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Influence of Phosphorus Precipitation on Wastewater Treatment Processes

Ján Derco, Rastislav Kuffa, Barbora Urminská,
Jozef Dudáš and Jana Kušnierová

Additional information is available at the end of the chapter

Abstract

Phosphorus stimulates aquatic plant growth and contributes to eutrophication process in rivers, lakes and the ocean. A large part of phosphorus is discharged into the receiving waters by wastewater. One of the solutions of this problem is represented by chemical precipitation. Simultaneous precipitation of phosphorus from wastewater with metal salts is commonly applied. Metal salts are dosed directly into aeration tank, and produced precipitates are wasted as a part of the secondary sludge. Thus, not only aerobic and anoxic processes of wastewater treatment plant are carried out in the presence of precipitant metals and precipitates but also the precipitates are, in many cases, accumulated in anaerobic sludge digesters. Operational research of phosphorus precipitation in lab-scale encompasses the impact of Fe^{2+}, Fe^{3+} and Al^{3+} salts on biological nitrification and denitrification processes, sedimentation and thickening characteristics of sludge as well as anaerobic sludge stabilisation processes. The measurements of specific oxygen uptake rate, nitrification and denitrification tests and monitoring of effluent values of quality standards were applied to evaluate the processes performance. Other objective of our research is to contribute to methodology for examination of thickening and dewatering characteristics of sludge with tested precipitation agents. Mathematically processed experimental results are used to compare sedimentation, precipitation and dewatering characteristics of activated sludge cultivated in the presence of selected precipitation agents. Better description of the experimental results was obtained with three parameters model of particles mass flow density curve. Comparison of minimum sedimentation tank size necessary for gravitational separation of individual sludge was used to examine sedimentation characteristics of activated sludge. Thickening characteristics of sludge were evaluated based upon thickening area needed to maintain the required sludge concentration in activated sludge model, which corresponds to maximum surface load in undissolved substances. Chemical precipitation of phosphorus produces metal precipitates. These are transported with the waste sludge to the digestion tanks. Impact of the precipitates on the anaerobic sludge

stabilisation process as well as on the sludge water quality was tested in the work. The main aim of the research and proposed chapter submission is a pursuit of decision making regarding selection of type of precipitating agent and strategy of chemical phosphorus precipitation.

1. Introduction

The requirement for removal of phosphorus from wastewater (WW) is rising due to increasing problem of eutrophication all over the world. Biologically enhanced phosphorus removal represents the most convenient way. The main disadvantage of this approach is the require-ment for an anaerobic bioreactor, that is, an increase of capital costs. As a result, chemical precipitation with ferric, ferrous, aluminium or calcium salts is usually applied. There are various technological strategies (**Figure 1**), which depend on the place of precipitants dosing with regard to the position of biological stage of the wastewater treatment plant (WWTP). Other reason for chemical phosphorus removal can be temporary solution during upgrading of a WWTP for enhanced biological phosphorus removal. There are also circumstances in WW treatment practice (e.g. lower organics content in WW for sufficient biological phosphorus removal, lower winter temperatures or more stringent effluent phosphorus standards) for application of chemical phosphorus precipitation as a complementary solution. Combined chemical and biological phosphorus removal is more effective and chemical saving.
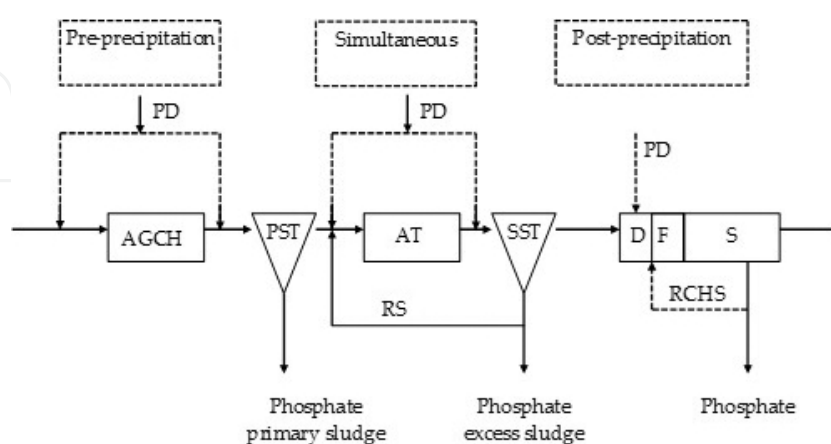

Figure 1. Phosphate removal processes (PD—precipitant dosing, AGCH—aerated grid chamber, PST—primary sedi-mentation tank, AT—aeration tank, SST—secondary sedimentation tank, D—dosing, F—flocculation, S—sedimenta-tion, RCHS—returned chemical sludge).

The addition of chemicals to raw wastewater for precipitation of phosphorus in primary sedimentation facilities is termed *"pre-precipitation"* [1]. Precipitates of phosphorus are withdrawn from the system as a part of primary sludge with low effect on activated sludge microorganisms. Increase in the amount of primary sludge is typical for this treatment technology. Precipitants are helpful to eliminate fluctuations of organic mass loading to biological stage of WWTP. However, simultaneous coagulation of organic matter occurs, leading to a decrease in BOD_5 and possible negative impact on efficiency of denitrification process.

Simple implementation of precipitating reagent dosing but no recovery of phosphorus from primary sludge is characteristic for this strategy.

The addition of chemicals to form precipitates that are removed along with wasted biological sludge is defined as *"coprecipitation"* [1]. Chemicals can be added to the effluent from primary sedimentation tank—the mixed liquor, that is, directly to the biological stage, or to the effluent from biological treatment process before secondary sedimentation.

Enhanced sedimentation of activated sludge is the advantage of phosphorus *coprecipitation* or *simulated precipitation*. Very simple dosing of precipitating chemicals and sufficient mixing and flocculation in biological treatment facilities are typical for this strategy. Concentration of mixed liquor in biological treatment tank increases, and solid retention time (SRT) decreases as a consequence of phosphorus precipitation. Phosphorus precipitates are removed from the treatment system as a part of excess sludge from which the phosphorus is not recoverable. Decrease in acid neutralisation capacity and pH in biological treatment tank and direct impact of precipitant agents on activated sludge microorganisms are also typical features of this phosphorus removal strategy.

"Post-precipitation" involves the addition of chemicals to the effluent from secondary sedimentation facilities and the subsequent removal of chemical precipitates. In this process, the chemical precipitates are usually removed in a separate sedimentation facilities or in effluent filters [1]. For this strategy, the elimination of effect of reagents on activated sludge microorganisms is characteristic. Main advantage is the achievement of minimal concentration values of total phosphorus in effluent (1 mg L^{-1}). Phosphorus is recoverable from chemical sludge. Main disadvantage of this technology is high investments related to separate flocculation and sedimentation tanks.

Simultaneous precipitation of phosphorus from wastewater with iron and aluminium salts is commonly used. Precipitation agents are dosed directly into the aeration tank, and produced precipitates are wasted as a part of the secondary sludge. Thus, not only aerobic and anoxic processes at WWTP are carried out in the presence of heavy metals, but precipitates are in many cases accumulated also in anaerobic sludge digester.

The most important operating parameter of simultaneous phosphorus removal is precipitating agent dosage. A lot of information about the dosing of precipitants can be found in the literature. Dosage of aluminium and iron salts usually falls into the range of 1–3 metal ion/phosphorus on a molar ratio basis [Eq. (1)] if the residual phosphorus in the secondary effluent

is >0.5 mg L^{-1}. To achieve phosphorus levels below 0.5 mg L^{-1}, significantly higher metal salt doses and filtration will be required [1]:

$$\beta = \frac{n_{Me}}{n_P}$$ (1)

where n_{Me} is the molar concentration of precipitating agent required for precipitation [mol L^{-1}], n_P the molar concentration of phosphorus to be precipitated [mol L^{-1}].

Recommended values of β ratio to achieve effluent concentration of phosphorus below 1.9 mg L^{-1} are 2–4 in simultaneous precipitation of phosphorus [2]. Under optimal function of separation stage, the concentrations of Al^{3+}, Fe^{2+} and Fe^{3+} in the effluent discharge for B = 1.5 are lower than 1 mg L^{-1} [3], that is, often lower than in the raw water. The separation by filtration enables to achieve metal concentrations below 0.5 mg L^{-1}. For urban wastewater with an average concentration of chloride 100 mg L^{-1}, sulphates 200 mg L^{-1} and the total phosphorus 10 mg L^{-1}, an increase in chloride concentration by about 50%, respectively 25% for the sulphate, will be the consequence of chemical precipitation process. It is also apparent that precipitation of phosphate contributes to the reduction in the total concentration of dissolved inorganic salts [4].

The required dose of coagulant/precipitant depends on the phosphate concentration, the pH and composition of the water. Due to the varying flow and phosphorus concentrations in raw water, it is advantageous to optimise the dosing of coagulants experimentally.

Significantly less data for the influence of precipitants on activated sludge activity and process efficiency appear in the literature. Mowat [5] published the data related to metal toxicity on microorganisms during biochemical oxygen demand test. At 20 mg L^{-1}, aluminium corresponded approximately to trivalent chromium and cyanide, and ferric iron showed similar toxicity. According to Bever and Teichman [3], ferric iron has a stimulation effect on nitrification process but ferrous iron causes an inhibition of this process. but inhibition of this process by ferrous iron was published by Bever and Teichman [3]. Because iron is usually introduced as not very toxic metal, there is a scarcity of literature about its toxicological and inhibitory effects on freshwater organisms. Aluminium and iron are commonly bioaccumulating in their salt form. Aluminium is a non-essential element, and it is mainly discussed in the context of its suspected detrimental role on the uptake of essential elements [6].

Extending spectrum of applied wastewater treatment processes and technologies follows the ever stricter requirements for discharged wastewater quality. Chemical precipitation of phosphorus is applicable in municipal wastewater treatment, and although being less environmentally favourable compared to enhanced biological phosphorus removal, the amount of investment funds is often decisive at this stage. Furthermore, enhanced biological phosphorus removal process frequently requires the application of chemical precipitation/post-precipitation as well, taking the increasingly stringent requirements for phosphorus removal from wastewater into account.

Simultaneous chemical phosphorus precipitation in biological stage of WWTP represents one of the most commonly used technologies when Fe^{2+}, Fe^{3+} and Al^{3+} salts are dosed into biological treatment facilities to precipitate the excess phosphorus in wastewater. These salts and their precipitates then become a part of the excess sludge and are thus transported also into anaerobic stabilisation tank.

Similarly to most treatment processes, chemical phosphorus precipitation is accompanied with generation of side products, interactions and impact on other simultaneously running processes. The aim of our research was to compare the impact of Fe^{2+}, Fe^{3+} and Al^{3+} salts on sedimentation and thickening characteristics of sludge, biological transformation processes and ammonia nitrogen removal, that is, nitrification and denitrification processes, as well as anaerobic sludge stabilisation processes. The objective of our research is to contribute to methodology for examination of thickening and dewatering characteristics of sludge with investigated precipitation agents. Mathematically processed experimental results of lab-scale-operated activated sludge models are used to compare sedimentation, precipitation and dewatering characteristics of activated sludge cultivated in the presence of selected precipitation agents, that is, Fe^{2+}, Fe^{3+} and Al^{3+} salts. Other purpose of this study is to find methods for quantification of precipitants influence on activated sludge activity.

2. Experimental and data processing methods

2.1. Influence of aerobic and anoxic biological processes

The process of simultaneous precipitation of phosphorus in aerobic biological WWTP was simulated in lab-scale. The activated sludge was cultivated in semicontinuous reactors in order to simulate plug-flow hydraulic regime at real aerated tanks of municipal WWTPs. The volume of one unit was equal to 1.5 L. The cultivation was carried out by applying different synthetic wastewater composition, that is, an individual substrate (methanol) or mixed substrates (methanol, glucose, natrium acetate and peptone or the mixture of natrium acetate and glucose) and ammonium nitrate in accordance with the ratio BOD_5:N = 100:5.

Operational conditions were changed during the experiments in order to investigate also the influence of these variables on activated sludge activity. The volumetric load related to COD varied between 1.0 and 2.0 kg m^{-3} d^{-1}. The bioreactors were operated over the solid retention time (SRT) of 8 or 10 days. The hydraulic retention time (HRT) of 46 h was maintained in the bioreactor. The amount of phosphorus added into the systems corresponded to its effluent concentration approximately 9.0 mg L^{-1}. Ferrous, ferric and aluminium salts were dosed as phosphorus precipitants and were applied after 50 days of cultivation (activated sludge acclimation). The amounts of precipitants required for dosing were obtained in accordance with metal/phosphorus molar ratios ranging from 1.5 to 3.0. The alkalinity was adjusted with sodium hydrocarbonate solution.

The analysis of chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS) and soluble phosphorus content was performed in accordance with

procedures described in the standard methods [7]. The content of total organic carbon (TOC) was obtained by TOC 2000 P analyser produced by IPU.

Respirometric measurements of oxygen uptake rate (OUR) which were performed by an oxygen Syland probe evaluated the influence of the above given precipitants on the activated sludge activity. These measurements were performed according to [8–10] and were carried out before the new aeration cycle started, that is, with endogenous biomass. With the resulting values, the maximum total oxygen uptake rates (the sum of exogenous and endogenous rates) were obtained. The effect of precipitants on activated sludge was evaluated from the total specific oxygen uptake rate (SOUR) values of metal-laden system related to the total SOUR values of the control system (without metals exposition). Thus, stimulation effect of metal to the activated sludge is calculated as follows:

$$SE = \left(\frac{r_{x,t}}{r_{x,t,con}} - 1 \right) \cdot 100 \ [\%]$$

(2)

where SE is the stimulation effect [%]; $r_{x,t,con}$ the total specific oxygen uptake rate of control sludge [mg g^{-1} h^{-1}]; $r_{x,t}$ is the total specific oxygen uptake rate of heavy metal-laden sludge [mg g^{-1} h^{-1}].

The measurements of specific substrate removal rate R_x at various substrate concentrations were performed by respirometric method [8, 9], and the values of maximum respiration rate $R_{x,max}$ and half saturation constant K_s of the Monod equation:

$$R_x = R_{x,max} \ \frac{S}{K_S + S}$$

(3)

where K_S is the half saturation constant [mg L^{-1}], R_X is the specific rate of substrate removal [mg g^{-1} h^{-1}], $R_{X,max}$ is the maximum specific rate of substrate removal [mg g^{-1} h^{-1}], S is the substrate concentration [mg L^{-1}],

were also evaluated in order to compare the influence of precipitants on activated sludge activity. Grid search method [11–13] was applied to evaluate respirometric measurements carried out at different substrate concentrations.

2.2. Impact on sedimentation, thickening and dewatering properties

Monitoring the impact of phosphorus precipitation agents to sedimentation, thickening and filtration characteristics of activated sludge formed another part in our research of the impact of precipitation agents to biological wastewater treatment processes and sludge treatment.

Real activated sludge process performed in systems with concentration gradient was simulated in the lab in semi-continuous models operated with default sludge age of 10 days. Retention time of synthetic wastewater was 2 days, and organic load rate expressed as COD was 1.5 kg m^{-3} d^{-1}. Salts of Fe^{2+}, Fe^{3+} and Al^{3+} were dosed to the systems together with the substrate. Fe was added as $FeSO_4 \cdot 7H_2O$. Trivalent Fe was added only after $FeSO_4 \cdot 7H_2O$ oxidation. Al^{3+} salts were added in form of $AlCl_3 \cdot 6H_2O$. Metals doses to precipitate excess phosphates were calculated for $\beta = 1.5$. A control model was operated in parallel, that is, without precipitation agents. Synthetic wastewater contained glucose and sodium acetate (COD = 3000 mg L^{-1}).

Solid flux method [1, 14–16] for the analysis of settling/thickening data and filtration equation [17–19] for processing of dewatering data were applied. Respiration measurements of SOUR were performed in order to evaluate the influence of precipitating agents on activated sludge microorganism activity.

In the case of non-standard sludge/suspension, it is possible to define the thickening area from experimental curve of particles mass flow density [18] that defines the relation of particles mass flow density q [kg m^{-2} h^{-1}] and sludge concentration [Eq. (4)]:

$$q = X \cdot u_0 \cdot \left(1 - \frac{X}{c_k}\right)^n \tag{4}$$

Particles mass flow density values may be gained as a product of sludge concentration values and respective measured precipitation rate or free sedimentation [15]. Analogically, the below formula applies for thickening rate u_z at specific solids concentration X:

$$u_z = u_0 \cdot \left(\left(1 - \frac{X}{c_k}\right)^n\right) \tag{5}$$

where X means sludge concentration [kg m^{-3}]; u_0, c_k and n are empirical parameters; c_k parameter value characterises the given suspension; it represents the maximal solids concentration (compression region). The constant u_0 represents thickening rate at unit suspension porosity. Simplified two parameters formula below may be used to describe the dependence of thickening rate and sludge concentration [18]:

$$u_z = k \cdot e^{-\beta \cdot X} \tag{6}$$

The values of k [m h^{-1}] and β [m^3 kg^{-1}] parameters describe the sludge thickening characteristics. Required thickening area may then be calculated from the equation:

$$A_z = \frac{Q_0 \cdot (1 + R) \cdot X_A}{q_{min}} \qquad (7)$$

where A_z means the required thickening area of thickening tank [m²]; Q_0 is wastewater flow [m³ h⁻¹]; X_a means concentration of solids [kg m⁻³]; and R means return sludge recirculation ratio. Minimum particles flow density q_{min} may be defined graphically pursuant to Yoshioka et al. [20] or calculated for example from the equation:

$$q_{min} = \frac{u_0 \cdot X_k \cdot X_r}{X_r - X_k} \left(1 - \frac{X_k}{c_k} \right)^{-n} \qquad (8)$$

If simplified two parameters thickening rate model is used [Eq. (6)], the below will apply for minimum flux of solids q_{min} (kg m⁻² min⁻¹) moving downward:

$$q_{min} = k \cdot \beta \cdot X_k^2 \cdot e^{-\beta \cdot X_k} \qquad (9)$$

Tuček and Koníček [18] describe how the Eqs. (8) and (9) are derived, as well as the formulae to calculate critical concentration value X_k and returned sludge concentration X_r.

Thickening rate corresponding to the sludge concentration [Eq. (5)] needs to be higher than solid flux of tank, that is, the below applies for minimum thickening area $A_{Z,min}$:

$$A_{Z,min} \geq \frac{Q}{u_z(X_a)} = \frac{Q}{u_0} \left(1 - \frac{X_a}{c_k} \right)^n \qquad (10)$$

where Q means sludge flow rate [m³ h⁻¹]

Assuming that flow rate is laminar when the filtrate flows through the porous material, filtration process may be described by the equation [16, 17]:

$$\frac{dV}{S \cdot d\tau} = \frac{\Delta p \cdot S}{\alpha \cdot \eta \cdot C \cdot (V + V_e)} \qquad (11)$$

where Δp means overall pressure difference [Pa] prior and after the filter that needs to be developed in order the required filtrate flow rate is reached; S means the filter size [m²]; dV means filtrate volume increment [m³] in time $d\tau$ [s]; u means filtration rate [m s⁻¹]; α means

specific cake resistance [m kg^{-1}]; η means dynamic filtrate viscosity [Pa s]; C means solids concentration in suspension [kg m^{-3}]; V means filtrate volume [m^3] in time τ [s]; and V$_e$ means fictive filtrate volume [m^3] that would be developed by a cake with the same resistance as the filtrate material resistance.

Integrating Eq. (11) and other adjustments lead into Eq. (12) for filtration at constant pressure [18]:

$$\left(\frac{V_2 - V_1}{2}\right)\frac{2}{k} + \frac{2V_e}{k} = \frac{\Delta \tau}{\Delta V} \tag{12}$$

Characteristic filtration constants, that is, V$_e$ and k quantities may be determined based upon measured values V$_i$, V$_{i+1}$ and τ_i a τ_{i+1}. Then, the filtration cake-specific resistance may be calculated from Eq. (13):

$$k = \frac{2\,\Delta p \,.\, S^2}{\alpha \,.\, \eta \,.\, C} \tag{13}$$

Another approach to determine filtration cake-specific resistance value is based on the assumption of negligible filtration material resistance with regard to filtration cake resistance [15]:

$$\alpha = \frac{\Delta p \,.\, S^2}{\eta \,.\, C \,.\, V_1 .\, \dot{V}_1} \tag{14}$$

Neglecting filtration support material resistance results in a relative error n defined as below:

$$n = \frac{\Delta \alpha}{\alpha}\,100 = \frac{\dot{V}_1}{\dot{V}_0 - \dot{V}_1}\,.\,100 \ \ [\%] \tag{15}$$

where V_1 means the volume of filtrate used to create the cake; $\dot{V}_0$ means filtrate volumetric flow rate through the filtration material; and $\dot{V}_1$ means volumetric filtrate flow rate through the cake and filtration material.

The dependence of specific resistance of compressible cake from pressure difference may be expressed as [15]:

$$\alpha = \alpha_0 + a \,.\, \Delta p^x \tag{16}$$

For certain suspensions $\alpha_0 = 0$ and Eq. (16) shall thus be transformed to Eq. (17):

$$\alpha = a \,.\, \Delta p^x \tag{17}$$

where a is constant.

Mathematically, the constant a equals to specific cake resistance at unit pressure difference for Eq. (16). Parameter x represents the filtration cake compressibility rate; $x = 0$ for non-compressible cake. Mathematically, α_0 represents specific cake resistance at $\Delta p = 0$.

Sedimentation characteristics of sludge from individual systems were evaluated based upon the minimum thickening area $A_{Z,min}$ values [Eq. (10)] that correspond to those of maximum hydraulic surface load of sedimentation tank in order to ensure for sludge separation conditions.

Thickening characteristics of sludge were examined by comparing the thickening area values calculated for measured solids concentration and the same flow rates of wastewater and return sludge. Three parameters model of particles flow curve [Eq. (4)] was applied onto the results of thickening curves measurements, or the dependence of thickening rate from sludge concentration [Eq. (5)], and two parameters dependence of thickening curve from sludge concentration [Eq. (6)] was applied.

Experimental values of filtration characteristics (specific filtration cake resistance α and fictive filtrate volume V_e) determined in filtrate rate measurement at constant pressure difference were used to assess dewatering sludge characteristics. At the same time, α dependence from pressure difference was also measured.

Grid search optimisation method [10, 12] was used to determine parameters in Eqs (4), (6), (16) and (17). Residual sum square S^2_R between experimental and calculated q, u and α values was applied as objective functions [12]:

$$S^2_R = \frac{\sum (y_i^{exp} - y_i^{cal})^2}{n - m} \tag{18}$$

where n represents the number of measurements and a means the number of model parameters.

2.3. Impact on anaerobic sludge stabilisation

Experimental models to simulate the processes occurring in the anaerobic digesters of stabilising raw sludge (**Figure 2**) consisted of three parts:

- reactor with volume 1.0 L which served as the digester with venting of generated biogas in the process,

- sorption of contaminants from produced biogas,

- device for measuring the resulting CH_4.

Reference model was also operated in parallel.

Anaerobically stabilised sludge sampled from the digester at WWTP Bratislava (applied as inoculum) was loaded with primary and excess sludge taken from the abovementioned WWTP. Anaerobic digesters were operated in batch mode at a residence time of 5 days. In both systems, during the tests carried out with the raw sludge the processes of the hydrolysis were investigated by measuring changes in the concentration of ammonia, and the methanogenesis process was investigated by measuring the production of biogas. Effect of iron on the processes of anaerobic digestion was evaluated by comparing the output values of the experimental (addition of Fe) and reference model. The pH was adjusted dosing systems $NaHCO_3$ and NaOH to the same value (about 7.8) to increase buffering capacity of both systems. The models were run at 37°C.
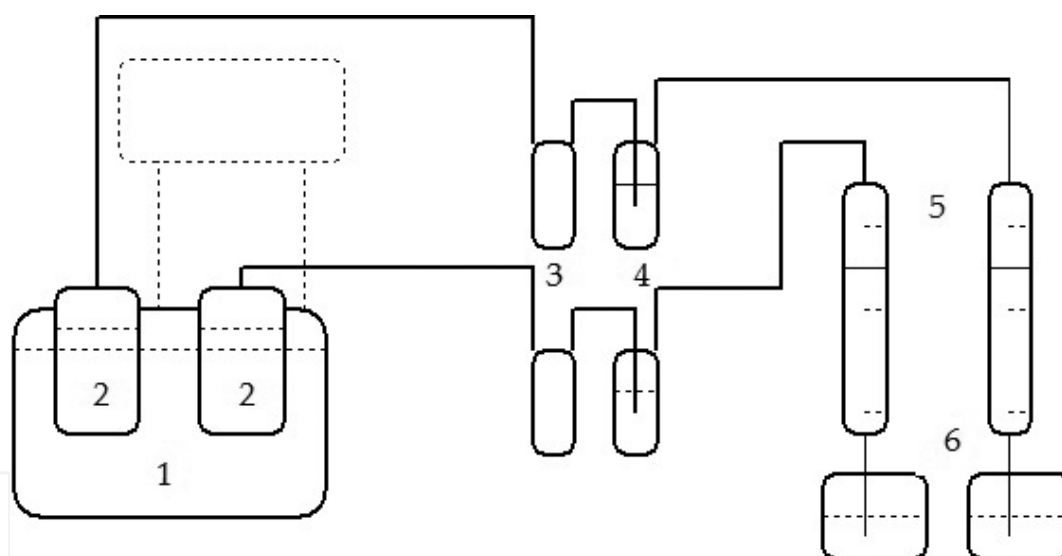
Figure 2. Schematic representation of lab-scale anaerobic stabilisation equipment (1-thermostat, 2—reactors, 3—safety vessels, 4—bubbler with KOH, 4—measurement of produced gas volume, 6—storage reservoirs for water).

3. Results and discussion

3.1. Impact on aerobic and anoxic biological treatment processes

The process of simultaneous precipitation of phosphorus in aerobic biological wastewater treatment system has been studied in semi-continuous lab-scale bioreactors. Operational conditions, type and dose of precipitants (ferric, ferrous and aluminium salts) were changed

during experiments in order to investigate the influence of these variables on activated sludge activity. Short-term and long-term effects of precipitants on activated sludge activity have been studied. Respirometric measurements were performed in order to evaluate the influence of precipitant metals on activated sludge activity. The effect of precipitants was evaluated with regard to specific oxygen uptake rate (SOUR) of the control activated sludge system operated at the same conditions excluding the precipitants dosing.

Figure 3 shows the effect of ferrous ($FeSO_4 \cdot 7H_2O$) and aluminium ($Al_2(SO_4)_3 \cdot 18H_2O$) precipitants on activated sludge respiration activity. Model wastewater containing glucose, methanol, sodium acetate and peptone was used as a substrate. Bioreactors including control system were operating at SRT of 8 days and the volumetric load of $1.0 \, kg \, m^{-3} \, d^{-1}$, related to COD. The precipitants during this set of experiments were dosed at metal to phosphorus molar ratios equal to 3.
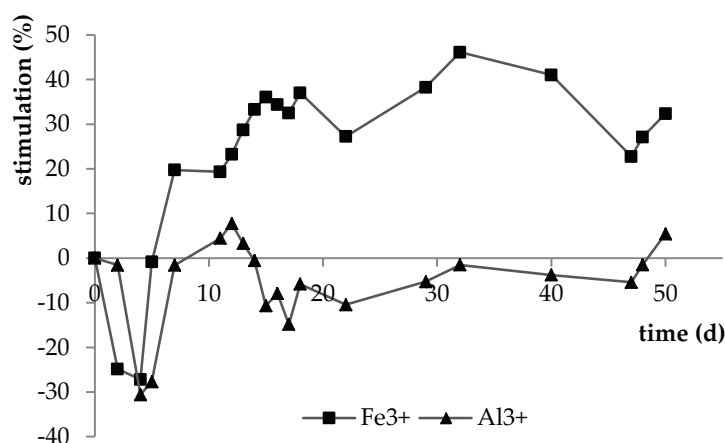

Figure 3. Stimulation effect of Fe^{2+} and Al^{3+} precipitating agents on activated sludge respiration activity.

The inhibition effect of about 30% for both precipitants few days after the beginning of the experiments follows from **Figure 3**. In the next period, after approximately 15 days from the beginning of the precipitants dosing, the stimulation effect of ferrous iron on activated sludge activity of about 30–40% [Eq. (2)] can be estimated from **Figure 3**. On the other hand, only small inhibition or insignificant stimulation influence of aluminium precipitant resulted from the measurements as can be seen in **Figure 3**.

The results on stimulation or inhibition effects of the precipitants on the activated sludge respiration activity can be influenced by the procedure applied in the evaluation.

From Eq. (2) follows that the values of relative SOUR can be considered to be a measure of these effects. The values of total suspended solids (TSS) are usually applied as a basis of specific rate expressions in wastewater engineering. It is obvious that the values of TSS concentration in the systems with precipitant dosing increase due to the precipitates formation and accumulation in activated sludge and will be higher in comparison with the control system.

Significant differences between the values of VSS versus the duration of experiments duration were observed in all three bioreactors maintained the same values of operational parameters (HRT, SRT, volumetric load) and used equal substrate composition [21]. These differences can be related for example to possible influence of heavy metals on biomass yield or to thermal decomposition of precipitates with hardly defined composition during performing the VSS content determination procedure. For example, the value of VSS for Fe precipitate based on our experiment is about 13% and for Al precipitate about 27% (both precipitates were prepared by coagulation, precipitation and filtration) [21]. It is also assumed that the differences between the VSS content in the studied systems can be partially ascribed to absorption of both dispersed form of biomass and slowly biodegradable products of microorganisms. This assumption follows from higher treatment efficiency of organic pollution removal in the systems with phosphorus precipitation with regard to dissolved as well as dispersed organic substances observed in our previous work [21]. Thus, adsorbed organics on activated sludge flocs practically decrease the observed values of activated sludge SOUR. This is due to the higher values of biomass concentration approximated by VSS content to which the values of SOUR are related.

The TOC content in biomass was also analysed in order to evaluate SOUR and compare the influence of the studied heavy metals on activated sludge activity. The values of TOC content in activated sludge from operated lab-scale bioreactors are given in **Table 1** [22].

Aerated system	TOC [%]
Fe^{2+}	17.10
Fe^{3+}	16.37
Al^{3+}	19.84
Control	21.33

Table 1. TOC content in activated sludge cultivated in observed lab-scale aerated system.
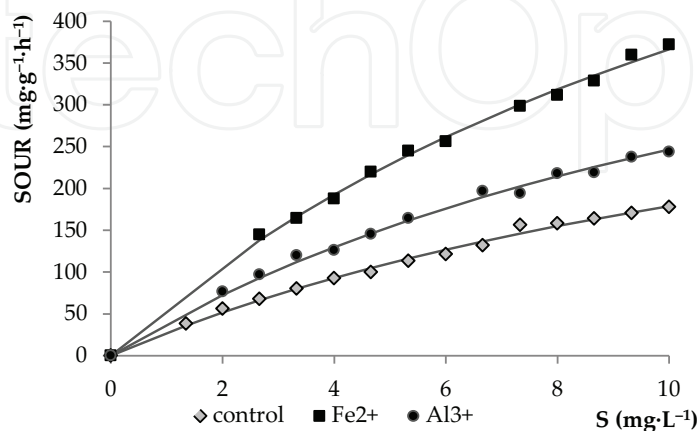

Figure 4. Dependence of SOUR (related to TOC mass unit) on substrate concentration.
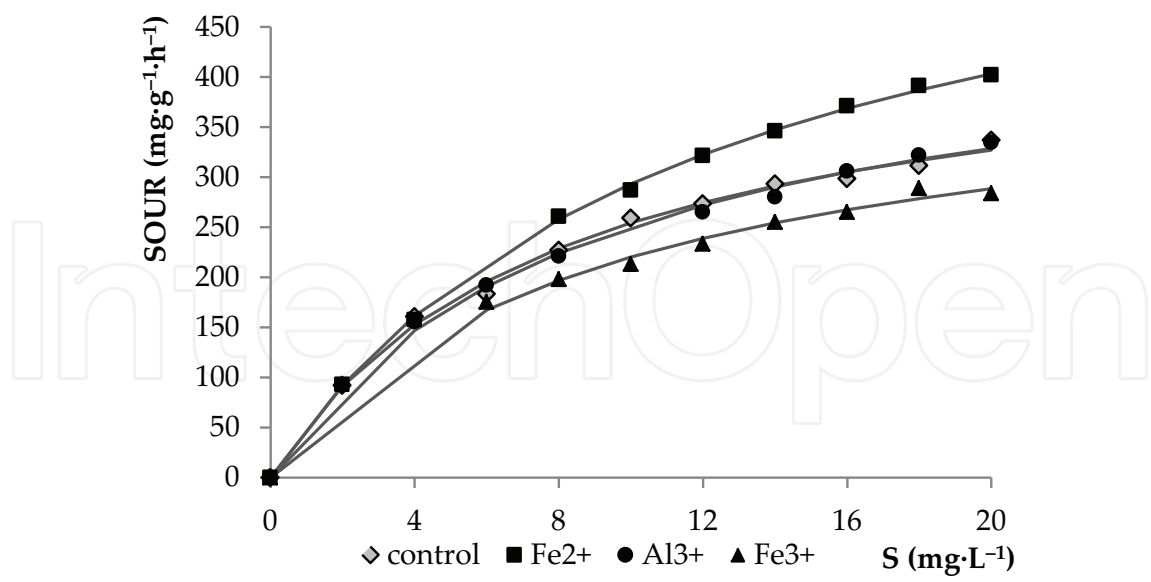
Figure 5. Dependence of SOUR (related to VSS mass unit) on substrate concentration.

The courses of the experimental and calculated values of SOUR (related to TOC concentration values) at different values of substrate concentration are presented in **Figure 4**. The highest values of SOUR can be concluded for the activated sludge cultivated in the presence of ferrous precipitant. On the other hand, this figure indicates only small differences between the SOUR courses obtained for activated sludge, which was cultivated in the control system and in the presence of ferric iron or aluminium precipitate. In **Figure 5**, similar concentration dependencies are plotted, but the values of SOUR for the same measurements are related to VSS content in individual bioreactors. Similarly to **Figure 4**, the highest values of SOUR have been achieved with activated sludge cultivated in the bioreactor with ferrous precipitant dosing. The values of Monod equation parameters obtained by the evaluation of SOUR values shown in **Figure 4** are given in **Table 2**.

	Control	Al^{3+}	Fe^{2+}	Fe^{3+}
$R_{X,max}$ [mg g^{-1}MLSS h^{-1}]	457.3	476.3	644.8	417.9
$R_{X,max}$ [mg g^{-1} TC h^{-1}]	1176.4	1326.6	2031.4	1252.1
K_S [mg L^{-1}]	10.0	10.0	15.0	10.0
$R_{X,max}$ [mg g^{-1}TOC h^{-1}]	2553.0	2533.3	4091.3	2659.1

Table 2. The values of biokinetic parameter values [Eq. (3)] related to different forms of activated sludge in aerated systems.

The courses of calculated values of SOUR with the same parameter values are also presented in **Figure 4**. A very good agreement between the experimental values (points) and the calculated ones (lines) follows from this figure. The values of maximum specific substrate removal

rates confirm the stimulation effect of ferrous ion on activated sludge respiration activity. As it was mentioned earlier, only small differences between the values of maximum SOUR obtained for ferric iron, aluminium precipitant and control systems resulted from the work. The values of maximum SOUR given in **Table 2** also confirm the stimulation effect of iron salts on activated sludge respiration activity.

From **Table 2** is obvious that $R_{x,max}$ value for the sludge cultivated in presence of Fe^{2+} is significantly higher than the value for the sludge cultivated in presence of Al^{3+} indicating a stimulatory effect of ferric salts to the respiration rate. However, sludge cultivated in the presence of ferrous salts showed the lowest measured respiration activity. From this knowledge, it leads to the conclusion that the ferrous and ferric forms of iron have different effects on the activity of the sludge. Stimulation effect of ferric salts is highly dependent on the pH in aeration tank.

Higher stimulation of heterotrophic microorganisms activity by ferrous salts in comparison with ferric precipitant is also of technological importance, for example, with regard to the place of ferrous precipitant dosing. This form of iron salts should be preferable dosed directly into the aeration tank. In other words, ferrous sludge should not be metered prior to aerated sand traps because the presence of oxygen would oxidize ferrous iron to ferric. Ferric iron has significantly less stimulation effect on the activity of the sludge in the aeration tank as ferrous salts dispensed directly to this aeration tank. In addition, ferrous salts dosing will save operating costs for the simultaneous precipitation of phosphorus in comparison with ferric salts. However, one should keep in mind when designing activated sludge process with simultaneous phosphorus removal that dosing of the ferrous salts will increase oxygen consumption in this part of aeration tank.

The courses of the experimental and calculated values of SOUR (related to TOC content in activated sludge) at different values of substrate concentration are presented in **Figure 4**. The highest values of SOUR can be concluded for the activated sludge cultivated in the presence of ferrous precipitant. On the other hand, this figure indicates only small differences between the SOUR courses obtained for activated sludge, which was cultivated in the control system and in the presence of ferric iron or aluminium precipitate. In **Figure 5**, the similar concentration dependencies are plotted, but the values of SOUR for the same measurements are related to volatile suspended solids (VSS) concentration in each bioreactor. Similarly to **Figure 4**, the highest values of SOUR have been achieved with activated sludge cultivated in the bioreactor with ferrous precipitant dosing.

Effluent phosphorus concentration varied between 1.0 and 2.0 mg L^{-1}.

3.1.1. Nitrification tests

The aim of preliminary short-term nitrification tests was to evaluate the effect of precipitating salts on nitrification activities of individual sludge after approximately one month of sludge acclimation in presence of individual precipitating agents. Kinetic assays were performed after feeding semi-continuous models by the model substrate composed of peptone, glucose, ethanol, sodium acetate, ammonium chloride, sodium dihydrogen phosphate and of the

precipitating agent. During the test, the pH was maintained at about 7.5. Measured values of different forms of nitrogen compounds during one cycle of each model are listed in **Tables 3–5**. Evaluation and comparison of nitrification rates of each activated sludge are shown in **Table 5**.

Time [h]	$N - NH_4^+$ [mg L^{-1}]	$N - NO_2^-$ [mg L^{-1}]	$N - NO_3^-$ [mg L^{-1}]
0	22.7	6.4	23.8
0.5	23.7	3.3	24.5
1.0	–	2.6	25.0
2.0	21.4	0.9	27.5
3.0	18.3	0.4	32.0
4.0	15.1	0.4	–

Table 3. Time variation in nitrogen compounds in control activated sludge model.

Comparing the rate of nitrification of second stage given in **Table 5**, one can conclude stimulatory effect of ferrous salts to the second stage of nitrification. The nitrification rates are based on the value of the total organic carbon (TOC) in individual models that best represent the active part of the biomass of activated sludge. The values of biomass concentrations in systems with the addition of the precipitants contain sufficient portions of the chemical sludge, and therefore, they are not suitable for expressing concentration of active biomass.

| Time [h] | Al^{3+} | | Fe^{2+} | | Fe^{3+} | |
| | $N - NH_4^+$ | $N - NO_3^-$ | $N - NH_4^+$ | $N - NO_3^-$ | $N - NH_4^+$ | $N - NO_3^-$ |
	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg l^{-1}]	[mg l^{-1}]
0	26.1	–	24.4	14.0	23.0	16.9
1	20.9	13.3	21.2	13.9	23.6	16.5
2	17.0	14.9	14.6	14.9	16.8	–
3	14,3	–	9.9	19.1	11.2	20.7
4	9.1	21.3	7.7	–	8.3	23.5
5	7.2	24.1	3.0	24.5	4.6	–
6	–	26.7	1.4	29.7	1.9	26.8
7	1.2	29.7	0.2	29.4	0.6	32.6

Table 4. Time variation in nitrogen compounds in activated sludge models with precipitating agents dosing.

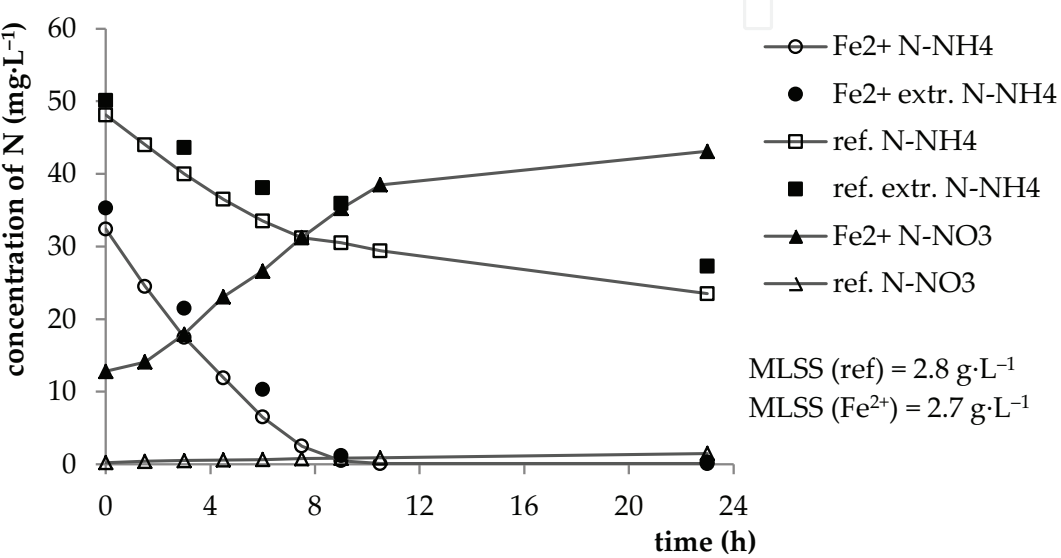|	Control	Al^{3+}	Fe^{2+}	Fe^{3+}
VSS $[g\,L^{-1}]$	2.78	3.10	3.16	3.13
TOC $[g\,L^{-1}]$	0.96	1.05	0.98	0.99
r_X $[mg\ N\text{-}NO_3\,g^{-1}\,h^{-1}]$	0.97	0.90	1.11	0.80
r_{TOC} $[mg\ N\text{-}NO_3\,g^{-1}\,h^{-1}]$	2.80	2.67	3.58	2.53

Table 5. Nitrification rate values.

Figure 6. Time dependencies of various forms of nitrogen compounds during 24-hour cycle in the reference model and in the model with ferrous salts.
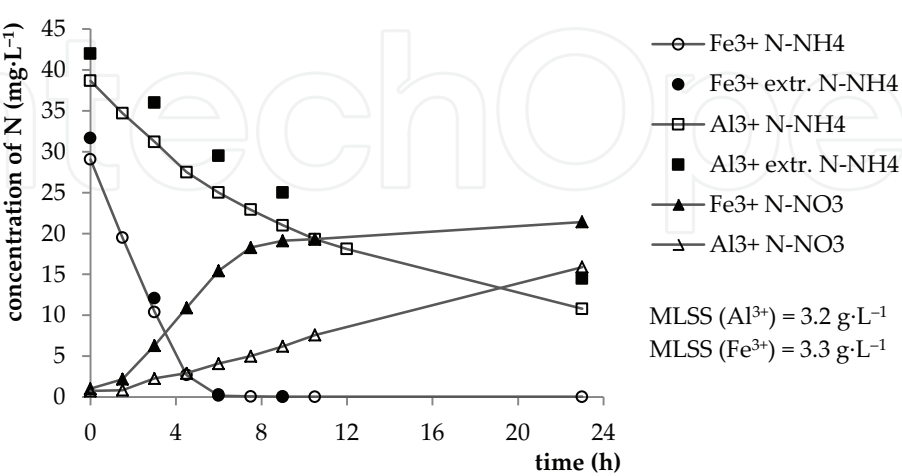

Figure 7. Time dependencies of various forms of nitrogen compounds during 24-hour cycle in the model with ferric and aluminium salts.

The rate of transformation of N-NH$_4$ to nitrite (1st nitrification step) cannot be taken as a benchmark to determine the impact of metal on oxidation of ammonia nitrogen since this value covers not only the rate of oxidation of N-NO$_3$, but also the consumption of N-NH$_4$ for the synthesis of biomass. Moreover, it is also influenced by the formation as a result of hydrolysis and ammonification of organically bound nitrogen.

The next kinetic tests were aimed at the investigation of nitrification during the whole reaction cycle in individual laboratory semi-continuous models. The results of the measurements are shown in **Figures 6** and **7**.

In order to compare individual models, the rates of ammonium nitrogen removal in the first hours of the test (rate includes the process of assimilation and nitrification) were calculated from the experimental data. The measured rates are shown in **Table 6**. In order to thoroughly verify coagulants influence on the process of nitrogen removal, the process of ammonium nitrogen adsorption on biomass was performed. The results of sorption of ammonia nitrogen are shown in **Figures 6** and **7**. From the results follows approximately equal and constant sorption of ammonium nitrogen during the whole cycle in all models. The value of adsorbed ammonia nitrogen is actually the difference between value of nitrogen extraction and the value of ammonia nitrogen measured without extraction. The concentration of ammonium nitrogen adsorbed on the biomass flakes reached 15–40% of the concentration of dissolved ammonium nitrogen, which is in good agreement with published values which ranged from 18 to 30% [23]. These values of sorption of ammonia nitrogen are characteristic for the semi-continuous system operation laboratory models.

	Control	Al^{3+}	Fe^{2+}	Fe^{3+}
Maximal rate of assimilation and nitrification R$_{x,N,m}$ [mg g^{-1} h^{-1}]	0.92	0.78	1.69	1.77
Rate of simultaneous nitrification R$_{x,N,m}$ [mg g^{-1} h^{-1}]	0.05	0.23	0.99	0.89

Table 6. The measured rate of assimilation and simultaneous nitrification during the daily cycle.

3.1.2. Denitrification test

The aim of the denitrification test was to monitor the degradation rate of nitrate nitrogen in individual models. For the better approximation of the active biomass, the denitrification rates were based on the concentrations of total organic carbon (TOC) in the individual sludge. The measured concentrations of nitrate and nitrite nitrogen during the denitrification tests are shown in **Table 7**. Experimental values of total suspended solids (TSS) and TOC are shown in **Table 8**.

Experimental and calculated dentrification rates based on TSS and TOC unit values in individual operated lab-scale models are shown in **Table 9**. From these results follow the stimulatory effects of both forms of iron salts, that is, ferrous and ferric salts on denitrification rate. However, about two times higher denitrification rate follows for ferric salts in comparison with ferrous salts when comparing specific denitrification rates based on TOC values. The

experimental values of denitrification rates are comparable with those published in the literature, that is, 5–20 mg g^{-1} h^{-1} (based on unit mass of TSS).

t (h)	Control		Al^{3+}		Fe^{2+}		Fe^{3+}	
	N-NO$_2^-$ (mg L^{-1})	N-NO$_3^-$ (mg L^{-1})	N-NO$_2^-$ (mg L^{-1})	N-NO$_3^-$ (mg L^{-1})	N-NO$_2^-$ (mg L^{-1})	N-NO$_3^-$ (mg L^{-1})	N-NO$_2^-$ (mg L^{-1})	N-NO$_3^-$ (mg L^{-1})
0	4.4	49.0	5.2	43.9	1.6	46.1	2.7	46.1
1	5.9	42.1	8.2	34.3	7.1	35.2	6.2	18.5
2	7.3	33.0	15.4	23.2	13.7	26.2	13.7	6.6
3	7.3	21.5	17.6	15.7	15.3	10.2	14.6	6.0
4	–	16.7	19.5	10.9	19.3	5.5	19.3	5.5
5, 6	–	15.1	19.5	3.0	19.3	3.9	19.3	3.2

Table 7. Concentration values of N-NO$_2^-$ and N-NO$_3^-$ in individual models.

	Control	Al^{3+}	Fe^{2+}	Fe^{3+}
X (g L^{-1})	1.28	1.36	1.32	1.32
TOC (%)	34.5	33.75	31.02	31.62

Table 8. Concentration values of TSS and TOC in individual models.

	Control	Al^{3+}	Fe^{2+}	Fe^{3+}
R$_{X,N-NO3}$ (mg/g h)	7.2	6.9	9.1	15.0
R$_{TOC, N-NO3}$ (mg/g h)	20.9	28.4	29.3	47.4

Table 9. Denitrification rates in individual models.

3.2. Impact on sedimentation, thickening and dewatering characteristic

Table 10 shows experimental values of dry mass concentration for each lab model and calculated values of u_0, c_k and n parameters in the particles mass flow density Eq. (4). The minimum thickening area values are also given for individual sludge determined from point of view of maximum hydraulic surface load or establishment of conditions for sludge separation in sedimentation tank [Eq. (10)]. Eq. (5) was applied to calculate thickening rate values corresponding to experimental values of sludge concentration in each model (**Table 10**). The same value of activated sludge flow rate ($Q_0 = 250$ m^3 h^{-1}) was applied to calculate minimum thickening area for each operational activated sludge.

The smallest value of minimum thickening area results from **Table 1** for aerated tank with Fe^{3+} doses; the same area is larger by approximately 16% for reference activated model sludge (without precipitation agents). Minimum thickening area for Fe^{2+} is larger by app. 19% than

in the reference model. The least thickening rate or the largest minimum thickening area are characteristic for sludge with Al^{3+} doses; this area is almost doubled in size compared to the sludge with Fe^{2+} dosing. It results from the above that this sludge shows the best sedimentation characteristics despite the highest solids concentration in the system with Fe^{3+} dosing (thickening rate decreases with growing sludge concentration).

Model	X_A [kg m^{-3}]	u_0 [m h^{-1}]	c_k [kg m^{-3}]	n [–]	u_z [m h^{-1}]	A_{min} [m^2]
References	2.5	19.2	12.2	1.58	13.3	18.8
Fe^{2+}	3.0	16.9	82.6	11.14	11.2	22.3
Fe^{3+}	3.4	24.8	88.1	12.00	15.5	16.2
Al^{3+}	3.3	10.0	77.3	13.15	5.7	44.0

Table 10. Values of dry mass concentration, parameters of particles mass flow density equation [Eq. (1)] and minimum thickening area for each sludge [Eq. (7)].

Table 11 shows experimental values of volatile suspended solids (VSS) in each lab model sludge, calculated values of k and ß parameters in thickening rate equations [Eq. (6)] and relevant values of minimum thickening area [Eq. (10)]. The same above specified activation mixture flow rate was used to calculate minimum thickening area for individual sludge.

Model	$X_{Sž}$ [kg m^{-3}]	k [m h^{-1}]	β [m^3 kg^{-1}]	u_z [m h^{-1}]	A_{min} [m^2]
References	2.20	27.6	2.50	14.6	17.1
Fe^{2+}	2.24	21.1	0.16	12.9	19.4
Fe^{3+}	2.49	24.8	1.41	15.3	16.3
Al^{3+}	2.61	9.9	0.18	5.6	44.8

Table 11. VSS concentrations, thickening rate equations [Eq. (3)] parameters and minimum thickening area [Eq. (7)].

Minimum thickening area values calculated with the simpler two parameters model [Eq. (6), **Table 11**] also prove the above evaluation of sedimentation characteristics of each sludge. **Table 12** shows minimum particles mass flow density values and the necessary thickening area (sedimentation tank) calculated with both above presented mathematical models for individual sludge with dosed precipitation agent. Values of $q_{min,5}$ [Eq. (8)] and A_{Z1} [Eq. (10)] correspond to the three parameters model and $q_{min,6}$ [Eq. (9)] and A_{Z3} [Eq. (10)] correspond to the two parameters model. Calculations were made for dry matter concentrations in each activation model presented in **Table 10**, and the above specified wastewater flow rate and the same value of return sludge recirculation ration.

It results from comparison of values presented in **Table 12** that the largest necessary thickening area is required for sludge with aluminium salts dosing in order to reach the required return sludge thickening to maintain the above specified activated sludge concentrations in each system (**Table 10**) at the same flow rate condition (wastewater flow rate and return sludge

recirculation ratio), while five to ten times smaller thickening area corresponds to sludge with iron salts dosing. The values of required thickening area for sludge with Fe^{2+} and Fe^{3+} dosing calculated with individual mathematical thickening models [Eqs. (4) and (6)] are contradicting. Values higher by app. 23 up to 70% result for simplified, two parameters model from comparison of the measured and calculated residual variation values of particles mass flow density figures. Thus, three parameters model was better in describing experimental values [Eq. (4)].

Model	$q_{min,5}$ [kg m^{-3} h^{-1}]	$A_{Z,1}$ [m^2]	$q_{min,6}$ [kg m^{-3} h^{-1}]	$A_{Z,3}$ [m^2]
Fe^{2+}	30.1	27.5	36.2	22.8
Fe^{3+}	24.1	38.9	52.7	17.8
Al^{3+}	2.7	331.0	9.5	94.5

Table 12. Values of q_{min} a A_Z for sludge with dosed precipitation agents.

The relations among thickening rate of sludge from models with precipitation agents dosing are also obvious from **Figure 8** that shows the particles mass (MLSS/TSS) flow density curves. The highest particles mass flow density value corresponds to the selected sludge concentration and thus, also the largest thickening sludge rate with Fe^{3+} dosing. The least values of these parameters are characteristic for sludge with Al^{3+} dosing. Alongside the parameters of the applied mathematical model, the value of particles mass flow density depends also on the requested sludge thickening, which relates to sludge concentration maintained in the activation tank and also to the return sludge recirculation ratio. This may also explain the seemingly contradicting calculated values of required thickening area for sludge with Fe^{3+} and Fe^{3+} (compared to the course of particles mass flow density curves depicted in **Figure 8**). Higher sludge concentration with Fe^{3+} dosing compared to Fe^{3+}, at the same recirculation ratio, results also in higher required thickening, which was also reflected in smaller minimum particles mass flow density value or higher value of the required thickening area.
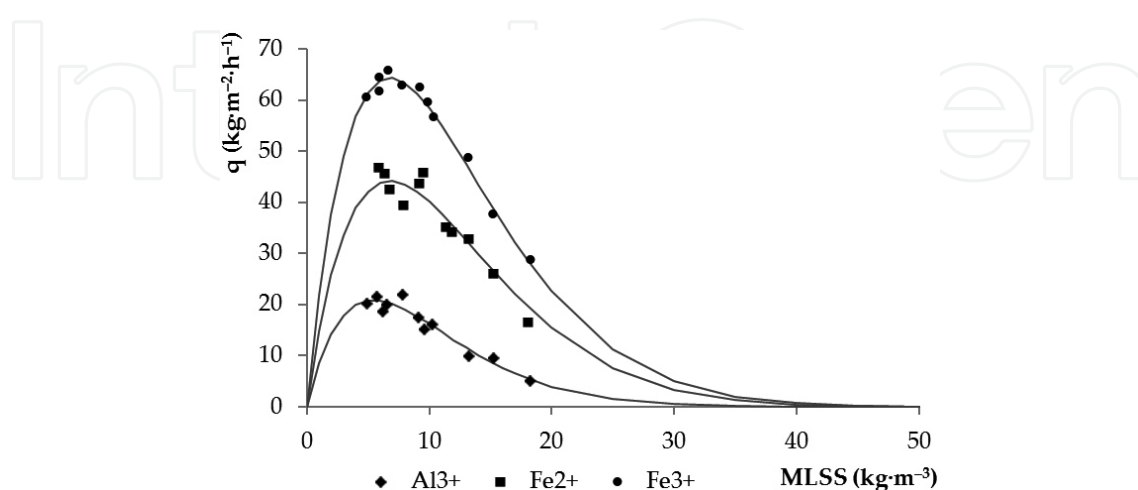

Figure 8. Particles solids flux flow curve for sludge in models with precipitation agents dosing.

Model	X_R [kg m^{-3}]	X_K [kg m^{-3}]	A_Z [m^2]
References	12.2	12.2	139.0
Fe^{2+}	32.0	27.6	135.0
Fe^{3+}	45.2	40.8	154.0
Al^{3+}	42.8	38.3	151.0

Table 13. Values of A_Z corresponding to maximum surface load in undissolved substances pursuant to.

Table 13 presents return sludge concentration X_R for each sludge required to maintain the above specified sludge concentrations in the system (**Table 10**), critical concentration X_K and the necessary minimum thickening area corresponding to the requirements of maximum surface load in undissolved substances (mass surface load) in compliance with the standard STN 75 6401 [24], that is, 6 kg m^{-3}h^{-1}. Respective values of sedimentation rates are given in **Table 13**.

It is obvious that activated sludge process intensification with the purpose of chemical phosphorus precipitation is accompanied with its increased concentration in the system, when unchanged sludge age is maintained. Thus, mass surface load may occur with insufficient sedimentation tanks dimension. It is obvious from **Tables 1** and **3** that the higher sludge concentration in the system, the higher the required thickness of returned sludge, and thus, also higher thickening area.

Figure 9 shows particles mass flow density curve for reference sludge (no agents dosed). The below sludge volume index (SVI) values were measured in individual bioreactors:
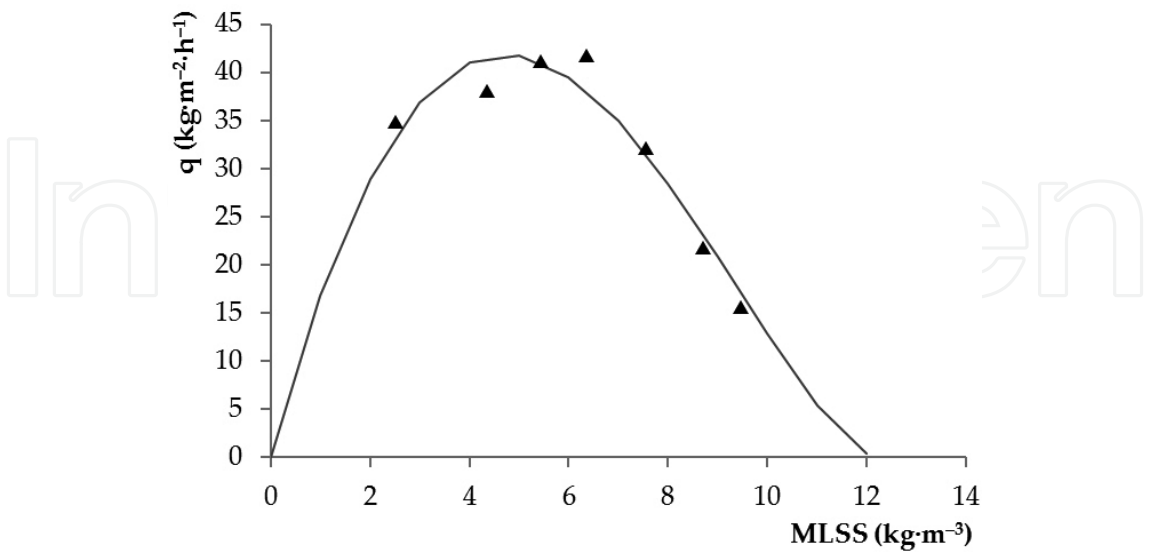

Figure 9. Particles mass flow density curve for reference sludge.

Fe^{2+}: 29.8 mL g^{-1}, Fe^{3+}: 36.3 mL g^{-1}, Al^{3+}: 42.5 mL g^{-1}and Ref: 69.9 mL g^{-1}.

These figures show high sedimentation characteristic of each sludge. SVI, however, is not a good parameter to compare sedimentation and thickening characteristics of these different sludge due to the different dry mass concentrations in each sludge, mineral portion and morphology of floccules.

Table 14 presents filtration characteristics for each sludge gained by processing filtrate volume increment measurements in individual time intervals, that is, applying Eqs. (12) and (13). The highest specific filtration resistance value for sludge cultivated with additional iron salts is obvious from **Table 14**. The lease values of fictive volume V_e correspond to this value, which also proves the least transitivity of the sludge cake. Relatively higher specific filtration resistance value and lower throughput are characteristic also for sludge with Al^{3+} dosing. The highest throughput results for reference sludge and the least specific filtration value are characteristic for sludge with addition of iron salts.

	α [m kg^{-1}]	k [s m^{-6}]	V_e [m^3]
References	0.929×10^{12}	3.05×10^{-11}	129×10^{-6}
Al^{3+}	9.750×10^{12}	0.48×10^{-11}	18.9×10^{-6}
Fe^{2+}	16.900×10^{12}	0.26×10^{-11}	0.6×10^{-6}
Fe^{3+}	0.319×10^{12}	$15,30 \times 10^{-11}$	26.0×10^{-6}

Table 14. Filtration characteristics for individual excess sludge measurements at $\Delta p = 19.6$ kPa—Eq. (12).

Table 15 presents specific filtration resistance values corresponding to measurement of filtrate volumetric flow rate through filtration material, filtration material and cake and filtrate volume corresponding to the developed filtration cake. Measurements were made at the same pressure difference as in the previous case, that is, $\Delta p = 19.6$ kPa. Measured data were evaluated with Eq. (17). Relative errors [Eq. (15)] did not exceed 4%. The lowest specific filtration resistance values result for sludge with dosed iron salts also from these results. When the same method is applied to define the specific filtration resistance values for other sludge used in our research, the results are very much the same while exceeding the sludge with Fe^{3+} dosing by approximately one order.

	α [m kg^{-1}]	Relative deviation [%]
References	4.56×10^{12}	0.13
Al^{3+}	4.16×10^{12}	0.55
Fe^{2+}	5.18×10^{12}	0.43
Fe^{3+}	0.63×10^{12}	3.95

Table 15. Filtration characteristics of sludge measured at $\Delta p = 19.6$ kPa—Eq. (14).

	α_0	A	x	S^2R
Control, (16)	2.552×10^{12}	0.426×10^{12}	0.0005	2.457×10^{25}
Control, (17)	–	2.958×10^{12}	0.0005	2.457×10^{25}
Al^{3+}, (16)	0.051×10^{12}	0.310×10^{12}	0.2048	0.099×10^{25}
Al^{3+}, (17)	–	0.554×10^{12}	0.1941	0.103×10^{25}
Fe^{2+}, (16)	0	0.005×10^{12}	0.6878	0.192×10^{25}
Fe^{2+}, (17)	–	0.005×10^{12}	0.6878	0.192×10^{25}
Fe^{3+}, (16)	0.008×10^{12}	0.106×10^{12}	0.2500	0.034×10^{25}
Fe^{3+}, (17)	–	0.001×10^{12}	0.7603	0.009×10^{25}

Note: numbers 16, and 17 mean that Eq. (16), or Eq. (17) were applied.

Table 16. Parameters of specific filtration resistance dependence from pressure difference Eqs. (16) and (17).

Table 16 presents the values of specific filtration resistance dependence from pressure difference, that is, the parameters of Eqs. (16) and (17). The data for calculation of specific filtration resistance values at different pressure differences were obtained by measuring volumetric flow rates through filtration material, filtration material and cake and also the filtrate volume when filtration cake was developed. Relative errors calculated with Eq. (15) did not exceed 4% for these measurements. The above mentioned equation describes the experimental data also for reference sludge and sludge containing aluminium precipitates, with approximately the same quality. The value of α_0 equals zero for sludge from model where iron salts was dosed. Better agreement of experimental and calculated α_0 values was gained with equation using zero value of α_0 also when iron salts were dosed, that is, Eq. (17).

The highest α_0 value corresponds to sludge from reference model (lower by app. two orders compared to sludge with Fe^{3+} or Al^{3+} dosing). Very low values of x parameter result for activated sludge from reference model or low specific filtrate resistance dependence on pressure difference.

4. Influence on anaerobic sludge digestion

Chemical precipitation of phosphorus produces metals' precipitates (Fe, Al). These are transported with the waste sludge to the digestion tanks where they occur at relatively high concentrations. The Fe precipitation's influence on the sludge anaerobic stabilisation process as well as on the sludge water quality was tested in this part of the work.

The Fe concentration increased in the digestion tank to app. 1000 mg L^{-1}. This, as a result of the simultaneous P precipitation in the activation, partially inhibited the CH_4 generation. When the load in the digestion tank reached 1.9 kg m^{-3} d^{-1} (kg sludge TS), the inhibition was 15–50%, depending on the number of the sludge inputs during the day. When the load decreased to 1.6 kg m^{-3} d^{-1}, the inhibition decreased to 5–20% depending on the number of sludge additions. The concentration of NH_4 and volatile fatty acids (VFA) in the digestion tank with Fe increased probably because the hydrolysis was stimulated and methanogenesis inhibited. Fe and P concentrations in the supernatant (sludge water) were minimal. On the other hand, the

stimulation effect on the process of anaerobic stabilisation was measured when applying lower concentration (below 400 mg L^{-1}) of the metal salts. These phenomena can be the consequence of the stimulation of hydrolysis as a first step of organic matter degradation or the elimination of sulphides by Fe precipitation.

The most important characterisation of situation in operated reactors with the anaerobic sludge stabilisation in relation to added Fe precipitates ($FePO_4$) wasted from lab-scale aerobic models with simultaneous phosphorus removal. Anaerobic digestion reactor under current conditions contains only trace Fe concentrations from the wastewater. However, anaerobic stabilisation reactor is subsequently filled with Fe precipitates due to the application of precipitation. Lower part of **Figure 10** shows the course of Fe concentration increase in the reactor during the experiments. Calculated courses predict the experimental Fe concentrations (calculation was done based on the Fe mass balance). Two breaks on the curve represent periods when the reactor was turned off, and no sludge was added to the reactor. The ratio of produced CH_4 volume in reactors with and without Fe feeding clearly shows that during the first phase of the experiment the biogas production was stimulated by added Fe. Since Fe concentration reached app. 400 mg L^{-1} (related to reactor volume) inhibition of the process was observed. During the interruption of the reactor's feeding, both long-term (18th–33rd day) or short-term (57th–60st day) biomass regeneration occurred. When the sludge was fed again, very significant stimulation of methanogenesis was observed. Within several days, the process was inhibited again. The inhibition is shown in details in **Figure 10** where are set daily produced amount of CH_4.

Relatively high differences in daily biogas volume production can be explained by the fact that digestion reactors were operated with small amounts of a real raw sludge for which the differences in organic content occur. For characterisation of Fe influence on methanogenesis, the most important is the top part of **Figure 10** showing the ratios of biogas volumes produced. After 50 days of experiment at Fe concentration over 800 mg L^{-1}, (reactor volume) the inhibition reached almost level of 50% compared with control model. During this period, that is, from the beginning of experiment to its 75th day, the digestion reactors were fed once a day. During following days, the feeding procedure was changed in order to eliminate significant level of inhibition. The sludge was added in the same way as at real WWTP, that is, more times a day (3 times a day). It is recommended to add raw sludge more than 2 times a day [25].

From **Figure 11** follows that the decrease in methanogenesis rate was related also to COD accumulation in the sludge supernatant, while the analysis shown preferable presence of acetate. The facts that the decrease in methanogenesis rate increased the COD of the sludge water and that the sludge regeneration stimulated the process indicate that not only the Fe but probably also the presence of volatile fatty acids (VFA) caused the inhibition. The accumulation of VFA could result not only due to the fact that slower methanogenesis did not remove all VFA, but also due to the fact that the Fe presence probably significantly increased the rate of hydrolysis and acidogenesis, which caused COD accumulation. Increased concentration of NH_4–N concentration can be also considered the factor of methanogenesis inhibition. From **Figure 11**, it can be seen that inhibition of methanogenesis rate, that is, the amount of removed COD/sludge is higher in the system without Fe.
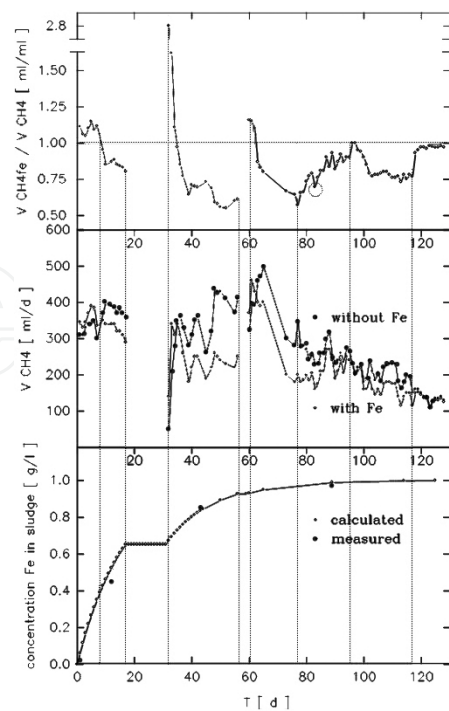
Figure 10. Time dependencies of concentration of iron precipitates and their influence on methane production during anaerobic sludge digestion.
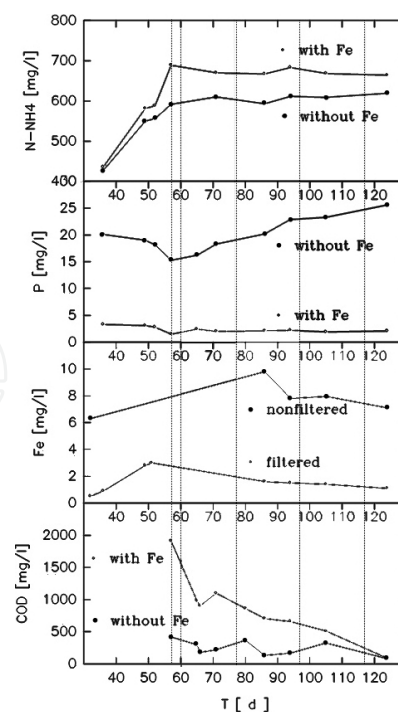

Figure 11. Time dependencies of concentration of ammonium nitrogen, phosphorus, iron and COD in sludge water during anaerobic sludge digestion.

5. Conclusions

Commonly used approaches to evaluate activated sludge activity through SOUR or specific substrate removal rate related to TSS are not fully satisfactory due to the presence of precipitates in activated sludge.

The content of VSS is a more representative quantity to relate the values of the specific rates performed by activated sludge from biological reactors operated with simultaneous chemical precipitation of phosphorus. The evaluation of respirometric measurements related to TOC content in activated sludge has proven to be the most convenient method of quantification of the effect of precipitant metals on activated sludge activity.

The decrease in SOUR of activated sludge microorganisms was observed at the initial stage of ferrous salts application. The maximum inhibition impact ranged from 2 to 6 h after the metal dosing. After the operation period of about 10 days, the values of SOUR increased. Stimulation of SOUR was observed at ferrous salts dosing. Only a small differences between the SOUR values with ferric or aluminium precipitants dosing and with sludge from control system were observed.

The highest efficiency of phosphorus removal was achieved in the bioreactor with aluminium precipitant. However, application of ferrous iron precipitant seems to be a more convenient technology of simultaneous precipitation of phosphorus due to the stimulation effect on activated sludge microorganisms activity.

Stimulation effects of ferric/ferrous salts on nitrification processes are evident. Stimulation of denitrification rates was observed for all systems with the higher stimulation in the ferric system.

The influence of dosed Fe^{2+}, Fe^{3+} and Al^{3+} salts on the sedimentation, thickening and dewatering characteristics of activated sludge was monitored with simultaneous precipitation of excess phosphorus. In addition to phosphorus elimination and activated sludge activity increase, also the improvement of sludge thickening and dewatering properties was observed.

Better description of experimental results was obtained with three parameters model of particles mass flow density curve. Comparison of minimum sedimentation tank size necessary for gravitational separation of each sludge was used to examine sedimentation characteristics of activated sludge.

Sedimentation and thickening rates increase when appropriate structure of activated sludge floccules is reached due to the higher mineral portion. Metals precipitates act as enhancement thickening agents when compared with control activated sludge thickening. The best sedimentation/thickening characteristics were reached for sludge from bioreactor where Fe^{3+} salts were dosed, while the worst sedimentation characteristics were observed in sludge with Al^{3+} dosing.

Maintaining the required sludge age with simultaneous chemical precipitation of phosphorus and unchanged volume of activation tank is accompanied with higher sludge concentration in activation, which results in higher values of particles mass flow to sedimentation tank.

Application of iron salts seems to be the best option for intensification of biological stage in existing WWTP with chemical phosphorus precipitation. Problems with creating conditions for gravitational sludge separation may occur when aluminium salts are dosed as this sludge is characterised with small and slowly settling floccules.

Thickening characteristics of sludge were evaluated based upon thickening area needed to maintain the required sludge concentration in activation or that corresponding to maximum surface load in non-dissolved substances.

The highest specific filtration resistance value was measured for activated sludge cultivated with iron salts doses, which is characterised also with the least throughput. The least value of specific filtration resistance was measured for sludge with iron salts dosing. Reference sludge was characterised by high throughput and low dependence of specific filtration resistance.

Precipitates in anaerobic digestion reactor resulted in partial inhibition of the methane generation. The concentrations of ammonium and volatile fatty acids increased, hydrolysis was stimulated, and methanogenic process was inhibited. The stimulation effect was measured for iron salts concentration lower than $400 \, mg \, L^{-1}$. The feeding procedure of raw sludge into digestion reactors three times a day resulted from performed lab-scale operation research on chemical precipitation of phosphorus impact on wastewater and sludge treatment processes as the most convenient one to eliminate significant level of sludge digestion process inhibition.

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Author details

Ján Derco[*], Rastislav Kuffa, Barbora Urminská, Jozef Dudáš and Jana Kušnierová

*Address all correspondence to: jan.derco@stuba.sk

Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, Slovak Republic

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