BioDEN

A biorefinery approach to exploit digestate as key feedstock in
the energy – nutrient nexus

D3.3 – Mineral P-fertilizer, extracted and re-precipitated from solid fraction of digestate

Objective

With the goal of recovering phosphorus (P) in the form of biobased fertilizers, acid-leaching is performed on the solid fraction of cow manure-based anaerobic digestate, followed by precipitation tests conducted on the supernatant derived from the leaching step. The potential of citric acid to leach P from the digestate is tested against the common practice of using sulfuric acid. Additionally, calcium hydroxide ($Ca(OH)_2$), magnesium hydroxide ($Mg(OH)_2$), and sodium hydroxide (NaOH) are further used in the precipitation step to obtain P-fertilizer in the form of Ca- and Mg-phosphate, or struvite.

Set-up/Parameters

The digestate used in the experiments is derived from bench-scale anaerobic digestion (AD) of cow manure, operated by KU Leuven. The N-stripped digestate samples are generated from the stripping-scrubbing tests performed by KU Leuven, using the same cow manure-based digestate. The solid fraction of the N-rich and N-stripped digestates are then used as the initial source of P. The characterization of the digestates is presented in Table 1.

Table 1 **-** *Characterization of cow manure digestate, Nitrogen-stripped cow manure digestate, and their respective liquid and solid fractions.*

Parameter	**Samples**					
	Digestate	**N-stripped digestate**	**Solid fraction of digestate**	**Solid fraction of N-stripped digestate**	**Liquid fraction of digestate**	**Liquid fraction of N-stripped digestate**
pH-KCl	8.43 ± 0.12	8.42 ± 0.02	9.11 ± 0.02	8.91 ± 0.05	8.47 ± 0.03	8.27 ± 0.03
EC (mS/cm)	20.36 ± 0.20	13.60 ± 0.25	3.17 ± 0.05	3.53 ± 0.02	24.32 ± 0.26	16.48 ± 0.16
Total solids (%)	5.76 ± 0.26	8.58 ± 0.66	12.09 ± 0.30	19.65 ± 0.59	2.21 ± 0.11	2.77 ± 0.25
Volatile solids (%)	79.27 ± 0.07	67.56 ± 0.22	76.78 ± 0.86	82.34 ± 0.18	91.42 ± 2.15	84.69 ± 2.34
Total N (g/kg FM)	4.15 ± 0.10	2.27 ± 0.06	6.08 ± 0.31	4.17 ± 0.07	3.42 ± 0.08	1.27 ± 0.02
Total NH_4^+ (g/ kg FM)	2.32 ± 0.01	0.18 ± 0.01	1.99 ± 0.04	0.22 ± 0.02	2.36 ± 0.08	0.06 ± 0.01
	----------------------------------g/kg DM------------------------------------				---------------------g/kg FM------------------	
P (g/kg)	8.81 ± 0.14	7.15 ± 0.08	11.01 ± 0.62	8.55 ± 0.17	0.068 ± 0.001	0.113 ± 0.001
K (g/kg)	44.60 ± 0.41	40.78 ± 0.36	20.82 ± 1.31	27.79 ± 1.97	3.19 ± 0.01	4.04 ± 0.02
Ca (g/kg)	16.74 ± 0.25	13.80 ± 0.21	24.06 ± 1.56	19.84 ± 0.78	0.12 ± 0.02	0.17 ± 0.03
Na (g/kg)	6.55 ± 0.14	23.77 ± 0.52	2.26 ± 0.36	6.02 ± 0.46	0.56 ± 0.01	1.21 ± 0.01
Mg (g/kg)	9.60 ± 0.09	7.88 ± 0.10	11.56 ± 0.89	10.38 ± 0.37	0.18 ± 0.01	0.16 ± 0.01

Note: The values of Total N and Total NH_4^+ are expressed in grams/kg of fresh matter of either the digestate, solid fraction, or liquid fraction.

The P in the solid fraction is extracted using citric acid addition (concentration of 0.1 mol/L) in liquid: solid ratio 2:1 for 24 hours and its leaching performance is compared against sulfuric acid under the same conditions.

After leaching, the liquid and pellet from the mixture are separated via a centrifuge at 3500 rpm for 10 minutes. The pH of the supernatant is measured and a precipitating agent (either $Ca(OH)_2$, or $Mg(OH)_2$), or NaOH is added until a pH of 8-8.5 is maintained for 30 minutes to achieve P precipitation. In cases where the pH is quickly raised above pH 8.5, drops of HNO_3 (0.01 mol/L) are added to adjust the pH between 8-8.5.

Centrifugation follows the precipitation step to separate the solid precipitate rich in P from the solution. The precipitate is dried in an oven at 50 °C and the dried precipitate is crushed to powder form, resulting in the final form of the potential biobased fertilizer. The final products are then sent for XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy), and EDX (Energy Dispersive X-Ray) analyses to determine their composition. An overview of the experimental set-up is illustrated in Figure 1.

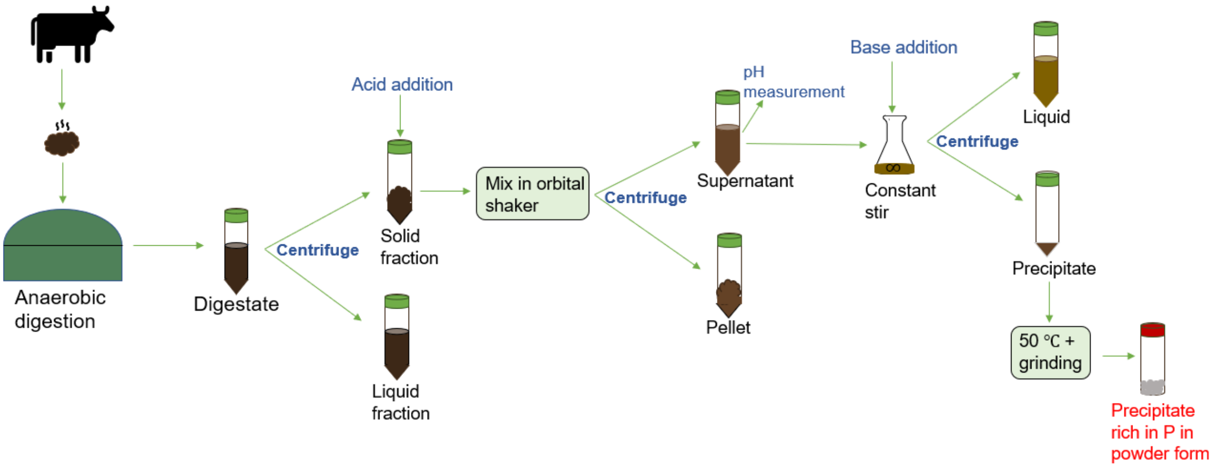

Figure 1 – Set-up for phosphorus precipitation from the solid fraction of digestate.

Results

The maximum P concentration was achieved as 48.2 mg P/g precipitate when sulfuric acid was applied as a P-leaching agent on the solid fraction of N-rich digestate (SFD), and $Mg(OH)_2$ was used as the precipitating agent. An overview of the P concentrations obtained in the final precipitates is shown in Figure 2.

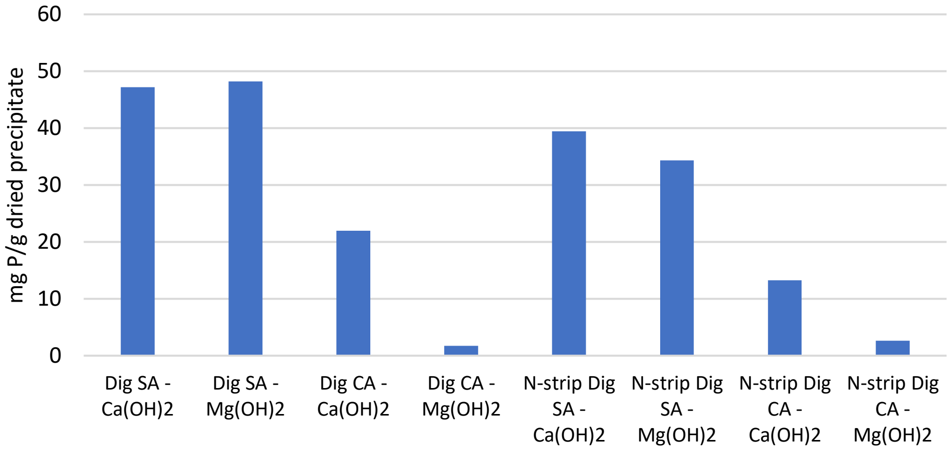

***Figure 2** - Phosphorus concentration of the final dried precipitates, originated from P-leached solutions from the solid fraction of N-rich and N-stripped digestate.*

Note: The initial sample in all the tests was a solid fraction of digestate, either N-rich or N-stripped. “Dig” refers to N-rich digestate; “SA” corresponds to sulfuric acid as a P-leaching agent; “N-strip. Dig” is N-stripped digestate and “CA” corresponds to citric acid as a P-leaching agent. “$Mg(OH)_2$” or “$Ca(OH)_2$” present in the figure are the precipitating agents used.

The precipitate originated from the SFD, in which sulfuric acid was used as the leaching agent, and $Ca(OH)_2$ as the precipitation agent, was composed of struvite ($NH_4MgPO_4.6H_2O$), calcite ($CaCO_3$), and gypsum ($Ca(SO_4)(H_2O)_2$). Since there was no Ca-phosphate indicated in the XRD result, we can assume that the addition of $Ca(OH)_2$ in the supernatant only contributed to the precipitation of phosphate (PO_4^{3-}) due to the increase of pH, since the added Ca^{+2} did not bind to PO_4^{3-}, and instead it was present in the form of calcite and gypsum. The precipitate resulting from a similar experiment, but using citric acid as the leaching agent, was composed of calcite, similar to the precipitate formed when sulfuric acid was used; however, no crystalline form was identified.

New precipitation tests using only NaOH to control the pH were further conducted. In the samples in which the SFD was used in the P-leaching step and either H_2SO_4 or citric acid was the P-leaching agent, the final proportion of NH_4^+:PO_4^{-3} and Mg^{+2}:PO_4^{-3} were both above 1, a minimum proportion expected to promote struvite formation. Therefore, NaOH was the only addition to the solution, used to reach a pH range between 8-8.5 for possible struvite formation.

The graphs obtained in the XRD analyses were analysed via the software QualX to identify the main composition of the solid product from the precipitation experiments. In the case of using sulfuric acid as the leaching agent, the composition of the precipitate exhibited struvite. On the other hand, the precipitation product resulting from the experiment with citric acid as the leaching agent did not present any significant crystalline formation.

The P-rich supernatants derived from solid fraction samples from N-stripped digestate (SFND), which were P-leached with both sulfuric and citric acid, had the proportion of NH_4^+:PO_4^{-3} lower than 1. Therefore, NH_4Cl was added to obtain the minimum proportion of $1NH_4^+$:$1PO_4^{-3}$.

In the final precipitate, obtained in the sample in which sulfuric acid was the P-leaching agent, struvite was also identified in the composition. On the other hand, in the precipitation product derived from SFND, P-leached with citric acid, no significant crystalline form was identified after the addition of NH_4Cl and NaOH, similar to the precipitate obtained from the SFD leached with citric acid.

Overall, the precipitation products in which citric acid was used as the P-leaching agent did not result in any crystalline material identified in the XRD. This result can be explained by a very low amount of crystalline form present, or it might indicate that citric acid acted at a level as a precipitation inhibitor, the latter already described in the literature. Kofina et al. (2007) observed up to 75-80% of struvite inhibition when citric acid was present. An increasing amount of citric acid additive in solution with conditions propitious to struvite formation resulted in a decrease in struvite formation in the study by Perwitasari et al. (2017). Therefore, although citric acid presented good P-leaching capacity in the present study, its influence on the precipitation step resulted in no crystalline formation with P in its composition at the end of the process.

The four samples mentioned previously were sent to SEM-EDX for further characterization of the products, and their elemental composition is presented in Table 2. For all the precipitation products O, Ca, and P were the elements present in the highest total percentages by weight, indicating a significant presence of P in all the products. The concentration of Mg in total percentage by weight; on the other hand, was the highest in the precipitate derived from the solid fraction of digestate and P-leached with sulfuric acid.

Table 2 - Elemental composition of precipitation products obtained via SEM-EDX.

Dig-SA			N-Strip. Dig-SA			Dig-CA			N.Strip.Dig-CA		
Element	Wt(%)	At (%)	Element	Wt(%)	At (%)	Element	Wt(%)	At (%)	Element	Wt(%)	At (%)
O	50.95	66.99	O	50.49	67.63	O	49.67	66.77	O	53.62	69.95
Ca	13.01	6.83	Ca	17.98	9.63	Ca	19.63	10.54	Ca	16.27	8.47
P	12.92	8.77	P	9.91	6.87	P	10.30	7.15	P	8.12	5.47
Mg	7.78	6.74	S	6.59	4.41	Si	5.65	4.33	Na	5.20	4.72
S	7.30	4.79	K	3.66	2.01	Na	3.95	3.70	Si	5.07	3.76
K	2.52	1.36	Mg	3.62	3.19	K	3.37	1.85	K	4.56	2.43
Na	2.50	2.29	Na	3.38	3.15	Mg	2.90	2.57	Mg	2.60	2.23
Si	2.14	1.61	Si	2.42	1.85	S	2.24	1.50	Cl	1.91	1.12
Al	0.50	0.39	Cl	1.54	0.93	Cl	1.18	0.71	S	1.79	1.16
Cl	0.41	0.24	Al	0.44	0.35	Al	1.10	0.88	Al	0.87	0.67
Total	100	100	Total	100	100	Total	100	100	Total	100	100

Note: “Dig” refers to N-rich digestate; “SA” corresponds to sulfuric acid as a P-leaching agent; “N-strip. Dig” is N-stripped digestate and “CA” corresponds to citric acid as a P-leaching agent.

Conclusions/Remarks

- Compared to citric acid, the solutions with sulfuric acid as the leaching agent resulted in the highest concentrations of P in the final precipitates, which corresponded to the experiments with $Mg(OH)_2$ (48.2 mg P/g precipitate) and $Ca(OH)_2$ (47.2 mg P/g precipitate) as the precipitating agent, with N-rich (non-stripped) digestate as a P source.
- In the sample of solution derived from a P-leached solid fraction of digestate, in which sulfuric acid was used, only the addition of NaOH as a base to reach the pH of 8 was already sufficient for the formation of struvite.
- Struvite was only obtained in the samples in which sulfuric acid was used as a P-leaching agent, for both digestate an N-stripped digestate.
- Citric acid used in the P-leaching step showed inhibition aspects in the P-precipitation step, after the addition of base.

References:

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Perwitasari, D. S., Jamari, J., Muryanto, S., & Bayuseno, A. P. (2017). Influence of Citric Acid on Struvite Precipitation. *Advanced Science Letters*, *23*(12), 12231-12234.

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More information about the project: check out the project website.

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