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

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Abstract

The phosphorus cycle of agricultural land in the European Union is not balanced. The amount of livestock waste produced cannot be applied on agricultural land due to restrictions in the phosphate and nitrogen application standards. In the near future, phosphate application limits for agricultural land tend to be stricter, while the production of livestock waste continues to increase. The need to process this waste is therefore urgent.

Phosphate is a valuable and vital resource, finite and irreplaceable, and the organic matter that is also present in livestock waste is necessary to maintain the fertility of agricultural soils.

One of the most promising methods of recovering phosphorus and nitrogen from agricultural waste is the crystallisation of struvite (an ammonium, phosphorus and magnesium salt) which can then be used as a slow-release biofertiliser.

Phosphate is mainly present in the solid fraction of livestock waste and can be released in the liquid fraction as soluble inorganic phosphate as the pH decreases. Therefore, it is necessary to carry out some pre-treatment to the crystallisation reaction of struvite.

The main objective of this study was to recover the phosphorus (P) in the digestate from the anaerobic digestion of pig manure by means of an acid pre-treatment.

Two digestate samples (one fresh and one old) were studied. The old digestate was stored for 6 months before the experimentation was carried out. Fresh and old digestate were treated using different techniques to recover the phosphorous. First the recovery of the phosphorous from the raw digestate was studied, then from the solid fraction of the digestate and finally from the liquid phase of the digestate. Solid and liquid fractions were obtained by centrifugation.

In the last part of the experimentation, a comparison was made between the reaction yield for obtaining struvite (NH_4MgPO_4-$6H_2O$) from $MgCl_2 \cdot 6H_2O$ and for obtaining calcium phosphate ($Ca_3(PO4)_2$) from $Ca(OH)_2$, using as raw material both the pre-treated digestate and the non-pretreated digestate.

The main factor influencing the release of phosphorus contained in the organic phase of livestock waste is the pH. In order to study the influence of this variable, an experimental design has been carried out.

Table 1. Design of experiments (DOE) for phosphorus release study

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 age	Fresh digestate			Old digestate	

Experimental procedure

The experiments were carried out using 100 mL of digestate as raw material in 250 mL beakers. Sulphuric acid (96-98% purity) was used for the acid treatment. This acid was dosed in the quantities required in each sample to reach different pH levels (from 8.0 (the initial pH) to 4.0).

In the first stage, after adding the acid to the raw digestate samples, effervescence occurred because the carbonates contained in the digestate was released in the form of CO_2. Once the effervescence ceased, the samples were allowed to react by stirring for 1 hour. Finally, the solid phase was separated by centrifugation and the concentration of phosphorus in the liquid phase of each sample was determined.

In the second stage of the study, acid was added to solutions containing 100 mL of water and 1.0 g of dry solid digestate. Again, the samples were allowed to react for 1 hour and the liquid phase was recovered by centrifugation to determine their phosphorus concentration.

In the third stage, first a separation of the raw digestate by centrifugation was perfomed and the acid treatment was carried out to the liquid phase of the digestate directly. The acid was added to the different samples of 100 mL of the liquid phase of the digestate and it was left to react during 1 hour, to determine the amount of phosphorus at the end of the digestate.

Finally, different experiments were carried out on samples of the raw digestate. 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. Both pre-treated and non-pre-treated samples were made to react with Mg and Ca. In the reactions with Mg to obtain struvite, $MgCl_2 \cdot 6H_2O$ was added to have a molar ratio Mg/P=1.5 and the pH of the solution was modified to 9.0 by the addition of NaOH; whereas in the reactions with Ca, $Ca(OH)_2$ was added to the samples with a molar ratio Mg/P=3 to obtain ($Ca_3(PO_4)_2$).

Results

In the first stage (treatment of the raw digestate), 90% phosphorus is released into the liquid phase with a pH value close to 5.0. However, in the second stage (treatment of the dry solid fraction of the digestate), only 50% phosphorus recoveries are achieved. For the third stage, the phosphorus recoveries obtained, in general, reached 90%; although the phosphorus concentrations in this stage (260 mg/L) were lower than the concentrations of the first stage (1,800 mg/L). The latter was due to the fact that, in the third stage, much of the initial phosphorus was lost when the solid phase of the digestate was removed by centrifugation prior to acid treatment.

Regarding the recovery of phosphorus through struvite formation and $Ca_3(PO_4)_2$ formation, in both cases phosphorus recoveries of more than 90% and 80% respectively have been obtained when acid pre-treatment of the digestate is performed. On the contrary, when these same reactions were carried out without acid pre-treatment, phosphorus recoveries only reached values close to 20%.

In addition, it highlights that, when fresh digestate is used, the phosphorus recoveries obtained are slightly higher than those obtained with the old digestate.

All these results agree with what has been obtained by other authors (Daumer et al., 2010; Shen et al., 2012; Szogi and Vanotti, 2009; Tasistro et al., 2007; Zhang et al., 2010). According to these results, when the pH of pig manure or pig manure fractions decreases, phosphorus is released from solids and solubilised in the liquid phase, mainly as inorganic P (ortho-P).

Conclusions

Acid treatment is presented as a promising alternative to improve the recovery of phosphorus from agricultural waste, as well as a determining factor to increase the technical and economic feasibility of the struvite process, one of the most important routes for the recovery of this phosphorus.

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