

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 NH₄⁺ 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 $\text{Ca}(\text{OH})_2$, or $\text{Mg}(\text{OH})_2$, 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.

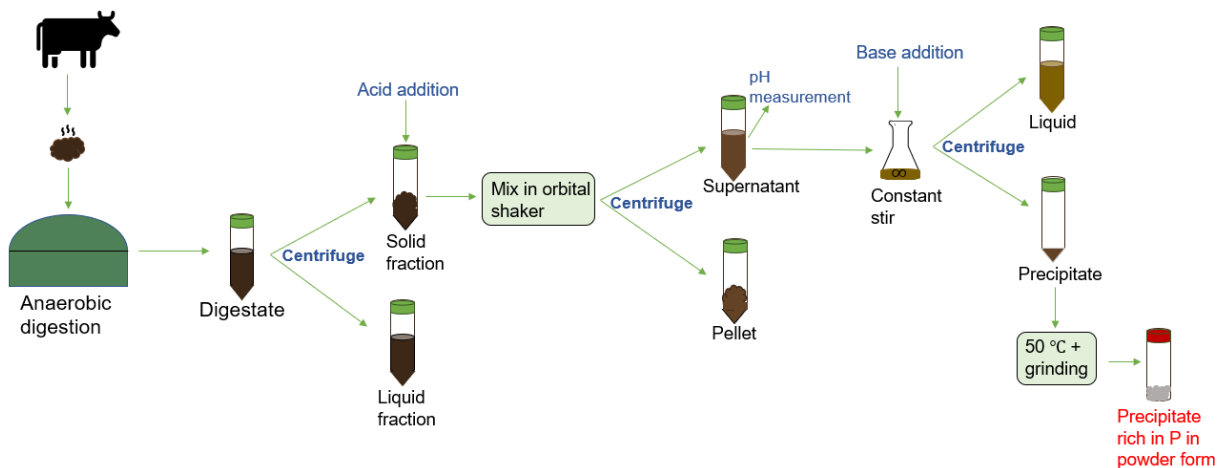


Figure 1 – Set-up for phosphorus precipitation from the solid fraction of digestate.

Results

The P-recovery from the solid fraction of digestate obtained with sulfuric and citric acid as leaching agents is presented in Figure 2. **Verwijzingsbron niet gevonden..**

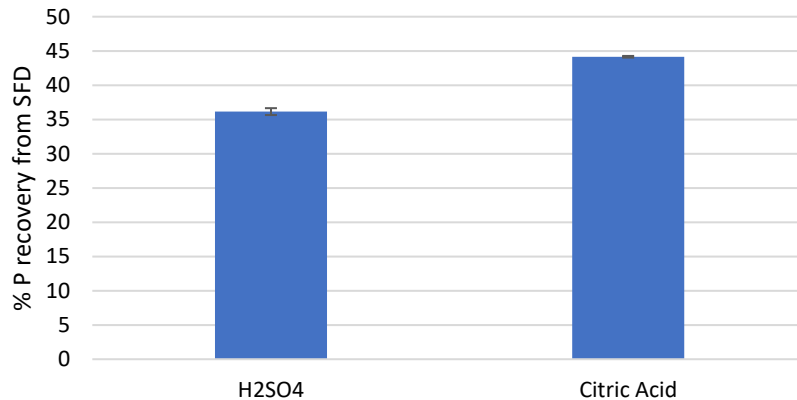


Figure 2 - Phosphorus recovery after acid leaching of the solid fraction of digestate with sulfuric and citric acid.

Note: “SFD” corresponds to the solid fraction of digestate.

The citric acid performed better as a leaching acid than sulfuric acid, recovering 44% of the P initially present in the solid fraction of digestate, whereas the sulfuric acid recovered only 36%. Therefore, citric acid is shown as a good alternative to sulfuric acid in the P-leaching step. As a result of the precipitation step using $Mg(OH)_2$ and $Ca(OH)_2$, 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 after the different tests performed is shown in Figure 3.

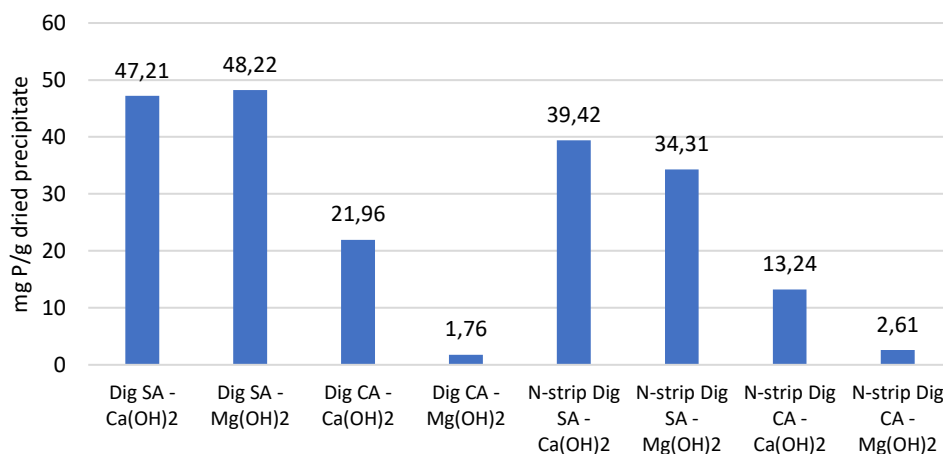


Figure 3 - Phosphorus concentration of the final dried precipitates, originated from P-leached solutions from the solid fraction of N-rich and N-stripped digestate.

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 samples mentioned previously in which $\text{Ca}(\text{OH})_2$ was used in the precipitation 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.

To identify the main composition of the solid product from the precipitation experiments, the graphs from the XRD analyses were analysed via the software QualX.

The precipitate originated from the solid fraction of digestate, in which sulfuric acid was used as the leaching agent, and $\text{Ca}(\text{OH})_2$ as the precipitation agent, was composed of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$), calcite (CaCO_3), and gypsum ($\text{Ca}(\text{SO}_4)(\text{H}_2\text{O})_2$). Since there was no Ca-phosphate indicated in the XRD result, we can assume that the addition of $\text{Ca}(\text{OH})_2$ 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 the experiment using citric acid as the leaching agent, was composed of calcite, similar to the precipitate formed when sulfuric acid was used; however, no struvite-like crystalline form was identified.

New precipitation tests using only NaOH to control the pH were further conducted. In the samples in which the solid fraction of digestate was used in the P-leaching step and either H_2SO_4 or citric acid was the P-leaching agent, the final proportion of $\text{NH}_4^+:\text{PO}_4^{3-}$ and $\text{Mg}^{+2}:\text{PO}_4^{3-}$ 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.

In the case of using sulfuric acid as the leaching agent, the composition of the precipitate exhibited struvite only for the precipitate derived from the experiment with the solid fraction of digestate, with a final concentration of 60.8 mg P/g precipitate. The lack of struvite in the precipitate composition

from the N-stripped digestate experiment could be explained by a possible formation of a very small amount of struvite, not being identified in the XRD, or possible formation of other compounds with the ions Mg^{+2} , NH_4^+ , and PO_4^{-3} , reducing their availability to form struvite. Although in the latter product no struvite was identified, the concentration of P identified was 40.6 mg P/mg precipitate.

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 exhibited 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.

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 leachate derived from P-leaching of the 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.
- In the final product derived from sulfuric acid as the P-leaching agent in the solid fraction of digestate, followed by the addition of NaOH in the precipitation step, struvite was identified, and a product concentration of 60.8 mg P/mg precipitate was obtained.
- The formation of other products might have competed with the formation of struvite in the leachate from the solid fraction of N-stripped digestate, therefore no struvite was identified; however, the final product had a concentration of 40.6 mg P/mg precipitate.
- Citric acid as the leaching acid resulted in the highest P-recovery (45%) from the solid fraction of digestate when compared to sulfuric acid (36%), while the citric acid showed inhibition aspects in the P-precipitation step after the addition of base.



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

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More information about the project: check out the [project website](#).

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