

Phosphorus removal and recovery from wastewater

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Abstrakt

Informácie o neustále sa zmenšujúcich zásobách ľahko dostupného fosforu či nehospodárne nakladanie s uvedeným makrobiogénnym prvkom sa stávajú predmetom intenzívnych debát mnohých vedeckých skupín. Najnovšou aktivitou pri výskume a aplikácii alternatívnych procesov odstraňovania fosforu na ČOV je v súčasnosti aj jeho opätovné získavanie a využitie. Odborná literatúra potvrdzuje fakt, že problematika predkladaného projektu sa netýka len SR a mestských, resp. priemyselných odpadových vôd v nej produkovaných, ale celej EÚ, kde sa práve tejto téme venujú výskumné pracoviská v podstate vo všetkých krajinách.

V uvedenom príspevku sú uvedené všeobecné informácie o recyklácii fosforu (P) a zároveň aj výsledky laboratórnych testov chemického zrážania P v biologicky vyčistených vodách, kalových vodách po aeróbnej i anaeróbnej stabilizácii a surových odpadových vodách na prítoku do ČOV. Zrážanie sa uskutočnilo so soľami železa (Fe^{3+}), hliníka (Al^{3+}) a horčíka (Mg^{2+}). Zrážaním P v terciárnom stupni za biologickým čistením bolo možné dosiahnuť koncentrácie $\text{PO}_4\text{-P}$ až pod 0,1 mg/l. V prípade zrážania v kalových vodách sa dosiahlo zníženie koncentrácie $\text{PO}_4\text{-P}$ pod 5 mg/l, avšak v prípade kalovej vody po anaeróbnej stabilizácii iba použitím Fe^{3+} pri molárnom pomere $\beta = 4$ a viac. Zrážaním so zmesou $\text{Fe}^{3+}/\text{Al}^{3+}$ a Mg^{2+} koncentrácie klesli len na 10 – 30 mg/l. Výsledkom experimentov so surovou odpadovou vodou je zníženie koncentrácie $\text{PO}_4\text{-P}$ až pod 0,3 mg/l, resp. 0,1 mg/l.

Zrážaním sa P odstránil veľmi účinne, čo predstavuje perspektívu pre jeho prípadnú recykláciu. Zaujímavé je najmä účinné vyzrážanie P v kalových vodách do struvitu, ktorý je potenciálnym hnojivom. Pri zrážaní s Fe^{3+} a $\text{Fe}^{3+}/\text{Al}^{3+}$ je potrebné zvážiť, či fosfor nebude potrebné zmeniť na zlúčeniny s vyššou hnojivou hodnotou. Okrem zrážania P dochádzalo aj ku koagulácii a zníženiu koncentrácie CHSK a v osobitných prípadoch i odstráneniu časti $\text{NH}_4\text{-N}$. Rovnako sa v práci overovalo, aké množstvo zrazeniny vzniká v jednotlivých typoch vôd počas daného procesu. Momentálne tiež prebieha overovanie, ktoré organické zlúčeniny zostanú v zrazeninách a ako budú recyklované v prípade ich využitia ako hnojiva. Zaujímavé je to najmä u mikropolutantov, akými sú zvyšky liečiv, drog, mikroplasty atď., ktoré by mohli znižovať kvalitu recyklovaného hnojiva.

Annotation

This research is focused on possibilities of phosphorus removal and recovery from various types of wastewater. Besides that, the report also introduces the results of the laboratory experiments of chemical precipitation of phosphorus from biologically treated wastewater, sludge water after aerobic and anaerobic stabilization and raw wastewater at the inflow to the wastewater treatment plant.

Keywords

Phosphorus precipitation; phosphorus recycling; struvite; wastewater and sludge water

Anotácia

Táto práca je venovaná možnostiam odstraňovania a znovuzískavania fosforu z rôznych typov odpadových vôd. Okrem toho správa tiež uvádza výsledky laboratórnych experimentov chemického

zrážania fosforu v biologicky vyčistených odpadových vodách, kalových vodách po aeróbnej i anaeróbnej stabilizácii a surových odpadových vodách na prítoku do čistiarne odpadových vôd.

Kľúčové slová

Zrážanie fosforu; recyklácia fosforu; struvit; odpadová a kalová voda

1 Introduction

Phosphorus is one of the essential biogenic elements necessary for the existence of all living organisms. Reports of dwindling reserves of the available phosphorus (P) and the uneconomical use of this biogenic element are the subject of intense scientific debate. Over the past decades rose the consciousness of the importance of phosphorus recovery. The current situation of phosphorus use is largely inefficient, especially in agriculture, which may contribute eutrophication of water bodies. To reduce the concentration of P, its removal by chemical and biological processes has been introduced at the WWTPs since the 1990s. The latest activity in the research and application of P removal processes at WWTPs focuses on its recovery and reuse. The need of phosphorus recycling is related to ecological, economic and geopolitical aspects. The problem is that more than 90 % of P is imported into the European Union (mainly from geopolitical instable supplier countries). Other risk is also fluctuation in prices. With the phosphorus reserves dwindling the price increases. For example, in 2008 the phosphate rocks prices jumped by up to 700 % due to customs measures (European Commission, 2013) and they dropped again in 2011. Analysis of P-flows in several EU countries has also shown that 50 % of used phosphorus is lost (20 % in wastewater, 10 % in food and biological waste and 20 % by erosion or leaching). These facts have contributed to the adoption of measures aimed at more efficient management of phosphate ore (European Commission, 2013).

The current recovery technologies are focused on obtaining the phosphorus from wastewater and its sludge (extraction of P from sewage sludge ash) due to their high P content. The usual method of phosphorus recovery at WWTPs is the application of treated wastewater sludge onto farm fields. Opinions on these processes are different, especially in the case of phosphorus recycling obtained from sewage sludge. Some people are more inclined to apply these sludges on soils (directly or after composting), others prefer the recycling of P from the water and sludge line within the WWTP by special processes. With this recycling it is possible to obtain 10 to 70 % of P at the WWTP (Egle et al., 2015). The recommended processes for recycling P from wastewater are mainly tertiary precipitation from biologically treated wastewater and precipitation from sludge water (but specific processes are also available, such as precipitation from "yellow waters" with a high concentration of P).

In Slovakia, a significant part of sewage sludge is composted and applied onto agricultural land (primary process for recycling P). The secondary way is material and energy recovery of sludge (Kos, 2016). Between 2007 and 2016, sludge production was around 53 – 59 000 tons per year, whereby 60 – 86 % was applied to agricultural land (Kozáková, 2017). In recent years, the focus is on the risks of the application of sewage sludge as the final product onto agricultural land. The main reason is the presence of micropollutants in the sludge. A specific problem of P recovery is the quality of the precipitates due to the occurrence of pharmaceuticals, endocrine disruptors, microplastics, etc. The results of monitoring in many countries, including the Slovak Republic, have shown that these compounds occur in wastewater and are significantly sorbed to sewage sludge. The results of the first screenings of micropollutants (pharmaceuticals, illicit drugs, and their metabolites) in sewage sludge in Slovakia show that median concentration of 51 different measured compounds (out of a total of 93 screened) were within the range of ones up to hundreds of ng/g (1 compound more than µg/g). The amount of these compounds in Slovak sludge production has been estimated at ones up to tens of kg/year (maximum value was 170 kg/year) (Bodík et al., 2018). If the micropollutants present in sewage water will coagulate and accumulate in formed phosphorus precipitates (especially in struvite), a paradox can occur. On the one hand, we aim to reduce the application of sludge onto soil to prevent

recontamination of agricultural crops, and on the other hand, within phosphorous recycling requirement a fertilizer is produced that can contain these micropollutants to an even greater extent. This aspect is also one of the topics for our further research.

An available method for phosphorus removal from wastewater is chemical precipitation with iron (Fe^{3+}), aluminium (Al^{3+}), magnesium (Mg^{2+}) and calcium (Ca^{2+}). It is a relatively simple, financially acceptable and effective method. The process consists of adding the optimal dose of coagulant agent to the wastewater with intensive stirring. The result of the coagulation process is the formation of salts precipitate. The resulting value of the $\text{PO}_4\text{-P}$ concentration of the effluent is dependent on mainly the pH value, the molar ratio of metal/P, as well as the value of the input concentration of $\text{PO}_4\text{-P}$ (Pitter, 2015; Bodík et al., 2016). The optimal value of the pH parameter in the precipitation process depends on the character of the wastewater (dissociated and undissociated compounds in water, etc.), as well as on the molar ratio P:Fe or P:Al. A molar excess of precipitating agent is recommended, which should be higher than 1.5 in precipitating process with Fe^{3+} and Al^{3+} (Drtil and Hutňan, 2013). Considering further use in agriculture, chemical precipitation into the form of struvite (ammonium magnesium phosphate hexahydrate) seems most promising and suitable. Struvite, or $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ contains NH_4^+ , PO_4^{3-} ions and Mg^{2+} in molar ratio 1:1:1. Struvit can be used as a slow-release fertilizer with low leach rates, which ensures a more continuous supply of nutrients for the plants during the growing season. Struvite precipitates after the addition of Mg^{2+} and pH adjustment (pH above 8.5). Increase in pH level will decrease its solubility and enhance its precipitation potential. In anaerobic processes, the conditions for its formation are fulfilled by sludge waters with higher concentrations of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ (Drtil and Hutňan, 2013).

The paper presents laboratory tests of P removal from biologically treated wastewater, sludge water after anaerobic/aerobic stabilization and raw municipal wastewater. The experiments were performed with the aim to obtain information about the phosphorus removal, as well as about the side-effects of precipitation process (COD removal efficiency, $\text{NH}_4\text{-N}$ and amount of formed precipitates per mg of precipitated P).

2 Experiment

Materials and Methods

This paper presents results of laboratory experiments focused on P precipitation from 2 biologically treated wastewaters (effluent: EF_1 , EF_2), 2 sludge waters (SW_1 , SW_2) after aerobic and anaerobic stabilization and centrifugation and 2 raw municipal wastewaters (influent: IN_1 , IN_2). The wastewaters were from real municipal WWTPs. The experiments were aimed at obtaining information not only about phosphorus removal, but also about the side-effects of precipitation ($\text{NH}_4\text{-N}$, COD removal efficiency). For precipitating phosphorus from wastewater were used following coagulant agents: 40 % solution of Fe^{3+} and 40 % mixture of Fe^{3+} and Al^{3+} . In the case of sludge water, Fe^{3+} , $\text{Fe}^{3+}/\text{Al}^{3+}$ and Mg^{2+} was used.

Characterization of WWTPs

WWTP_A with a capacity of over 100 000 population equivalents (PE) contains: screens, grit chambers, primary sedimentation tank, activated sludge tank (anaerobic stage + pre-denitrification process + nitrification process + regeneration of return sludge + precipitation of P with $\text{Fe}^{3+}/\text{Al}^{3+}$), mesophilic anaerobic sludge stabilization, dewatering of sludge by centrifuge. The samples from this WWTP were EF_1 , SW_1 and IN_1 .

WWTP_B with a capacity of 75 000 PE contains: the same objects as WWTP_A , however precipitation of P is realized with Fe^{3+} . The samples from this WWTP were EF_2 and IN_2 .

WWTP_C with a capacity of 10 000 PE contains: screens, grit chambers, activated sludge tank (pre-denitrification + nitrification process; without precipitation of P), sludge storage tank (aerobic stabilized sludge), centrifuge. The sample from this WWTP was SW₂.

Procedure of phosphorus precipitation

The first step of experiment was analysis of unadjusted sample (effluent, sludge water, influent). The original sample was filtered and in case of need diluted. The experiment continued with 100 ml of unfiltered sample whereby the pH was measured before coagulant addition (40 % solution of Fe³⁺, 40 % mixture of Fe³⁺/Al³⁺, solution of Mg²⁺). Then the commercially supplied coagulant agent was added to the sample with different dosage. Molar ratios of metal/PO₄-P doses were $\beta = 2, 4, 6 (8)$. The sample was then mixed quickly for 5 minutes and slowly for 15 minutes using a magnetic stirrer (flocculation of precipitates). The next step was measurement of pH after coagulation and the pH adjustment by adding 1 M NaOH (to neutral pH or in case of Mg²⁺ to pH above 10). This was followed by 30 minutes of sedimentation (the sample clearly shows 2 layers, as seen in Figure 1). The sedimented sample (without filtration) was used for the analysis of individual parameters (COD, PO₄-P, NH₄-N) using standard methods (Horáková et al., 2015).

A UV/VIS spectrophotometer (Hach Lange DR 5000) was used, and pH values were determined using a Hanna Instruments HI2002-02 EDGE pH meter.

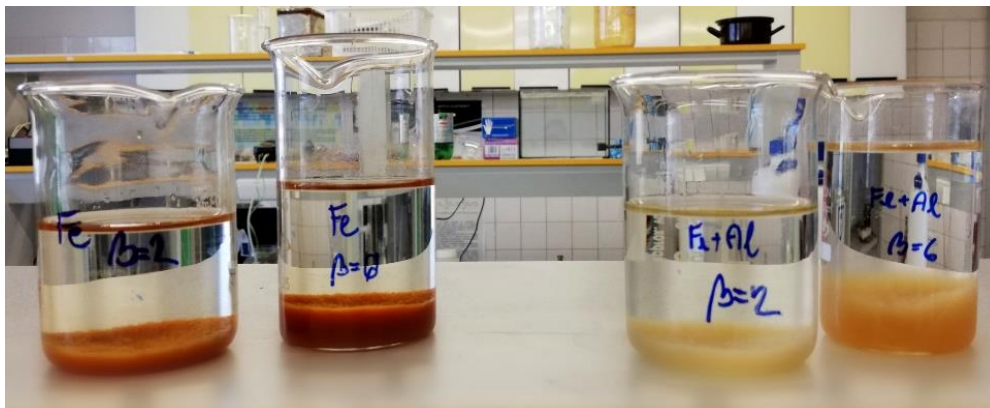


Figure 1: Samples of effluent after precipitation with Fe³⁺ and Fe³⁺/Al³⁺ and after sedimentation ($\beta = 2$ and 6)

3 Results and discussion

Influence of precipitation process on water quality

All the results of phosphorus precipitation from biologically treated wastewater (EF₁ and EF₂), sludge water (SW₁ and SW₂) and raw municipal wastewater (IN₁ and IN₂) are summarized in Tables 1 – 3. Changes in the concentrations of PO₄-P depending on the types of wastewater, used precipitating agent and the molar ratio β are shown in the Figures 2 – 4.

Table 1: The results of phosphorus precipitation in effluent EF₁ and EF₂ depending of the molar ratio β (β values in mol/mol; SS values in mg of precipitates per mg of precipitated P)

EF ₁						EF ₂					
β	PO ₄ -P	COD	NH ₄ -N	pH	SS/P	β	PO ₄ -P	COD	NH ₄ -N	pH	SS/P
(-)	(mg/l)	(mg/l)	(mg/l)	(-)	(-)	(-)	(mg/l)	(mg/l)	(mg/l)	(-)	(-)
Analysis of effluent (unadjusted sample)						Analysis of effluent (unadjusted sample)					
-	0.09	46	14	7.2	-	-	0.15	19	1.2	6.9	-
Coagulation with Fe ³⁺						Coagulation with Fe ³⁺					
2	0.006	23	13	7.0	10 680	2	0.022	19	1.1	6.5	6 622
4	0	20	13	6.4	23 977	4	0.001	14	1.2	6.7	12 191
6	0	23	11	6.7	34 727	6	0.002	14	1.2	6.5	16 599
Coagulation with Fe ³⁺ /Al ³⁺						Coagulation with Fe ³⁺ /Al ³⁺					
2	0.002	25	14	6.8	5 127	2	0.006	13	0.7	6.5	2 999
4	0	23	13	7.2	9 568	4	0.002	11	0.7	6.4	8 252
6	0	21	11	6.9	14 750	6	0.003	22	0.7	6.5	8 921

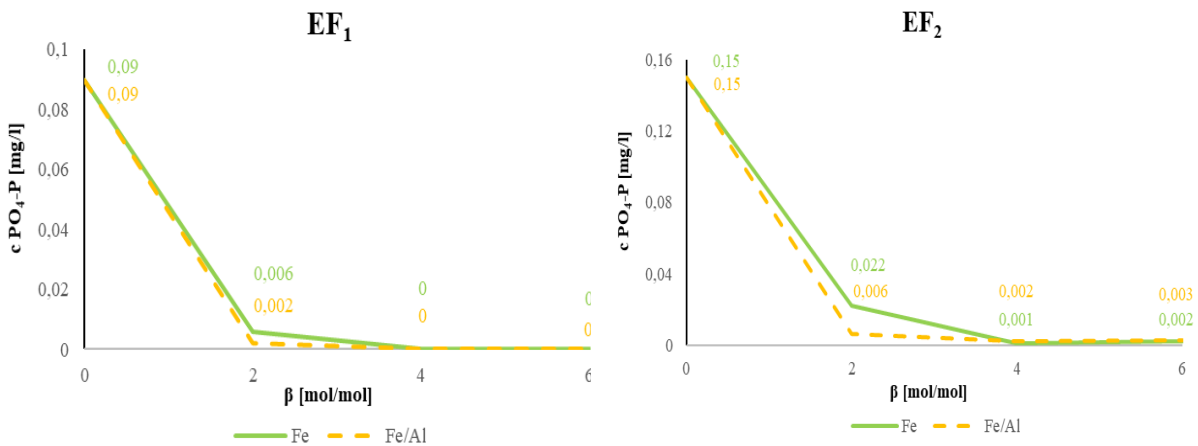


Figure 2: Changes in the concentrations of PO₄-P depending on the used precipitating agent and the molar ratio β in the sample EF₁ and EF₂

In case of biologically treated wastewater, precipitation tests were performed only with coagulant agents containing Fe³⁺ and Fe³⁺/Al³⁺ because alkaline pH is required to precipitate with Mg²⁺ to form a struvite. Before discharging the effluent from the WWTP to the recipient, it would be necessary to adjust the pH back to neutral range. The outflow concentrations of PO₄-P reach very low values at doses $\beta = 2$ to 6. The difference between precipitation with Fe³⁺ and Fe³⁺/Al³⁺ was not observed. According to quality of purified water and the recycling of phosphorus, the results can be considered very positive. The results showed that the side-effect of precipitation was the COD removal. The COD removal efficiency in test with E₁ using iron coagulant and mixture of iron and aluminum coagulant was about 50 %. In the case of more polluted wastewater, this COD reduction can help to achieve lower values of effluent COD and to eliminate fines or to reduce fees. In the case of effectively treated wastewater (EF₁: from 46 mg/l to 20 – 25 mg/l), COD reduction could eliminate both fines and fees. Comparing the NH₄-N concentrations, the decrease in concentrations is negligible both operationally and analytically. However, in the case of E₂ (from 1.2 mg/l to 1.1 mg/l for Fe³⁺ and to 0.7 mg/l for Fe³⁺/Al³⁺) the decrease in concentration may be interesting according to strict effluent limits for nitrogen forms (ones of mg/l). We assume that NH₄-N is sorbed on the formed precipitates (need to

verify). The question is also how much precipitate (the amount of suspended solids) is formed in individual types of wastewaters during the precipitation process. In addition to aim of achieving the best quality of purified water there is also interest in obtaining as much phosphorus as possible in a concentrated form suitable for its next recycling. Tests with E₁ and E₂ showed that in the tertiary stage, precipitation of P produced up to grams of precipitates per 1 mg of removed P (3.0 to 34.7 g/mg). This is extremely high value and in case of need of recycling P we recommend not to use simultaneous chemical precipitation (P becomes a part of excess sludge).

Table 2: The results of phosphorus precipitation from sludge water SW₁ and SW₂ depending of the molar ratio β (β values in mol/mol; SS values in mg of precipitates per mg of precipitated P)

SW ₁					SW ₂				
β	PO ₄ -P	COD	NH ₄ -N	pH	β	PO ₄ -P	COD	NH ₄ -N	pH
(-)	(mg/l)	(mg/l)	(mg/l)	(-)	(-)	(mg/l)	(mg/l)	(mg/l)	(-)
Analysis of <i>sludge water</i> (unadjusted sample)					Analysis of <i>sludge water</i> (unadjusted sample)				
-	61	504	1 142	7.8	-	32	371	508	7.6
Coagulation with Fe ³⁺					Coagulation with Fe ³⁺				
2	24	506	-	7.4*	2	0.28	276	-	7.2*
4	5	476	-	7.3*	4	0.21	301	-	6.8*
6	4	376	-	7.2*	6	0.13	226	-	6.6*
Coagulation with Fe ³⁺ /Al ³⁺					Coagulation with Fe ³⁺ /Al ³⁺				
2	30	461	-	7.8*	2	0.53	324	-	7.2*
4	27	437	-	7.7*	4	0.49	324	-	7.0*
6	11	409	-	7.4*	6	0.39	209	-	6.7*
Coagulation with Mg ²⁺					Coagulation with Mg ²⁺				
2	17	429	977	10.0	2	3.8	261	472	10.1
4	15	451	909	10.0	4	2.1	279	479	10.1
6	10	476	850	10.1	6	1.7	279	504	10.1
8	10	451	930	10.1	8	1.7	284	455	10.1

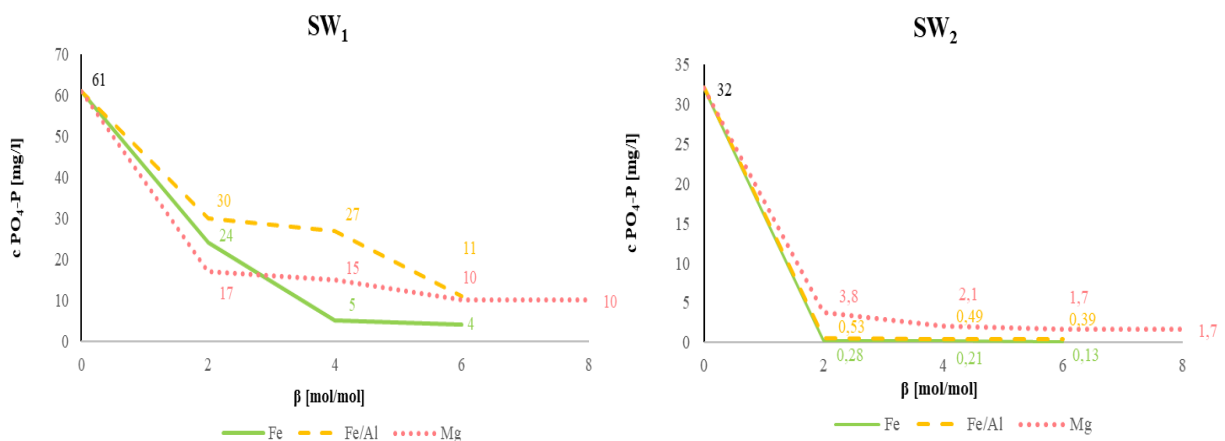


Figure 3: Changes in the concentrations of PO₄-P depending on the used precipitating agent and the molar ratio β in the sample SW₁ and SW₂

The results shown that the highest efficiency of P removal in the experiments with SW₁ was achieved in precipitation process with Fe³⁺ (molar ratio $\beta = 4$ and higher; PO₄-P: from 61 mg/l to 4 – 5 mg/l). With the mixture of Fe³⁺/Al³⁺ and Mg²⁺, the concentrations decreased only to 10 – 30 mg/l. In the case of SW₂ the concentrations of PO₄-P decreased from 32 mg/l to 0.13 mg/l – 0.53 mg/l using Fe³⁺ and Fe³⁺/Al³⁺. Using precipitating agent Mg²⁺ the coagulation efficiency was lower (from 32 mg/l to 1.7 mg/l – 3.8 mg/l). Unlike the biologically treated wastewater, it wasn't needed to adjust the pH to neutral range. The buffer capacity of sludge water was sufficient to prevent the pH dropping below 7 (even at $\beta = 6$). In case of phosphorus precipitation using Mg²⁺ addition of 1 M NaOH was required to increase pH (pH = 10 – 10.1). Since the sludge water is returned to the inflow and mix with raw wastewater, reversing pH with acid is not necessary. Phosphorus precipitation produce hydroxyapatite and/or struvite. Their advantages are easy dewatering of the product and potential phosphorus recycling. Since all elements in the struvite are nutrients, this mineral seems to be an ideal fertilizer. Same as in the case of effluent, decrease of COD was observed due to coagulation process. The efficiency of COD removal in laboratory tests with SW₁ was in average 11 %. The highest decrease in concentration was observed using Fe³⁺ in a molar ratio $\beta = 6$, when COD concentration decreased from 504 mg/l to 376 mg/l. Less effective coagulation was achieved by mixture of Fe³⁺/Al³⁺ (from 504 mg/l to 409 mg/l), resp. Mg²⁺ (from 504 mg/l to 429 mg/l). In the case of SW₂ the decrease in COD parameter wasn't significant. The COD concentration decreased from the original 371 mg/l in the unadjusted sample to approximately 200 – 300 mg/l. The highest decrease was observed in precipitation experiments with a mixture of Fe³⁺/Al³⁺ and with molar ratio $\beta = 6$, where the value decreased by almost half (from 371 mg/l to 209 mg/l). The decrease in COD parameter does not have a significant operational effect (COD is in the water line diluted and removed from SW). According to use of the precipitate as a recycled fertilizer, lower coagulation in the formation of struvite is an advantage. Due to the high pH value in the precipitation experiments with Mg²⁺, precipitation process led to the production of undissociated ammonia NH₃. This form is easily stripped/evaporated, as evidenced by the decrease of NH₄-N after precipitation. It is evident that the decrease of NH₄-N is usually reported in the precipitation process of P, but its removal in the struvite is minimal due to the concentrations of NH₄-N in sludge water. Although quality and settling ability of the precipitates were not quantified during laboratory tests, after using coagulant agent containing Mg²⁺ it was possible to visually observe their smaller size and worse settling ability.

Table 3: The results of phosphorus precipitation in influent IN₁ and IN₂ depending of the molar ratio β (β values in mol/mol; SS values in mg of precipitates per mg of precipitated P)

IN ₁						IN ₂					
β	PO ₄ -P	COD	NH ₄ -N	pH	SS/P	β	PO ₄ -P	COD	NH ₄ -N	pH	SS/P
(-)	(mg/l)	(mg/l)	(mg/l)	(-)	(-)	(-)	(mg/l)	(mg/l)	(mg/l)	(-)	(-)
<i>Analysis of influent (unadjusted sample)</i>						<i>Analysis of influent (unadjusted sample)</i>					
-	6.50	1 246	91	6.8	-	-	3.60	330	36	6.8	-
<i>Coagulation with Fe³⁺</i>						<i>Coagulation with Fe³⁺</i>					
2	0.10	209	83	6.9	300	2	0.03	65	34	6.9	285
4	0.04	189	87	6.5	361	4	0.02	66	34	7.1	276
6	0.02	194	89	6.6	451	6	0.01	60	37	6.8	687
<i>Coagulation with Fe³⁺/Al³⁺</i>						<i>Coagulation with Fe³⁺/Al³⁺</i>					
2	0.27	226	82	7.0	231	2	0.07	81	33	7.0	287
4	0.07	220	84	6.5	352	4	0.02	82	36	6.5	359
6	0.07	209	92	6.5	332	6	0.01	75	36	6.6	484

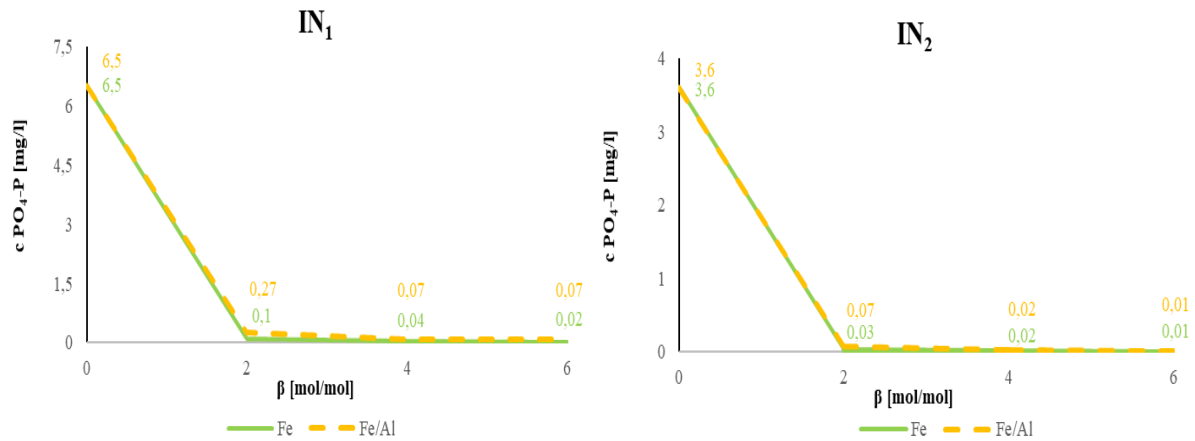


Figure 4: Changes in the concentrations of PO₄-P depending on the used precipitating agent and the molar ratio β in the sample IN₁ and IN₂

Significant decrease of the PO₄-P concentration by precipitation from raw municipal wastewater was achieved (IN₁: below 0.3 mg/l; IN₂: below 0.1 mg/l). The table 3 shows the common trend in which the higher the dose of coagulant agent, the higher efficiency of removal. The decrease in COD concentration was also very significant. The COD coagulation efficiencies were up to about 80 %. The most significant decrease was in precipitation tests with IN₁ using mixture of Fe³⁺/Al³⁺ and with molar ratio $\beta = 4$ (from 1 246 mg/l to 189 mg/l). In tests with IN₂ the value decreased from 330 mg/l to about 70 mg/l. However, according to eventual recycle of phosphorus, these results may not be an advantage (COD may impair quality of precipitate). The decrease of NH₄-N can be neglected. A positive result is that the amount of precipitate per 1 mg of precipitated P is significantly lower than in the case of effluent (only hundreds of mg per mg of P; an average of 370 mg of precipitate per 1 mg of removed P).

4 Conclusion

The Tables 1 – 3, resp. Figures 2 – 4 include the following findings:

- coagulation tests in biologically treated wastewater, sludge water and raw municipal wastewater showed, that PO₄-P can be precipitated with all three coagulating agents (Fe³⁺, Fe³⁺/Al³⁺ and Mg²⁺),
- the phosphorus removal efficiency using iron coagulant, mix of iron and aluminium coagulant and magnesium salt is in the range of 75 % – 99 %,
- significant decrease of COD and partial decrease of NH₄-N are considered to the side-effects of phosphorus precipitation. However, according to recycle of phosphorus these results may not be an advantage (COD may impair quality of precipitate),
- due to the usability of precipitates, precipitation process using Mg²⁺ (into struvite) is the most suitable,
- in precipitation tests with Fe³⁺ and Fe³⁺/Al³⁺, the need to change P to compounds with a higher fertilizer value is questionable (this is one of the topics for further research).

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