RELEASE AND RECOVERY OF PHOSPHATES FROM SEWAGE SLUDGE

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ABSTRACT

Some treatment plants in operation have not been designed to fulfill the required standards of phosphorus removal. A possibility to upgrade the efficiency of phosphorus removal could be elimination of the phosphorus returned with sludge processing liquors by releasing and recovering from sewage sludge. The phosphorus recovery can occur from sewage sludge by chemical methods or from supernatant liquor by phosphate precipitation in the form of struvite. The leaching process with base or acid has shown phosphorus release from sewage sludge in the range from 70 to 100 % of the total phosphorus amount. For struvite precipitation from digested sludge supernatant a decrease was observed of phosphate concentration in the order of 95 % in the liquor.

KEYWORDS

Activated sludge, chemical leaching, phosphates precipitation, struvite.

INTRODUCTION

The allowable standards of the fundamental pollutions indexes of treated sewage discharged into receiving water (Act of Environmental Minister, November 29, 2002) caused that the intensive progress of the high effective biological technologies of wastewater treatment for carbon compounds and nutrients (nitrogen and phosphorus) removal was observed. The present standards of the wastewater quality discharged from municipal wastewater treatment plants, which are in conformity to the 91/27/EWG directives are admitting a total phosphorus concentration below 1 and 2 mg/l, respectively, to the size of the wastewater treatment plant. Some of the treatment plants in operation in Poland, like at Jaslo, Zamosc, Nowy Targ or Węgorzewo, (Kurbiel and Żeglin, 1997) have been designed to fulfill the required standards, i.e. to have an effective biological technology of organic substrate and nutrients removal. Another treatment plants, like e.g. in Szczecinek are using in addition chemical precipitation with iron salts, like PIX in order to increase the effectiveness of phosphorus removal. There are also wastewater treatment plants, for example at Bielsko-Biala Komorowice, which has not been designed for biological phosphorus removal and in consequence large amounts of chemical precipitants have to be applied. At many treatment plants the biological phosphorus removal efficiency is not satisfactory and efforts are made to upgrade the removal rate. The reasons of not attaining the required effects of phosphorous removal can be of various natures. One possible reason can be the unfavorable ratio of the carbon compounds to phosphorus in the sewage during the biological treatment process. A possibility to upgrade the effects of phosphorous removal could be elimination of the phosphorous returned with sludge processing liquors. Phosphorus accumulated in the activated sludge can in the following steps of thickening and anaerobic sludge digestion processes be again released in the form of phosphates, and increase the concentration in treated sewage. The phosphates re-dissolution is not only true in the case of anaerobic digestion of surplus sludge originating from the biological phosphorus removal process, but also true in the case of chemically precipitated phosphates with iron salts (Suschka et al., 2001). One of the possibilities to reduce the load of recirculated phosphates could be phosphorus recovery from sewage sludge. Based on a rough estimation, the recirculated load of phosphorous amounts up the 25 % of the influent to the sewage treatment plant load with raw sewage. Recovered phosphorus can be used as a raw material by the phosphorus industry, or can be directly utilized as a fertilizer of prolonged activity. The phosphorus recovery can occur immediately from sewage sludge by chemical methods – acid or base leaching or by the primary sludge combustion and next the leaching process. The alternative solution could be phosphorus recovery from supernatant liquor by controlled phosphate precipitation in the form of magnesium ammonium phosphate (MAP) - known as struvite.

Chemical release of phosphorus from sewage sludge

As the second step in phosphorus recovery is to release phosphorus from the sludge bound compounds that may be done by different methods for example through the use of physical, mechanical, biological or chemical means. During this step phosphorus is transferred into a relatively small stream compared with the influent flow. The phosphate concentration in this stream may be 10~50 times higher than the influent phosphate concentration (Stark, 2002).

Chemicals may be used directly on the sewage sludge or the sludge may be pre-treated with incineration or supercritical water oxidation before addition of chemicals. The chemicals are used to change the pH of the sludge mixture and cause phosphorus release. Briefly, supercritical water oxidation is using temperature above 374 ºC and pressure above 22.1 MPa to destruct organic materials.

When sludge is acidified to a pH-value below 3, most of the phosphate salts are dissolved (Hansen et al., 2000). If acidification is combined with a thermal hydrolysis, parts of the biologically bound phosphorus are also released. Depending on the sludge quality, it is possible to dissolve more than 90% of the phosphorus in sludge. If the sludge is merely acidified, the yield is about 70%. Compared to biological phosphorus removal the maximum recovery yield is about 50%.

When the sludge is treated with acid, this dissolves not only phosphorus but also precipitating chemicals (if present) and metals, including heavy metals. Organic micro pollutants remain in the organic fraction. The acid that does not react with sludge components or dissolved alkali-consuming material as hydrogen carbonate and organic acids will decrease the pH. In a similar way the addition of base will react with different sludge components and dissolve hydrogen carbonate and ammonia and the hydroxide ions that are left will increase pH.

MATERIAL AND METHODS

The following methods have been tested experimentally (Stark, 2002) for phosphorus release.

Sludge from wastewater treatment plant (WWTP)

Three different types of sludge were used (primary sludge mixed with excess sludge, digested sludge and post-precipitated iron sludge from the deep-bed filters). Hydrochloric (HCl) was used as acid while sodium hydroxide (NaOH) was used as base. The chemicals were added to a given amount (200 ml) of sludge and were stirred in a beaker by a mini-flocculator for 2 h. The sludge was mixed at different pH-values (2, 4, 10 and 12, respectively). The sludge was centrifuged for 15 min at 3500 rpm and the liquid phase was filtrated through 0.45 μm filter. The samples were stored frozen before analyses. In another experiment hydrochloric acid (HCl) was added to digested sludge at different pH-values (2, 3, 4 and 5) and a mixing time of 2 h was used. The release of total phosphorus, the chemical demand and the change in suspended solids were studied. The sludge was centrifuged after mixing for 15 min at 3500 rpm and the liquid phase was filtrated through 0.45 μm filter. The samples were stored frozen before analyses. Experiments were performed in triplicate.

Pre-treated sludge

Sludge residue samples from a pilot plant with supercritical water oxidation (SCWO) process were used. Five milliliters of sludge sample were centrifuged at 4000 rpm for 20 minutes. The liquid phase was poured out and was filtered through a 0.45 μm filter and the soluble phosphate content was analysed. To the remainder of the sludge, 25 ml of different concentrations of acid (hydrochloric acid) or base (sodium hydroxide) were added. Sample and liquid were shaken for 2 hours. Thereafter the samples were centrifuged at 4000 rpm for 20 minutes. The liquid phase was poured out and filtered through a 0.45 μm filter. The solutions were diluted before analysis of phosphate. The experiments were performed (in duplicate) in room temperature. It is the same procedure for experiment performed with ash sample with the difference that 1 g of ash is used instead of 5 ml.

RESULTS AND DISCUSSION

The results from the described experiments with sludge from WWTP indicate a high release of phosphorus at low pH-values with only use of acid, without heat or pressure. Acid addition seems to be more useful for total phosphorus release in digested sludge than use of base. The phosphorus release is 80% of total phosphorus amount at pH 2 for digested sludge (Stark, 2002), see Figure 1.

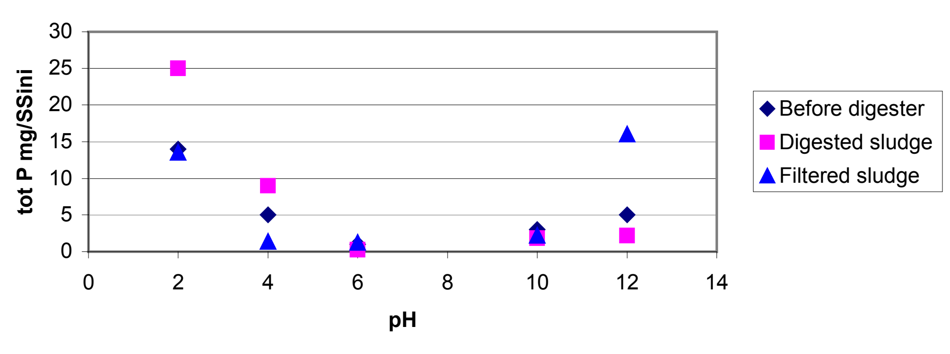

Figure 1. Total phosphorus/ SS initial at different pH with different types of sludge (modified from Stark, 2002).

The experiments with pretreated sludge using SCWO show that phosphorus was leached out more easily with the acid (hydrochloric acid) at room temperature than the base (sodium hydroxide), which is shown in Figure 2. At 0.1 M the acid showed a 100% phosphorus release while the base had a slower release. The leaching with base showed at 1 M approximately 70% phosphorus release. The organic material is not remaining in the sample, which simplify the leaching but still the problem remains of dissolving also the heavy metals.

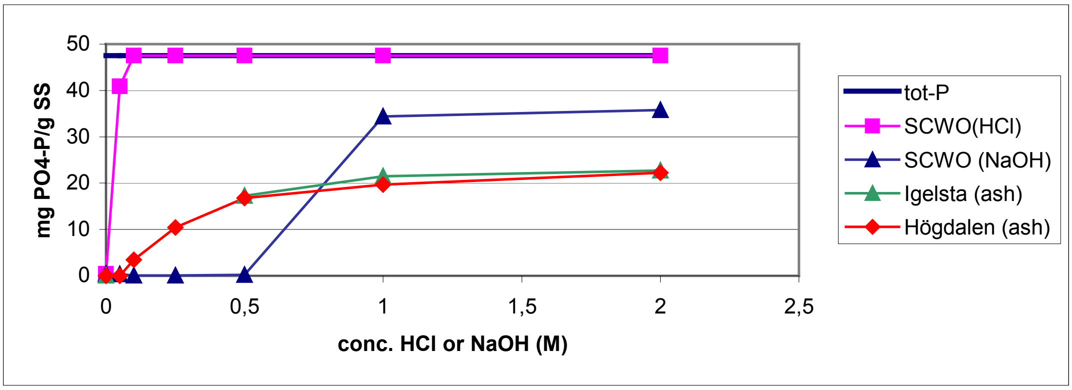

Figure 2. Phosphorus release (mg Phosphate/g SS) for sludge residual from SCWO treated with acid HCl or base NaOH together with leaching from ash, which is only treated with acid. Modified from Stark, 2002.

Comparison with incineration

In the same figure (Figure 2) the results from leaching with ash are shown. The result indicates that phosphorus is more easily leached with acid from the sludge residue from supercritical water oxidation (SCWO) than from ash via incineration.

Fractionation of sludge by use of acid or base is an important step to release different components from the sludge, including phosphorus. With the addition of acid, a large fraction of the inorganic material can be dissolved, and thereby also sludge bound phosphorus compounds. The performed experiments show that a lower pH gives increase of phosphorus release, which is accordingly to literature. Heavy metals are also dissolved in different degree.

The experiments with pre-treated sludge indicate that a higher dose of base seems to be needed to reach the amount of released phosphorus using acid. When phosphorus is released, heavy metals are also dissolved in different degrees that create a problem to obtain a pure phosphorus product. It also seems to be easier to dissolve phosphate from the residue of supercritical water oxidation compared to leaching of ashes. The reason may be that, after the supercritical water oxidation, the metal ions are not so tightly bound as by incineration, where crystallisation and glassification may occur. This comparison is under investigation at KTH.

RECOVERY OF PHOSPHATE

So far many attempts have been made to control the process of recover MAP as fertiliser, which can be used directly for agricultural purposes. While only slightly soluble in water and soil solutions, MAP was found to be a highly effective source of phosphorous nitrogen and magnesium for plants through both foliar and soil application (Lunt et al., 1964; CEEP, 2001).

MATERIAL AND METHODS

Investigations on struvite precipitation were carried out as jar tests, and as continuous flow semi-technical model with centrate (Suschka et al. - in press (A), Suschka et al. - in press (B)) The model had a volume of 100 litres, and is shown in Figure 3.

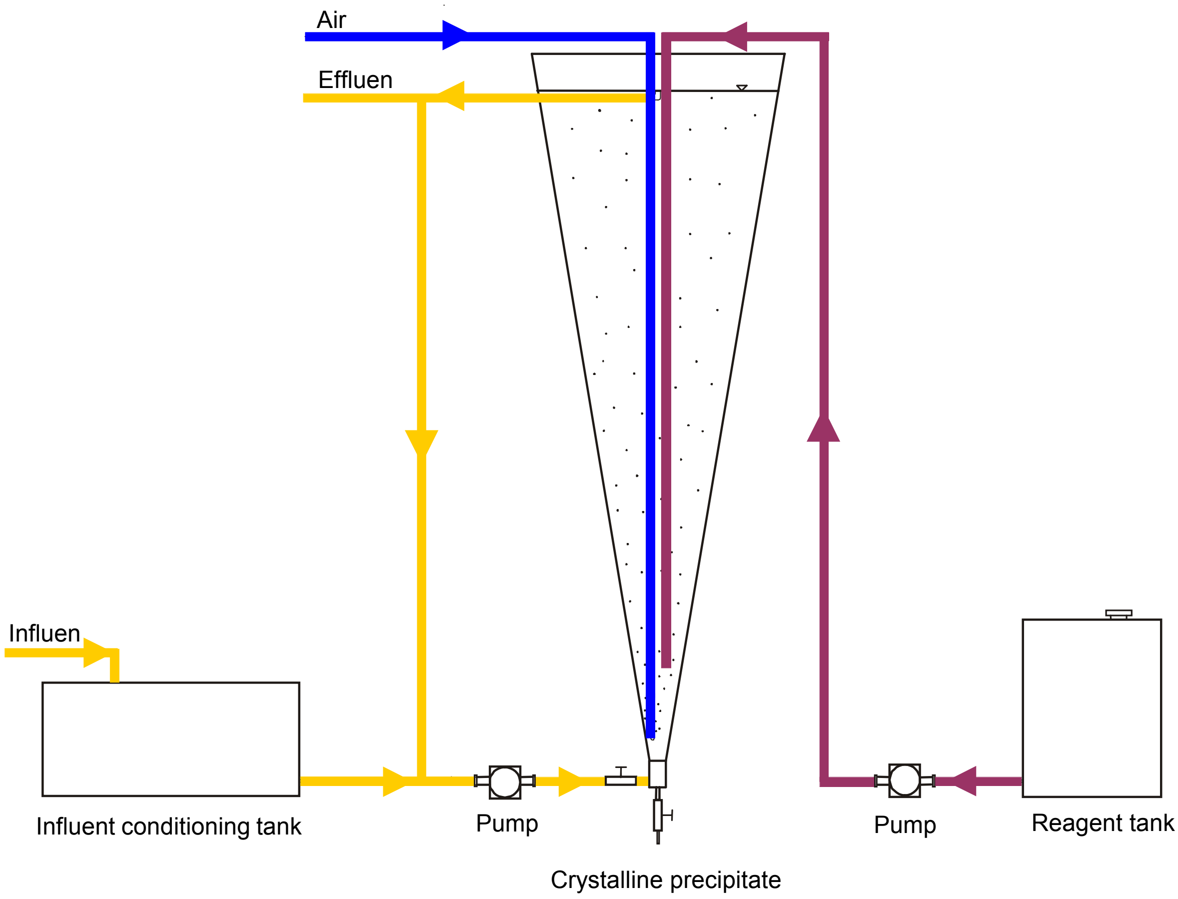

Figure 3. Semi-technical model.

The model was conical on the full high. The conical lower part of the reactor had an obtuse angel of 20^o .

The sewage filtrate from the digested sludge dewatering press and required chemicals were supplied from the bottom. The recirculated reactors content entered at the bottom. The streams have been tangentially oriented in order to activate a spiral upward flow. The principle of that type of a reactor is based on varying flow velocity across the reactor. There is a decrease of velocity with the increase of the distance from the bottom in the conical part of the reactor. Slow mixing in the upper sections follows intensive mixing at the bottom. In the upper section therefore the formation and growth of crystals is allowed. An important feature was recirculation of the reactors content from a point above the suspended sludge blanket. Precaution was therefore taken to avoid disintegration of clusters of crystals (aggregates) in the recirculation pump.

Centrate of anaerobic digested sludge was used in the experiments of phosphorous recovery. The concentrate had a phosphates content of 130 to 160 mg PO_4/dm^3. The concentration of ammonia varied from 700 to 900 mg $N\text{-}NH_4/dm^3$, and the concentration of magnesium was in the range of 10 to 20 mg Mg/dm^3. Evidently the concentration of magnesium was distinctively below the stoichiometric requirement according to the given formula below:

$$Mg^{2-} + NH_4^+ + PO_4^{3-} \rightarrow MgNH_4PO_4 + 6H_2O$$

Magnesium was added in the form magnesium oxide, magnesium chloride and magnesium sulphate. Samples were mixed mechanically or by supply of pressure air, for a period of 24 hours. After that period samples were filtered through a 0.45 µm filter and analysed for phosphate, ammonia and magnesium. A microscope observed the precipitated crystals.

Methodology of determinations

Most of the chemical determinations were carried out according to the Standard Methods (1995). For determination of the concentration of magnesium, an atomic absorption spectrophotometer Aanalyst 100 – Perkin Elmer was applied.

In order to ascertain that the precipitate was really struvite, X-ray diffraction analyses have been done. A wide angel X-ray (WAXS) apparatus, with a diffraction meter HZG-4 was used.
Also to observe the form of precipitated out crystals microscopic pictures have been made. The microscope used – NIKON ALPHAPHOT- 2 YS2 coupled with a camera PANASONIC GP-KR222 allowed also for size measurements by a programme LUCIA ScMeas Version 4.51.

RESULTS AND DISCUSSION

For struvite precipitation from digested sludge supernatant, pH increase was required. The optimum pH for struvite precipitation is in the order of 8.5. If the samples with magnesium chloride or magnesium sulphate was added and pressured air was used for mixing an increase of pH was observed due to stripping of the free carbon dioxide.

When magnesium oxide was applied and stirrer or hydraulic mixing mixed the samples, pH was raised by addition of magnesium oxide. The results of investigations have shown a decrease of phosphate concentration in supernatant liquor in the order of 95 %.

The crystals formed are of regular orthorhombic structure (Photo 1 and 2) independently of the substrate used. This was also true for the various magnesium salts used. The regularity of formed crystals is however depending on the quality (the origin) of centrate. At many occasions performing the investigations exactly according to the adopted procedure the formed crystals resembled broken pieces.

Sometimes however, the struvite crystals can have a totally different shape and have a needle like appearance (Photo 3 and 4). Performed research has shown that the structure of formed crystals depends on the mode of mixing and reactor operation. Needle like crystals are formed in the presence of high concentration of free ammonia in the liquid. The critical issue for struvite crystals separation from the liquid is aggregation in large enough granules to be ready separable. It is not clear which crystallisation form has a higher affinity for aggregation into granules. More research is required to clarify the mentioned problem above.

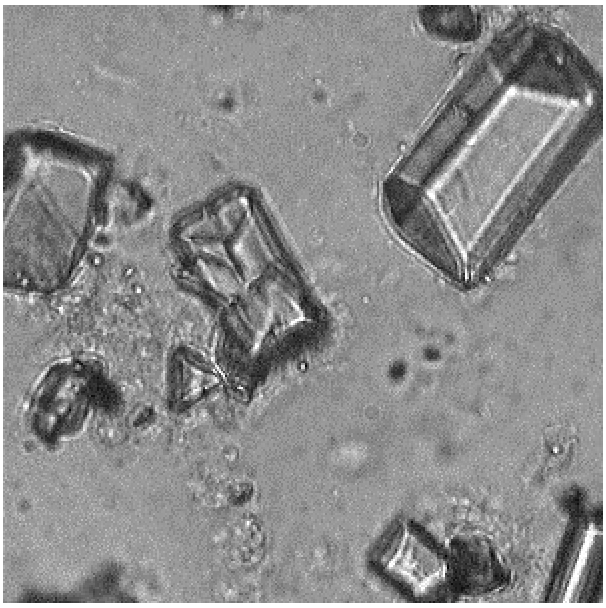

Photo 1. Struvite crystals with magnesium oxide used as the source of magnesium. (x 176) (S. Popławski).

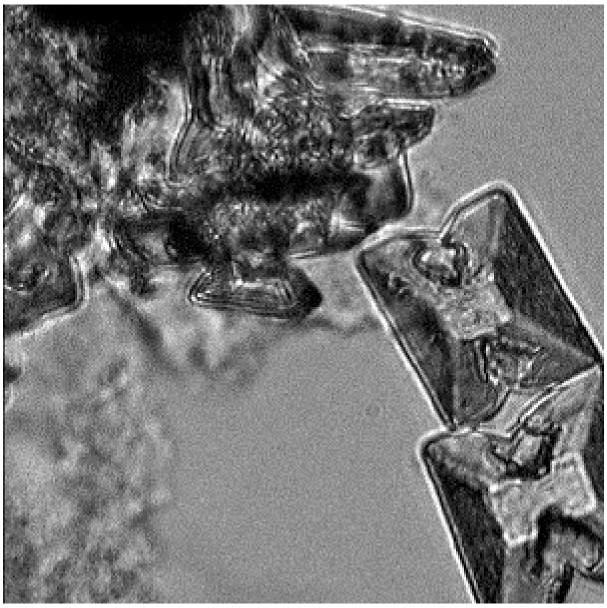

Photo 2. Orthorhombic crystals structure of precipitate struvite using magnesium chloride. (x 176) (S. Popławski)

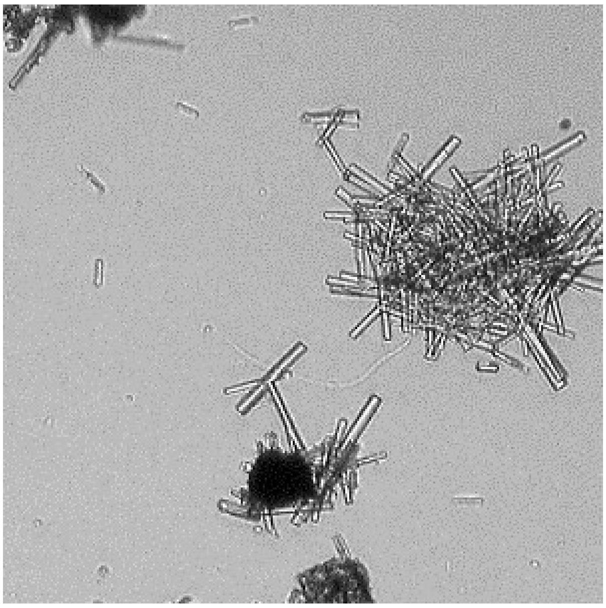

Photo 3. Needle like structure of struvite crystals. (x 176) (S. Popławski)

Photo 4. Needle like struvite crystals with magnesium oxide. (x 176) (S. Popławski).

SUMMARY

The performed investigations have shown a high effect of the phosphorus release and recovery from sewage sludge. The leaching process with acid could be used to achieve an almost total phosphorus release (100 %) from pretreated sludge. Leaching with base a lower effect of phosphorus release was observed, on the level 70 %. The released phosphorus could be utilized by the phosphorus industry. The phosphorus recovery by the controlled precipitation in the form of magnesium ammonium phosphate – struvite could be utilized as a fertilizer of prolonged activity. The release and phosphorus recovery from sewage sludge is an important limiting factor to decrease phosphorus returned with sludge processing liquors. Both of the methods of phosphorus recovery could be used in parallel, or separately depending on treatment and disposal of sewage sludge processes.

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