Study of pig manure digestate pre-treatment for subsequent valorisation by struvite

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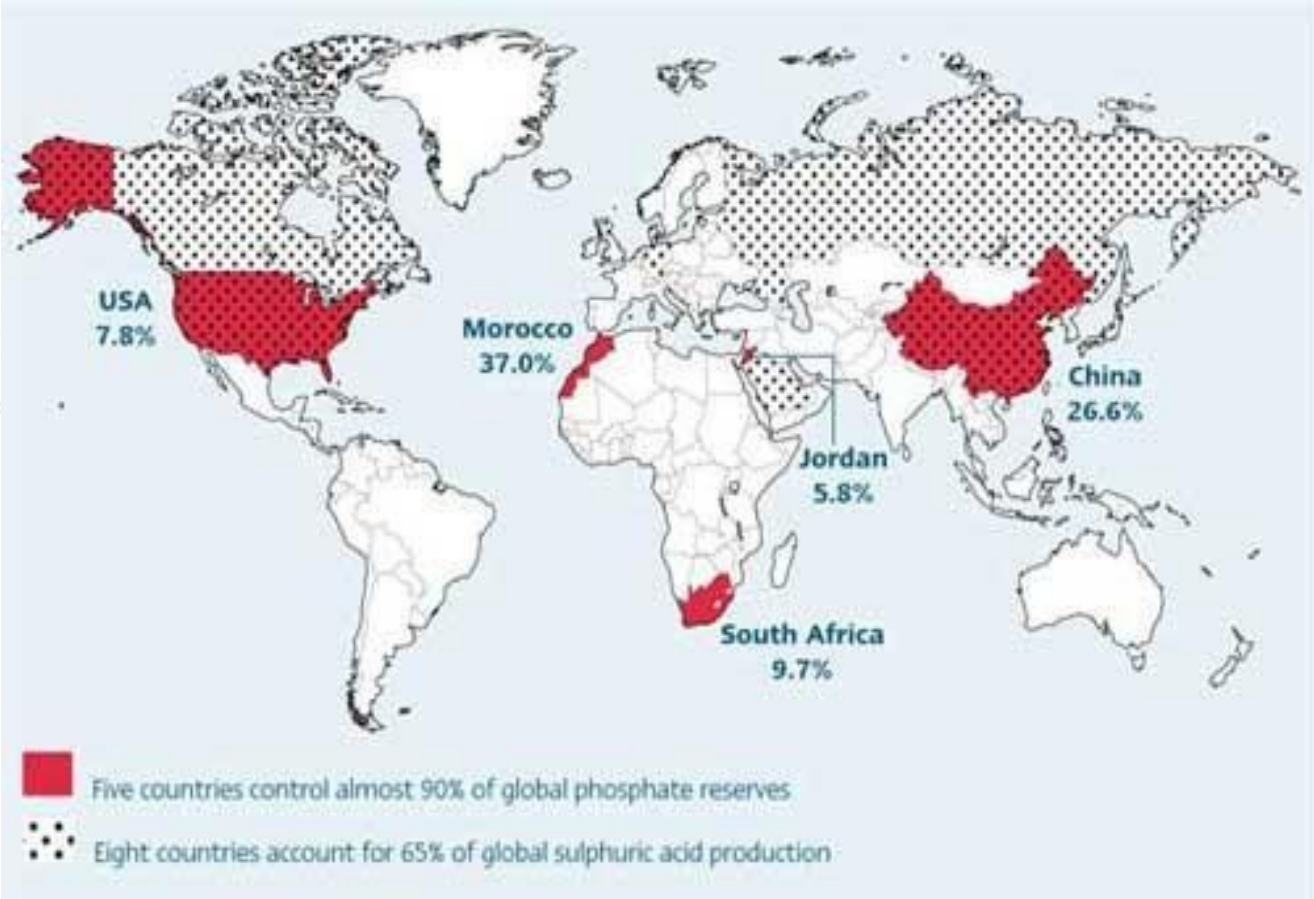
Introduction

- Agricultural demand for **mineral fertilisers** is steadily **increasing** and should be considered a very serious threat to future human food security.
- World fertiliser (N, P, K) demand is estimated to reach **199 Mt** by the end of **2019**.
- Modern industrial agriculture depends on continuous inputs **of non-renewable extracted P**.
- The **phosphate rock reserves** used to make fertilisers are finite and there is concern that they are in **danger of depletion**.

Introduction

- Phosphorous reserves

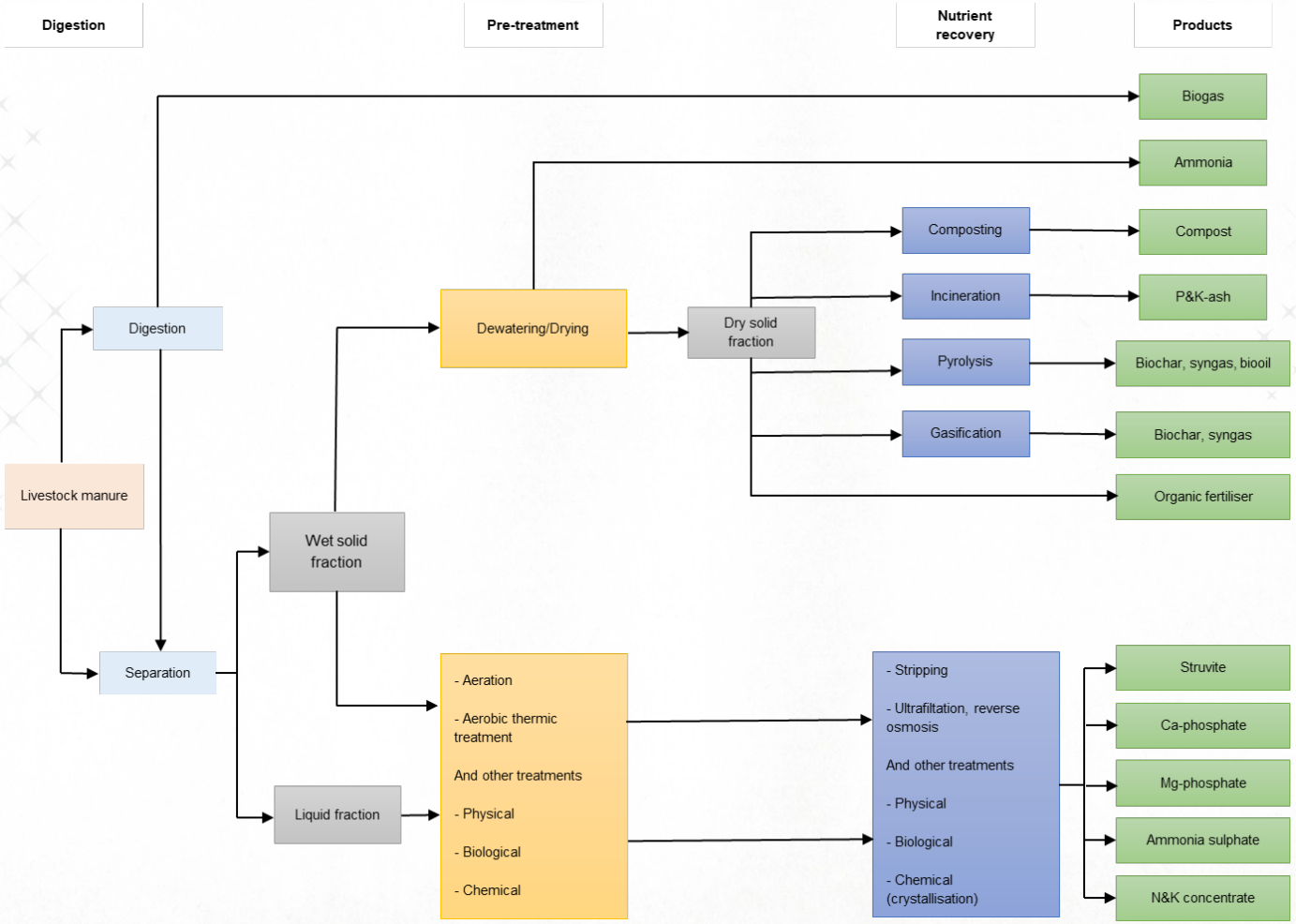


Introduction

- Food production in Europe is dependent on imported P fertilisers, but **P use is inefficient** and losses to the environment high:
  - Deterioration of the water quality.
  - Eutrophication.
  - Loss of biodiversity.
- It is necessary to carry out a **recovery of P** and other nutrients from waste generated in various productive products.
- Two of the **waste** that have the most potential for **P recovery** are:
  - Livestock waste: manure, digestate, etc.
  - Wastewater.
- Both residues are generated in **large quantities** and contain a **high P concentration**.

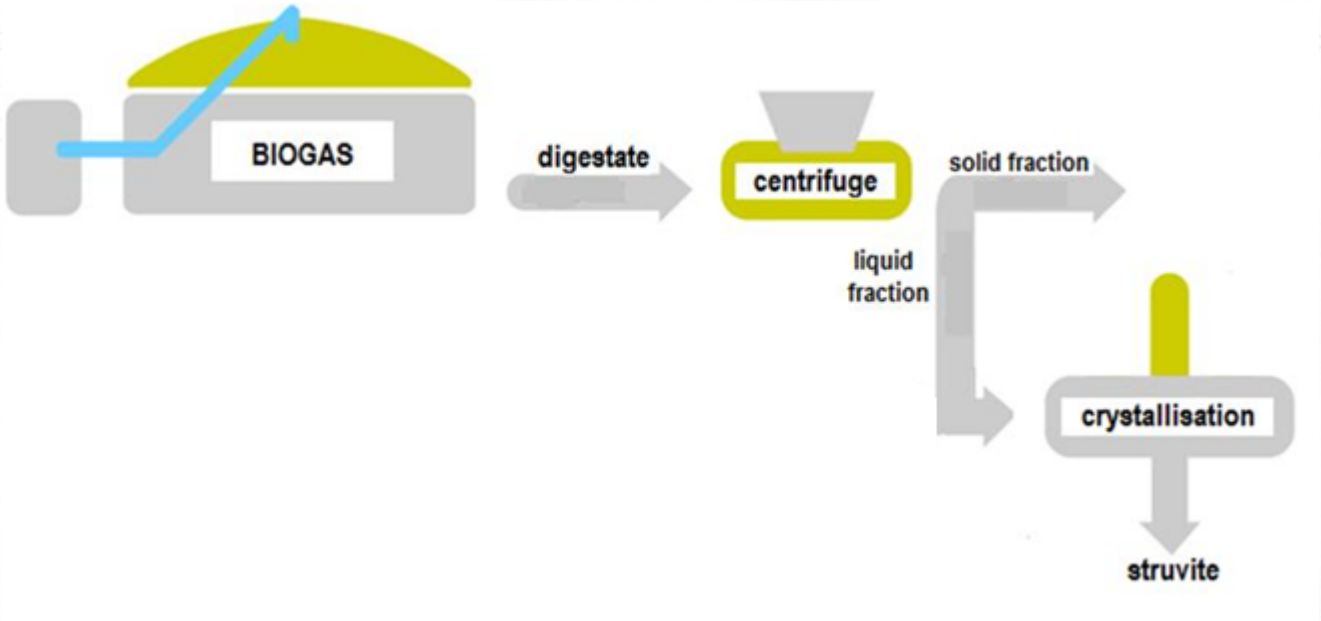
Introduction

- Various techniques for the nutrient recovery from waste can be used.



Introduction

- **Struvite precipitation** is one of the most promising livestock waste and wastewater treatment techniques.
- Struvite can be obtained from digestate generated as by-product in a biogas production plant (using livestock waste as raw material).

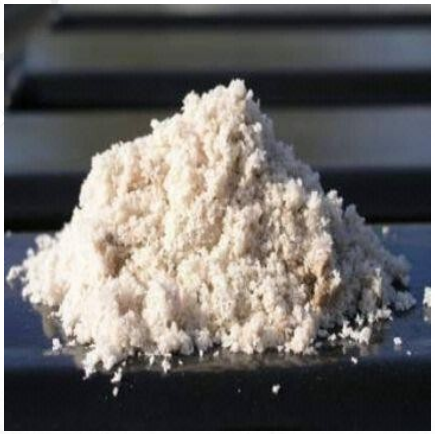


Introduction

- Phosphate and Ammonium can be **recovered** from the digestate by precipitation of **struvite**, also known as MAP (ammonium magnesium phosphate).

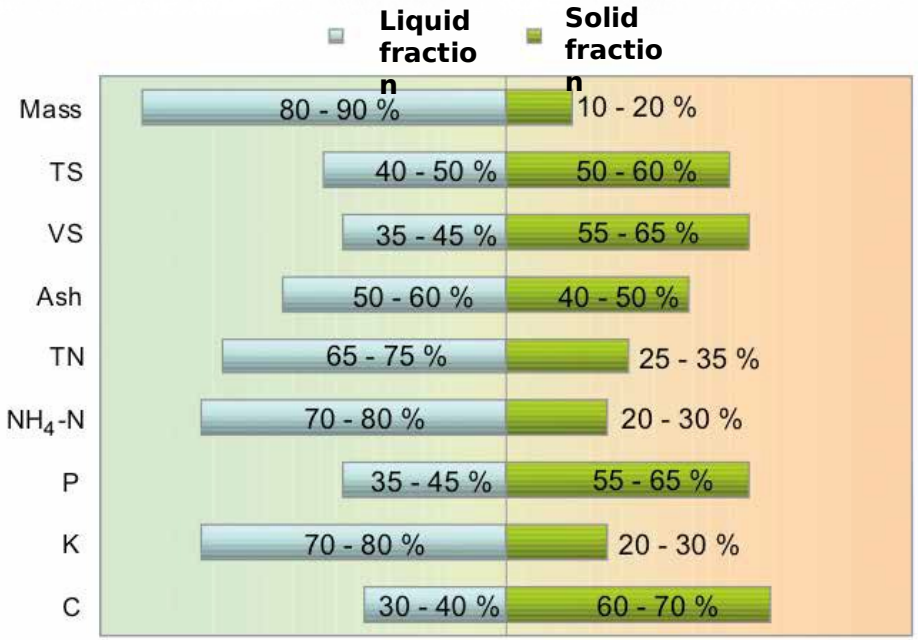
$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O$$

- The resulting **struvite** is a **good fertiliser** because nitrogen, phosphorus and magnesium are valuable nutrients for plants.



Introduction

- The great problem of the struvite process: phosphate is mainly present in the **solid fraction** of livestock waste.



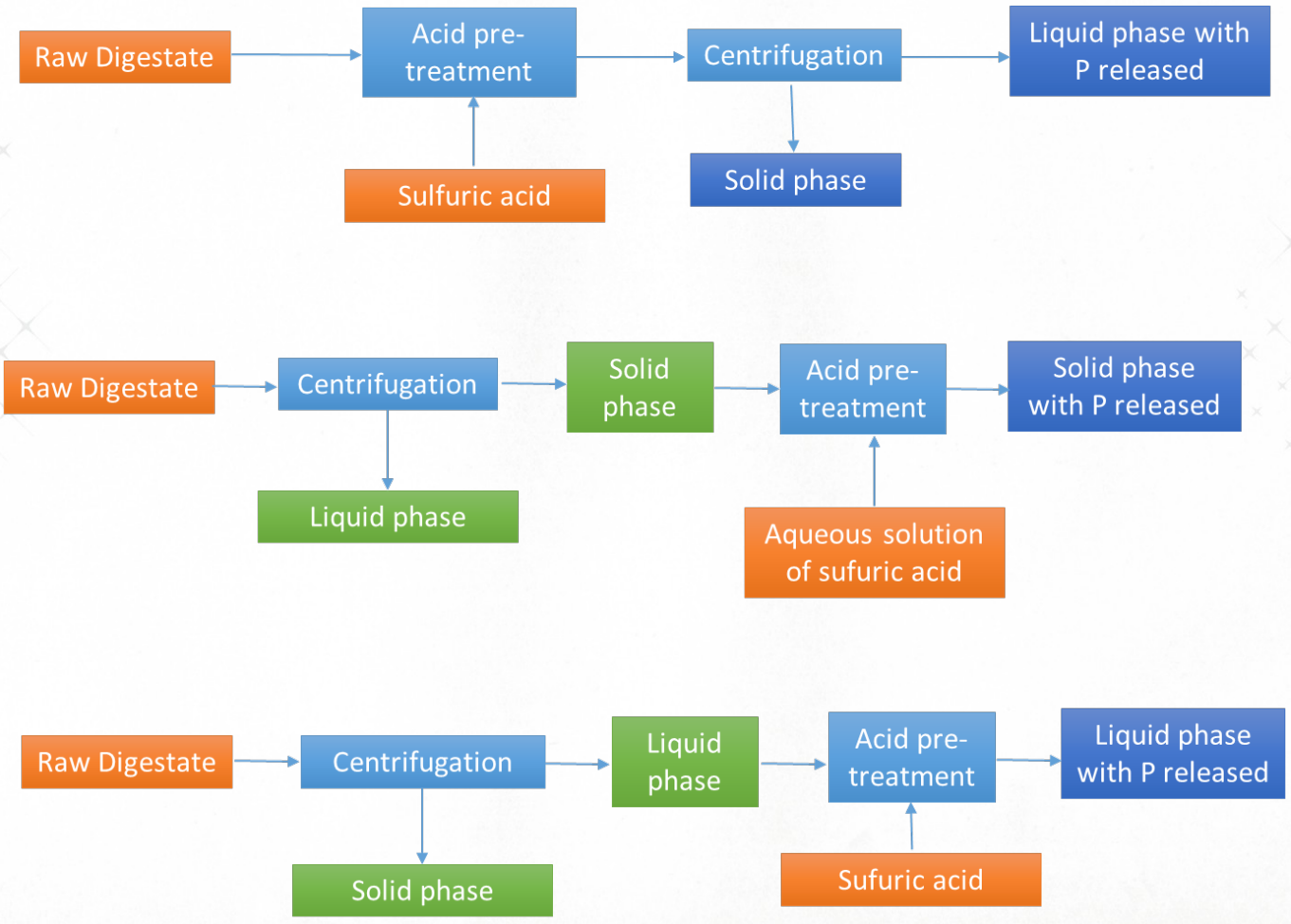
- It is necessary to carry out some **pre-treatment** to the crystallisation reaction of struvite.

- There are **several methods** of pre-treatment of the digestate but the one that has more projection is the **acid pre-treatment**.

Objectives and methodology of the study

- The main objective of this work was to **recover the P in the solid fraction of the digestate** from the anaerobic digestion of pig manure by means of an **acid pre-treatment**.
- Two digestate samples were studied:
  - **Fresh digestate** sample.
  - **Old digestate** sample (stored for 6 months).
- Fresh and old digestate were treated using **different techniques** to recover the phosphorous:
  - Acid pre-treatment to the **whole digestate** (raw digestate).
  - Acid pre-treatment to the **solid phase** of the digestate.
  - Acid pre-treatment to the **liquid phase** of the digestate.

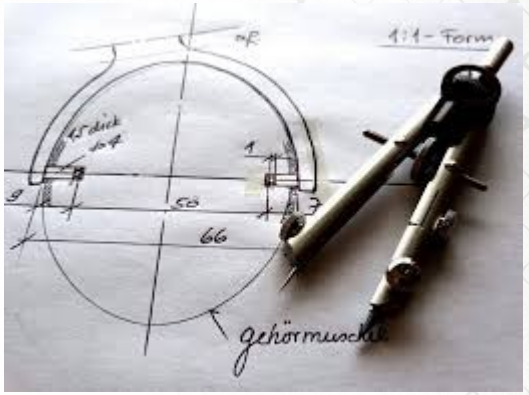
Objectives and methodology of the study



Design of the experiments

- An **experiment design** was carried out that allowed the number of experiences to be reduced to a minimum without losing relevant information.
- The main factor influencing the release of phosphorus contained in the solid phase of livestock waste is the pH.

Factors	Levels				
pH	4.0	5.0	6.0	7.0	8.0
Fraction of material	Raw digestate	Solid fraction of digestate		Liquid fraction of digestate	
Storage	Fresh digestate			Old digestate	



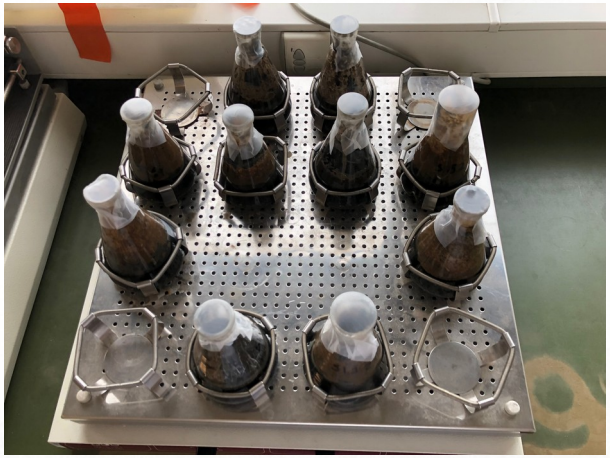
- All the experiments were carried out at room temperature.

Experimental procedure

- Experiments were carried out using **250 mL** batch stirred tank reactors.
- Sulphuric acid (**96-98% purity**) was used for the acid treatment.
- Samples were allowed to react by stirring for **1 hour**.

Experimental procedure

- **Raw digestate** as raw material
  - **100 mL** of raw digestated was introduced into each reactor.
  - The required amount of **acid** was added to each sample.
  - The samples were agitated and reacted for **1 hour**.
  - **Solid phase** was separated by **centrifugation** and the concentration of phosphorus in the liquid phase of each sample was determined.



Experimental procedure

- **Solid phase** digestate as raw material.
  - **100 mL** of water and **1.0 g of dry solid** digestate was introduced into each reactor.
  - The required amount of **acid** was added to each sample.
  - The samples were agitated and reacted for **1 hour**.
  - **Solid phase** was separated by **centrifugation** and the concentration of phosphorus in the liquid phase of each sample was determined.

Experimental procedure

- **Liquid phase** digestate as raw material.
  - **Separation** of the raw digestate by centrifugation was performed.
  - **100 mL** of liquid phase digestate was introduced into each reactor.
  - The required amount of **acid** was added to each sample.
  - The samples were agitated and reacted for **1 hour**.
  - **Solid phase** was separated by **centrifugation** and the concentration of phosphorus in the liquid phase of each sample was determined.

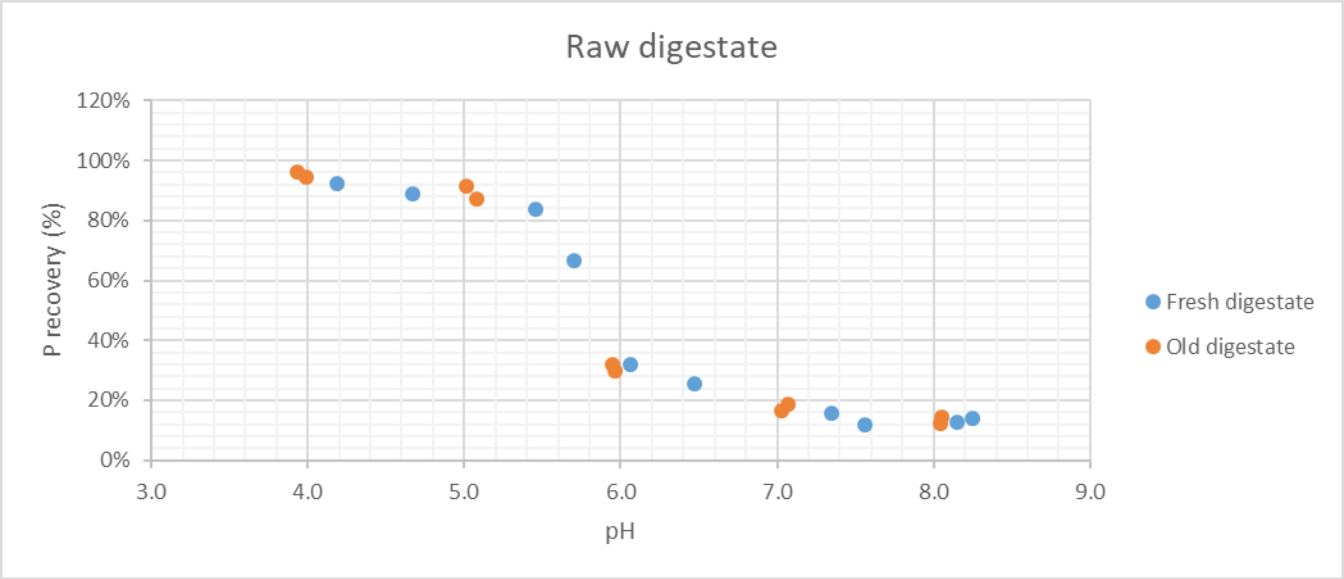
Results

- Initial characterisation

Parameters	Fresh digestate	Old digestate
pH	8.20	8.05
Total Solid (g dm/g digest)	0.11	0.01
P concentration (mg/L)	2098.83	181.12
%w liquid phase (g liq phase/g total)	60.51	85.23

Results

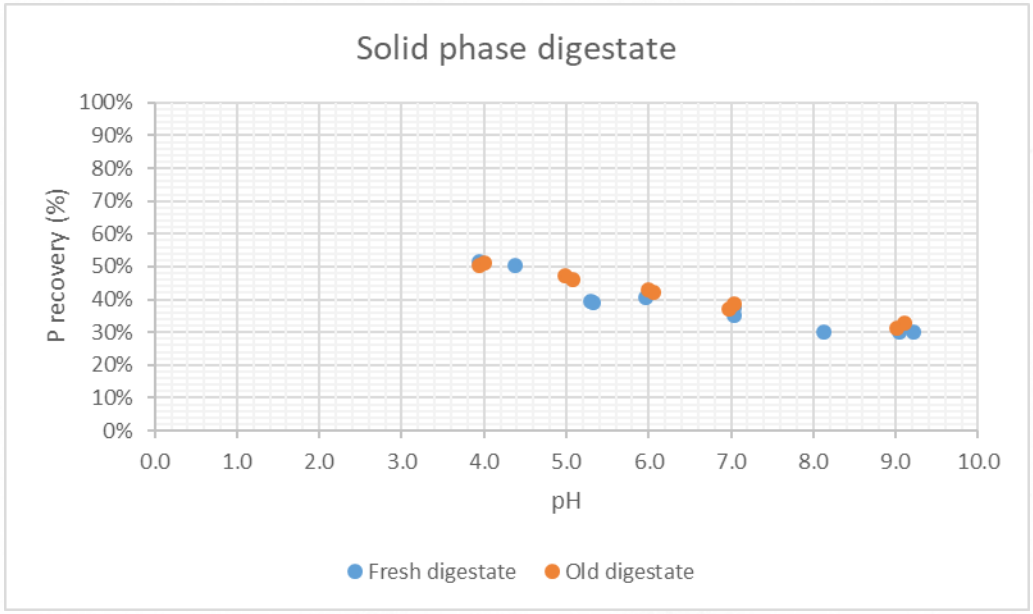
- Influence of **pH** on raw digestate.



- The P recovery generally **increases** with the reduction of pH value. 90% P is released into the liquid phase with a pH value close to 5.0

Results

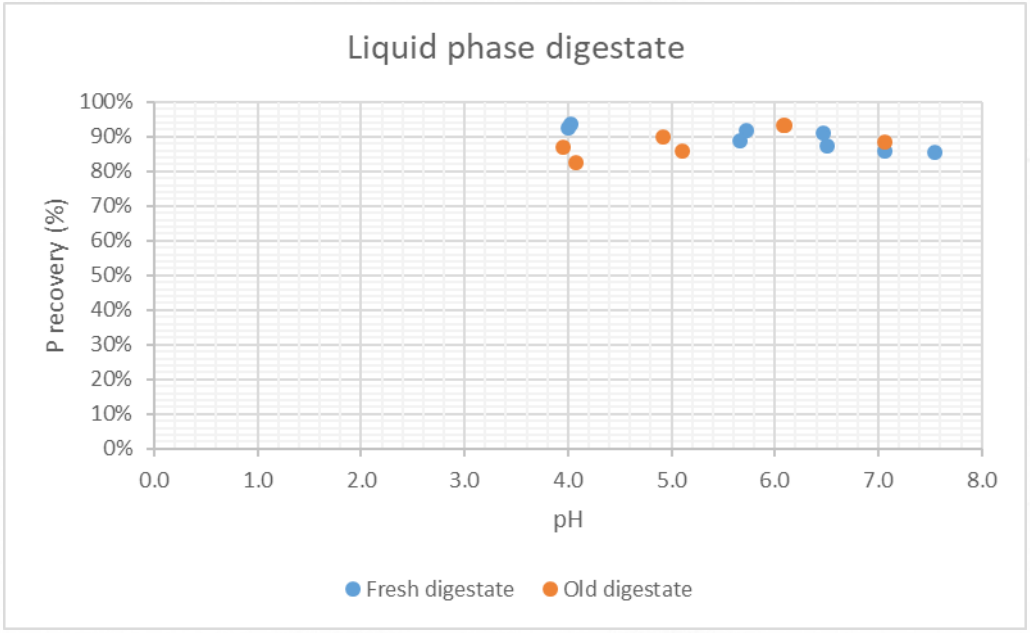
- Influence of **pH** on solid phase digestate.



- Only **50%** P recovery are achieved.

Results

- Influence of pH on liquid phase.



- P recovery reached **90%**. Although, P concentrations in this stage were lower than the concentrations of the first stage.

Results

- Recovered P concentrations at **pH ≈ 5-6**

Raw material	Recovered P concentration (mg/L)		% P recovered	
	Fresh digestate	Old digestate	Fresh digestate	Old digestate
Raw digestate	1755.69	156.82	83.65	86.58
Solid digestate	49.75	21.27	39.35	46.03
Liquid digestate	248.29	50.80	85.79	89.97

- Results are similar but more P is recovered for the **fresh digestate** because it contains many more solids.

Final experiments

- **Struvite** was obtained from raw digestate.
- A comparative study of **struvite reaction yield** was performed by carrying out an acid pre-treatment to the digestate and not performing it.
- To some samples the amount of acid needed to reduce the **pH value to 6.0** was added, while to others no pre-treatment was performed.

Final experiments

- The yield of the struvite crystallisation reaction is **higher** in the case of carrying out an **acid pre-treatment**.
- By means of acid pre-treatment a large amount of P is released, so there will be a **higher concentration of P** available in the **liquid phase** of the digestate before the crystallisation reaction.

Raw material	pH initial	pH final	Acid volumen (mL)	P initial (mg/L)	P final (mg/L)	% P recovered as struvite
Raw digestate without pre-treatment (fresh)	8.14	8.14	0.00	226.69	39.53	83.31
Raw digestate with pre-treatment (fresh)	8.05	6.15	3.50	1085.44	43.77	93.47
Raw digestate without pre-treatment (old)	8.07	8.07	0.00	108.75	19.02	82.46

Conclusions

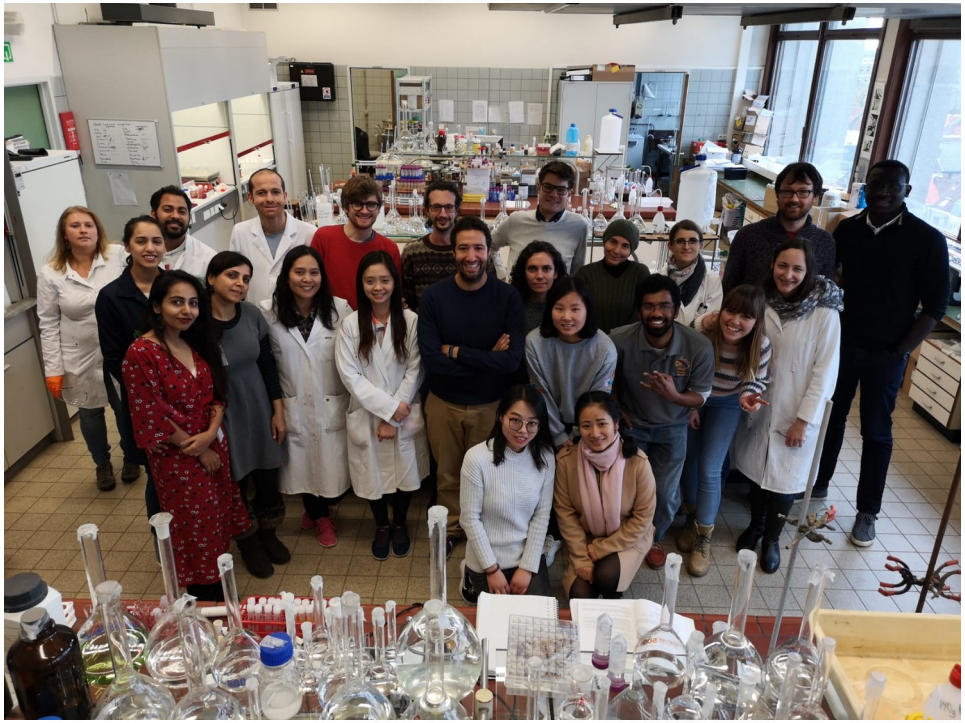
- Through acid pre-treatment, more than **90%** of the phosphorus present in the raw digestate can be recovered.
- The **concentrations of phosphorus** available in the liquid phase of the digestate to carry out the struvite crystallisation reaction are 5 times higher when acid pre-treatment has been performed than when it has not.
- The **age of the digestate** does not have a great influence on the amount of phosphorus recovered.
- The most **optimal pH** at which acid pre-treatment could be carried out should be in the range of **5.0** to **6.0**.

Future works

- Conduct an **economic assessment** for the introduction of the acid pre-treatment step in the struvite crystallisation process.
- Optimise the struvite crystallisation process on a **pilot scale**, including the pre-treatment step.

Stay at Ghent University

- This research was carried out through a stay at the Laboratory of Analytical Chemistry and Applied Ecochemistry belonging to the Department of Green Chemistry and Technology of Ghent University.



Thank you for your attention

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If you have any question, do not hesitate to contact me

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