BIOLOGICAL RELEASE OF PHOSPHATES FROM SEWAGE SLUDGE AFTER CHEMICAL PRECIPITATES

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ABSTRACT
Phosphates present in municipal sewage in the main stream as well as in the side stream (sludge processing stream) are often removed by precipitation with ferrous sulphates. This results in sulphates increase in treated sewage on one hand, and production of sludge of limited agricultural use on the other. Investigations on biological release of phosphates under anaerobic conditions has been carried out on a relatively large laboratory scale model. An anaerobic fixed bed filter of a volume of 12 litres was used. With a hydraulic load of 0.013 $m^3/m^2 \cdot h$ the hydraulic retention time (HRT) was 5 days. The filter was thermostated at a constant temperature of 30 $^{\circ}C$. Phosphates present in treated waste water have been precipitated out with ferrous sulphate - $Fe_2(SO_4)_3$. With the increase of the amount of ferrous sulphates added, a decrease in pH was observed. In the range of pH 4 to 6, phosphates were precipitated as $FePO_4$, while at pH above 7 in the from of $Fe_3(PO_4)_2$. Under anaerobic conditions ferrous sulphides are produced but no free hydrogen sulphide was detected. In parallel to sulphates reduction an increase in phosphates in the solution was measured. Efficiency of biological processes of phosphates release was assessed on base of microbiological investigations of sulphates reduction and phosphates concentrations in the supernatant liquor. The carried out investigations have shown the feasibility of biological phosphates recovery.

KEY WORDS
Phosphates, chemical precipitation, SRB bacteria, phosphorus bacteria.

INTRODUCTION

Phosphates compounds are present in high concentrations in several municipal and industrial wastewaters. Chemical phosphates removal is the most often applied method at sewage treatment plants. Chemical precipitation of phosphorus is possibility with alum or iron salts. Most often iron salts are used, both forms as ferrous Fe (II) and/or ferric (III) sulphates.

$$3\,FeSO_4 + 2\,PO_4^{3-} \rightarrow Fe_3(PO_4)_2\downarrow + 3\,SO_4^{2-} \qquad \text{(i)}$$
$$Fe_2(SO_4)_3 + 2\,PO_4^{3-} \rightarrow 2\,FePO_4\downarrow + 3\,SO_4^{2-} \qquad \text{(ii)}$$

They are used in the from of chloride to:

$$FeCl_3 + PO_4^{3-} \rightarrow FePO_4\downarrow + 3\,Cl^{-} \qquad \text{(iii)}$$
$$3\,FeCl_2 + PO_4^{3-} \rightarrow Fe_3(PO_4)_2\downarrow + 6\,Cl^{-} \qquad \text{(iiii)}$$

The effects of phosphates removed with alum or iron salts are 70 to 90 % , and depend on: pH, phosphates concentration, kind and portion of salt, suspended mater etc. The molar ratio of Fe : P is 1 : 1 (reaction ii and iii). That is that 163.3 g of $FeCl_3$ will react with 95 g PO_4^{3-} to form 150.8 g $FePO_4$. The weight ratio of Fe : P is 1.8 : 1, while the weight ratio of $FeCl_3$: P is 5.2 : 1. The molar ratio of Fe : P is 3 : 2 (reaction i and iiii), while the weight ratio of the ferrous ion to phosphorus is 2.7 : 1.

Medium and large wastewater treatment plants are obliged to remove phosphates respectively to the level of 2.0 to 1.0 mg $P_{tot.} \cdot l^{-1}$. Chemical precipitation is a relatively easy and not very expensive process. Phosphate precipitation with ferric ion is more effective in anaerobic conditions. Most of the retained phosphorus from biological processes (surplus sludge) and from chemical precipitations (chemical precipitate) is commonly transferred to the anaerobic sludge digestion processes at treatment plants. In the anaerobic sludge digestion process phosphates from surplus sludge and chemical precipitates are released to the supernatant liquor. Sulphate reducing bacteria can effectively release phosphate from Fe-P sludge, (Suschka, 2001). Rydin (1996) studied in the laboratory, the release of phosphates from Fe-P and Al-P sludge at several municipal sewage treatment plants and found a much higher release rate from sludge under anaerobic conditions. The aforementioned author (Rydin, 1996) also noted that water passing through a sewage sludge layer spread over the land will remove phosphates under anaerobic conditions and there could be a smell of hydrogen sulphide – H_2S noticed. In the literature no other reference could be found about the correlation between sulphide development in anaerobic conditions and phosphorus release. The processes of phosphorus release and sulphates reduction were carried out due to microbiological activity, in this case the Sulphur- Reducing Bacteria (SRB). The SRB bacteria cells are spherical, ovoid, rod – shaped, spiral, or vibroid-shaped. They are occurring as singly, in pairs, or sometimes in aggregates. The morphology and feasibility to produces spores and the growth ability in the characteristic temperature range for mezo- and thermophilic micro-organisms have been determined. The SRB bacteria are strictly anaerobic. Under anaerobic conditions sulphate is converted by SRB to sulphide. Different source of carbon, such as: lactate, acetate, malate, formate and glucose were utilised. Sulphur-reducing bacteria were identified in accordance to Bergey systematic.

MATERIALS AND METHODS

For the carried out experiments the material used was taken from municipal sewage treatment plants. Two parts of experiments can be distinguished. First, phosphates present in the supernatant liquor after sludge digestion process and centrifuged were precipitated chemically with iron sulphate – $Fe_2(SO_4)_3$, of a commercial name - PIX. Chemical sludge and raw municipal sewage were mixed in the ratio 3 :1, in order to increase COD to enhance the microbiological processes.

Secondly, the substrate the chemical sludge in admixture with sewage were supplied to the anaerobic biological filter. Phosphates from the substrate were released in the anaerobic biological process to the liquor and sulphates were reduced to sulphides. In the same process iron was reduced from Fe^{3+} to Fe^{2+} and iron sulphides – FeS were precipitated.

Anaerobic biological filter.

A laboratory scale anaerobic filter of a diameter of 10 cm and a high of 1.5 m was used. The model of the anaerobic filter was shown in fig.1.The anaerobic reactor was constructed as a PVC tube filled with polypropylene rings. The active volume of the reactor was 12 liters. The substrate was continuously supplied to the reactor by a pump at a flow of 0.1 l/h, the hydraulic load was 0.013

m^3/m^2h. The anaerobic reactor was installed in a temperature-controlled chamber, where the constant temperature (30 ^oC) was maintained.

Analytical Techniques
Samples taken of the influent and effluent were analyses for: pH, temperature, redox (oxidation – reduction potential), phosphates, chemical oxygen demand (COD), sulfates, sulfites and iron. Samples were determined according to Standard Methods for the Examination of Water and Wastewater (1).

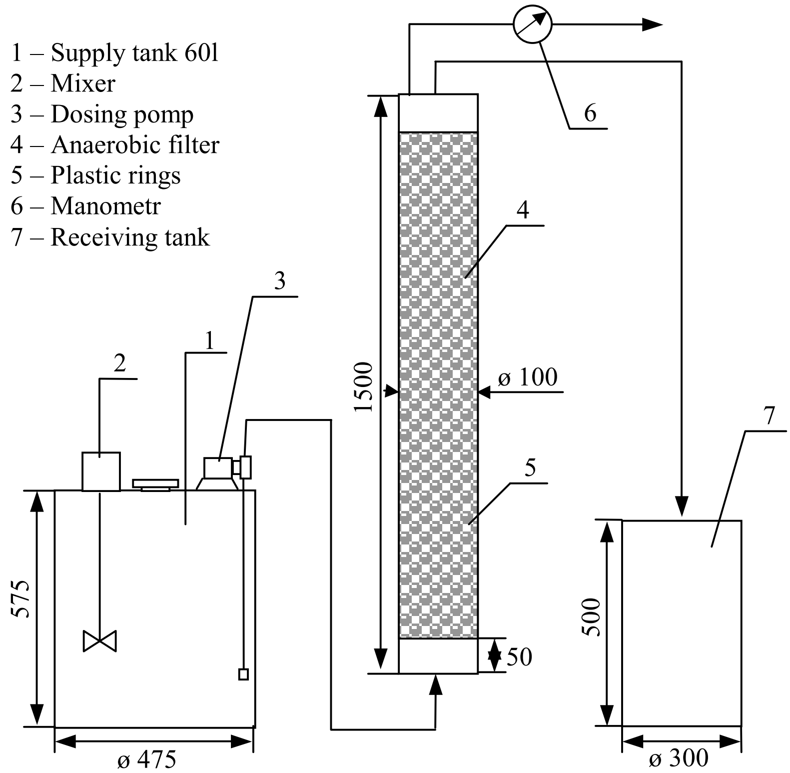

Figure 1. Anaerobic biological filter.

Bacteria identification
Sulphur-reducing bacteria were identified in accordance to Bergey systematic. The cells morphology was qualified as well as the ability of spores production, growth in optimum range – temperature for mezophilic and thermophilic bacteria, occurrence of flagellates. Different sources of carbon, such as: lactate, pyruvate, malate acetate, glucose were used for SRB growth. Also the *desulfoviridin* tests were performed for identification of the *Desulfovibrio* genus bacteria.

Results and discussion
Under anaerobic conditions phosphorus bacteria which have the ability of phosphorous accumulation in excessive amounts in comparison to the average requirement, are releasing Mg^{2+}, K^+ and Ca^{2+} ions in parallel with phosphates, (Comeau i in., 1987; Groenestijn i in., 1988a; Mino in., 1998). Degradation of polyphosphates is the result of polyphosphate AMP – phosphotransferase and adenylate kinase activity. Only for some . bacteria the hydrolysis of polyphosphates is catalyses by the polyphosphate glukokinase or polyphosphate fructokinase, resulting in the phosphorylation

of glucose and fructose respectively. Phosphates release by bacteria is the reaction during which the energy of two ADP molecules are delivered to a cell being next transformed to ATP + AMP (Groenestijn i in., 1988b).

In result of performed anaerobic microbiological processes, phosphates were released from sewage sludge containing phosphates precipitated out by addition of chemicals. (fig.2). The phosphates concentration in the substrate supplied to the anaerobic biological filter varied in a relatively wide range from 20 mg PO_4^{3-}/l to 53 mg PO_4^{3-}/l. The phosphates concentration in the anaerobic filter effluent increased to values in the range from 47 mg PO_4^{3-}/l do 157 mg PO_4^{3-}/l. It means, that there was a 2 to 5 times increase in the phosphates concentration as the result of microorganisms activity.

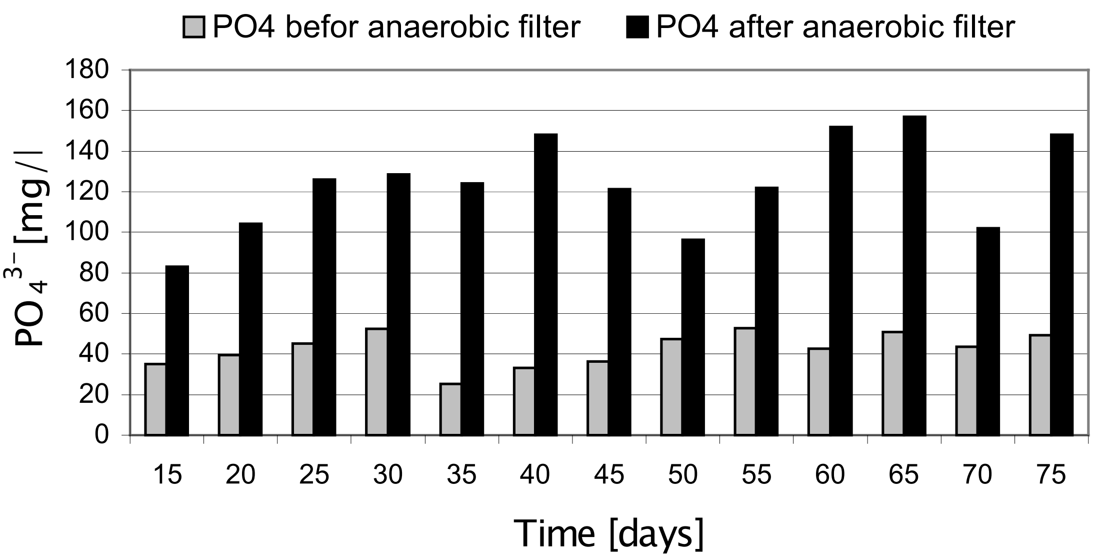

Figure 2. Phosphates concentration before and after the anaerobic biological filter.

As mentioned in the methodology the substrate used in the presented experiments was a mixture of sludge precipitated with the addition of [$Fe_3(PO_4)_2$], at pH in the range of 7 to 8 and raw municipal sewage. Municipal sewage was used as a source of organic carbon i.e. as the energy source of microorganisms. In conjunction to phosphates release, removal of organic substrate was measured expressed as COD changes. COD of the substrate supplied to the anaerobic filter varied in the range of 219 mg O_2/l to 373 mg O_2/l (fig.3 and 4). The COD of the anaerobic filter effluent was much lower and was in the range of 126 mg O_2/l to 223 mg O_2/l.

The maximum value of the COD equal to 223 mg O_2/l was measured in the effluent from the initial stage of the filter being in operation. After the preliminary period of about15 days, all measurements have shown values of COD below 200 mg O_2/l.

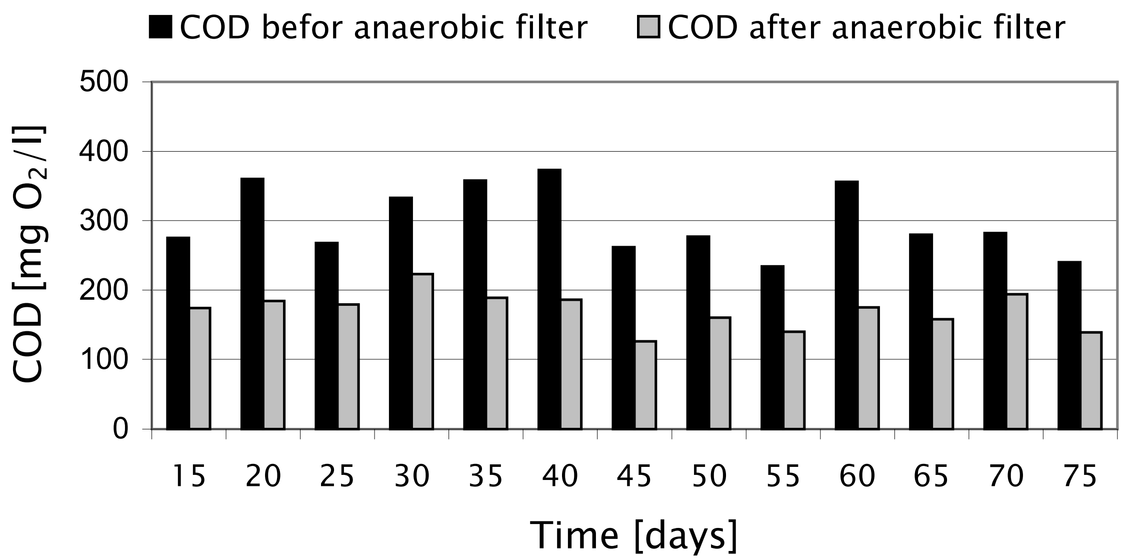

Figure 3. COD concentration before and after the anaerobic biological filter.

The effects of organic compounds removal expressed as COD decrease after the adaptation phase varied from 37 to 51 %. The COD values in the filter effluent were 1,45 to 2,08 times lower in comparison to the inflow. The variation of measured COD values in the effluent are reflected in phosphates concentration changes. (fig. 4).

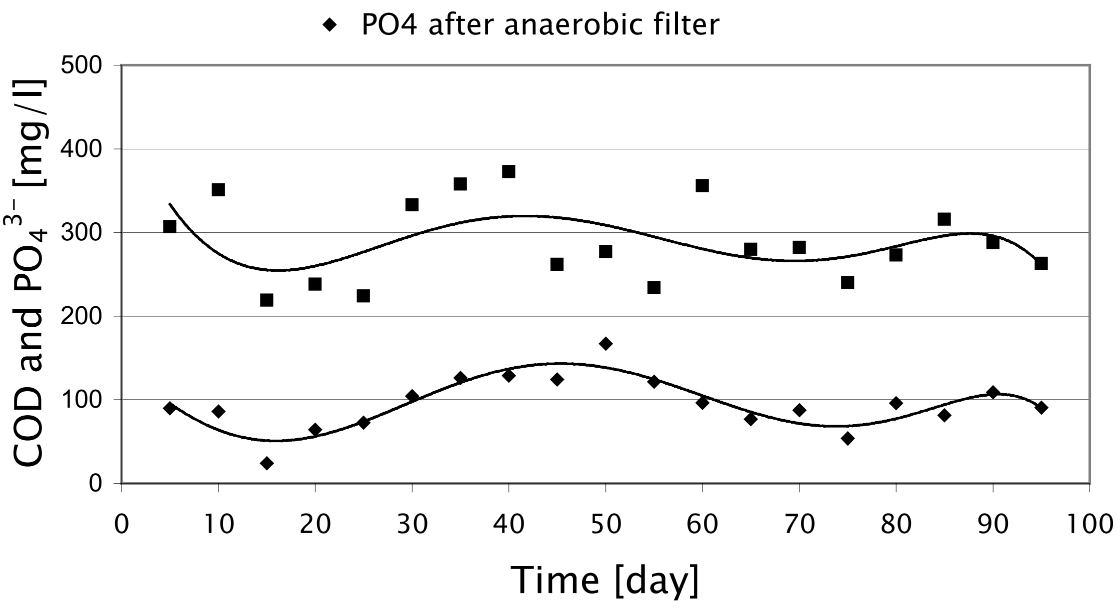

Figure 4. Changes of COD before anaerobic biological filter and changes of phosphates concentration after filter.

The presence of carbon source and energy is affecting the biological process of phosphates release from sludge. This is because in the anaerobic conditions, phosphorus bacteria are taking up organic matter. The favourable substrate is acetate. Nevertheless, acetic acid and volatile fatty acids can be replace by glucose, (Yan Hua Liu, 1998). The anaerobic phosphates release process is enhanced by easy biodegradable digestion products. In this phase, bacteria are taking up the products of acidic stage of fermentation – mainly acetate, which are next transformed to complex organic compounds – mainly poly-β-hydroxybutyrates (PHB), stored in cells. It is the important feature of phosphorus bacteria, which enable them to live, in contrast to most of bacteria, which can not take up organic matter under anaerobic condition. Some authors, (Brodisch and Joyner, 1983) suggest, that the anaerobic stage is the environment where the fermentation processes are occurring, and microorganisms like i.e. *Aeromonas* sp. are producing volatile fatty acids (acetic acid) which are next used to phosphates accumulation and poly-β-hydroxybutyrates. The maximum increasing of organic carbon reserves in the anaerobic conditions can be achieved by supplying of simple organic sources e.g. specific sewage or acetic acid salts, whereas the minimization of the reserves will happen in the case of electron acceptors, like O_2 and NO_3^- addition (Comeau et. al., 1987; Wachtmeister et al., 1997).

In anaerobic conditions (measured values of ORP in the biological filter effluent was on the level of – 200 mV) the decrease of sulphates concentration, (fig.5) and the processes of the sulphates reduction to sulphides and free hydrogen sulphide were observed. The transformations took place with the participation of identified SRB bacteria, belonging to *Desulfovibrio* genus. The desulphurication process was accompanied with the process of phosphates release (fig.5).

Simultaneously decrease of ferrous ion Fe^{2+} (not earlier precipitated) concentration was probably the result of ferrous sulphide precipitation.

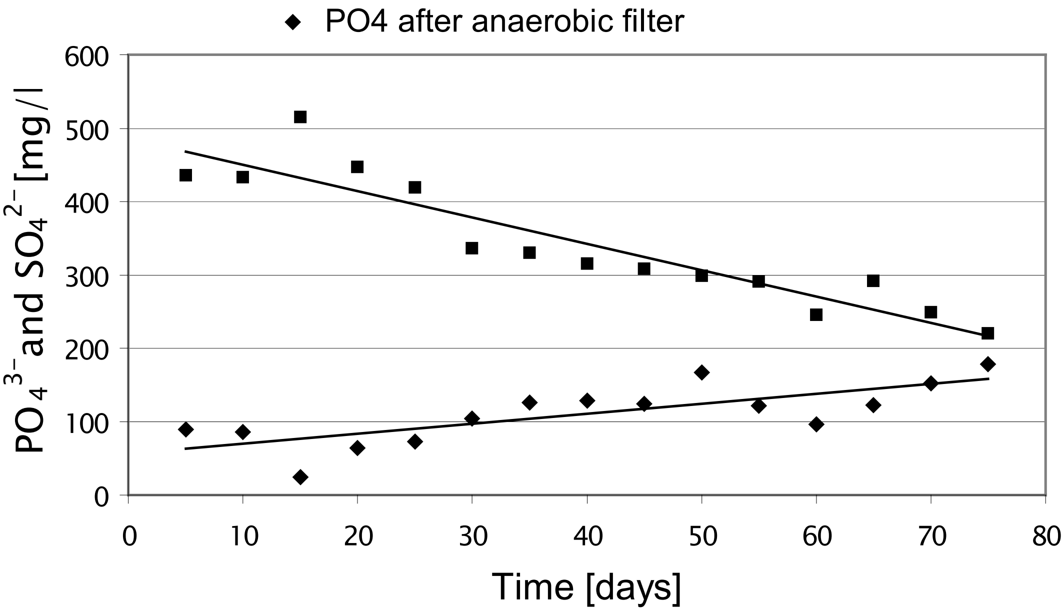

Figure 5. Phosphates and sulphates concentrations after the anaerobic biological filter.

The COD to SO_4^{2-} ratio have had a distinct impact on the effects of phosphates release (fig.6).

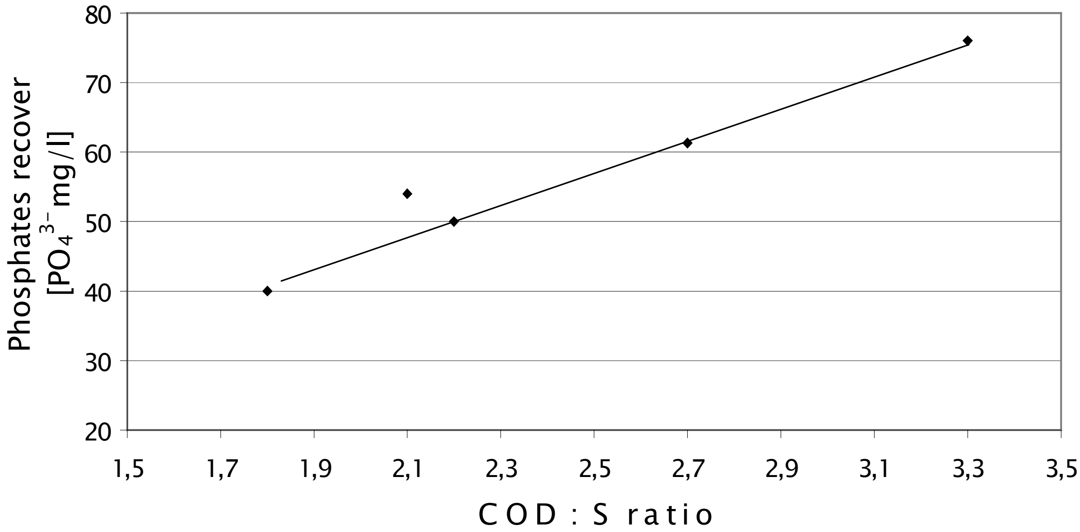

Figure 6. Effect of phosphates release in relation to COD/S ratio.

Together with the value of the COD/S weight ratio increase an increase of released phosphates was observed. The decrease of sulphates concentrations was strictly correlated to the phosphates release process, (fig. 7). This is considered to be an important parameter describing the right course of the anaerobic microbiological process.

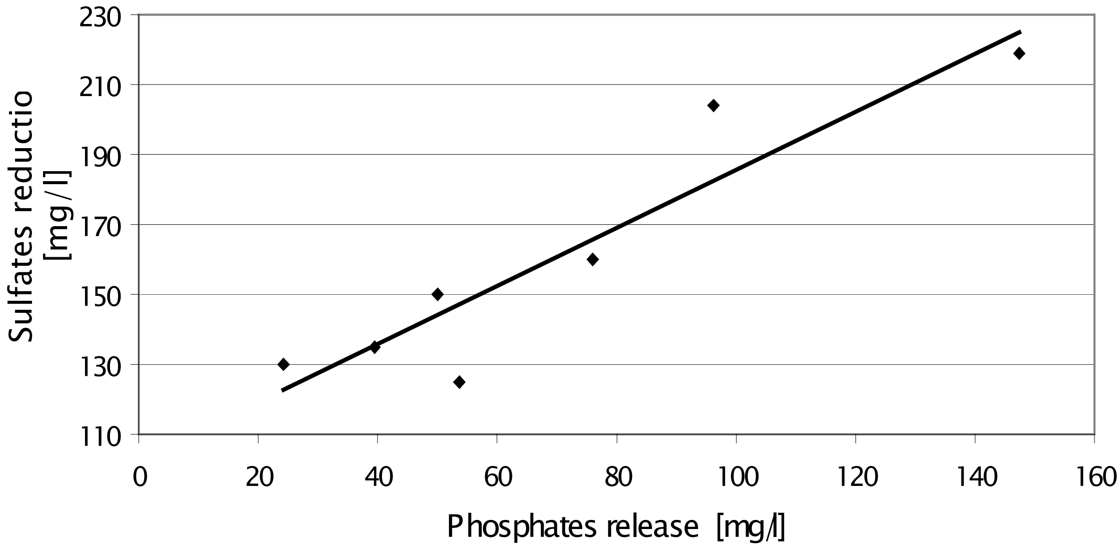

Figure 7. Relationship between phosphates release and sulphates reduction in the anaerobic microbiological process

CONCLUSIONS

On the base of performed investigations it could be concluded that:

1. The chemical phosphates precipitation with ferric sulphides occurred at pH value from 7 to 8 is resulting in $Fe_3(PO_4)_2$ precipitation
2. Under anaerobic conditions in the biological filter phosphates were released. The phosphates concentrations in the effluent increased from to 2 to 5 times in comparison to the inflow.
3. The phosphates release has been accompanied with sulphates reduction to sulphides, gaseous hydrogen sulphide and ferrous sulphides. That process could be considered as a confirmation of anaerobic conditions in the biological filter.
4. During the phosphate release process the changes of the organic compounds concentrations were observed. COD concentrations were decreased in the range from 37% to 51% (from 1,45 to 2,08 times).
5. The rate of the phosphorus release process was COD/S ratio dependent and an increase of phosphates release with the increase of the initial sulphates concentration in substrate could be observed..
6. The phosphates release process could be correlated to sulphate reduction.
7. Anaerobic, biological filter could be used as an effective method for microbiological phosphates release from sewage sludge after chemical precipitation.

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