

MODELLING OF PHOSPHORUS REMOVAL IN PRESENCE OF NITRATES AND ITS INFLUENCE ON AN ENERGY RECOVERY FROM SLUDGE

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ABSTRACT

The paper describes second stage of investigations on specific operational problems which may occur in wastewater treatment plants of long term problem of nitrate presence in raw wastewater. Basic mechanism of EBPR i.e. release and uptake of phosphorus are based on growth and decay of microorganisms with the use of easy biodegradable carbon sources, presence of nitrites being active electron acceptors may adversely impacts this process. One of its unwanted results is higher than assumed consumption of easy biodegradable carbon. With the system supplying these electron donors via acidic fermentation may lead to direct overload of the biological reactor with pre-fermentation products. Finally in system with mesophilic fermentation of sludge as a processing method, it may lead to an unfavourable decrease of a biogas composition with diminishing of an energy recovery potential. Based on Wentzel's model of biodegradable matter circulation and use, some modelling proposal were prepared and data for verification came from operational tests on existing WWTP.

KEYWORDS

Phosphorus, modeling, sustainable development, WWTP operation optimization,

INTRODUCTION

Product of mesophilic fermentation of wastewater sludges i.e. methane rich gas called a 'Biogas' can be utilized as fuel for boilers and gas generators. This way, the overall energy costs at the WWTP can be substantially reduced. The volume of biogas produced during a mesophilic digestion phase as well as the methane content in the biogas can vary depending on the nature of the substrates delivered with raw (unstabilized) sludge. Investigation on this matter were presented by authors in previous papers of this series. The laboratory method selected for this study is the respirometric batch tests (Cimochowicz-Rybicka 1999, 2001). It appears to be the most precise method for determination of digestion parameters. The method focuses on biogas generation, which remains proportional to organic matter decomposition. Digestion is a biochemical decomposition of organic matter from sludge by bacteria. It is performed in four consecutive stages:

- ↓ hydrolysis
- ↓ acidification
- ↓ acetogenesis
- ↓ methanogenesis

The basic pre-requisite of proper operation of this process is a balance between substrates and quantity of bacterial microorganisms. As particulate matter cannot transfer through the

microorganisms cell it is required that organic and inorganic substrates are in soluble form. Conversion of an organic matter into methane and carbon dioxide leads to decrease of degradable organic matter content in sludge down to 50-55%. In some systems with enhanced biological phosphorus removal systems supported by acidic fermentation of a primary sludge lower net unit gas production has been observed. The problem which has been presented in this paper is related to study on estimation of a technically feasible digestion time for mixed (raw and WAS) sludges of a different composition focused on maximization of a methane-rich gas production under varying operational conditions. As a case study, the process of a sludge digestion process was examined in the sludge samples collected at the Nowy Sacz WWTP. This paper itself does not present final results, as it is still under tests. Some questions being asked, have not been answered yet so this paper reflects present status of experiments and modeling, related to common Polish-Swedish co-operation.

Case study highlights the problem

The problem arose during tests on Nowy Sacz WWTP which is the main test field for authors of this paper regarding optimization of methane recovery from sludges. As it was described previously (Rybicki S.M., Kurbiel J 2000), the Nowy Sacz WWTP has been designed for municipal wastewater treatment, servicing a community of 60000 inhabitants. It is in operation since 1996. Process layout is based on a UCT system. Sludge processing is of combined type:

- ◆ primary sludge is passing through a fermenter used for VFAs generation to gravity thickener where it reaches 3.5-5% of dry solids content then is pumped to a digester operated in mesophilic condition . Stabilized sludge is dewatered by centrifuge to 25% SS;
- ◆ WAS is simultaneously stabilized aerobically in the activated sludge reactors then thickened mechanically in drum screen; final dewatering is done by a centrifuge to approx. 18% SS;
- ◆ mixed dewatered sludge is blended with a quicklime (or with a cement) then transported to utilization in a landfill recovery;
- ◆ At present (September 2003) the sludge process is under conversion to common digestion of all process sludges on a mesophilic digestion way to increase energy production as well as to improve sludge dewatering characteristics (Kurbiel J., Rybicki S.M. 2000,2001; Kulig M., Rybicki S.M. Stanisz J., 2001). This was the first technical effect of long-term co-operation between Cracow University of Technology and WWTP owner i.e. Sadeckie Wodociagi Ltd.

Recognition of the problem occurred when it has been observed that respirometric tests on both raw-only and mixed sludges showed lower net unit gas production than it had been expected. Unit gas production reflects amount of gas produced, expressed in standard cubic meter per 1 kilogram of volatile suspended solid removed (similar results were obtained when amount of gas being produced per one kilogram of VSS supplied was measured). Results from full scale operation in year 2000 (1st half) has been presented in Fig.1. below. One should note than expected value is usually assessed as 0.9 to 1.0 Std m³ per 1 kG of VSS removed.

This relatively low unit gas production tended to decrease in summer months. Operational check of the plant's operation showed that this might be credited to intensive use of fermenters to decompose some part of an organic matter in raw sludge to less complexed carbon compound, mostly volatile fatty acids (VFAs), which in further step of biological treatment can serve as electron donors for EBPR and biological denitrification processes.

The WWTP based on a general MUCT concept was designed basing on a general assumption that no electron acceptors are present in raw wastewater, this included absence of nitrates which might disturb biological processes of phosphorus release and uptake in the reactor. The necessity for phosphorus removal was obvious (see Fig.2.), as a receiving water body was a Roznowskie Lake, an artificial reservoir. This requires until now 1.0 g TP/m³ concentration in an outlet as a maximum value, which was underlined in a water permit.

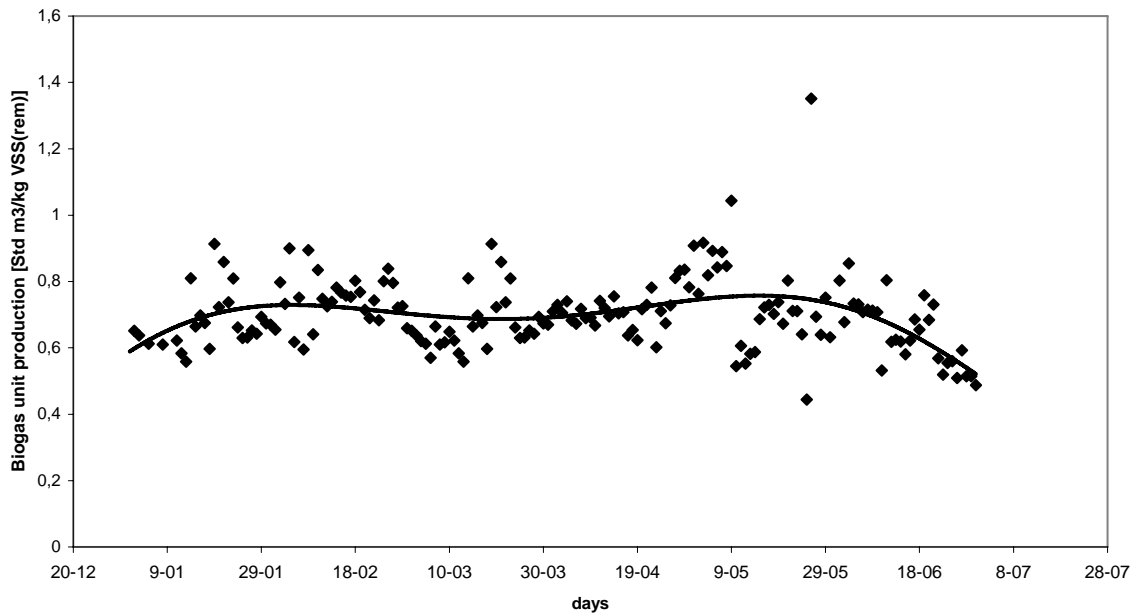


Figure1. Operational results and trendline of a biogas production in 1st period of observation – Nowy Sacz case study .

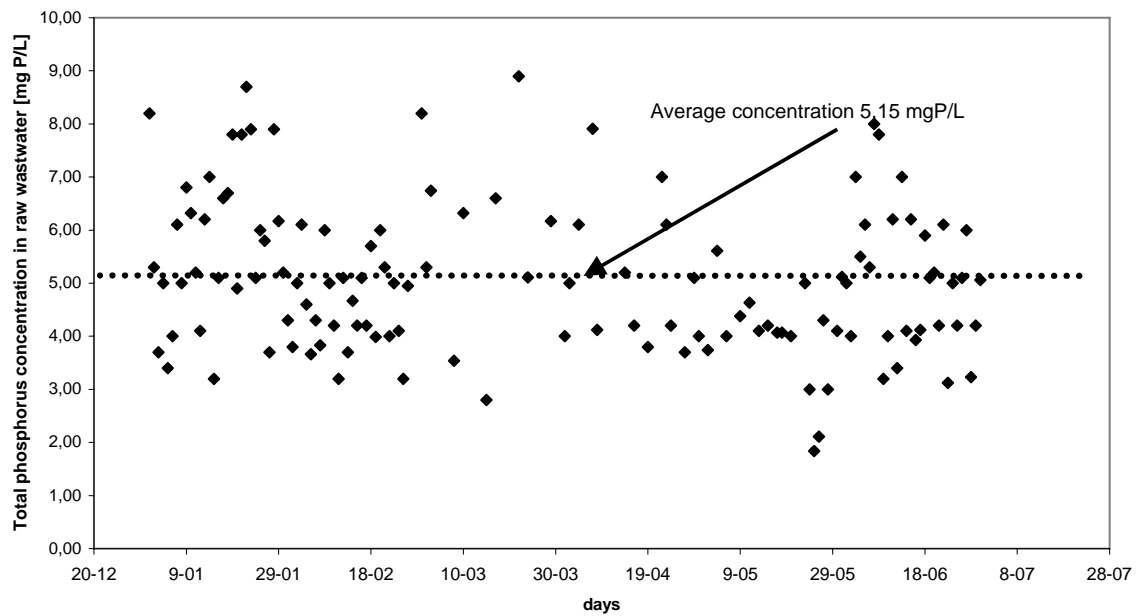


Figure2. Operational results and average value of total phosphorus concentration in raw wastewater in 1st period of observation – Nowy Sacz case study.

Identification of source of additional electron acceptors

Initial grab samples in 1998-1999 and later routine twice a week tests showed significant concentration of nitrates in raw wastewater with an increase in summer period. It was shown in Fig.3 for first half of year 2001 i.e. second period of study.

As it has been stated before, tests were made to identify source of electron acceptors in a wastewater train, with a specific seasonal changes. First concept was an identification of potential industrial (food processing) wastewater, but no such large load was identified within a service area. It was finally stated that these nitrates came from tap (potable water). This problem was not reported before due to local conditions:

- Nitrate concentration in raw water was not considered as significant problem as it was lower than maximum concentration level (10 mg N-NO₃/L – in accordance with Polish regulations);
- Seasonal changes was due to change of proportion of raw water withdrawn for potable water production which was in fact a mixture of groundwater, surface water and artificial infiltration; in case if majority of water volume originated from ground water increase of nitrite concentration in tap water than raw wastewater was observed;
- No significant regression was found between nitrate concentration in tap water and raw wastewater, however these values are bound as it was shown on Fig. 3.

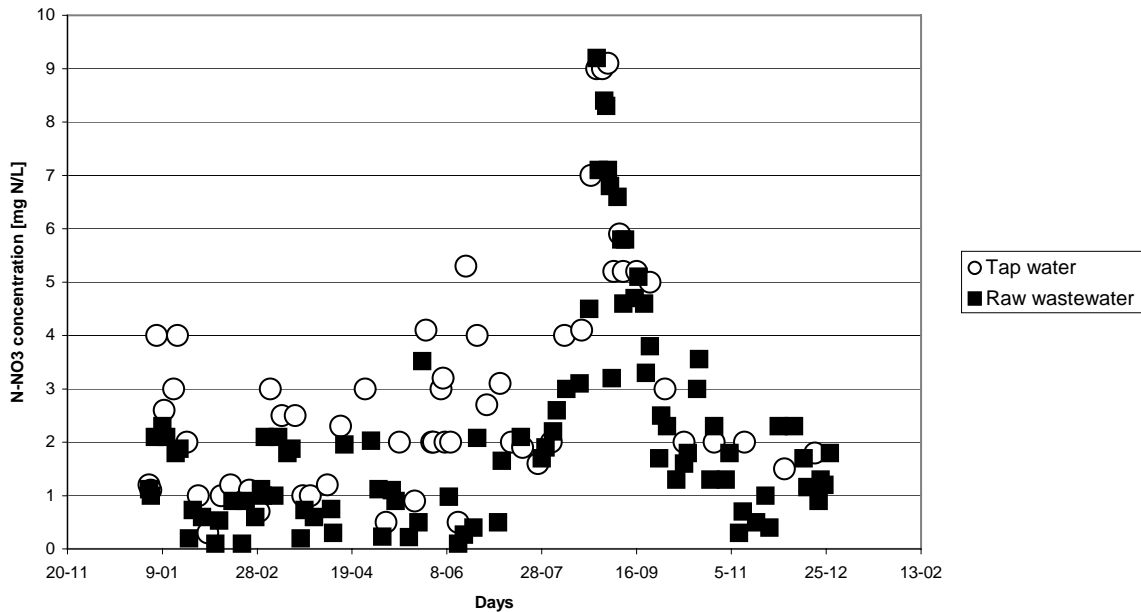


Figure 3. Nitrate nitrogen concentration in raw wastewater and in tap water in 2nd period of observation.

SELECTED ASPECTS OF PHOSPHORUS REMOVAL MODELLING

Necessity for phosphorus removal modeling in presence of nitrates

Presence of nitrates created two various group of problems. First is necessity for quick denitrification i.e. use nitrates as electron acceptors in anaerobic zone with such an intensity, that phosphorus removal process would take place, second – however related to the first is higher consumption of easily biodegradable carbonaceous matter.

Solving this problem in full scale operation is a proper choice of carbon source dosing (internal or external) control procedure: either feedback or feed forward mode. At first a feedback mode was used, mainly due to good experience in this type of control applied at first two years of operation for P-precipitation control (Rybicki, 1998). The simplified rule can be described as:

- Use of enhanced biological phosphorus removal process without continuous precipitation;
- Data regarding phosphates concentration in an effluent zone of secondary clarifiers were utilized as control factor; its increase resulted in higher demand for biodegradable carbon compounds, simply – higher volume of supernatant supplemented with some mass of hydrolyzed (fermented) primary sludge was added to treatment train;

Due to relatively longer response time, typical effect was that not only a supernatant large but also significant load of VFA-rich mass of hydrolyzed sludge was passing through sludge thickener being discharged to the treatment line prior to the reactor. Proportion between dry mass of sludge directed to treatment train and mass of sludge flowing to the digestion chamber thus being a source for a methane gas production has been presented in Fig.4. Another result of a feedback control strategy was extension of hydraulic retention time of sludge caused by operator, trying to produce as much VFAs as possible via extension of acidic phase of fermentation. Total (summarized) HRT in pre-fermentation unit and in gravity thickener was presented in Fig. 5. further.

Decrease of unit gas production mentioned above was credited by authors to the fact, that extended VFA production based on feed back control mode combined with limited possibility of sludge discharge control led to two unfavorable results:

- Lack of control of real need for easily biodegradable carbon source for processes;
- Decrease of potential substrate for mesophilic fermentation due to conversion of large load of primary sludge to VFA to be used in a wastewater treatment train.

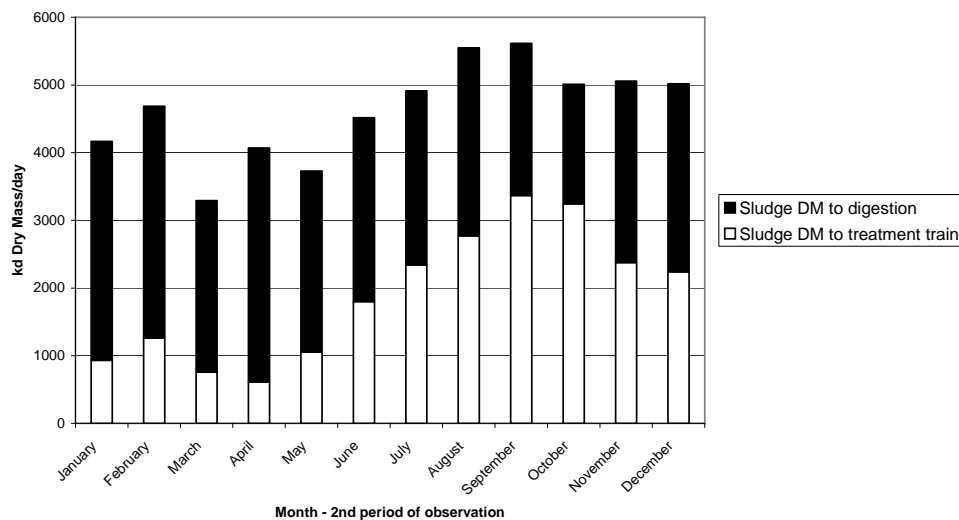


Figure 4. Distribution of fermented sludge by dry mass – monthly average value, 2nd period, feed back control mode.

Modeling processes related to organic matter consumption in denitrification for process control

Observations, mentioned above led to one general conclusion that process control should be considered as feed-forward mode. Existing commercial modelling Tools (e.g. steady state SASSPro V2 model) as well as dynamic models based on ASM 2 models are not developed for nitrate presence in anaerobic zone of multi-stage biological reactor (ASM 1 as well as all IWA Model Nr 1

– related models does not incorporate fully applicable biological phosphorus removal. Such an attempt require application of process model which will show real requirements for carbon source for phosphorus release and uptake with occasional occurrence of nitrates.

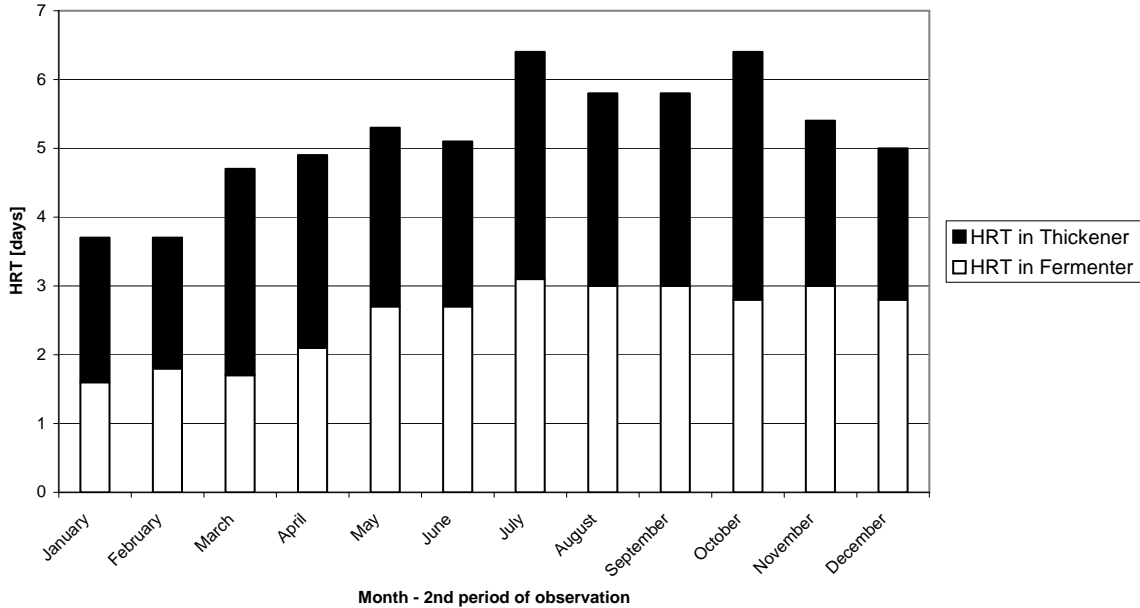


Figure 5. Real HRT in prefermentation module – monthly average value, 2nd period, feed back control mode.

Similar problem of design tool for existing WWTP was considered among others by Wik et al (Wik et al. 2003). They described procedure of modeling nitrate conversion with exact calculation of organic matter use (carbon compounds) with a special emphasis on feed forward control, solving this problem assuming that the WWTP can be illustrated as $i=1,2,\dots$ reactors connected in series. Wik however did describe Anoxic/Oxic type reactor, but this attempt seems to be applicable in solving problem described. Based on double Monod kinetics, chosen for assessment of degradation rate of readily biodegradable substrate by denitrification in anoxic conditions.

Starting point was a double Monod kinetics:

$$r(S_N, S_C) = \eta * \frac{\mu}{Y} * X * \frac{S_N}{S_N + K_N} * \frac{S_C}{S_C + K_C} \quad (1)$$

Nitrate concentration mass balance in the reactor's stage was proposed:

$$V_i \frac{dS_{N,i}}{dt} = Q_i * (S_{N,i+1} - S_{N,i}) - \frac{V_i}{K_{C,N}} * r(S_N, S_{C,i}) \quad (2)$$

Donor inlet to the reactor is represented by COD in accordance with the equation (3):

$$V_i \frac{dS_{C,i}}{dt} = Q_i * (S_{C,i+1} - S_{C,i}) - V_i * r(S_{N,i}, S_{C,i}) \quad (3)$$

Nomenclature for equations (1) to (3)

Q	Flow through the reactor/stage of the reactor
S_N	Nitrate concentration
S_C	Carbon source concentration
η	coefficient expressing lowered efficiency due to use of nitrate instead of oxygen
V_i	Reactor's volume
r	rate

Authors (Wik et al. 2003) assumed that no nitrate was present after primary settling tank, so even if the general description of the model could be applied for specific part of the WWTP being described, the way of solving problems was to consider technical changes. These suggested changes were based on construction of additional pre-denitrification chamber, as a part of original anaerobic zone (stage) of the reactor. This was proposed to ensure lack of electron donors in the Bio-P stage. Wik et al also simulated a feed-forward control system basing on theoretical assumptions presented above. Process PLC is to get signal regarding nitrate level in the wastewater flow to the reactor. Three feed forward control strategies:

1. Use of signal for full strength at all times;
2. Blocking control signal, when the effluent concentration of nitrites is low
3. Mixed strategy.

All these strategies are workable with no limitation of degradable carbon source. In case of the Nowy Sacz WWTP, this attempt seems to be useful for denitrification chamber control, and was abandoned by authors of this paper as first attempts of modelling for real values.

Modelling phosphorus release and uptake

Since presentation of a SIPHOR model for EBPR by P. Johansson (Johansson, 1994), some proposals were made, all based on a general observation from laboratory tests on uptake VFAs (SCFAs) by phosphorus accumulating organisms (PAO) and storage as polyhydroxyalkanoates (PHA) (Hu et al. 2002). This however requires purely anaerobic conditions thus rapid denitrification is a kind of prerequisite for this process. Regarding a biomass growth it must be noted that (according to Wentzel et al.) PAOs show real growth only in aerobic conditions and no significant growth was observed under anoxic conditions. Developing a UCTHO model Wentzel suggested however, that in specific case of nitrate presence in anaerobic chamber PAO denitrification parallel with anoxic P uptake should be considered. These observations led to ASM 2 model. This model calculated growth based on two groups of carbonaceous matter: VFA (SCFA) and fermentable RBCOD, with the general observation that in properly working process, almost all VFAs are taken by PAOs. ASM model incorporated some new description of the hydrolysis as it was stated, that hydrolysis of slowly degradable organic matter can take place in anaerobic conditions. A reducing factor n_F was proposed for real modelling. Metabolism of PAO microorganisms under aerobic conditions (phase) were described using five stoichiometric pathways ((HU et al. 2003):

- Polyhydroxybutyrate (PHB) degradation
- Oxidative phosphorylation
- Biomass synthesis from PHB as substrate
- PolyP synthesis and P transport
- Glycogen production using

Modification of ASM model named ASM2d was the first one to incorporate anoxic processes for PAOs:

- Growth of PAOs under anoxic conditions and with the use of stored PHA;
- Use of energy stored in PHAs to take up P and store it in a form of Polyphosphates.

Szetela and Dymaczewski (2002) suggested modification of this model. They modified the equation describing organic compound storage (rate) from its original ASM 2d form (equation 4):

$$\rho_{10} = q_{PHA} * \frac{S_A}{K_A + S_A} * \frac{S_{ALK}}{K_{ALK} + S_{ALK}} * \frac{\frac{X_{PP}}{X_{PAO}}}{K_{PP} + \frac{X_{PP}}{X_{PAO}}} * X_{PAO} \quad (4)$$

to the more complexed form, which contains two additional factors against built-in of PHAs into a biomass in anaerobic as well as anoxic conditions equation (5).

$$\rho_{10} = q_{PHA} * \frac{S_A}{K_A + S_A} * \frac{K_O}{K_O + S_O} * \frac{K_{NO}}{K_{NO} + S_{NO}} * \frac{S_{ALK}}{K_{ALK} + S_{ALK}} * \frac{\frac{X_{PP}}{X_{PAO}}}{K_{PP} + \frac{X_{PP}}{X_{PAO}}} * X_{PAO} \quad (5)$$

Nomenclature for equations (4) to (5) is standardized for IWA models

$K_A, K_O, K_{NO}, K_{ALK}, K_{PP}$	- kinetic constants
S_O	- dissolved oxygen concentration;
S_{NO}	- nitrate concentration;
X_{PP}	- polyphosphates concentration;
X_{PAO}	- concentration of PAOs
S_{ALK}	- alkalinity,

The ASM 3 model (Koch et al. 2001) included facts that phosphorus effluent concentration depends on more factors. Important was identification of particulate phosphorus removed with excess sludge. In real term it is a sum of three ‘sub-fractions’:

- Inorganic calcium precipitated phosphates;
- Physiological P i.e. used for growth of the activated sludge biomass;
- Polyphosphat taken by PAOs (to some extent this part is responsible for a ‘luxury uptake’ as this process phenomena was named in 70s)

General decryptions of phosphorus concentration in effluent is as shown in equation (6):

$$C_{P,e} = C_{P,o} - X_{P,org} - X_{P,inorg} - X_{PP} + i_{P,COD} i_{COD,TSS} X_{TSS,e} \quad (6)$$

where: $i_{P,COD} i_{COD,TSS} X_{TSS,e}$ represents particulate phosphorus in suspended solids leaving the system. But still modelling of phosphorus removal processes is recognized as not final one due to relatively margin of uncertainty.

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CONCLUSIONS

- Paper describes results of first stage of investigations on phosphorus removal control in temporary presence of nitrates in raw wastewater; it describes problems recognized and selection of a way to solve these problems.
- Proper model of phosphorus removal is necessary for feed forward control of biological treatment plant with enhanced biological phosphorus removal, especially while optimisation of plant's performance is difficult due to untypical factors. In the specific case, being described, nitrates create this problems;
- Improper control system may adversely affect not only biological reactor itself, but also may create operational problems in other part of a WWTP for example it may significantly decrease energy recovery.
- Of recognized process models ASM 2d and ASM 3 ones seems to be applicable; modification proposed by Szetela and Dymaczewski should be verified as promising description of the model.

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