# SELECTED IMPACT OF ENHANCED PHOSPHORUS REMOVAL ON WASTEWATER SLUDGE PROCESSING

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**Abstract**
The paper presents some problems related to enhanced biological phosphorus removal. In case of municipal wastewater need for electron donors leads either to addition of external sources of carbon such as ethanol, methanol or acetic acid or an internal source must be applied. The internal source means usually a mixture of short chained fatty acids produced from sludge on the way of hydrolysis. Full-scale investigations supported by laboratory tests enlightened some specific operational problems which may occur in wastewater treatment plants with an intensive acidic generation. Higher then assumed consumption of biodegradable carbon is usually one of adverse unfavorable effects. During full-scale tests on supplying the treatment train with required electron donors via acidic fermentation it was found that it frequently led to direct overload of the biological reactor with pre-fermentation products. The system with mesophilic fermentation of sludge as a stabilization method a significant decrease of a biogas production was proved.

**Key Words** Phosphorus removal, nutrient removal, biogas generation, sustainable development, WWTP operation optimization, EBPR, sludge processing,

## INTRODUCTION

Multi-phase biological reactors are at present most commonly applied process technology in municipal wastewater treatment. These reactors create proper technical conditions to perform three main groups of processes in one technical facility. These are:

- Conversion of an organic matter contained in raw sewage into an 'activated sludge' which is a biomass (also its products of respiration such as; carbon dioxide and water). Extension of this biomass is wasted from a system as so called "sludge (wasted activated sludge);
- Incorporation of surplus amount of phosphorus into a biomass during consecutive exposure of a biomass to anaerobic and aerobic conditions;
- Conversion of an organic nitrogen and ammonia which are main nitrogen compounds in raw wastewater into oxidized form: nitrites and nitrates (nitrification) and finally release a gaseous nitrogen into an ambient atmosphere (denitrification);

The most sensitive process appears to be an enhanced biological phosphorus removal (EBPR), so these multiphase reactors used to be dimensioned with respect to ensure proper amount of readily biodegradable carbon compounds prior an anaerobic zone. In case of municipal wastewater a significant need for electron donors leads either to addition of external sources of carbon such as ethanol, methanol or acetic acid or an internal source must be applied. The internal source means usually a mixture of short chained fatty acids produced from sludge on the way of hydrolysis and acidic fermentation. These compounds are usually expressed as the easy biodegradable COD.

In the process of the EBPR bio-P bacteria (usually *Acinetobacter* but also *Klebsiella* species ) release phosphate under anaerobic conditions from polyphosphates being stored within the cell. The energy which is available from the hydrolysis (from breaking polyphosphate chains) is being used for storage of organic material within the cell. Under aerobic conditions this stored material is utilized while energy for growth and energy for phosphate storage is obtained via respiration.

The net overall effect is storage of phosphorus within an activated sludge cells in proportion higher than under normal conditions. Phosphorus creates as high as 6-8% of a total biomass weight while under normal conditions it is approximately 2%. This phenomena is called "luxury uptake"(Carlsson et al, 1996, Ekama et al 1999, Barnard 2000). Some authors reported as high as 20% P in biomass while pure cultures of bacteria were tested but it is not a min focus of this paper.

## SCFA ROLE IN EBPR PROCESSES

Ratio of phosphate released to substrate taken up during the anaerobic phase is a crucial parameter in determination whether an overall process is performed properly. Access of proper substrate for release (and further uptake) of phosphorus is necessary. Until beginning of 1990s main source was of an 'external' type such as: ethanol, glucose, glucose, starch or specific fruit processing wastewater. Since mid 1990s performance of a primary sludge fermentation to obtain a mixture of a short chained fatty acids – SCFA (or volatile fatty acids – VFA) became a standard routine procedure in WWTPs operation. These soluble easily biodegradable compounds should be delivered in such amount (concentration) that both needs for enhanced phosphorus and biological denitrification processes must be ensured. (Barnard 1994).

### Methodology

Data regarding wastewater quality (raw, settled, treated) as well as sludge parameters were completed by the WWTP laboratory on daily composite samples. Cracow University of Technology laboratory completed tests on phosphorus release rate (PRR). As a source of the SCFA a supernatant from pre-fermenter were applied. The pre-fermenter was a full-scale operational unit with SRT = 3,75 d, being fed with a primary sludge only.

The ratio of phosphate release to substrate uptake is calculated the difference between the phosphate release during an uptake and the substrate release without substrate uptake (Moser-Engeler et al, 1998). They were re-calculated in molP/mol SCFA in Figure 1. This figure shows average, minimum and maximum values from tests also some data for single SCFA as published by Moser-Engeler et al. were presented.

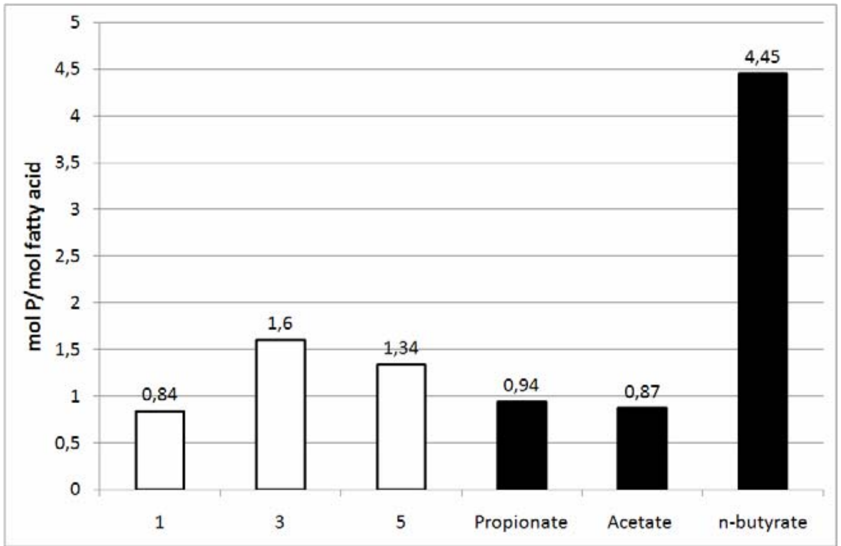


**Figure 1.** Substrate release rates for real-terms values (white ribbon) and single fatty acids (by Moser-Engeler – black ribbon), T=20$^{O}$C.

In the uptake phase the kinetics also differs with respect to a type of fatty acids, data from the same sources were presented in Figure 2, when a differences in uptake rates, expressed in mg COD/mgCOD (p)/d. COD(p) means particulate COD of an activated sludge.

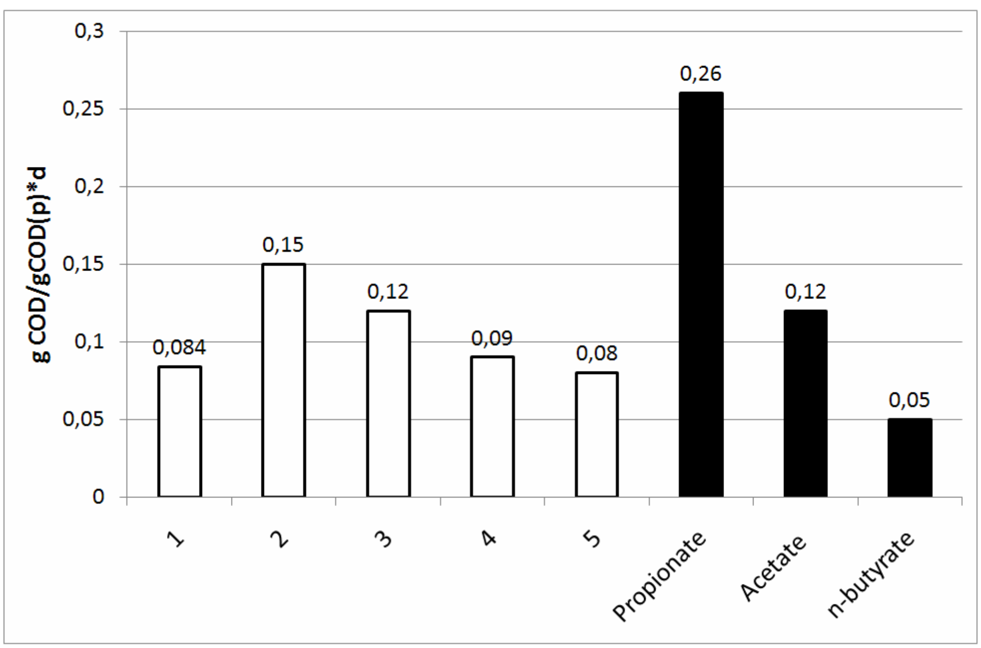


**Figure 2.** Substrate uptake rates for real-terms values (black ribbon) and single fatty acids (by Moser-Engeler – white ribbons), T=20$^{O}$C.

In general terms both author's experiments and literature references confirmed that linear fatty acids are initially being degraded but the decrease of branched fatty acids is very slow. When these lnear fatty acids were consumed, the substrate uptake rates for an iso-butyrate and also 2-methyl butyrate increased.

Presence of nitrates is a specific problem which may adversely impact release/uptake sequence. Main operational problem appears to be a necessity for efficient denitrification i.e. use nitrates as electron acceptors in anaerobic zone with such intensity, that phosphorus removal process would take place. Related to this is second problem i.e. higher consumption of easily biodegradable carbonaceous matter (Rybicki 2005). It was earlier recognized by some authors (Shung-Hsing et.al, 1996, Kuba et al. 1997) that nitrate presence reduced phosphorus release rate. Also a denitrification had a higher activity than P-release mainly due to sequestrating of easy biodegradable COD.

**Role of fermentation products in EBPR systems**

Mixture of short chain fatty acids produced during the first step of anaerobic digestion (hydrolysis and acidogenesis) can be applied in conventional flow-through WWTPs. Its simplified description is a conversion of substrate organic matter through a hydrolysis into a fermentable soluble carbon compounds into fermentation products. Diagram on Fig.3. (Mino et al,1995) shows an organic substrate transformation process under anaerobic conditions. The overall process is as follows:

- Slowly biodegradable substrates ($X_S$) are hydrolyzed to fermentables ($S_F$);
- Fermentable substrates are fermented to fermentation products ($S_A$)– mixture of SCFA, also expresses as $COD_{EB}$
- Bio-P bacteria (phosphate accumulating organisms) utilize only $S_A$ to for anaerobic storage of polyhydroxyalkanoates (PHA)
- In successfully operated reactors the specific rate of $X_S$ hydrolysis is considerably lower then the specific rate of $S_F$ fermentation and $S_A$ utilization; this phenomena one can check comparing concentration of $S_A$ and $S_F$ versus $X_S$ in an activated sludge. It means that the hydrolysis is the rate limiting process of substrate utilization.

$$X_S \xrightarrow[\text{Hydrolysis}]{} S_F \xrightarrow[\text{Fermentation}]{} S_A \xrightarrow[\text{Storage}]{} X_{PHA}$$

**Figure 3.** Organic substrate transformation under anaerobic conditions

**IMPACT OF PRIMARY (ACIDIC) FERMENTATION ON SLUDGE PROCESSING**

The paper describes first phase of investigations on specific problem when intensive generation of SCFAs from a primary sludge created operational problems in sludge processing train. Initial attempt in full-scale operation was to improve a SCFA production in a side-stream pre-fermenters through increase of the sludge SRT in pre-fermentation unit. It resulted in higher volume of supernatant supplemented with some mass of hydrolyzed (fermented) primary sludge was added to treatment train. Due to relatively longer response time, two effects were observed:

- High TSS concentration in a supernatant
- Significant load of VFA-rich mass of hydrolysed sludge passing through sludge thickener being discharged to the treatment line prior to the reactor.

The mass balance at this stage differed from expected values (Oleszkiewicz et. al. 2000), however eeffluent total phosphorus concentration (i.e. below 1 ppm) was obtained at proper frequency.

Recognition of the problem occurred when it has been found that respirometric tests on both raw-only and mixed sludge showed lower net unit gas production than it had been expected. Results from full scale operation have been presented in Fig.4.

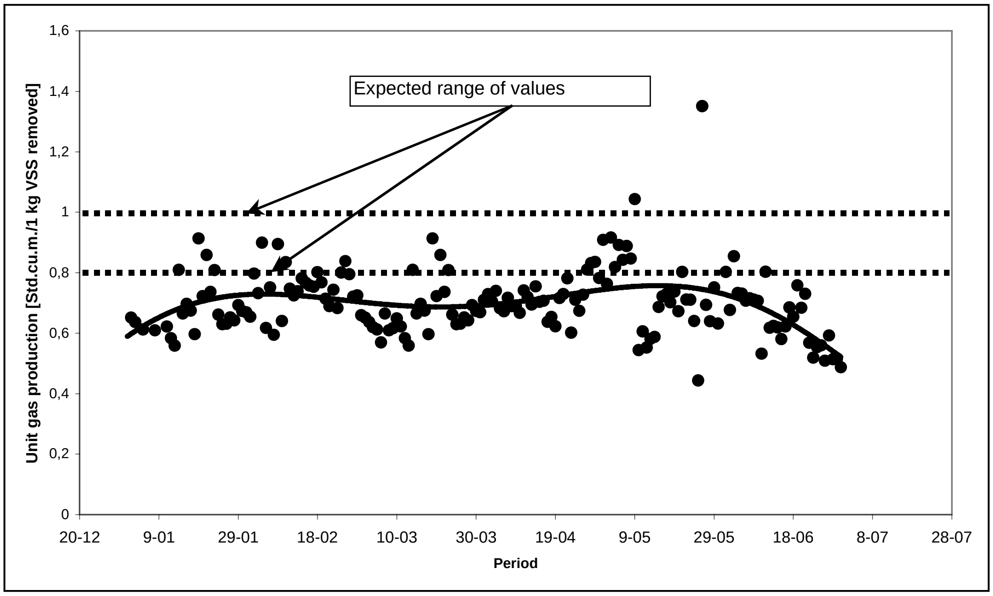


**Figure 4.** Operational results and trend line of a unit biogas production

In the sludge digestion process a decrease of organic matter content (VSS) is achieved through a conversion of organic material, captured in raw sludge, to a mixture of methane and carbon dioxide. The process is conducted in anaerobic conditions. The mixture is commonly known as “digestion gas” or “biogas”.

Biogas with a high methane content 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. Operational check of the plant’s practice showed that this might be caused by an intensive use of pre-fermenters to decompose some part of an organic matter in raw sludge to less complexed carbon compound, mostly SCFAs which in further step of biological treatment can serve as electron donors for EBPR and biological denitrification processes. Decrease of unit gas production mentioned above was credited by author to the fact, that extended SCFA production with limited possibility of sludge discharge control led to use of potential substrate in a wastewater treatment train instead of an use for mesophilic fermentation. Further experiments and modeling attempts were addressed towards a hypothesis that intensive acidic fermentation if pre-fermenters may adversely impact a biogas production. That means that generation of easily biodegradable COD ($S_A$) may use such a portion of slowly degradable matter ($X_S$) that it may influence a methanogenesis in anaerobic digesters. This observation may help in operational optimization of municipal WWTPs.

**Methodology**

The laboratory method selected for this study was the respirometric batch tests (Cimochowicz-Rybicka, 2001) for checking a net biogas production from a sludge from thickeners after full-scale

pre-fermentation. The method focuses on batch test on a biogas generation, which remains proportional to organic matter decomposition. Initial investigations covered year-and-half period of 2003-2004 divided into three periods of investigations with regard to mode of phosphorus removal.
Main test confirming proper operation of a EBPR plant were phosphorus release rate (PRR) tests. These were conducted in grab samples to check process performance with a surplus of carbon sources. Representative results (4 out of 15) obtained are summarized in table 1, they were slightly different than expected i.e. release of phosphorus was sometimes below 3.0 mgP/gMLSS/h . (One can note different units of PRR – due to modeling reasons – than applied in Fig 1 this paper).

## METHODS AND MATERIALS

### Laboratory equipment for the respirometric test

The experimental instruments applied for tests on productivity of the digestion gas included:

- ANR-100 respirometer for anaerobic experiments, US made by the CHALLENGE Syst. Int.;
- Water bath with magnetic mixer
- Computer program for automatic data collection and processing

### Assumptions for batch test investigation

| | |
|---|---|
| *Experimental methodology:* | batch tests |
| *Period of experiment:* | ca. 30 d, this period is to be adjusted due to sludge acclimation |
| *Temperature*: | the incubation temperature: 35$^{o}$C. |
| *Experimental system*: | a magnetic stirred system |
| *Volume of samples*: | 500 mL glass vessels |
| *Chemical analyses*: | |
| - basic: | suspended solids (SS), volatile suspended solids (VSS) |
| - reference: | pH, alkalinity, COD, ammonium |
| *Gas measured system*: | anaerobic respirometer ANR-100 |
| *Determination of methane percentage of gas volume*: | gas chromatographic analysis |

**Table 1.** Phosphorus release tests under various conditions – grab samples.

| Sample No | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| Sludge SRT [day] | 1,6 | 3,3 | 3,45 | 4,1 | 5,5 | | |
| P-release [mgP/gMLSS/h] | 2,4 | 3,9 | 4,12 | 4,6 | 4,0 | | |

According to the literature data, the volume of biogas generated during anaerobic decomposition of 1 kg of organic material amounts to 900-905 $dm^3$. However, in the tests these values ranged between 500 -750 $dm^3$/kg VSS removed. The volume of biogas produced per 1 kg of VSS supplied to the system ranges from 400 to 600 $dm^3$. An average biogas volume, produced at the wastewater treatment plant is assumed as 480 $dm^3$/kg VSS removed.

**Mathematical formulation of problem being tested**

Mathematical formulation of the problem was based on a general idea that further investigation results will be re-calculated for a $COD_{EB}$ as a measurement of a easily available carbonaceous matter. Assumption based on previous observation was that two parallel hydrolysis processes take place i.e. fast and slow hydrolysis. Probably in case of long SRT pre-fermentation is based on fast stage mostly so with the SA products available after this stage slow fermentation will takes place which impacts on overall biogas production. This will standardize – to some extent – further experiments with an ASM models. The concept was based on Vollersten et al (2006).

**Table 2.** COD characterization in hydrolysed sludge (by Vollersten et al)

| Process | $S_A$ | $X_{S,fast}$ | $X_{,slow}$ | $X_{Bw}$ | $-S_0$ | Process rate |
|---|---|---|---|---|---|---|
| Hydrolysis, fast | 1 | -1 | | | | $k_{h,\,fast} * \frac{X_{S,\,fast}/X_{Bw}}{K_{X,\,fast} + X_{S,\,fast}/X_{Bw}} * X_{Bw}$ |
| Hydrolysis, slow | 1 | | -1 | | | $k_{h,slow} * \frac{X_{S,slow}/X_{Bw}}{K_{X,slow} + X_{S,slow}/X_{Bw}} * X_{Bw}$ |
| Maintenance energy requirement | -1 | | | *See NOTE below* | 1 | $q_m * X_{Bw}$ |

**Parameters:**

| | | |
|---|---|---|
| $k_{h,\ fast}$ | hydrolysis rate constant of $X_{S,\ fast}$ | $[d^{-1}]$ |
| $k_{h,\ fslow}$ | hydrolysis rate constant of $X_{S,\ slow}$ | $[d^{-1}]$ |
| $K_{X,\ fast}$ | Saturation constant, hydrolysis of $X_{S,\ fast}$ | [gCOD* gCOD $^{-1}$] |
| $K_{X,\ slow}$ | Saturation constant, hydrolysis of $X_{S,\ slow}$ | [gCOD* gCOD $^{-1}$] |
| $q_m$ | Maintenance energy requirement rate constant | $[d^{-1}]$ |
| $X_{Bw}$ | Heterotrophic biomass | [gCOD*m$^{-3}$] |
| $X_{S,\ fast}$ | Fast hydrolysable substrate | [gCOD*m$^{-3}$] |
| $X_{S,slow}$ | Slow hydrolysable substrate | [gCOD*m$^{-3}$] |

NOTE: If $S_A$ concentration is not sufficient, the $X_{Bw}$ is used as a source of $COD_{EB}$ via endogenous respiration.

Also one should remember that pre-fermenters' operation takes place in temperature approx 20$^o$C, while temperature in a digestion chamber working in a mesophilic mode is almost twice higher (35$^o$C).

**CONCLUSIONS**

- Enhanced biological phosphorus removal systems usually require higher concentration of easily biodegradable carbonaceous matter that it is available in municipal raw wastewater. Short chainy fatty acids appear to be reliable source to be used in routine operation of WWTPs.
- SCFA generation of primary sludge delivers required amount of an electron donors and the multi-pase reactor in the treatment plant, can be successfully operated without chemical addition

- Proper strategy of phosphorus removal is necessary, especially while optimisation of plant's performance is difficult due to untypical factors. In described specific case, contradiction between needs for acidic fermentation products for EBPR processes and a biogas production were main obstacle in proper operation.
- Improper system control – overloading of pre-fermentation unit 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.

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