D3.4 – Alternative P-leaching process with recovered acids

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, and Nitrogen (N)-stripped anaerobic digestate, for further struvite precipitation. Sulfuric acid is the common P leaching agent in this practice, while finding more sustainable and environmentally friendly alternatives to sulfuric acid (e.g., recovered acids, waste acids from industry) is important. In that sense, recovered scrubbing waters from a stripping/scrubbing process (as ammonium sulfate and ammonium citrate) and a waste sulfuric acid from a chemical industry (47% sulfuric acid + 4% hydrogen peroxide) are investigated as alternatives to sulfuric acid.

Set-up/Parameters

The digestate used in this work is derived from a bench-scale anaerobic digestion (AD) of cow manure together with the N-stripped digestate collected after the stripping-scrubbing of 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 both digestates is reported in "*D3.3 Mineral P-fertilizer, extracted and re-precipitated from the solid fraction of digestate*".

The P in the solid fraction is further extracted using alternative acids to sulfuric acid: ammonium sulfate (3.6x diluted), ammonium citrate, and waste sulfuric acid (44x diluted). The characterization of the alternative acids is given in Table . The liquid:solid ratio is maintained at 2:1 in the leaching step, and the mixture is then continuously stirred for 24 hours. The acid dilutions are performed to obtain a final pH in the range of 4.5-5.5. The leaching performance of the alternative acids is then compared against sulfuric acid under the same conditions. A follow-up precipitation step was performed by adding NaOH until the pH 8-8.5 was reached, to obtain a P-rich product in the form of struvite, with potential fertilizer application. More details on the precipitation step are described in "*D3.3 Mineral P-fertilizer, extracted and re-precipitated from the solid fraction of digestate*". Figure 1 shows the P-leaching and P-precipitation steps.

Table 1 - Characteristics of the acids tested in the P-leaching of the solid fraction of cow manure digestate.

Parameters	Alternative acids applied in P-leaching		
	Ammonium sulfate	**Ammonium citrate**	**Waste sulfuric acid**
pH	< 2.00	4.35 ± 0.02	< 2.00
EC (mS/cm)	232.33 ± 2.47	21.24 ± 0.28	> 9999
Total N (g/kg FM)	4.52 ± 0.07	4.41 ± 0.06	< 0.10
P (mg/L)	< 0.15	0.21 ± 0.02	0.82 ± 0.01
K (mg/L)	1.00 ± 0.23	0.46± 0.18	1.00 ± 0.25
Ca (mg/L)	1.05 ± 0.37	0.49 ± 0.25	2.90 ± 0.10
Na (mg/L)	< 0.15	3.76 ± 0.03	4.98 ± 1.00
Mg (mg/L)	< 0.15	< 0.15	0.49 ± 0.07

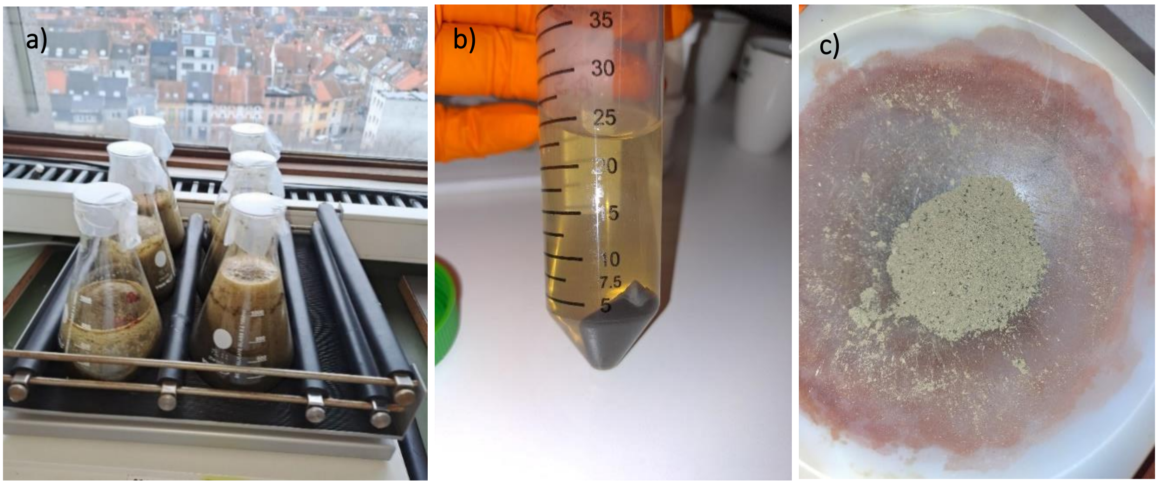

Figure 1 - P-leaching and precipitation: a) SFD and SFND being mixed with P-leaching agents in an orbital shaker; b) products after P-precipitation and a centrifuge separation (P-rich product corresponds to the solid part); c) struvite-like precipitate after drying and grinding.

Results

An overview of the P recovery rates from the solid fractions of digestate (SFD) and N-stripped digestate (SFND) is shown in Figure 2 and Figure 3, respectively.

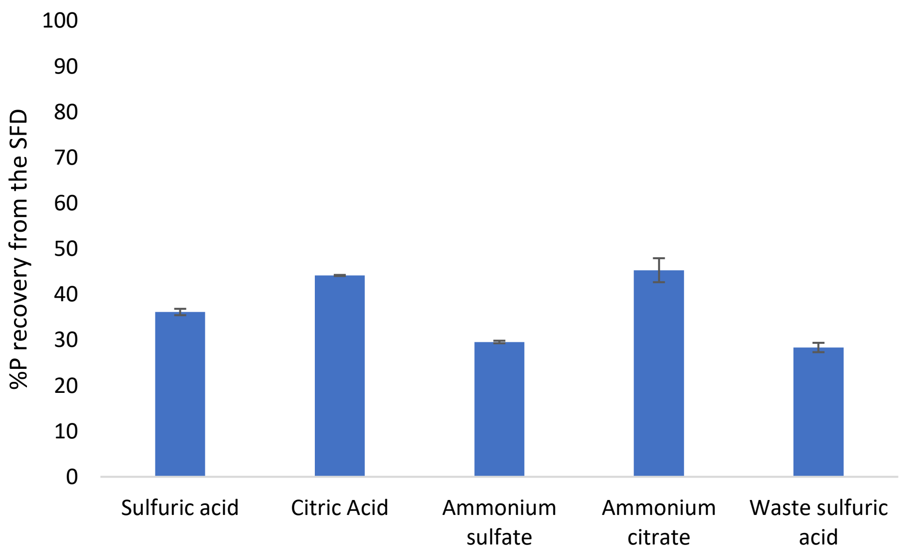

Figure 2 - Phosphorus recovery (%) from the solid fraction of digestate via acid leaching with alternative acids, compared with sulfuric acid.

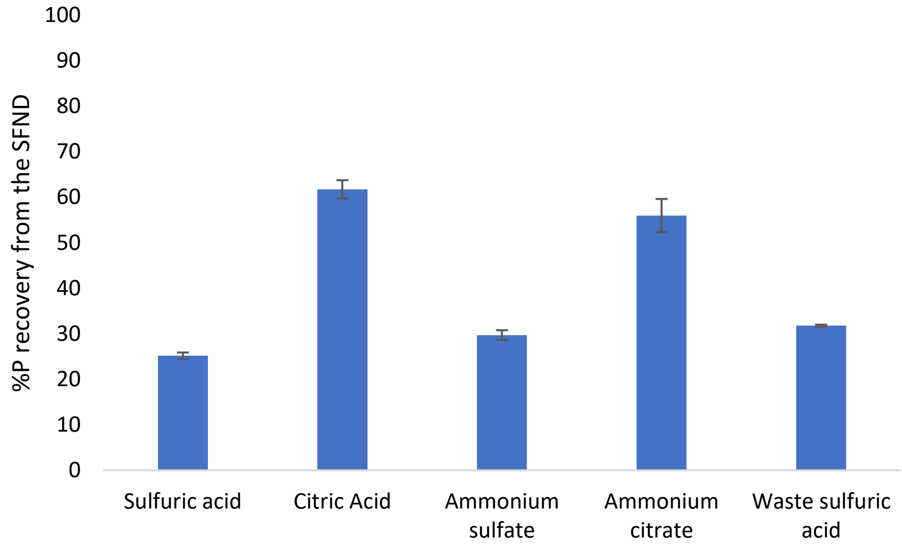

Figure 3 – Phosphorus recovery (%) from the solid fraction of N-stripped digestate via acid leaching with alternative acids, compared with sulfuric acid.

The ammonium sulfate and waste sulfuric acid, for both SFD and SFND, perform similarly to the sulfuric acid, the latter with 36% of P recovery for SFD and 25% for SFND. In the case of SFD, the sulfuric acid slightly outperforms the waste sulfuric acid and ammonium sulfate, whereas for the SFND, the waste sulfuric acid slightly outperforms the conventional acid, reaching a P recovery of up to 32%. However, compared to the conventional sulfuric acid, both ammonium citrate and citric acid result in the highest P recovery from the SFD, with 45% and 44%, respectively. The same behavior is observed with the SFND, with even higher recoveries of 62% and 56% when citric acid and ammonium citrate are applied as leaching agents, respectively.

Considering the recovery of phosphorus from the solid fraction of digestate to an acidic solution, ammonium citrate would result in fewer risks involved with its handling due to its higher pH when compared to sulfuric acid, besides being a more sustainable option since it is recovered and reused from the N-stripping of digestate. Its choice as a leaching acid would possibly bring a valorization of this product as a P-leaching agent, and possibly a higher interest in the N-stripping/scrubbing method itself, due to an extra income source for its users.

Although both citric acid and ammonium citrate outperform the other acids tested, the recovery of the P from the acidic solution to the struvite form in a follow-up precipitation step does not occur when these two acids are used as leaching agents. Both citric acid and ammonium citrate hinder the formation of struvite, a product with a potential as P-fertilizer. A reduction in the rates of struvite formation was observed by Kofina et al. (2007) when citric acid was applied in synthetic wastewater solutions supersaturated for struvite, with a reduction of up to 75-80% in struvite formation reported. Perwitasari et al. (2017) also observed a reduction in the struvite precipitation rate constants when an increased amount of citric acid was added to crystallizing solutions, in conditions propitious to struvite formation.

The ammonium citrate results in a similar inhibition most probably due to its similar chemical composition to citric acid, since it is the citric acid after capturing ammonia in the N-stripping/scrubbing process. In that sense, when struvite-like P precipitate is aimed as the final product, both ammonium citrate and citric acid are not recommended as leaching agents, unless the aim is to obtain the P in the final liquid product. Since the main goal of this study is to obtain a potential P fertilizer in the final solid form, ammonium sulfate, the by-product of the stripping/scrubbing, and the waste sulfuric acid would be the recommended alternatives to sulfuric acid among the ones tested. These recovered acids stand as more sustainable options as P leaching agents, since they could reduce the dependence on pure sulfuric acid and create a new market potential for them.

Conclusions/Remarks

- Citric acid and ammonium citrate outperform sulfuric acid as P-leaching agents, reaching 62% and 56%, respectively, when applied on the SFND.
- Although citric acid and ammonium citrate perform better than sulfuric acid and the other alternative acids in the P-leaching step, their presence in the precipitation step results in an inhibition of struvite formation.
- Ammonium sulfate and waste sulfuric acid perform similarly to the sulfuric acid as P-leaching agents in the SFD, with approximately 30% of P-recovery.
- Considering the aim to obtain a final product in the form of struvite as a potential P fertilizer, both ammonium sulfate and the waste sulfuric acid are more sustainable alternatives to sulfuric acid, due to their comparable performance and valorisation of these products.

References:

Kofina, A. N., Demadis, K. D., & Koutsoukos, P. G. (2007). The effect of citrate and phosphocitrate on struvite spontaneous precipitation. *Crystal Growth and Design*, *7*(12), 2705-2712.

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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