performance of Phoslock, a phosphorus binding clay. *Harmful Algae*, 7, 545-550.
- Saeed, T., Sun, G. (2012). A review on nitrogen and organics removal mechanisms in subsurface flow constructed wetlands: dependency on environmental parameters, operating conditions and supporting media. *Journal of Environmental Management*, 112, 429-448.
- Van Hulle, S., Yandeweyer, B. D., Meesschaert, P. A., Vanrolleghem, R., Dumoulin, A. (2010). Engineering aspects and practical application of autotrophic nitrogen removal from nitrogen rich streams. *Journal of Chemical Engineering*, 162, 1-20.
- Van Kempen, R., Mulder, J. W., Uijterlinde, C.A., van Loosdrecht, M.C.M. (2001). Overview: full scale experience of the SHARON process for treatment of rejection water of digested sludge dewatering. *Water Science and Technology*, 44, 145-152.
- Van Loosdrecht, M. C. M., Salem, S. (2005). Biological treatment of sludge digester liquids. *IWA Specialized Conference „Nutrient Management In Wastewater Treatment Processes and Recycle Streams”*, 13-22.
- Van Oosterhout, F., Lüring, M., (2013). The effect of phosphorus binding clay (Phoslock®) in mitigating cyanobacterial nuisance: a laboratory study on the effects on water quality variables and plankton. *Hydrobiologia*, 710, 265-277.
- Ward, B.B. (2013). *Reference Module in Earth Systems and Environmental Sciences*. Elsevier Inc.
- Wett, B., Alex, J. (2003). Impact of separate reject water treatment on the overall plant performance. *Water Science and Technology*, 48(4), 139-14.
- Wojciechowska, E., Gajewska, M., Ostojski, A. (2017). Reliability of nitrogen removal processes in multistage treatment wetlands receiving high-strength wastewater. *Ecological Engineering*, 98, 365-371.
- Zamparas, M., Gavriil, G., Coutelieris, F.A., Zacharias, I. (2015). A theoretical and experimental study on the P-adsorption capacity of Phoslock™. *Applied Clay Science*, 335, 147-152.

Zastosowanie innowacyjnych technologii do usuwania związków biogenych ze ścieków – studium przypadku (BARITECH)

Streszczenie

Innowacyjne technologie stosowane podczas oczyszczania ścieków powinny spełniać nie tylko wysokie wymagania dotyczące jakości oczyszczonych ścieków, ale także zapewnić maksymalny potencjał odzysku energii i surowców z ścieków. Jednym ze sposobów poprawy skuteczności usuwania związków azotu i fosforu w istniejących konwencjonalnych oczyszczalniach ścieków, jest wstępne oczyszczanie odcieków powstających podczas mechanicznego odwadniania osadu ściekowego po biologicznym oczyszczaniu ścieków. Celem badań było określenie charakterystycznych parametrów procesów technologicznych, dla zapewnienia skutecznego usuwania związków biogenych (N, P) ze ścieków po oczyszczaniu w procesie nityfikacji/anammox zachodzącym w reaktorze typu SBR. Badanie zostało podzielone na dwa etapy. Pierwszy etap przeprowadzono w celu optymalizacji procesu usuwania związków azotu ($\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ i $\text{NO}_2\text{-N}$) z odcieków powstających z mechanicznego odwadniania przefermentowanych osadów ściekowych. Odcieki oczyszczane były w reaktorze SBR w procesie ANAMMOX. Instalacja pilotowa składała się z pojedynczych złożeń o przepływie pionowym umieszczonych w zbiornikach ze stali nierdzewnej, pracujących równolegle oznaczonych odpowiednio jako złożo "0", "I", "II". Próbkę do analizy pobierano w celu określenia zmian $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ i $\text{NO}_2\text{-N}$ w ściekach w każdym ze złożeń. W złożu "0" (nie zasiedlonym trzcina) usuwanie związków azotu spowodowane było jedynie przed sorpcją, aż do wyczerpania jego pojemności sorpcyjnej. Natomiast zmiany stężenia $\text{NH}_4\text{-N}$ i wytwarzanie $\text{NO}_2\text{-N}$ przy jednoczesnych zmianach stężenia $\text{NO}_3\text{-N}$ wskazywały na zachodzący proces nityfikacji w złożach "I" i "II" (oba zasiedlone trzcina). Doświadczenia wykazały różne mechanizmy procesów odpowiedzialnych za przemiany związków azotu i skuteczność ich usuwania, w zależności od podłoża i wegetacji. W drugim etapie badań przeprowadzono optymalizację procesu usuwania fosforanów. Natomiast doświadczenia związane z usuwaniem fosforu zostało przeprowadzone w laboratorium w warunkach nieprzepływowych przy zastosowaniu modelu z czterema reaktorami. Każdy reaktor zawierający ścieki syntetyczne o stężeniu fosforanów 15 mg/dm^3 poddano mieszaniu. Próbkę do analizy zostały pobierane z każdej zlewki po założonym czasie sedymentacji. Badania przeprowadzono w celu określenia optymalnej dawki preparatu Phoslock® przy znanym stężeniu anionów fosforanowych PO_4^{3-} w roztworze modelowym, oraz znalezienia optymalnego czasu mieszania i sedymentacji. Próbkę poddano analizie i określono następujące parametry: pH, zawiesinę, przewodnictwo, mętność, barwę i stężenie fosforanów. Przeprowadzone badania potwierdziły wy-

soką skuteczność usuwania PO_4^{3-} (ponad 95%). Badanie nie wykazało zależności między czasem mieszania a stopniem redukcji związków fosforu.

Abstract

Eco-innovative technologies in wastewater treatment should provide not only stringent standards for the quality of treated wastewater but also ensure maximum recovery of energy and raw materials from wastewater. One of the ways to improve the removal efficiency of nitrogen and phosphorus compounds in existing conventional wastewater treatment plants is pretreatment of reject water generated during the mechanical dewatering of the digested sewage sludge. The aim of this research was to select the technological parameters of processes to ensure effective removal of nutrient elements (N, P) from RW treated in a SBR reactor in the nitrification/anammox process. The study was divided into two stages. The first stage was carried out to optimize nitrogen compounds removal in the effluent from ANAMMOX process used to treat reject water after centrifugation. The installation consists of single vertical subsurface flow (VSSF) beds located in stainless steel containers working parallel marked as BED control "0", "I", "II". Samples have been taken for analysis to determine the changes of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ in the effluent of each filter. In bed "0" the removal of nitrogen compounds was caused only by sorption at last until its capacity was reached. In bed "I" and "II" the $\text{NH}_4\text{-N}$ concentration in effluent and production of $\text{NO}_2\text{-N}$ with simultaneous changes of $\text{NO}_3\text{-N}$ indicated that nitrification was occurring. The investigation has shown different pattern of processes responsible for nitrogen compounds transformation and removal efficiency, depending on the bed substrate and vegetation. In the second stage the optimization of phosphates removal was carried out. The investigation was conducted in steady conditions in laboratory model with four batch reactors. Each batch reactor of synthetic wastewater with given concentration of phosphates (15 mg/dm^3) was subjected to mixing. Samples for analyzing were taken from each beaker after assumed time of sedimentation. Studies were conducted to determine the optimal dose of Phoslock[®] with known concentration of phosphate anions PO_4^{3-} in model solution, time of mixing and time of sedimentation. Samples were analyzed with following parameters: pH, total suspended solids, conductivity, turbidity, color and phosphate concentration. The carried out investigations confirmed high efficiency of phosphate anions PO_4^{3-} removal (over 95%). Also study showed no relationship between the mixing time and the degree of reduction of phosphorus compounds.

Słowa kluczowe:

Usuwanie azotu, usuwanie fosforu, odcieki, oczyszczalnie hydrofitowe

Keywords:

Nitrogen removal, phosphorus removal, reject water, constructed wetlands

