

Contribution to the Study of Ammonia Removal from Digestate by Struvite Precipitation

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Abstract. This study deals with an issue of ammonia removal from anaerobic digestion's by-product - digestate. The aim of the research is ammonia removal by chemical precipitation using the combination of Mg^{2+} , NH_4^+ and PO_4^{3-} ions in struvite ($MgNH_4PO_4 \cdot 6 H_2O$). Laboratory tests were carried out using the sample of digestate liquor. The final product of the treatment may have the potential to be used as a fertilizer.

1. Introduction

Anaerobic digestion is a combination of processes leading to breaking down biodegradable materials in the absence of oxygen. It is a combination of physical, physicochemical and biological processes caused by functional groups of anaerobic microorganisms of transformation into final products – biogas and digestate [1]. Because residual biomass is generated mostly in agriculture, the most widely spread type of biogas plants are the agricultural ones. Such biogas plants process wastes from livestock production, crop residues or farm animals' excrements; recently also purpose-grown plants are used as feedstocks [2]. As it is forbidden to process wastes in the agricultural biogas plants according to Czech national waste legislation Act 185/2001 Coll., and other materials according to Regulation (EC) 1774/2002 of the European Parliament and of the Council, these biogas plants' digestates are the most suitable for their subsequent use. According to the Czech and also European legislation, digestates are considered to be organic fertilizers in most cases. The digestate's content of nutrients and also their subsequent availability for plants is affected by the input substrate; properties may also vary over time within one biogas plant. However, a common feature is the low dry matter content (for agricultural biogas plant between 2.5 and 8.5 %). C:N ratio is often between 10:1 and 2:1.

The issue is that the chemical composition of digestate is closer to a mineral fertiliser rather than an organic one, and almost all easily degradable organic material has already decomposed during anaerobic digestion resulting in only minimum of beneficial substances usable by plants. Nitrogen content in fresh digestate is about 0.25-0.75 %, of which 25 to 75 % are in the form of ammoniacal nitrogen (i.e. $N-NH_4^+$) causing a weak alkalinity of digestate (pH = 7-8) [3]. Thus, land spreading of digestates can cause a discharge of large quantities of nutrients into the environment, which contributes to eutrophication and depletion of dissolved oxygen in water bodies. Owing to the expansion of biogas plants and the associated quantity of digestate production, it is necessary to look for other means of its application or properties enhancement. One of the options is the chemical precipitation of $N-NH_4^+$ in the form of struvite, which is a mineral that can be reused as a slow-release fertilizer [4]. Frequently precipitation of struvite is an undesirable accompanying phenomenon at



urban waste water treatment plants. In many countries, commercially available reactors are used in large waste water treatment plants for phosphorus recovery and it is further used as a certified fertilizer [5]. These days there is an increasing interest in the application of this method. According to [6] there are already published studies in combined wastewater from bovine and leather tanning factories, swine waste, anaerobic supernatant from a centrifugation section of a civil biological nutrient removal plant, effluent from the biologically treated opium alkaloid wastewater, anaerobic treatment of the baker's yeast industry, domestic wastewaters, landfill leachate, etc. In addition, this study deals with the precipitation of ammoniacal nitrogen (N-NH_4^+) in struvite from the liquid phase of digestate, digestate liquor, from an agricultural biogas plant.

2. Materials and methods

2.1. Materials

All laboratory experiments were conducted in real digestate samples provided by Stonava Farm. The Stonava Farm's Biogas Plant is a purely agricultural. The input material for anaerobic digestion is pig slurry in combination with maize silage and crushed corn grain. Two fermentation stages operate at 42-45 °C.

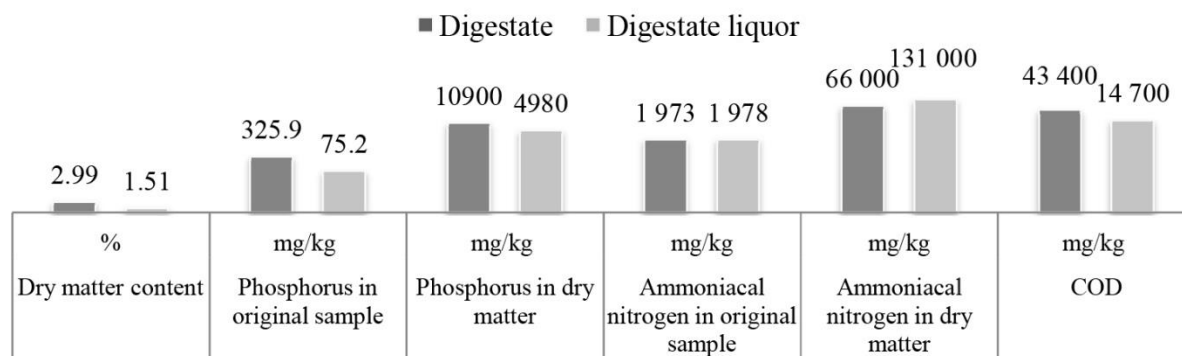
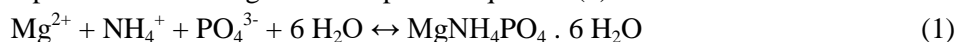


Figure 1. Model chemical composition of digestate and digestate liquor from Stonava Farm. The phosphorus and ammoniacal nitrogen concentrations were converted to the original weight of the sample depending on the dry matter content.

As digestate can be dewatered there are two components: the liquid phase – digestate liquor and the solid phase – digestate fibre. These two phases differ in their properties. In particular, they differ in the dry matter content and amounts of ammoniacal nitrogen, which can be separated by precipitation into the form of the magnesium ammonium phosphate – struvite. The amount of ammoniacal nitrogen in dry matter also differs in digestate and digestate liquor as can be seen in figure 1. For this reason, the experiments were conducted only with digestate liquor.

2.2. Experimental

Struvite precipitation begins by exceeding the equilibrium concentrations of the reaction ions Mg^{2+} , NH_4^+ and PO_4^{3-} and proceeds according to the simplified equation (1).



The solubility of struvite thus depends on the concentration of magnesium, nitrogen and phosphorus and usually decreases along with increasing pH when the minimum is at pH = 9-11 [7]. In order to guarantee that the product of solubility of the potential struvite precipitate as in equation (1) would be exceeded, Mg^{2+} and PO_4^{3-} were added to the sample of the centrifuged digestate. In the first part of the research, summarized in this contribution, Magnesium sulphate anhydrous – MgSO_4 (Penta s.r.o) and Disodium hydrogen phosphate dodecahydrate $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ (Penta s.r.o) were used for this purpose. Chemical reagents were dosed according to the chemical analysis carried out in

the laboratory of the *Institute of Environment Engineering at HGF, VSB-TUO*. The results of the digestate liquor analysis are shown in Table 1.

Table 1. Input parameters of digestate liquor after centrifugation in centrifuge *BEHO CHC 61A*

Parameter	Dry matter content	PO_4^{3-}	NH_4^+	N-NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	COD
Unit	%	[mg.l ⁻¹]	[mg.l ⁻¹]	[mg.l ⁻¹]	[mg.l ⁻¹]	[mg.l ⁻¹]	[mg.l ⁻¹]	[mg.l ⁻¹]
Value	2.17	640	2 138	1 660	279	136	215	34 000

Experimental procedure was drawn up based on experiments already carried out according to expert articles [8, 9]. Initial sample temperature was ± 20 °C. The pH value was adjusted using 30% NaOH. The pH value = 8.90-9.25 was tolerated, because in accordance with [10] struvite has the lowest solubility at this interval. Also samples were tested without pH adjustment. Stirring was carried out on a *Lovibond* 4-position mixing column at 250 and 150 RPM. Volume of the samples was $V = 150$ ml. First, PO_4^{3-} ions were added, stirring was done, pH was measured, and Mg^{2+} reagent was added, and the sample was homogenized. pH was repeatedly measured or adjusted by NaOH. Subsequently, RPM were reduced and the time of precipitation was measured from this moment. For samples at the temperature of $t = 35$ °C, the *Lavat Chotutice* magnetic stirrer *MM4* with the heating function was used and the temperature was measured by pH meter *WTW pH 330i* with a temperature measurement function. Upon expiration of the precipitation time the samples were subjected to separation. The tested separation methods were:

- Vacuum filtration on a Vacci-Space 30 apparatus through a KA-2 quantitative analysis paper (high speed) at a pressure $p = -0.2$ MPa (-3 psi) according to recommendations of [8].
- Centrifugal centrifugation of *Merici* type *NF 800* for 10 minutes at a frequency of 4 100 RPM according to recommendations of [6].

3. Results and conclusions

To find a suitable ratio of precipitating agents $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ and MgSO_4 in various stoichiometric ratios were dosed. Tested ratios of the reactants are given in Table 2.

Table 2. Tested weight ratios and appropriate concentration of ions.

Tested weight ratio	Mg^{2+} [mg.l ⁻¹]	NH_4^+ [mg.l ⁻¹]	PO_4^{3-} [mg.l ⁻¹]
3.2 : 1.0 : 1.7	9 363	2 138	18 725
2.0 : 1.0 : 0.5	5 618	2 138	5 618
3.2 : 1.0 : 0.8	9 363	2 138	9 363
1.3 : 1.0 : 0.8	3 745	2 138	9 363

After the first experiments, we found that the samples could not be separated by vacuum filtration through a KA-2 filter paper for quantitative analysis. Therefore, the solid phase was separated using the second method. The first tested ratio was $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 3.2:1.0:1.7$. Results obtained were: The NH_4^+ removal efficiency was approximately identical in case of 15 min. precipitation at a) pH = 6.9 (without pH adjustment), and b) pH = 9.0 (with pH adjustment). For the first case a) was NH_4^+ removal 77.3 % and 81.3 % for the second case b). However, for the sample b) with pH adjustment there were obtained lower residual concentrations of PO_4^{3-} and Mg^{2+} ions compared to sample a). These ions could be precipitated in the form of $\text{Mg}_3(\text{PO}_4)_2$. Residual PO_4^{3-} concentration was very high (equals 3 700 mg.l⁻¹). At weight ratio of 2.0:1.0:0.5 there was the influence of pH adjustment (mostly pH = 9.0), duration and temperature on ammoniacal nitrogen removal tested (see figure 2). Ions were removed from these samples in average of 56.4 %. In the samples where precipitation was using increased temperatures at $t = 35$ °C, no significant increase in ammonium ion removal efficiency was observed. On the contrary, prolongation of the precipitation time to $t = 60$ min. led to the slightly increased efficiency. Because the ammonia removals are noticeably lower due to small amounts of PO_4^{3-} ions added another essential ions ratio was tested. At ratio 3.2:1.0:0.8 the

maximum NH_4^+ removal efficiency (82.5 %) was obtained in a sample after 15 minutes precipitation with pH adjustment to pH = 9 and raised temperature to $t = 35^\circ\text{C}$. According to the calculations of removed ions ratio, N-NH_4^+ should be removed from this sample from up to 80.0 % in struvite. For total NH_4^+ ions removal, see in figure 3.

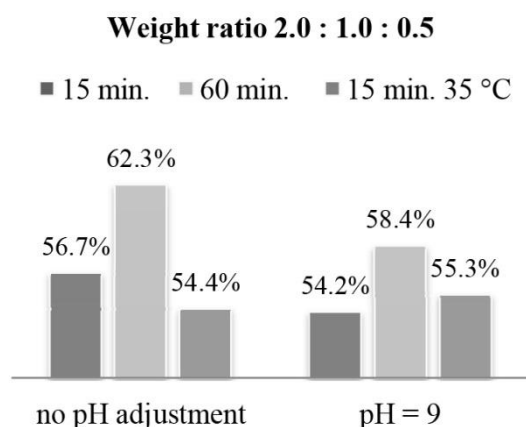


Figure 2: Total NH_4^+ ions removal. Tested weight ratio 2.0 : 1.0 : 0.5.

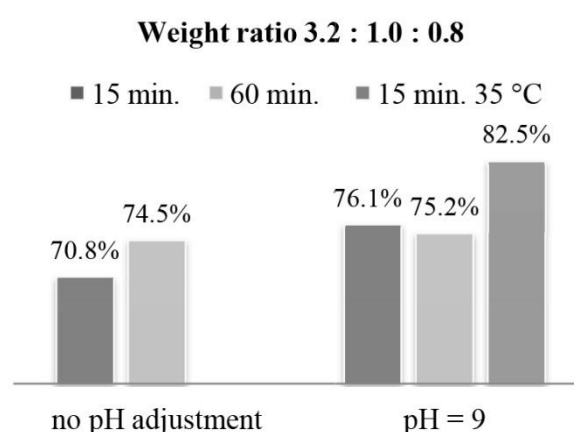


Figure 3: Total NH_4^+ ions removal. Tested weight ratio 3.2 : 1.0 : 0.8.

Due to the high residual concentrations of magnesium in acquired digestate liquor - $c(\text{Mg}^{2+}) = 3200 \text{ mg.l}^{-1}$, lower amount of Mg^{2+} ions added was tested along with the last tested amount of PO_4^{3-} ions. It means the ratio 1.3: 1.0: 0.8. Over 75.9 % of ammonium ions were removed in spite of low Mg^{2+} doses. Ammonium ions could be from 72.0% removed as struvite precipitate according to the calculations.

According to all the obtained results, the list of best removals in certain conditions was assembled (see table 3). One experiment was chosen from the list to be examined in detail.

Table 3. The best chosen removals of NH_4^+ ions and residual concentrations of ions.

Tested weight ratio	NH_4^+ Removal [%]	t [min]	pH [-]	t [$^\circ\text{C}$]	Mg^{2+} [mg.l $^{-1}$]	PO_4^{3-} [mg.l $^{-1}$]	NH_4^+ [mg.l $^{-1}$]
3.2 : 1.0 : 1.7	81.3	15	9.0	20	1 980	3 700	400
2.0 : 1.0 : 0.5	62.3	60	no	20	2 320	160	805
3.2 : 1.0 : 0.8	82.5	15	9.0	35	3 220	192	375
3.2 : 1.0 : 0.8	74.5	60	no	20	3 101	700	545
3.2 : 1.0 : 0.8	76.1	15	9.0	20	3 252	280	510
1.3 : 1.0 : 0.8	77.8	15	no	20	129	603	475
1.3 : 1.0 : 0.8	78.5	60	9.0	20	768	525	460

Chosen dose of reagents was in a ratio of 1.3: 1.0: 0.8. The precipitation lasted for 15 minutes and the pH value was not adjusted in advance. Input concentrations of used ions corresponded to 3 745 mg.l^{-1} Mg^{2+} ions and 9 363 mg.l^{-1} PO_4^{3-} ions. The precipitated sludge after separation was analysed for the presence of struvite by X-Ray Powder Diffraction (XRD), for the dry matter content and sum of SO_4^{2-} ions. Total dry matter was 15.76 % and the sum of SO_4^{2-} in the sludge was 35 076 mg.kg^{-1} of dry matter. According to XRD the sludge contained the most the precipitating agent as a mineral in its hydrated form - $\text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$ (Precisely 37.29 %). Even though the struvite was represented in this sample less than was expected, namely 33 %, N-NH_4^+ was removed from the sample with an efficiency of $\eta = 77.8$ %. N-NH_4^+ , which was not detected as struvite, may be present in an amorphous form in which cannot be distinguished by XRD analysis. Other minerals monitored in a sludge were:

Quartz - SiO₂ (15.96 %), Calcite - CaCO₃ (10.26 %), Brucite - Mg(OH)₂ (3.01%) and Sylvite - KCl (0.49 %). Parameters of supernatant liquor gained after precipitation and centrifugation are in table 4.

Table 4. Parameters of supernatant liquor gained after precipitation.

Parameter	COD [mg.l ⁻¹]	NH ₄ ⁺ [mg.l ⁻¹]	N-NH ₄ ⁺ [mg.l ⁻¹]	PO ₄ ³⁻ [mg.l ⁻¹]	Mg ²⁺ [mg.l ⁻¹]	Ca ²⁺ [mg.l ⁻¹]	Na ⁺ [mg.l ⁻¹]	SO ₄ ²⁻ [mg.l ⁻¹]
Value	14 200	475	369	603	129	13	2 184	9 275
Removal	-58.2 %	-77.8 %	-77.8 %	-5.78 %	-5.14 %	-95.3 %	+90.2 %	-34.7 %

4. Conclusions

The aim of the research was to verify the possibilities of struvite precipitation in the liquid phase of the digestate using MgSO₄ reagent, which is not a commonly used reagent according to summary in [6]. The experiments proved that struvite was able to precipitate at various Mg²⁺:NH₄⁺:PO₄³⁻ ratios, whereby the stoichiometric ratio of 1.0:1.0:1.0 is not necessary to keep up, since the full use of the introduced ions will never be achieved. Furthermore, it was found that the combination of increased pH to a level of 9.0 and increased temperature can achieve the maximum removal of NH₄⁺ ions. However, almost identical results under lower energy demands can be achieved by appropriate ion ratio. In general, it is not advisable to use MgSO₄ as a source of Mg²⁺ ions, because the need of high concentrations of SO₄²⁻ permits a subsequent use only with further treatment.

Acknowledgments

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