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PHOSPHORUS RECOVERY FROM SWINE SLURRY BY ACIDIFYING ULTRAFILTRATION AND STRUVITE CRYSTALLISATION

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Abstract: *Recovering nutrinets form waste is an alternative to the continues phosphorus mining and fertilizers productin. Domestic wastewater and waste streams from livestock are among the most promising sources of recycled phosphorus with potential application in the agriculturing. The paper reviews a method of phosphorus recovery from swine slurry using stages of acidifying, ultrafiltration and cryzstalisation with an aim to extract phosphorus, purifying the fluid and sediment struvite crystals. The purpose was to examine the application of swine slurry, to establish pH-optimum for acidifying and crystallization. Testings of orto-phoshorus, ammonium and magnesium were carried out on every step of the examination, also they were accompanied with supporting tests which indicated the decreasing of organic matter.*

Based on the results obtained, a procedure for acidic mobilization of the phosphates was developed as an initial step which significantly increased efficiency and recovery rate (up to 65%). Thereby the precipitation of struvite from wastewater and manure could be a step toward the development of hybrid technologies for simultaneously wastewater treatment and resource recovery which will contribute to the transformation of the economy from linear to circular approach.

Keywords: *phosphorus, swine slurry, manure, ultrafiltration, struvite.*

INTRODUCTION

Globally, intensification of agricultural systems increases the environmental footprint of food production. Larger livestock production units result in higher local emissions of pollutants (Peterson, S.O., et al., 2007). In the same time, the animal manure could be considered as a source of plant nutrients like phosphorus (P), nitrogen (N) and potassium (K). It is well-known that phosphorus is a valuable and life-essential, finite, irreplaceable resource and that organic matter that is also present in manure is needed to maintain the fertility of the agricultural soils (Schoumans, O.F et. al., 2014). Taking into account the fact that EU do not have significant phosphorus rock to mine, recycling this resource form waste flows is recommenced as an alternative to ensure food production security in the whole community. One opportunity for P-recovery is its concentration in the form of phosphate mineral named struvite (magnesium ammonium phosphate - $NH_4MgPO_4 \cdot 6H_2O$). It is slow P-releasing fertilizier with potential application in the organic and conventional farming.

EXPOSITION

Investigation of Swine Slurry Characteristics

Two swine slurry samples from a collector (SS1C and SS2C) and another two samples from a separator (SS1S and SS2S) were analized. The date obtained are presented in Table 1.

The values of total P and orto-P obtained showed that in SS1S- and SS2S sample phosphorus is dominantly in dissolved form, while in SS1C and SS2C it is presented in two fractions – mobilized (soluble) P and immobilized P - 29% and 45%, respectively. To uncover all the P potential of this substrate in soluble form, acidification procedure can be performed.

Table 1 Composition of swine slurry samples

Parameter	Unit	SS1C	SS2C	SS1S	SS2S
Total Solids	%	2.34±0.02	2.26±0.01	0.96±0.01	0.82±0.07
Volatile Solids	%	1.85±0.13	1.68±0.11	0.79±0.01	0.58±0.02
Total Inorganic Solids	%	0.48±0.12	0.58±0.11	0.17±0.01	0.24±0.02
C, d.w.	%	43.64±3.01	40.90±2.68	45.21±0.01	38.79±1.36
Total COD	mg O_2 L^{-1}	17,750±71	12,900±141	9,050±141	5,500±71
Dissolved COD	mg O_2 L^{-1}	9,725±21	3,620±14	5,650±71	3,173±11
Settleable Solids	ml L^{-1}	340	235±7	35.5±1	150±42
Total PO4	mg L^{-1}	1,967±97	1,292±20	357±16	490±45
orto-PO4	mg L^{-1}	1,401±12	889±14	357±19	486±2
NH4	mg L^{-1}	2,637±56	1,673±19	2,595±9	1,702±80

Note 1: SS1C – swine slurry 1 collector; SS2C – swine slurry 2 collector; SS1S – swine slurry 1 separator; SS2S – swine slurry 2 separator.

Note 2: The samples were tested in duplicate and the standard deviation is added to the value.

Titration of Swine Slurry with 0.4 n H_2SO_4 and 1 n NaOH

To determine quantities of H_2SO_4 and NaOH needed for acidifying and alkalizing the substrates 0.4 n H2SO4 (Fig. 1 and Fig. 2) and 1 n NaOH (Fig. 3 and Fig. 4) titration were performed. Durign the acid titration, orto-phosphates were examined (Fig. 5 and Fig. 6).

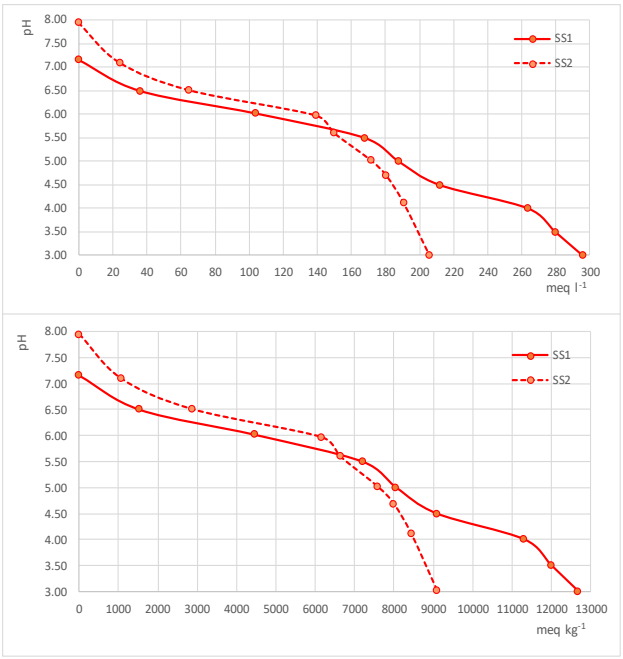

Fig. 1 Titration with 4 n H_2SO_4 of SS1C and SS2C

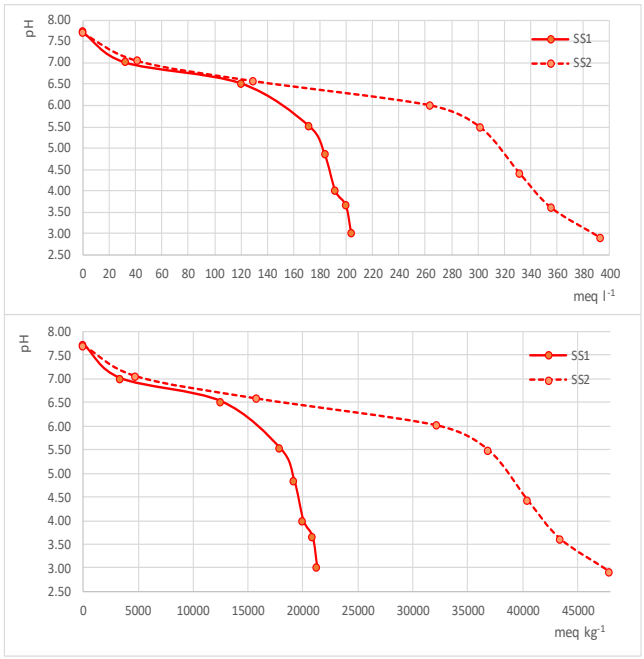

Fig. 2 Titration with 4 n H_2SO_4 of SS1S and SS2S

During this set of expiriments it was established that amount of acid needed is between 9,104 meq kg^{-1} dry weight for sample SS2C and 47,920 meq kg^{-1} dry weight for sample SS2S. In the same time, we have to take into account the fact that SS2S has total solids of 0.82%.

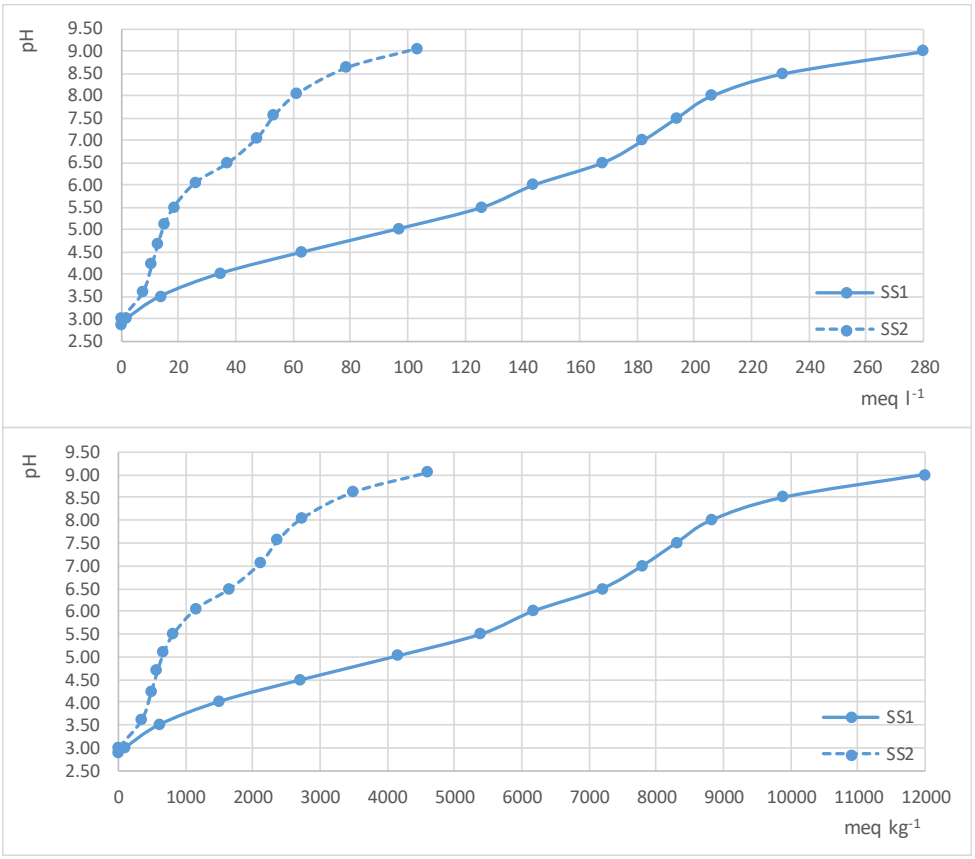

Fig. 3 Titration with 1 n NaOH of SS1C and SS2C

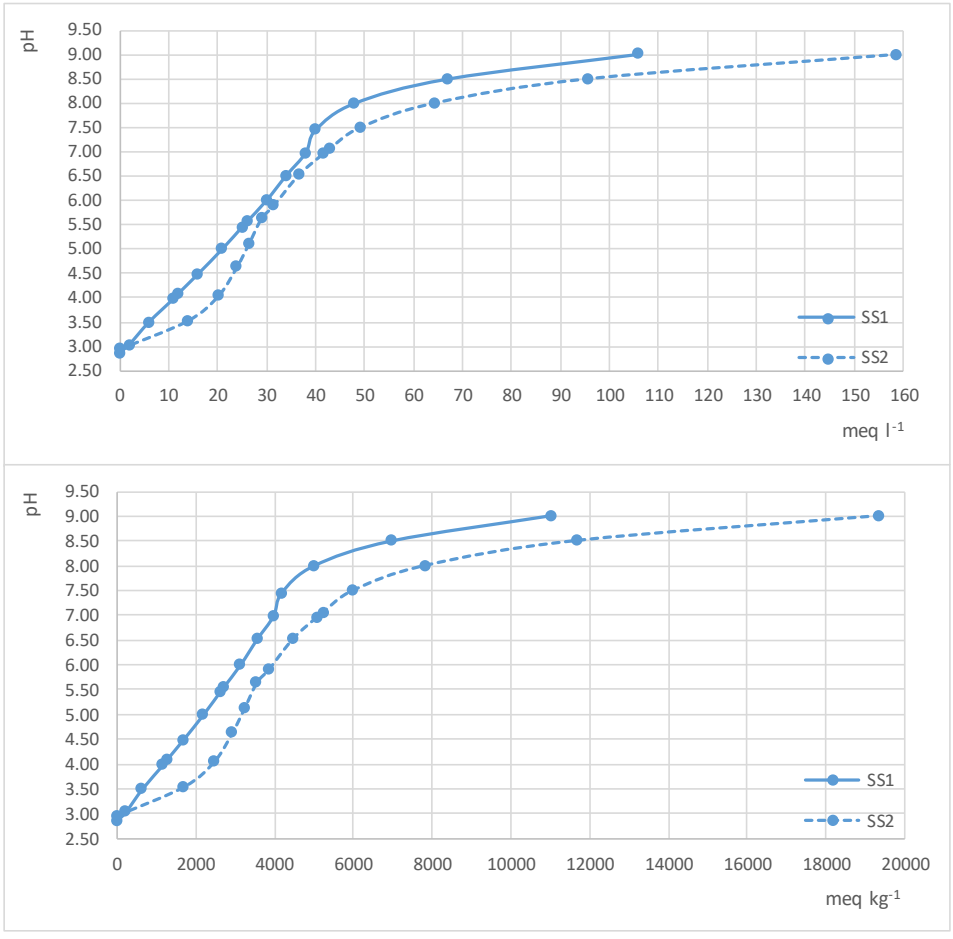

Fig. 4 Titration with 1 n NaOH of SS1S and SS2S

For alkalization of the acid treated samples, both samples (SS1S and SS2S) showed nearly same needs of NaOH.

After acid titration samples were tested for orto-P. The method used is according ISO 6878 (Ammonium molybdate spectrometric method), which pH range is 3.0 – 10.0, therefore it was not necessary a pH adjustment of the fluids.

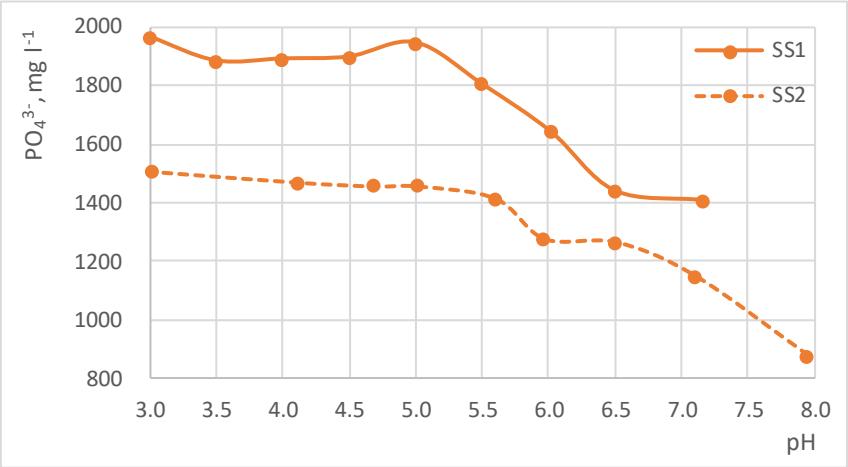

Fig. 5. orto-P during acid titration of SS1C and SS2C

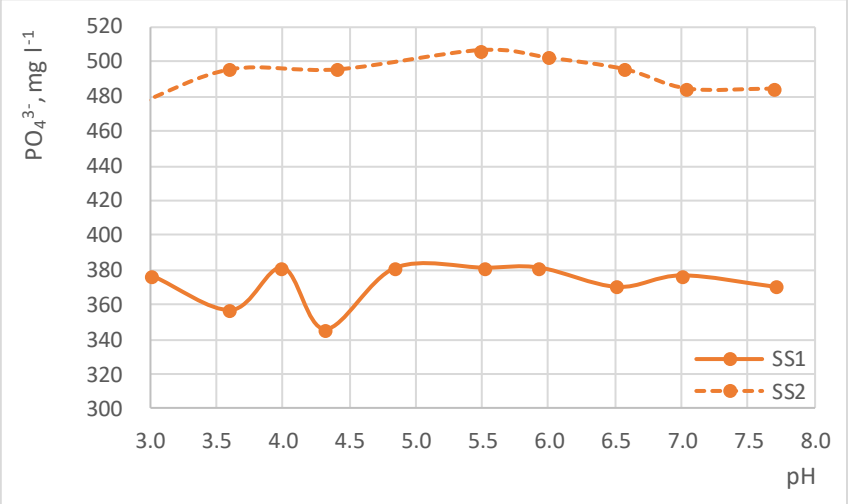

Fig. 6 orto -P during acid titration of SS1S and SS2S

It was established that in SSxS-samples there is no significant effect on the soluble phosphates fraction since initialy values, there is not unsoluble phosphates to be mobilized. On the contrary, in the case of SSxC samples, the soluble orto-phosphates were increased with 39.5% (at pH 3.0 - 1,967 mg L^{-1} orto-P) for SS1C and 71.8% for SS2C (at pH 3.0 - 1,508 mg L^{-1} orto-P).

Acidifying and Ultrafiltration

In this experiment we aimed to treat SS2C due to its large volume and high orto-P concentration. According to the results from the titration with sulphuric acid, pH point, up to which we examined the acidification with c.H_2SO_4, was pH 5.0. After that the sample was centrifuged for 10 min by 4,000 min^{-1} and the supernatant was collected for further processing.

Influent with volume of 5.7 L was filtered by laboratory ultrafiltation system EAUF-600 (Fig. 7) with pore size of 0.01 μm and the produced permeat was collected for struvite crystatallization. Characteristics of the influent, permeate and reject flows are shown in table 2.

The molar ratio of NH_4:PO_4:Mg of the permeate (table 3) shows that increasing the pH values could start spontaneously struvite formation.

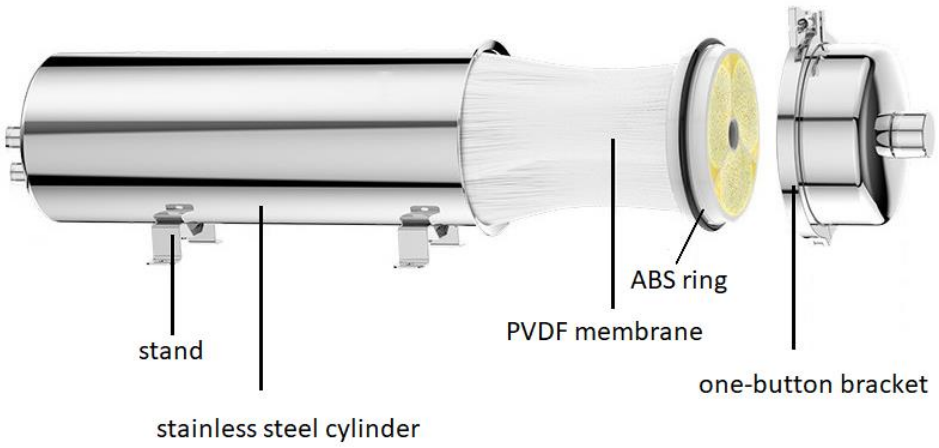

Fig. 7 Ultrafiltration system EAUF-600

Table 2 Flow characteristics of ultrafiltration process

Parameter	Influent	Permeate	Reject
V, ml	5,700	5,210	440
TS, %	3.09	1.72	17.66
TCOD, mg L^{-1}	2,720	1,379	16,977
NH4, mg L^{-1}	1,605	1,458	3,163
PO4, mg L^{-1}	2,130	1,951	4,032
Mg, mg L^{-1}	1,051	962	2,000
Ca, mg L^{-1}	200	170	519
Mass units			
V, L	5.70	5.21	0.49
TS, g	176	89,4	77,7
TCOD mg	15,504	7,861	96,771
NH4, mg	9,146	8,311	18,026
PO4, mg	12,141	11,121	22,983
Mg, mg	5,714	4,848	11,400
Ca, mg	1,142	967	2,958

Table 3 Molar ratio of the permeate

Permeate - molarity	mmol L^{-1}	NH4:PO4:Mg
NH4	80.9	3.9
PO4	20.5	1.0
Mg	39.6	1.9

Crystallization

The struvite cristalization was achieved after alkalization of the substrates with 30% NaOH to pH values of 8.02; 8.30; 8.87; 9.42 and 10.14. The crystallization was performed on floculator at 50 min^{-1} for 30 min. Beakers with the suspensions were led stay overnight and then the supernatant and cristals were harvested by centrifugation (for 10 min by 4.000 min^{-1}) The results for the liquid fraction before and after precipitation of struvite are presented in Table 4.

Table 4 Characteristic of the liquid fraction before and after precipitation of struvite

Parameter	Before	After Crystallization				
		s1	s2	s3	s4	s5
V, ml	5,210	500	500	500	500	250
pH	5.53	7.80	7.98	8.72	9.22	9.83
TS, %	1.72	-	-	-	-	-
Total COD, mg L^{-1}	1,379	836.0	848.0	853.0	846.0	814.0
NH4, mg L^{-1}	1,458	2,946	2,880	2,819	2,464	2,476
PO4, mg L^{-1}	1,951	190.3	97.80	39.65	17.62	2.64
Mg, mg L^{-1}	962	258.2	194.4	243.0	230.9	129.1
Ca, mg L^{-1}	170	250.5	320.6	160.3	120.2	175.4

The concentration of phosphorus in the supernatant after struvite formation was decreased significantly - in sample s1 it was fallen to 10% from the initial value, as in sample s5 phospates were dropped up to 0.14%. Magnesium also was decreased in all five samles, however there was significant increasing within the supernatants of calcium (sample s1 and s3), which can be explain with ion exchange reactions occurred with the dosing of NaOH. The concentration of ammonium ions was expected to decrease, but the opposite trend was observed. In this regard, it is necessary to analyze the total nitrogen in order to have better knowledge on the fate of this nutrient during the process.

CONCLUSION

This study demonstrates the potential of the swine slurry as a source of phosphorus. The acidification step supports the complete extraction of the initaly unsoluble forms of phosphorus wich increses the recovery proces efficiency. The fluid obtained after ultrafiltration showed suitable N/P/Mg molar ratio so there is no need to add external souce of magnesium or phosphorus for precipitation.

ACKNOWLEDGEMENTS

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REFERENCES

Petersen, S.O., S.G. Sommer, F. Béline, C. Burton, J. Dach, J.Y. Dourmad, A. Leip, T. Misselbrook, F. Nicholson, H.D. Poulsen, G. Provolo, P. Sørensen, B. Vinnerås, A. Weiske, M.-P. Bernal, R. Böhm, C. Juhász, R. Mihelic. (2007). Recycling of livestock manure in a whole-farm perspective. *Livestock Science* 112, 180–191.

Schoumans, O.F., P.A.I. Ehlert, J.A. Nelemans, W. van Tintelen, W.H. Rulkens, O. Oenema. (2014). *Explorative study of phosphorus recovery from pig slurry. Laboratory experiments.* Alterra Wageningen UR.