

AMMONIA REMOVAL FROM DIGESTED SLUDGE SUPERNATANT

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ABSTRACT

Wastewater Treatment Plants that make use of anaerobic processes for sludge digestion often have problems with phosphates and ammonia nitrogen “overloads” returned to biological sewage treatment process together with effluents coming from dewatering of digestion sludge. The high concentrations of phosphates and ammonium nitrogen in supernatant constitute 10 – 20 % of entire load brought to biological process. The aim of the study was chemical removal of ammonium nitrogen and phosphates from supernatant. Chemical process of ammonium nitrogen removal permits for its 95 % and 80 % of phosphates reduction.

KEYWORDS

chemical precipitation, high concentration of ammonia, phosphate removal, struvite

INTRODUCTION

At present biological processes of nitrogen and phosphorus removal, are well developed. Many different alternatives are in operation aiming at achievement of high removal rates in connection to the specific raw waste water quality and requirements. Stringent requirements for medium and large treatment plants can however, not always be reached only by biological methods.

In the case of phosphorous if the concentration of total phosphorous in the treated effluent should be below 1,5 mg P/l or even 1,0 mg P/l, and can not constantly be achieved by biological methods, simple chemical precipitation can be applied in addition. If iron or aluminium salts are added in conjunction to the biological process, they are referred in the literature as simultaneous process of phosphorous removal.

If high effects of nitrogen removal are required, e.g. the content of total nitrogen to be below 10 mg N/l in the effluent, no simple chemical processes exist to upgrade the effects of nitrogen removal. Most often the improvement of the effects of nitrogen removal are achieved by enlarging the overall volume of the biological reactors, and thus extending the nitrification and denitrification process reaction time, or by addition a post denitrification tank supplied with an external source of organic carbon. In the first case there are additional high investment costs, in the second case operational costs are increasing and in addition an increase of BOD or COD of the treated sewage is possible.

Medium and large sewage treatment plants often are conditioning excess sludge by anaerobic digestion. The liquor after digested sludge dewatering, which is returned to the main stream of sewage treatment contains phosphates and ammonia in high concentration. The amount of recirculated phosphates and ammonia constitutes about 10 to 20 % of the total load of entering to the biological sewage treatment process of phosphorous and nitrogen. Retaining that amount in the

side stream, i.e. removing phosphates and ammonia, from the returned dewatering liquor could have a distinct positive effect on the overall effects of phosphorous and nitrogen removal from treated sewage. Removal of phosphates could be achieved by addition of lime in the process of sludge sanitary quality improvement. A pH of at least 10,5 has to be reached for substantial precipitation of calcium phosphates. Complete removal of phosphates will require a pH of about 12. It is obvious that large quantities of lime are required.

Another possibility would be addition of magnesium salts and precipitation phosphates in the form of Magnesium Ammonium Phosphate MAP, known as **Struvite**. In this case keeping in mind the formula of struvite $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ - obviously also a part of ammonia nitrogen can be retained. Ammonia is always present in surplus to the struvite formula and thus if ammonia removal is the target more magnesium salts and phosphates have been provided. Removal of ammonia from high strength waste water was investigated by several authors, however, the practical implementation is very limited to pilot plants. Precipitation of struvite is feasible in the case of landfill leachates and/or from anaerobic digester supernatant. Landfill leachates can have a content of ammonia in the range between 1000 and 6000 mg N-NH₄/l (Li et al., 1999) and only stripping or struvite precipitation will be an appropriate solution. A comparison of different methods of ammonia removal in the case of digested sludge supernatant was given by Siegrist (1996).

The possibilities and advantages of ammonia removal from digested sludge superantant is discussed in this presentation based on carried out appropriate investigations.

EXPERIMENTAL

A full technical scale municipal sewage treatment plant with a flow of about 60 000 m³/d was the source of substrates and the base for evaluation of results. Supernatant of anaerobically digested surplus activated sludge was the main substrate used for experiments on magnesium ammonia phosphate precipitation with the aim of phosphorous and nitrogen removal effects upgrading. The quality of the supernatant varied, maintaining the concentration of ammonia and phosphates within a relatively narrow range. The concentration of ammonia varied between 1000 to 1500 mg N-NH₄/l, while the concentration of phosphates was mainly in the range of 180 to 220 mg PO₄/l.

Precipitation of struvite was based on batch tests, carried out in large 2 or 5 litre beakers. Tests were performed for digested sludge liquor and the digested sludge discharged directly from the digester before dewatering. To supply phosphates, superphosphate or phosphoric acid was applied. Superphosphate added, was a technical grade, commercially available product with a content of 46 % P₂O₅ – called triple superphosphate. Also for experiments technical grade 85 % phosphoric acid was used. Magnesium oxide used was also a commercially available product with a content of 92 % of MgO.

All reagents have been added as dry products. After addition, according to the chosen procedure samples have been mixed for 30 minutes. Some of the tests for digested sludge have been mixed for 24 hours to assure complete dissolution of the reagents and the expected reactions.

Determinations of ammonia, phosphates and total phosphorous were done according to Standard Methods. Potassium and magnesium were measured by atomic absorption spectrometry. Before performing of the chemical determinations, samples have been filtered on a medium paper filter.

RESULTS AND DISCUSSION

The used for investigations municipal excess sewage sludge was anaerobically digested in closed digesters at a temperature of 32 – 33 °C for about 30 days. The process can be considered as a classic or conventional one. The digested sludge dry solids was most often in the order of 35 g/l to 40 g/l, i.e. the water content was in the range of 96.5 - 96.0 %. The volume of digested sludge to be

discharged was approximately 6 times smaller as an effect of dewatering (centrifuges are used for dewatering) and as a consequence the dry solids increased to about 20 to 24 %.

The tested digested sludge had a relatively stable content of organic substances between 56 and 58 %. Also pH was in a narrow range of 7.4 to 7.7. Only occasionally the pH was higher and reached a value of 8.0. The digested sludge has a good fertilizer quality containing about 2.1 % of phosphorous and about 4.6 % of nitrogen.

The process of sludge dewatering results in relatively large quantities of liquor, which is normally returned to the main stream of sewage treatment. These liquors contained high concentration of phosphates and ammonia nitrogen. In average about 10 to 15 % of the total load of phosphorous entering a sewage treatment plant is returned. In the case of our investigations, the amount of ammonia nitrogen returned to the main sewage stream was extremely high, and amounts to 44 % of the total load. The quality of the centrate was given in Table 1. Such a high rate of ammonia recycling was specific to the WWTP under investigation and was very different from other cases studied in the past.

Table 1. Characteristic of centrate used for experiments

Parameter	Units	Measured range	Average
Temperature	°C	24 – 27	26
pH	-	7.49 – 7.84	7.7
COD	mg O ₂ /l	280 - 350	315
Ammonia nitrogen	mg N-NH ₄ /l	1000 – 1500	1150
Phosphates	mg PO ₄ /l	126 – 324	200
Total phosphorous	mg P/l	46 – 111	75
Magnesium	mg Mg/l	13 – 18	14
Potassium	mg K/l	152 – 195	160
Calcium	mg Ca/l	62 - 89	65

Addition of lime to digested sludge with the aim stabilization and destruction of pathogenic organism can result in practical total removal of soluble phosphates. An example of possible soluble phosphates removal is presented in Fig. 1.

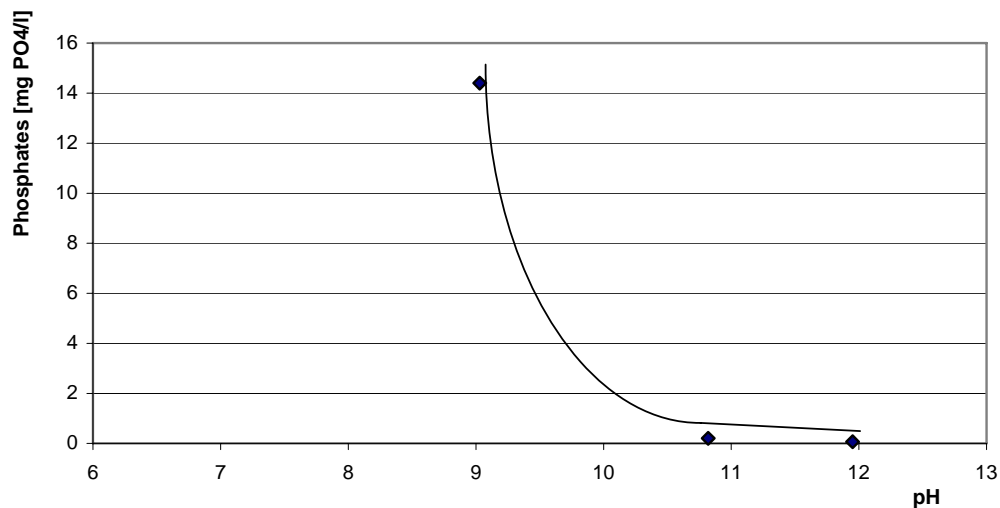


Figure 1. Residue phosphates in correlation to pH obtained by lime addition

Addition of magnesium salts to digested sludge or sludge supernatant results in struvite precipitation. As previously published (KTH) different crystals of struvite are formed in connection to the procedure of precipitation applied. (Fig. 2 and 3.). The effects of phosphates removal is in the order of 87 % (Fig. 4).

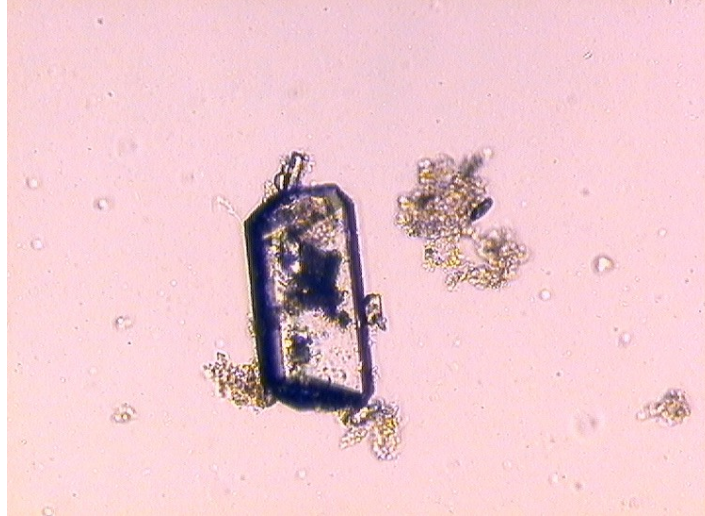


Figure 2. Struvite crystals with magnesium chloride used as the source of magnesium. (x 100)
(S. Popławski)

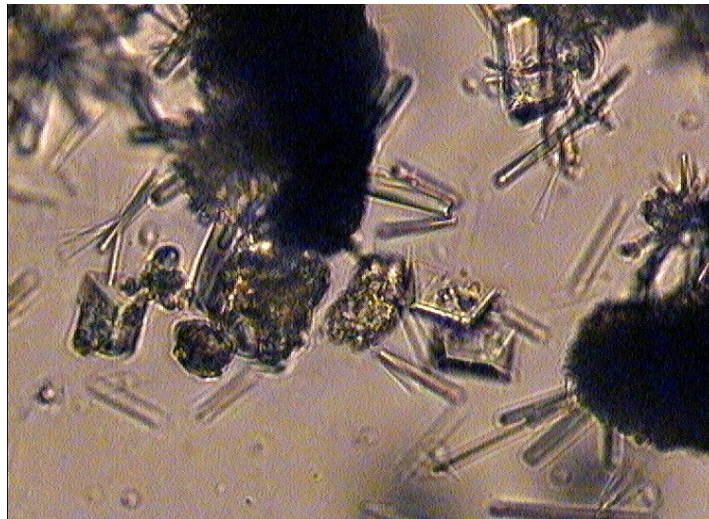


Figure 3. Needle like crystals with occasionally found orthorhombic structured crystals. (x 100)
(S. Popławski)

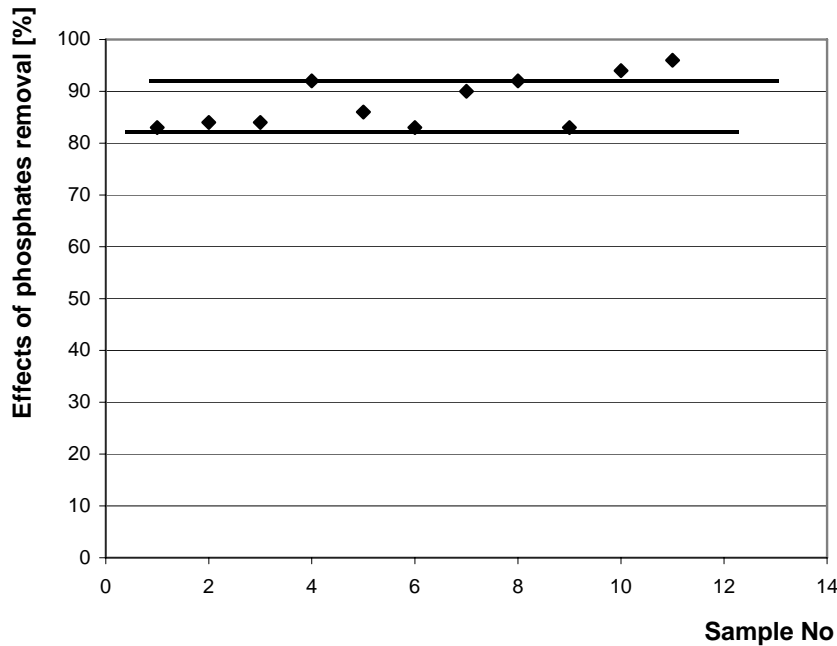


Figure 4. Achieved effects of phosphates removal from digested sludge supernatant.

Magnesium can be added as magnesium sulphate, magnesium chloride or magnesium oxide. In the case of $MgSO_4$ or $MgCl_2$ addition pH has to be raised to about 9.5 with e.g. NaOH. Magnesium oxide has a low solubility but in the process of hydrolysis (of higher solubility) there occur a simultaneous increase of pH, up to the required level. This process is relatively slow and reaction time of several hours is required. If compressed air is used for mixing, at the relatively high pH of 9.5, a partial stripping of ammonia takes place. Under laboratory conditions a removal of about 300 to 400 mg N-NH₄/l was measured. In the specific case of the mentioned sewage treatment plant, it means removal of a load in the range of 60 to 80 kg N/d. In comparison to the load of nitrogen introduced to the treatment plant it constitutes about 11 to 15 %. As a side effect to the process of struvite precipitation for phosphates removal it is a distinct result.

Adding phosphates as superphosphate or phosphoric acid to fulfil the formula of struvite, in respect to the concentration of ammonia in the supernatant or digested sludge, ammonia can be removed effectively. The effects of ammonia removal very found to be independent on the chemicals used. An example of the decrease of ammonia concentration using super phosphate was presented in Fig. 5. The residual ammonia can vary, but values as low as 22 mg NH₄/l can be obtained. (Fig.6).

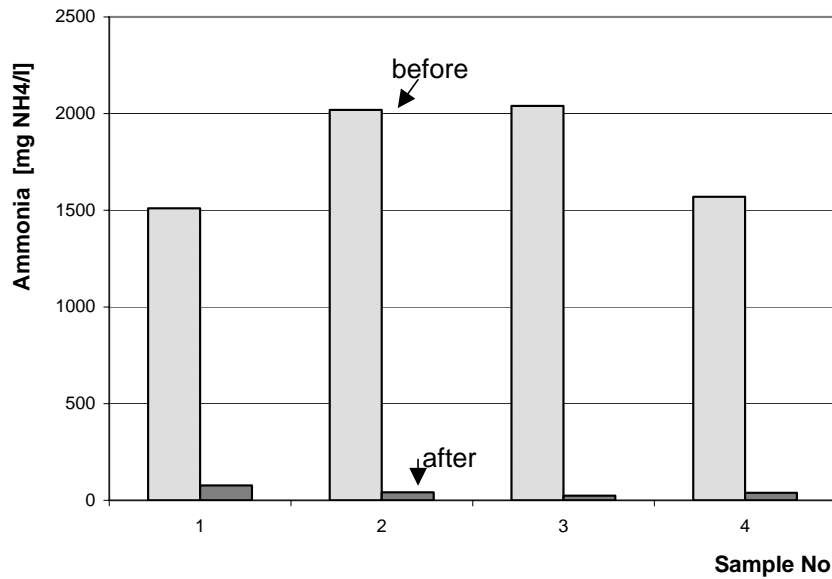


Figure 5. The concentration of ammonia in the centrate before and after addition of superphosphate and magnesium oxide.

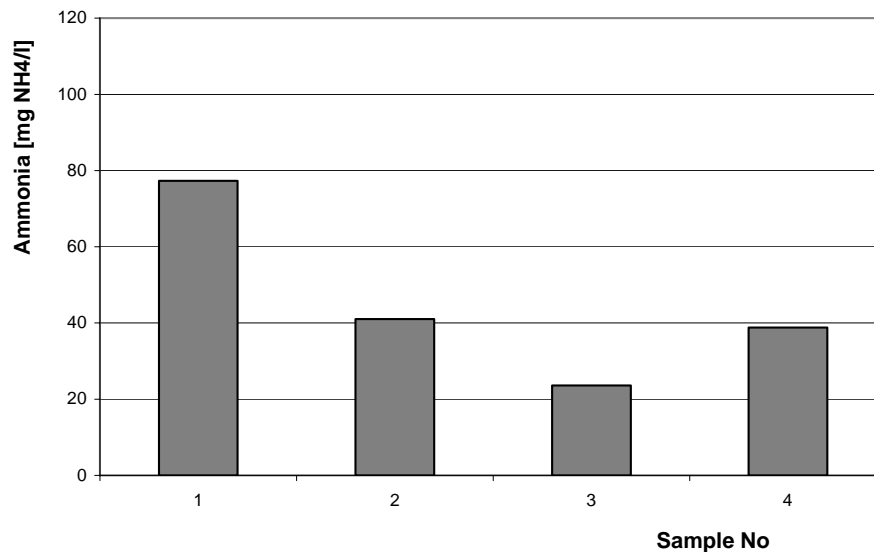


Figure 6. The concentration of ammonia in centrate treated with superphosphate and magnesium oxide.

Precipitation of struvite requires a pH above 8.5, preferable in the order of 9.5. If phosphoric acid was used as the source of phosphates, pH of the sludge has decrease to about 2.4. Consecutively the pH had to be raised in order to enable struvite precipitation. In our experiments NaOH was used. Using Na_3PO_4 , no pH correction is required. Adding next magnesium oxide a very high pH value of 11.8 can be achieved. As mentioned before, results of ammonia removal are very similar to those obtained by addition of other sources of phosphates. There was however a distinct difference in

capture of potassium. A decrease from a level of about (in average) 160 mg K/l to about 16 mg K/l, i.e. 90 % removal was obtained with use of Na_3PO_4 as the source of phosphates..

For the other sources of phosphates used in our experiments at maximum only about 40 % of potassium was retained.

The precipitated out magnesium ammonium phosphate has been shown to be a highly efficient source of magnesium, nitrogen and phosphorous for plants. The release rate is relatively slow and even if applied in massive does not cause plants burning. MAP is used primarily for horticultural applications. Wider use is hindered by relatively high cost. This can be dramatically changed aiming at production of biosolids or biofertilizer.

Table 3. The quality of sludge liquor before and after superphosphate and magnesium oxide addition

Parameter	Units	Digest sludge	Addition of MgO + $\text{Ca}(\text{H}_2\text{PO}_4)_2$	Addition of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ + MgO
Temperature	°C	21,9	21,7	21,5
pH – 1	-	7.10	8.93	6.09
pH - 2	-		8.78	8.69
COD	mg O_2 /l	258	747	363
Ammonia	mg NH_4 /l	1542	70	42
Phosphates	mg PO_4 /l	127	24	23
Magnesium	mg Mg/l	13.6	30	30
Potassium	mg K/l	120.9	117.4	97.3
Calcium	mg Ca/l	71.1	58.3	43.8

CONCLUSIONS

1. In order to achieve high nitrogen removal effects at medium and large sewage treatment plants removal of ammonia nitrogen from digested sludge supernatant is crucial.
2. To achieve this different chemical or biological processes can be applied. The process of struvite precipitation is advocated.
3. Precipitation of struvite is so far the unique process allowing simultaneous removal of excess phosphates and ammonia from the liquor.
4. If substantial, or almost complete removal of ammonia is required addition of phosphates is necessary to fulfill the stoichiometric formula of struvite
5. Addition of phosphates as superphosphate is feasible and have many advantages.
6. Depending on the ratio of sewage sludge to superphosphate added at least two different products can be obtained. If the amount of added superphosphate is limited only to the process of ammonia removal (fulfilling the formula of struvite) the product can be called **“biosolid”** if superphosphate would be added in much higher amounts, the product would be **“biofertilizer”** of different quality.
7. An additional benefit of ammonium removal and binding in the form of struvite is the increase of nitrogen concentration in obtained biosolid
8. Drying and pelletization results in obtaining a safe hygienic product. The effects of thermal biosolid treating, on availability of N and P applied to different soils is controversial and more studies are required.

REFERENCES

- Battistoni A., De Angeles, Priscicandro M., Boccadoro R., Bolzonella D. P. (2002). Removal from anaerobic supernatants by struvite crystallization: long term validation and process modelling. *Wat.Res.*, **36**, (8): 1927-19
- Doyle J.D, Parsons S.A., Wall F. Doyle J. Oldring K. Chuchley J. (2001). Assessing the potential for struvite recovery at sewage treatment works. *Environmental Technol.* **22**, 11, 1279-1286
- Hogan F. Mchugh M.. Morton S. (2001). Phosphorous availability of P-recovery from municipal wastewaters. *Environmental Technol.* **22**, 11, 1347-1354
- Li X.Z., Zhao Q.D. And Hao X.D. (1999). Ammonium removal from landfill leachate by chemical precipitation. *Waste management* 19, 409 - 415
- Richards I.R. Johnston A.E. (2001). The effectiveness of different precipitated phosphates as sources of phosphorous for plants. *Report prepared for CEEP Centre Europeen d'Etudes des Polyphosphates.*
- Siegrist H. (1996). Nitrogen removal from digester supernatant – comparison of chemical and biological methods. *Wat. Sci. Technol.* **43**, 1-2, 399-406
- Standard Methods for Water and Wastewater Examination*, 17th ed. (1995). American Public Health Association, Washington, D.C.
- Suschka J. (March/April 2002) Phosphorous removal and recovery . Agro Food Industry Hi-Tech.. Milano, Italia
- Ueno Y. Fujii M. (2001). Three years experience operating and selling recovered struvite from full-scale plant. *Environmental Technol.* **22**, 11, 1373-1377
- Van Voorneburg F. Van Veen H.J. (1993). Treatment and disposal of municipal sludge in The Netherlands. *J.IWEM.*, 7, 116-121