

RECYCLING OF PHOSPHORUS AND AMMONIA NITROGEN FROM DIGESTATE

Katrin Calábková, Petra Malíková, Silvie Heviánková, Michaela Červenková

¹VŠB-Technical University Ostrava, Faculty of Mining and Geology, 17. listopadu 15, Ostrava, Czech Republic

ABSTRACT

Digestate from biogas plants, formed by dewatering anaerobically stabilized sludge, is characteristic of high concentrations of phosphates and ammonia nitrogen suitable for further use. Phosphorus is an element widely used to produce fertilizers, and because of its continually shortening natural supplies, recycling of phosphorus is gaining on significance. Both phosphorus and nitrogen are important elements and their presence affect the quality of water resources. Both elements can contribute to eutrophication. At the same time, both phosphorus and ammonia nitrogen, are important elements for agricultural production, and therefore greater demands are being made on the effort to connect sewage treatment processes and the process of recycling of these nutrients. A suitable product of phosphorus and ammonia nitrogen are phosphates in the form of a structurally-poorly soluble precipitate of magnesium ammonium phosphate (struvite). This form of slowly decomposing fertilizer is distinguished by its fertilizing abilities. Compared to direct use of digestate as a fertilizer, struvite is more stable and can gradually release ammonia nitrogen for a long time without unnecessary losses. In the reported experiments, the precipitation efficiency of the recycling of ammonia nitrogen and phosphorus from the digestate liquor (liquid discharge from digestate) was, at a stoichiometric ratio of $Mg^{2+}: NH_4^+: PO_4^{3-}$ (3.2: 1: 0.8) and a stirring time of 15 minutes, 87 % for ammonia nitrogen ions.

Keywords: digestate, biogas plants, ammonia recovery, precipitation

1 INTRODUCTION

Digestate, a nutrient-rich material produced by anaerobic digestion at biogas plants, can be applied as a fertilizer. All the nitrogen, phosphorous and potassium present in the feedstock remain in the digestate as none is present in the biogas. However, the nutrients are extensively more available in digestate, meaning it is easier for plants to utilize them.

The digestate handling options mainly depend on the resulting quality of the product generated after anaerobic digestion. This means that the way of disposal depends mainly on the properties of input raw materials entering the biogas plants [1].

Agricultural biogas plants are biogas plants where materials of plant nature and livestock manure, or bedding, are processed. The processing of wastes listed in Czech Waste Act 185/2001 Coll and other materials stated by Regulation (EC) 1774/2002 of the European Parliament and of the Council is forbidden in agricultural biogas plants. On the authority of the Czech and European legislation, digestates are considered organic fertilizers in the most cases. The digestate's nutrient content and its nutrient subsequent availability for plants is affected by an input substrate. However, a common feature for digestate is low dry matter content, which for agricultural biogas plant, is between 2 and 9 %.

The digestate's chemical composition is similar to the mineral fertilizer rather than organic one and almost all easily degradable organic materials decomposed during anaerobic digestion. This resulted in a presence of minimum beneficial substances in digestate which may be utilized by plants. Nitrogen content in fresh digestate ranges from 0.25 to 0.75 %, of which 25 to 75 % is in the form of ammoniacal nitrogen (i.e. $N-NH_4^+$) making up a weak alkalinity of digestate (pH = 7-8). Therefore, land spreading of digestates can cause a discharge of large quantities of nutrients into the environment, which participate in eutrophication and reduction of dissolved oxygen in water bodies [2].

In practice, there are two views of the use of digestate. One party believes it is necessary to modify the digestate in some way and then get rid of it. However, a more modern approach seeks to make the most of this raw material. Firstly, it aims to recycle all nutrients (nitrogen, phosphorus, potassium), use them as fertilizers and use the separated water to irrigate or dilute fermentor contents [3].

With the increase in population on Earth, the demand for raw materials and the associated need for fertilizers increased. Higher consumption of fertilizers results in a rapid decline in natural phosphates. Currently, 80 % of the extracted phosphorus is used to produce fertilizers. Phosphorus is mainly mined in South Africa, China, and Morocco [4]. If the phosphorus consumption remains the same, the natural phosphates supply will be

exhausted within 100 to 120 years. The mining of phosphorus will become increasingly demanding and expensive, as the available deposits diminish. During its cycle in nature, phosphorus is leached into surface water and groundwater, then taken into the sea, where it is deposited as insoluble phosphates into deep sediments [5,6].

2 MATERIALS AND METHODS

The used sample of digestate was from the Stonava biogas plant. The input material for anaerobic digestion is pork slurry in combination with maize silage and crushed corn grain. The digestate was firstly centrifuged and only the liquid part – digestate liquor – was used for precipitation. A Stonava Farm employee retrieved the sample.

Laboratory measurements were based on a chemical analysis of digestate liquor, which determined the concentrations of ammonia, phosphate, and magnesium ions. These ions are the basic components for precipitation of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$). The measured input values for digestate liquor are recorded in Table 1.

Table 1. Input values of digestate liquor sample

Parameter	Dry matter content	PO_4^{3-}	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	COD
Unit	%	$[\text{mg}\cdot\text{l}^{-1}]$	$[\text{mg}\cdot\text{l}^{-1}]$	$[\text{mg}\cdot\text{l}^{-1}]$	$[\text{mg}\cdot\text{l}^{-1}]$	$[\text{mg}\cdot\text{l}^{-1}]$	$[\text{mg}\cdot\text{l}^{-1}]$
Value	2.16	480	2 508	281	143	216	33 986

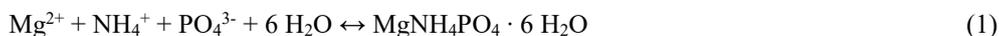
The Nessler reagent was used to determine the amount of ammonia nitrogen in digestate liquor. Concentration of magnesium ions was determined by a chelatometric method and absorption spectroscopy was used to determine the phosphates in the sample of digestate liquor.

The precipitation required an increase in the concentration of magnesium and phosphate ions, which was achieved by the addition of reagents. The source of Mg^{2+} ions was magnesium hydroxide and the source of PO_4^{3-} ions become orthophosphoric acid - H_3PO_4 .

The precipitation of magnesium ammonium phosphate was also affected by the pH value. The optimal pH for crystallization is between 8.5 and 9. The precipitate that occurs within this range is one of the worst-degradable forms [7,8].

Precipitation of struvite

The struvite precipitation begins when the equilibrium concentrations of the reaction ions Mg^{2+} , NH_4^+ and PO_4^{3-} is exceeded and the process acts according to the simplified equation (1).



The solubility of magnesium ammonium phosphate is thus dependent on the ion concentration of magnesium, nitrogen and phosphorus and typically decreases with increasing pH when the minimum is at pH = 9-11 [9].

150 ml of digestate liquor was used to precipitate struvite. Reagents were added to the stoichiometric ratio of 3.2: 1: 0.8 ($\text{Mg}^{2+} : \text{NH}_4^+ : \text{PO}_4^{3-}$).

First, 85% orthophosphoric acid - H_3PO_4 was pipetted into the beaker. 150 ml of the digestate liquor sample was added into the breaker. The mixture was then mixed with a glass rod. Further, magnesium hydroxide - $\text{Mg}(\text{OH})_2$ was weighed and added to the mixture. When it had ceased to foam, it was mixed again with the glass rod. Finally, the pH was measured. Mixing of the samples was carried out on a 6-position mixing column MK 6, the first sample was stirred for 15 min and the second sample was 60 min. First, the samples were mixed rapidly at 250 rpm and then at a slower speed of 150 rpm [9]. For separating the solid phase from the liquid phase, the centrifuge at a frequency of 4000 rpm for 10 minutes was used.

During the precipitation of struvite from the first digestate liquor sample, 2 217 $\text{mg}\cdot\text{l}^{-1}$ of ammonia nitrogen were transferred into precipitate. The precipitation with second digestate liquor sample was more successful, 2 280 $\text{mg}\cdot\text{l}^{-1}$ of ammonia nitrogen were transferred into precipitate. The results show that a longer precipitation time has a beneficial effect on the resulting residual values. The efficiency of ammonia nitrogen transfer was 86.9 % and 89.4 %. The results are shown in Table 2.

Table 2. Parameters of removals of NH_4^+ ions and residual concentrations of ions

N. of sample	t [min]	pH [-]	t [°C]	Mg^{2+} [$\text{mg}\cdot\text{l}^{-1}$]	PO_4^{3-} [$\text{mg}\cdot\text{l}^{-1}$]	NH_4^+ [$\text{mg}\cdot\text{l}^{-1}$]	NH_4^+ Removal [%]
Sample 1	15	9.4	20	135	117	333	86.9
Sample 2	60	9.4	20	129	63	270	89.4

3 RESULTS

After separation, the precipitated sludge was analyzed for the existence of struvite by X-Ray Powder Diffraction (XRPD) to detect the content of the dry matter, which was 15.8 %.

According to XRD, the most represented minerals in the precipitate were $\text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ (struvite). Other minerals present in the sludge were: Quartz - SiO_2 , Calcite - CaCO_3 , Brucite - $\text{Mg}(\text{OH})_2$ and Sylvite - KCl . The percentage content of the sludge can be seen in Figure 1. Ions of NH_4^+ were removed from the sample with an efficiency of 87 %, and while not detected as struvite, they may be present in an amorphous form that is not detected by XRD analysis or the ions may be removed by volatilisation of the ammonium gas.

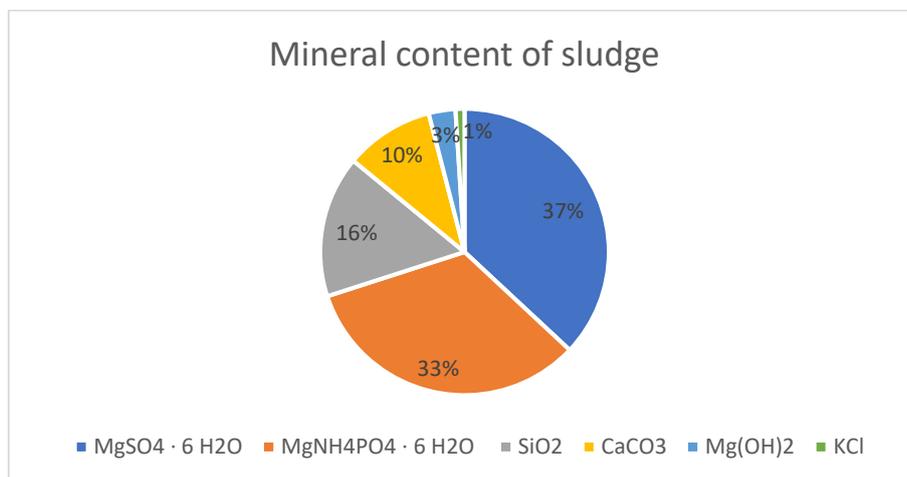


Figure 1. Composition of sludge

Parameters of supernatant liquor gained after precipitation and centrifugation are in Table 3.

Table 3. Parametres of supernatant liquor gained after precipitation

Parameter	PO_4^{3-}	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	COD
Unit	$[\text{mg} \cdot \text{l}^{-1}]$					
Value	117	333	12	135	2 194	14 198
Removal [%]	76	87	95	5	+90*	58

Note: *the amount of sodium increased by 90 %

CONCLUSION

Digestate contains high concentrations of ammonia and phosphate ions, which can be further processed. One of the possibilities of processing these ions is to convert them to a poorly soluble magnesium-ammonium phosphate precipitate. This compound can be further used as a fertilizer. The aim of the presented study was to precipitate phosphorus and ammonia into insoluble form from digestate using selected reagents and pH values.

The stoichiometric ratio of 3.2: 1: 0.8 ($\text{Mg}^{2+} : \text{NH}_4^+ : \text{PO}_4^{3-}$) was used to precipitate phosphates and ammonia ions from digestate liquor. During the precipitation, the ammonia ion removal efficiency reached 87 %.

The main contribution of this research is finding the possibility of reduction of ammonia nitrogen N-NH_4^+ in the products of digestate (digestate liquor) by the chemical precipitation method by the combination of Mg^{2+} , NH_4^+ and PO_4^{3-} ions in the form of poorly soluble structures - $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$. The result of the research is confirmation of the practical use of the liquid and sludge components of the digestate liquor as fertilizing irrigation, respectively mineral fertilizer.

Subsequent research shall focus on intensifying the precipitation process (length of process, change of pressure or temperature) to increase the quality of sludge obtained as a fertilizer, especially by obtaining larger $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$ crystals.

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