



Explorative study of phosphorus recovery from pig slurry

Laboratory experiments

O.F. Schoumans, P.A.I. Ehlert, J.A. Nelemans, W. van Tintelen, W.H. Rulkens and O. Oenema



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The manure surplus in the Netherlands is about 25% of the total manure produced, expressed in mass of phosphate. This surplus has to be processed into secondary fertilizer and/or exported. The other 75% can be applied on agricultural land in The Netherlands, within the current nutrient application standards for agricultural land. The costs of manure processing and export are high. New, simple and cheap innovative techniques are requested.

Here, we report on laboratory experiments with the aim to explore cheap and innovative techniques. The main focus of the experiments was to lower the P-content in pig slurry with 25%. In that case, in principle all manure produced in The Netherlands can be applied on agricultural land in The Netherlands itself, including the organic matter and other nutrients in the manure. The results show that with physical and chemical treatment techniques 25% of the phosphate can be rather easily recovered from the solid or liquid fractions of the pig slurry. The costs of chemicals depend highly on the buffer capacity of the studied (n=3) pig slurries, and are less than 5 € per ton pig slurry.

Keywords: phosphate, manure,, intensive livestock production, phosphate recovery, pig slurry, manure treatment.

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Preface

This project was funded by the Farmers organisation LTO and the Ministry of Economic Affairs in The Netherlands and is one of the projects within the 'Topsector agreement' between the government and the private sector called 'Meerwaarde Mest en Mineralen (Added value Manure and Minerals)' (project number AF12178). New innovative approaches are needed 'to close the phosphorus cycle' of agriculture in The Netherlands, because currently there is a surplus of manure phosphorus in agriculture. One promising perspective is to recover phosphorus from animal manure as secondary phosphate resource for the phosphate fertilizer industries.

Simple laboratory experiments have been carried out to test a number of techniques for an effective and efficient recovery of phosphate from pig slurry. The main aim of the experiments was to lower the P-content in pig slurry by at least 25%. By doing so, more manure can be applied on agriculture land in The Netherlands, while respecting the application limits for phosphate (and nitrogen). A second aim was to add value to recovered P, as secondary phosphate resource, for industries with a market outside the Dutch agriculture.

The research was carried out in 2013 by Alterra, WUR Department Soil Quality (CBLB) and ATV-ETE both research institutes of Wageningen UR.

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The authors

Summary

The phosphate (P_2O_5) cycle of agricultural land in The Netherlands is not in balance. The amount of manure produced annually in The Netherlands contains about 174 million kg of phosphate. About 40 million kg of this amount of phosphate cannot be applied on agricultural land due to the restrictions of phosphate application standards (and nitrogen application standards). To date, the major part of the manure surplus is exported as dried poultry manure pellets to Germany and France, while a significant part of the poultry manure (about 8 million kg P_2O_5) is incinerated to produce bioenergy, with the phosphate containing ash exported to the United Kingdom. In the near future, phosphate application limits for agricultural land in The Netherlands tend to become stricter, while the manure production may tend to increase due to the abolishment of the milk quota and the expiration of the pig and poultry production rights by 2015. Hence, the need to process and export more manure is urgent.

The costs of manure processing and export are high (about 15-20 € per ton pig slurry), and new cheap and innovative techniques are needed to be able 'to close the phosphate cycle' of agricultural land in The Netherlands. Ideally, the surplus (excess) amount of phosphate is recovered from the manure and used as secondary resource for the phosphate fertilizer industries, and sold to areas where the need for phosphate fertilizer is large. It is well-known now that phosphate is a valuable and life-essential, finite, irreplaceable resource, and that organic matter that is also present in manure is needed to maintain the fertility of the agricultural soils.

The main focus of the study reported here, was to reduce the phosphorus (P)¹ content in pig slurry with at least 25%. Only the recovered fraction of phosphorus will have to be exported. Also, if the manure surplus, expressed in terms of phosphate surplus is reduced, the value of manure on the national market will increase and livestock farmers will make smaller costs to redistribute their manure to arable farmers. Currently livestock farmers have to pay a substantial 'goodwill fee' to arable farmers in order to convince them to apply pig slurry on their land.

Three fresh (raw) pig slurry samples were studied and treated using different techniques to recover P. P-recovery is defined here as the extraction and separation of P from slurry in a solid and rather pure, inorganic form. Phosphate is mainly present in the solid fraction of manure and can be released into the liquid fraction as soluble inorganic phosphate by lowering the pH. This can be done using untreated pig slurry or in the solid or liquid fractions of pig slurry after using simple separation techniques like a screw press. The dissolved phosphates can be filtered and further treated with $Ca(OH)_2$ to recover a solid calcium phosphate precipitate. The pH of the slurry determines the phosphate release from the solid fraction into solution, and thereby the options for P-recovery.

There are options to recover up to 80% of the total amount of P in pig slurry with this 'acid-base approach'. However, the costs of chemicals to retrieve most of the P from pig slurry are high (2.63 – 10.85 € per ton pig slurry) due to the high pH-buffering capacity of the pig slurry. The cost of chemicals (expressed per ton raw pig slurry) for recovering 25% of the total P of the studied pig slurries varied between 0.33 to 1.32 €, for the treatment of raw pig slurry, 0.34 to 2.12 € for the treatment of the solid fraction of P slurry, and 0.17 to 3.39 € for the treatment of the liquid fraction of pig slurry.

Another approach is the treatment of the liquid fraction of pig slurry with Mg sources ($Mg(OH)_2$, $MgCl_2$ or MgO) to produce Mg-precipitates like NH_4 -struvite, K-struvite or Mg-phosphate. It is possible to

¹ With the term phosphorus (P) we refer to the element 'phosphorus'. With the term phosphate we refer to both (i) compounds containing the element phosphorus in general and (ii) to the chemical formula P_2O_5 , which is used in agriculture for expressing the phosphorus content in fertilizers and manures, including its treatment products and derivatives.

precipitate P with Mg at the prevailing pH of the manure (pH 8). NaOH might be added to increase pH but our research showed that this is not required; increasing the pH with NaOH to 9.5 did not improve the P'-recovery. Using a low tech separation technique a recovery of 25 to 50% seems to be realistic with this Mg-approach. The costs of the required chemicals are relative low (0.23 – 2.08 € per ton raw pig slurry), since the pH of the pig slurry does not have to be changed. A disadvantage of this method is the presence of organic matter in the precipitate of around 30% C. The compositions of the Mg~P-precipitate, after addition of $MgCl_2$ to a low tech separated liquid fraction, showed that a relative high P-content can be retrieved: 4.5 and 6.2% P_2O_5 per kg wet product which equals to 14-16% P_2O_5 per kg DM.

In short, this study shows that there are technical options to reduce the P-content of pig slurry by simple and relative cheap techniques, which are expected to be feasible at small industrial scale and larger innovative livestock farms. The treated (residual) pig slurry still has the original (high) organic matter and nitrogen contents, but a lower P-content than the original raw slurry, and is thereby better suited for use within a system of strict phosphorus application standards for soils with moderate to high phosphorus status (due to the higher N/P ratio). Tests with larger units of each treatment step are needed, followed by tests on pilot scale to demonstrate the practical feasibility.

The recovered P-precipitates can be used as secondary raw materials for the phosphorus fertilizer industries. But specific requirements of end users, regarding inorganic purities, physical characteristics and chemical composition (e.g. other co-precipitated minerals) still require additional study. Experiments are needed in collaboration with end users to optimize the conditions and final products. There are several options to change the quality of the end product by means of used separators, additions of coagulants, pH, and drying and pelleting options.

1 Introduction

In the period 2006 – 2011 the average animal manure production in the Netherlands was approx. 174 million kg P_2O_5 per year. About 92 million kg P_2O_5 in manure could be applied on the land of the farms where the manure was produced. The other 82 million kg P_2O_5 became available on the 'manure market' and was distributed to arable and horticulture farms (45%) and to small customers (6%) like the private sector, hobby farms and natural areas, or was processed and exported (about 50%) (Koeijer *et al.*, 2012). The manure production is larger than the area of land available for manure disposal, when expressed in phosphate² (kg P_2O_5). Or in other words, 'the manure phosphate cycle of the agricultural system is not in balance', since about an equivalent of 40 million kg P_2O_5 in manure has to be processed and exported outside the agricultural sector. The major part of the manure surplus is exported as dried poultry manure pellets to Germany and France and another part of the poultry manure (corresponding to about 8 million kg P_2O_5) is incinerated to produce bioenergy, while the phosphate-rich ash is exported (currently to the United Kingdom).

Various efforts are made to bring the manure phosphate cycle in a more 'sustainable balance' for The Netherlands. Efforts are undertaken to (a) lower the P-content in animal feed; (b) increase P-use efficiency by bio-refining of raw materials for animal feed; (c) increase P (and N) use efficiency of manure by separation into a thick (mainly organic matter and P) and a liquid fraction (mainly N, K) which can serve as secondary raw material for fertiliser production; (d) produce N/K mineral concentrates from manure to be used as chemical fertiliser; (e) market thick fractions of manure separation as secondary raw material for P-recovery.

At the short term (2015) 50% of the phosphate manure surplus has to be processed by each sector. The pig farms produces about 46 million kg P_2O_5 per year, which can be considered as surplus, and consequently about 20-25 million kg P_2O_5 has to be processed each year. It is expected that by lowering the P-content in feed the P-surplus in pig slurry can be reduced with about 10 million kg P_2O_5 . This means that approximately 25% of the P in pig slurry has to be processed and recovered at the short term. Current ways of processing and exporting substantial amounts of manure phosphate require a large effort and are rather costly. In addition, the exported manure to neighbouring countries is not always welcomed in these countries, because various farms also have a surplus of animal manure, which needs to be transported to other farms, that could have accommodated the Dutch manure surplus. Therefore, the current export to neighbouring countries may not be durable.

In the near future, phosphate application limits for agricultural land in The Netherlands tend to become stricter, while the manure production may tend to increase due to the abolishment of the milk quota and the expiration of the pig and poultry production rights by 2015. Hence, the need to process and export more manure is urgent.

If on the other hand a quick and inexpensive solution can be found to lower the P-content in manure by at least 25%, more manure can be used (applied within the set limits) within The Netherlands. This idea for 'closing the manure P cycle in The Netherlands' has been circulating for a while. The idea is for example included in current Public Private Partnerships (PPPs), but never brought into practice or thought well over. The general impression is that removal of part of the P from animal manure 'sounds well' but empirical information on the technical opportunities and practical feasibility are missing completely. The first step would be simple laboratory experiments to explore the technical opportunities.

² With the term phosphorus (P) we refer to the element 'phosphorus'. Both phosphorus and phosphate are used for compounds containing the element phosphorus or phosphate in general. The term phosphate is specifically used for the chemical formula P_2O_5 , which is used in agriculture for expressing the phosphorus content in fertilizers and manures, including its treatment products and derivatives. Note, 1 kg of P = 2.29 kg P_2O_5 .

Although there is ample information and experimental results on P-recovery from organic wastes – i.e. sewage sludge – information on P-removal from animal manure is limited. Available information is quite often limited to research on speciation of P, using chemical models. This study focusses on technical opportunities for P-removal from animal manure.

The study is restricted to pig slurry. Basically all poultry manure is already exported and/or incinerated³, while most of the cattle slurry can be accommodated on the grassland-based dairy farms where the slurries are produced. Pig slurry has a P-content of 3 - 4 kg P₂O₅ per ton, and this is for a significant part inorganic P (80 - 95%; (Gerritse and Vriesema, 1984)). This phosphate is found in the solid phase. Separation of animal manure leads to an organic matter and phosphate-rich solid fraction, and a liquid fraction with rather low concentrations of N and K and virtually no P (Schoumans *et al.*, 2010; Schröder *et al.*, 2009; Velthof and Hummelink, 2010). However, both products are still 'bulky', and the combination of organic matter and P in the solid fraction results in the export of organic matter while the aim is to export P. Therefore, the main focus of this research is to evaluate options of phosphate removal and recovery from manure via simple and relative cheap processing techniques, without the removal of organic matter.

1.1 Aims

The aims of the study are:

- I. To determine the quantity of phosphate that can be recovered from pig slurry by acidification followed by separation into a solid fraction and a liquid fraction from which P is removed by precipitation using a base.
- II. To determine the quantity of phosphate that can be recovered from the solid fraction of pig slurry by acidification.
- III. To determine the amount of phosphate that can be recovered from the liquid fraction obtained after mechanical separation of the pig manure. This recovery can follow two different routes:
 1. Separation of pig slurry into a solid fraction and a liquid fraction and acidification of the liquid fraction only to reduce acid use and subsequently recovery of P using a base followed by removal of precipitated P.
 2. Separation of pig slurry into a solid fraction and a liquid fraction, skipping the acidification step and recover P directly from the liquid fraction by adding a base (alkaline source) followed by removal of precipitated P.

³ At BMC Moerdijk. <http://www.bmcmoerdijk.nl/en/>

2 Design, materials and methods

2.1 Experimental design

2.1.1 P-recovery with an acidification step ('acid-base approach')

The pH of pig slurries varies usually between 7 and 8. The phosphates are largely associated with precipitates of calcium as dicalciumphosphate, or with ammonium and magnesium as struvite (Bril and Salomons, 1990). A large part of the available phosphate minerals in manure or manure fractions can be released by lowering the pH. Also phosphorus bound in organic matter may be released by hydrolysis by reducing the pH. Phosphorus that has been released (mainly as PO_4^{3-}), at the lower pH, can be recovered by separation of this acid liquid phase and addition of an alkaline source, for example $\text{Ca}(\text{OH})_2$, forcing precipitation of a Ca~P which finally can be removed from solution by filtering the suspension. This leads to a relatively small volume of P-rich precipitates. The remaining fractions (wet manure cake and liquid fraction after separation of the precipitate), can be combined again and manure with a lower phosphate content is formed. This manure with lower phosphate content can be applied as nutrient source depending on its N- and K-content on agricultural land in The Netherlands. Export to neighbouring countries can be avoided, so costs for export can be minimized by removing part of the phosphate from animal manure. Of course costs for P-removal have to be lower than the economic gain of P-recovery from animal manure and the lower cost of export.

Figure 1a gives a schematic visualisation of the concept/design of P-recovery from pig slurry. The slurry is acidified and homogenized after which separation in a thick (wet solid manure cake) and a liquid fraction takes place. An alkaline solution (base) is added to the liquid fraction to precipitate solubilized phosphate after which the phosphate rich precipitate is removed by for instance a filtration process. To reduce the pH of manure a substantial amount of H^+ is needed, because the buffer capacity of manure can be rather high. Research with liquid swine manure showed that approx. 100 meq H^+ per liter manure is needed to reduce the pH to 4 (Alitalo *et al.*, 2012), corresponding with 3.6 kg HCl or 4.9 kg H_2SO_4 per ton manure ($M_{\text{HCL}} = 36.46$ en $M_{\text{H}_2\text{SO}_4} = 98.08$). For the titration of dairy slurry with HNO_3 about 550 meq H^+ per kg manure was needed to obtain pH 4. (Oenema and Velthof, 1993) which is 5.5 times higher than for liquid swine manure. Danish research with pig slurry showed that about 7 kg H_2SO_4 per ton pig slurry was needed to reduce the pH to 5.5 (142 meq H^+ per kg manure). So the amount of acid needed to reduce the pH differs for different types of manure. It is well known that animal type, feed type and duration of manure storage influence the composition of manure and, as a result, the buffer capacity of the manure.

Although most of the phosphate in manure is accumulated in the solid fraction as precipitates and incorporated in organic matter, still a part of this fraction is suspended in the liquid phase that is obtained after a mechanical separation (particulate P). The amount of inorganic P in solution compared to the total amount of P in pig slurry is low. The amount of suspended material in the liquid fraction is highly dependent on the mechanical separation technique used. As already mentioned, much of the P is associated with fine particles (Peters *et al.*, 2011; Wendler Fernandes *et al.*, 2012) and the buffer capacity of pig slurry fractions is less than the pig slurry as a whole. Besides the treatment of pig slurry as a whole to recover P, there are also options, based on acidification, to recover P separately from solid manure (fractions) or from the liquid manure fraction obtained after the separation process. This liquid fraction contains a small amount of soluble P (PO_4) and an amount of P that is present in suspended particles. The design of treatment steps needed to recover P from a solid fraction and a liquid fraction is presented in Figure 1b and 1c, respectively. With respect to the P present in the solid fraction, the P-recovery from different particle size solid fractions of pig slurry was studied in detail. The main research questions were:

1. The quantity of acid required to reduce the pH of the different particle size fractions to the target pH (due to the differences in the buffer capacity). The target pH is the pH where a substantial part of the P is present as soluble P (as PO_4).

2. The P release from the different particle size fractions into the solution.
3. The amount of P that can be recovered from the different particle size fractions. The particle size studied were $> 500 \mu\text{m}$, $250\text{-}500 \mu\text{m}$, $106\text{-}250 \mu\text{m}$ and $\leq 106 \mu\text{m}$ obtained by sieving techniques. The detailed experimental design is presented in Figure 2. The overall aim of all experimental studies was to develop a procedure to retrieve at least 25% of the available P in the pig slurries and to concentrate the recovered P into a solid fraction.

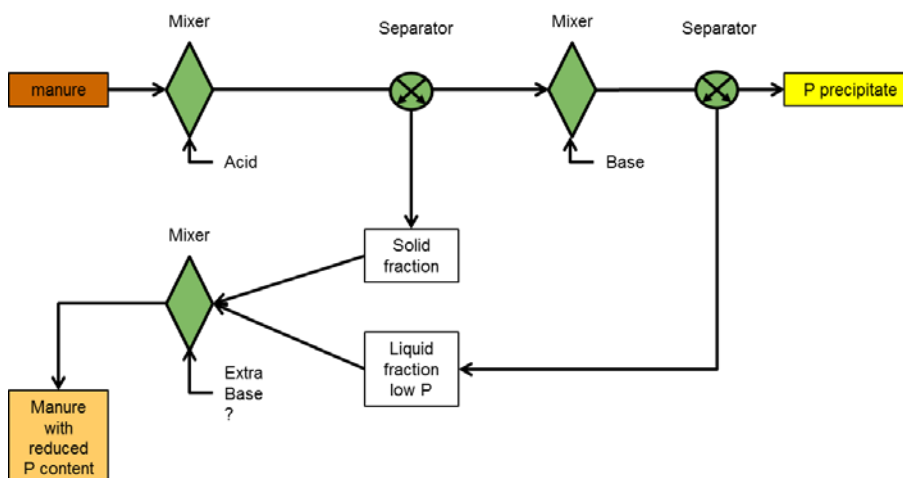


Figure 1a Schematic representation of proposed steps to reduce the P-content in pig slurry by treatment of the pig slurry as a whole.

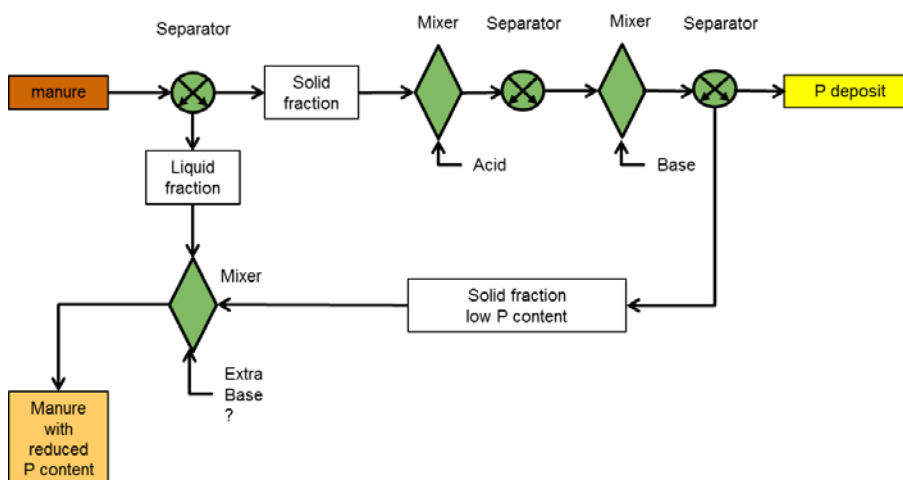


Figure 1b Schematic representation of proposed steps to reduce the P-content in pig slurry by treatment of the solid fraction of the pig slurry.

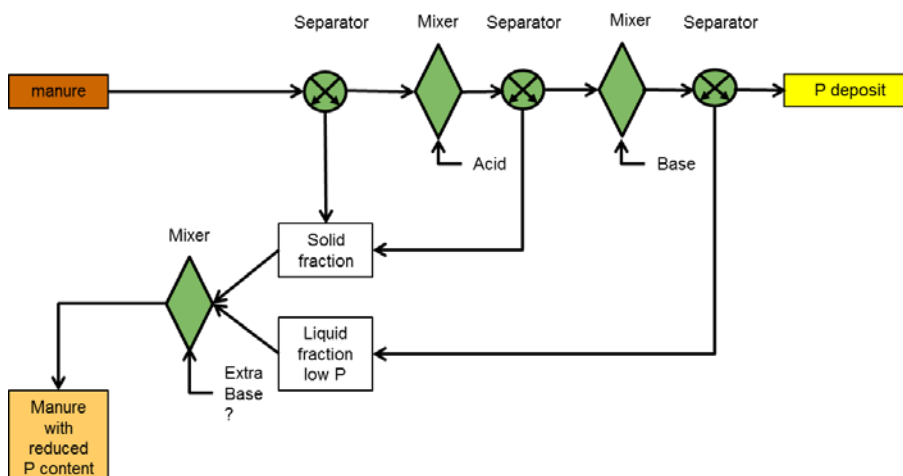


Figure 1c Schematic representation of proposed steps to reduce the P-content in pig slurry by treatment of the liquid fraction of the pig slurry.

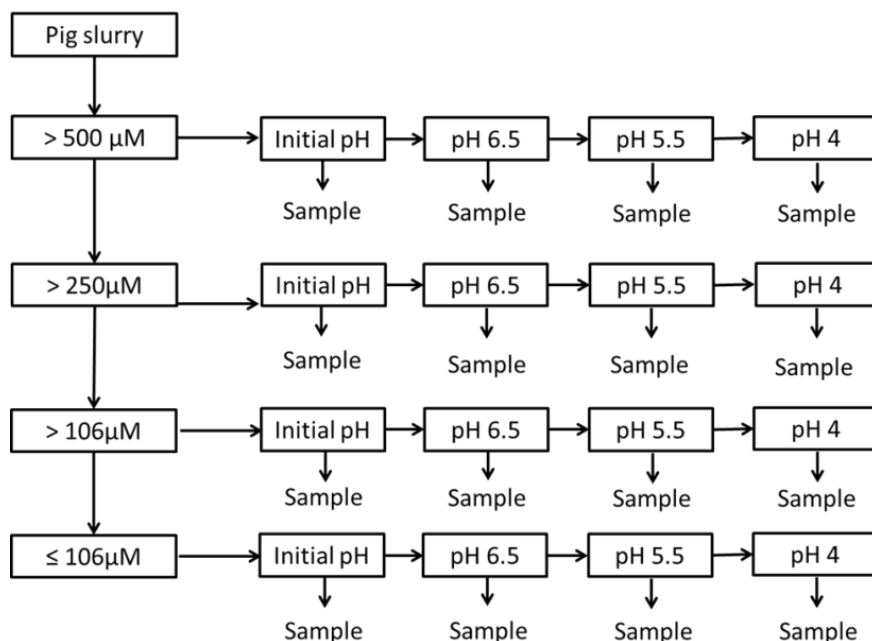


Figure 2 Experimental design and fractionating scheme of pig slurry and sampling of the solution at different pH.

2.1.2 P-recovery without an acidification step

Besides the acid treatment of whole pig slurry, specific solid fractions of pig slurry or the liquid fraction of pig slurry (which contains soluble PO_4 and a small amount of P-containing suspended and colloidal particles) to release and recover P, a second approach is to produce precipitates from the liquid fraction that has been separated mechanically from non-acidified manure at high pH, since soluble P can be precipitated with Mg^{2+} or Ca^{2+} at high pH. And during this precipitation process also P-containing colloidal and suspended particles, which are present in the liquid phase, might also precipitate.

By increasing pH with $\text{Ca}(\text{OH})_2$ soluble P can be precipitated as amorphous calcium phosphate (ACP, $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$) but also calcite (CaCO_3) can be formed (Ekama *et al.*, 2006) on which phosphate can be adsorbed or co-precipitated (Schoumans, in prep.). Other calcium phosphates have been identified (Fordhan and Schwertmann, 1977): $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$, dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), and inorganic salts of ammonium and calcium ($\text{NH}_4\text{CaPO}_4 \cdot \text{H}_2\text{O}$). The main points of interest regarding Ca-precipitates production are:

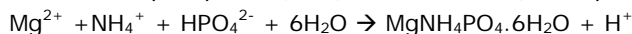
1. The amount of P that can be recovered by addition of Ca hydroxide to the liquid fraction.
2. The impact of increasing the pH of the liquid fraction (~pH 8) to 11.0 (with NaOH) in order to increase the CO_3 -concentration to improve the initiation of precipitation of Ca-phosphate-precipitates or formation of CaCO_3 -phosphate-adsorption complexes.
3. The composition of the precipitate, including dry matter and organic matter content.

Different forms for Mg-P products can also be formed, like magnesium ammonium phosphate (MAP, NH_4 -struvite or just called struvite), magnesium potassium phosphate (K-struvite), and magnesium hydrogen phosphate. This latest product is easily soluble when conditions are changed. The pH is an important factor for which products will be formed (Greaves *et al.*, 1999; Le Corre *et al.*, 2009; Lindsay *et al.*, 1989).

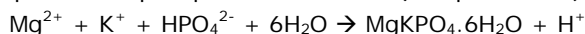
Struvite formation in animal manure is studied but mainly at laboratory scale (Çelena *et al.*, 2007; Greaves *et al.*, 1999; Luo *et al.*, 2001; Shen *et al.*, 2012; Szogi and Vanotti, 2009; Wahal *et al.*, 2011; Wendler Fernandes *et al.*, 2012). Formation of struvite in waste water is studied more intensively. Not only struvite but other minerals co-precipitate as well (De Graaff, 2010; Ekama *et al.*,

2006; Ganrot *et al.*, 2007; Lind *et al.*, 2000; Van Rensburg *et al.*, 2003; Wu and Zhou, 2012). The pH determines the phosphorus mineral that precipitates (Colsen, 2002; Gadekar *et al.*, 2009; Ehlert *et al.*, 2013). The following reactions may occur:

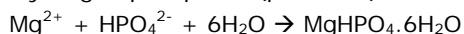
- 1) Magnesium ammonium phosphate (MAP): NH_4 -struvite ($8.5 < \text{pH} < 9.5^4$):



- 2) Magnesium potassium phosphate: K-struvite ($9 < \text{pH} < 10.5$):



- 3) Magnesium hydrogen phosphate ($\text{pH} < 8.5$):



The main points of interest/research questions regarding Mg-precipitates production from the liquid fraction that has been separated from the manure are:

1. The amount of P that can be recovered by addition of Mg to the liquid fraction.
2. The impact of increasing the pH to 9.5.
3. The impact of Mg source, like $\text{Mg}(\text{OH})_2$, MgCl_2 or MgO , on the P-recovery.

The advantage of this second approach is that the pH of the manure fraction can be kept high (no acid needed afterwards; less costs). The disadvantage could be that the P-recovery is too low and/or the quality of the product will be less. This would make it less attractive as secondary resource for industries, when compared to precipitates of soluble inorganic P obtained after acid treatment, which can be easily separated by mechanical separation techniques.

2.2 Materials

The study has been carried out with three slurries from fattening pigs:

- Pig slurry 1 (a sample from research location 'Sterksel').
- Pig slurry 2 (a sample from a pig fattening farm). From this fresh pig slurry the original material and both separated fractions (Distrimex/Bauer screw press) were available (liquid and solid fraction); the solid fraction looked like 'peat litter'.
- Pig slurry 3 (a sample from another pig fattening farm). This slurry had been stored approx. three months in a manure pit before samples were taken.

From pig slurry 1 and 3 only a non-separated manure sample was delivered. Therefore, the manure was separated in the laboratory by a laboratory centrifuge at 1000 rpm (pig slurry 1) and at 300 and 3000 rpm⁵ (pig slurry 3) or by sieving / filtering for some of the experiments.

The dry matter content (DM), organic matter content (OM) and total amounts of P, N and K were determined in the pig slurry samples and also in the solid fractions obtained after mechanical separation of the pig slurry. In the liquid fraction the total concentrations of P, N and K were determined (total of suspended and soluble) and also the ortho-P concentration. Furthermore, the separation efficiencies of water, DM, OM, P, N and K were determined as defined by Schröder *et al.* (2009):

$$\text{Separation Efficiency component} = \frac{[\text{quantity of this component in the solid fraction}]}{[\text{total quantity in the manure}]} \times 100 (\%) \quad (1)$$

The calculation of the Separation Efficiency (SE) for the LF also follows equation (1).

4 Indicative. Ranges of pH follow Colsen (2002). pH range depends on the composition of the matrix from which struvite is precipitated.

5 Conversion of rpm in g for the Rotor (Thermo Scientific. Fiberlite F1-6X250Y).

rpm	g
300	10
3500	1880
10000	15300

2.3 Methods

2.3.1 Sampling, sample pretreatment and analysis conditions

Laboratory samples were taken after homogenising the pig slurry or the liquid fraction with a mixing tool (paint mixer). The solid fraction (wet manure cake) was homogenised by hand.

Analyses of pig slurries and its fractions followed two different pre-treatments. One pre-treatment was acidifying with 2 M H_2SO_4 and drying of samples at 70°C. Dried samples were ground and sieved (< 2 mm). Analyses in liquid fractions were conducted in a subsample taken from the homogenised fresh sample.

P-recovery was measured in acidified or alkalinized samples at the required pH. To retrieve the required pH sample material was acidified or alkalinized in 500 ml beakers according to the measured titration curves to modify the pH to the required value. Some sample material reacted vividly on acid addition and caused foaming due to the production of CO_2 . After this reaction had stopped, the beakers were sealed and stirred during 60 minutes (50-60 rpm). Samples were centrifuged (3000 rpm, ten minutes) to separate solids from the liquid fraction. Solids were carefully removed and the liquid fraction was used to analyse the P-concentration. Weight of solids and liquid fraction was registered.

For instrumental analyses (ICP, SFA) samples require filtering over 0.45 μm filters. Pig slurries differ in their filtration characteristics. Filtering slurries over this filter size appeared extremely difficult for some samples. If filtering over 0.45 μm filters appeared difficult, the following procedure was followed. To facilitate filtering samples were centrifuged (10,000 rpm) during ten minutes, followed by a 5 times dilution with demineralised water followed by filtering over 0.45 μm filters. Even then some samples could not be filtered, not even after a second centrifugation step (10,000 rpm, 10 minutes). These samples (obtained in the experiment with $\text{Ca}(\text{OH})_2$ -addition) were measured as they were on the Segmented Flow Analyser (SFA).

Analyses on $\text{PO}_4\text{-P}$ on the SFA followed within 48 hours after sampling. Analyses on total-P were conducted in acidified samples (0.14 M HNO_3).

P-recovery was determined by the decrease in P-concentration before and after the precipitation reaction.

2.3.2 Titration of pig slurry and its fractions

Titration curves were determined by adding H_2SO_4 or NaOH to samples of whole pig slurry and its fractions. Per titration 100 ml or 150 ml sample was added to a 400 ml beaker of known weight. The weight of the sample was registered. The sample was stirred with a magnetic stirrer. The pH was measured with a pH electrode (Thermo Scientific. Orion. 8115BNUWP Ross Ultra Semi-Micro pH). Next 1 ml 2 M H_2SO_4 was added and the pH was registered after stabilisation. Then the next addition of one ml 2 M H_2SO_4 followed. In general, stabilisation was reached within minutes. After reaching the required pH, the solution was centrifuged and the P-concentration was measured in the supernatant. Titration with 1 M or 5 M NaOH , to increase the pH of manure (fraction) samples, followed the same procedure.

2.3.3 Recovery of P from the liquid fraction by increasing the pH and adding calcium or magnesium compounds

Recovery of P from the liquid fraction, obtained after mechanical separation of acidified whole pig slurry, was conducted via precipitation with a calcium or a magnesium compound. Calcium sources tested were $\text{Ca}(\text{OH})_2$ and CaCl_2 . The influence of the final pH was tested at pH 8 and pH 11. The pH was raised by adding NaOH before adding the Ca-compounds. The idea of raising the pH to 11 with NaOH was to increase the CO_3^{2-} concentration to improve the condition of precipitation of CaCO_3 products (after Ca-compounds addition), on which phosphate can adsorb and co-precipitate. The setup of this experiment is presented in Figure 3.

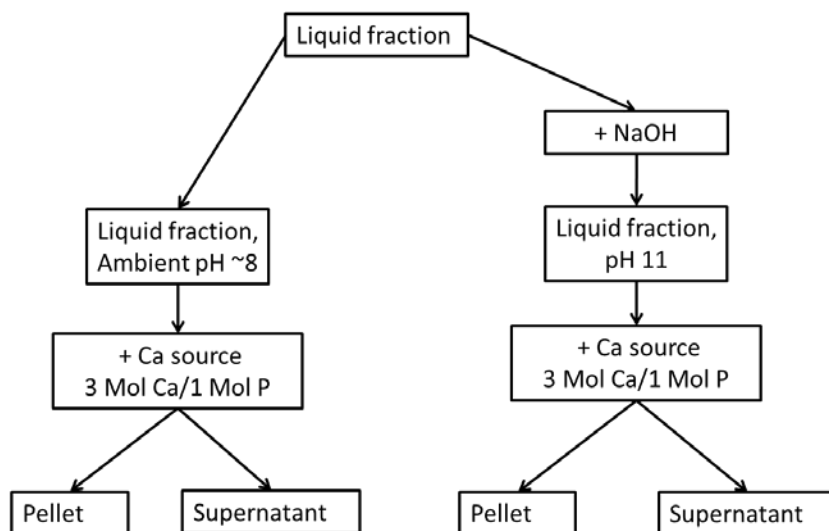


Figure 3 Scheme for calcium addition as $\text{Ca}(\text{Cl})_2$ or $\text{Ca}(\text{OH})_2$, with and without alkalisation to pH 11. The solid particles and liquid fraction separated in the laboratory are called pellet and supernatant, respectively.

Magnesium phosphate precipitate was tested with the following magnesium sources: MgCl_2 , MgO and $\text{Mg}(\text{OH})_2$. The influence of the pH was tested at pH 8 and pH 9.5 by means of addition of NaOH (Figure 4). A molar ratio of 1.3 Mg to 1 mol P was used. This is a 30% higher amount of Mg than needed to precipitate NH_4 -struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) and was applied to facilitate flocculation. After Mg addition, samples were stored during 24 h at $4 \pm 3^\circ\text{C}$ before precipitates were collected. The P-recovery was determined by the decrease in P-concentration in the solution before and after the precipitation reaction.

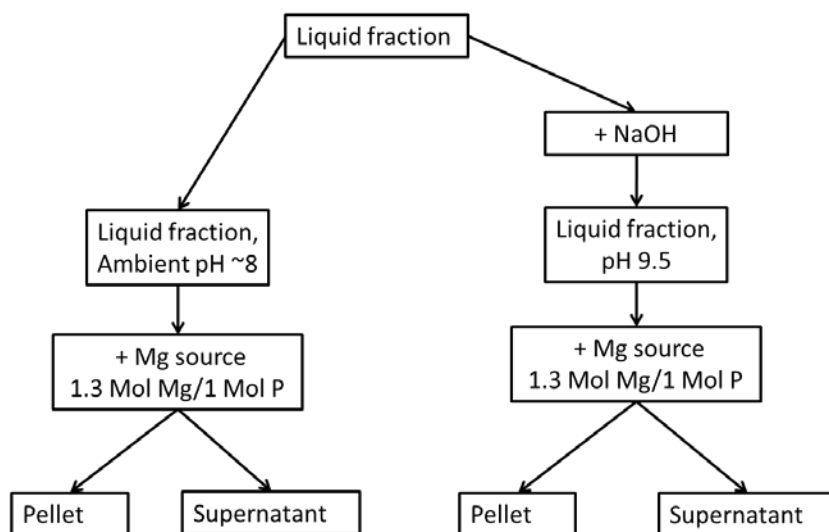


Figure 4 Scheme for magnesium addition as MgCl_2 , $\text{Mg}(\text{OH})_2$ or MgO with and without alkalisation to pH 9.5.

2.3.4 Recovery of P from the solid fraction by acidification

P-recovery from the solid fraction was studied to investigate if:

1. The solid fraction requires less acid than the whole pig slurry to solubilize P.
2. The use of acid can be further reduced to solubilize P solely from the finest fraction.

P-solubilisation from the solid fraction of pig slurry was tested with pig slurries 2 and 3. The experiments started with both original pig slurries⁶ which were centrifuged at 300 rpm during ten minutes to produce a solid and liquid fraction. The liquid fraction was centrifuged for a second time at 10,000 rpm during ten minutes. From the solid fraction, liquid fraction and pellet⁷ the dry matter content was measured. Both solid fraction and pellet from the liquid fraction were examined on their P-release characteristics. Samples of 600 mg dry matter of both solid fraction and pellet were added to 40 ml demineralised water and treated with H₂SO₄ to create pH values of 5.0, 5.5, 6.0, 6.5 and 8.0. Quantities of acid were calculated from titration curves of not-separated pig slurry. However, these calculated quantities of acid did not lower the pH to the desired level: more acid was needed. It seems that the buffer capacity of the solid fraction (per unit weight) was higher than the buffer capacity of the whole pig slurry (per unit weight). The quantity of acid was registered⁸. Samples not treated with acid also received 40 ml demineralised water. Samples were shaken during 30 minutes after which they were centrifuged at 20.000 rpm. P (SFA) and pH was measured in the resulting supernatant.

2.3.5 Chemical analyses

Dry matter content was determined according to the gravimetric method and NH₄-N was measured by 1:40 (v/v) extraction with 1 M KCl (shaking time 30 minutes) followed by filtering. The amount of total N and total P were measured after H₂SO₄-H₂O-Se destruction (both dried samples and liquid samples). All analyses were conducted by the Chemical and Biological Soil Laboratory (CBLB). CBLB is a testing laboratory certified by the Dutch Accreditation Council (scope: 342). Followed procedures are based on:

E0101 based on NEN-EN-15934.

E1408 own procedure based on NEN-EN-ISO-13395 and NEN-EN-ISO-15681-2 (measuring N and P using SFA).

E1410 own procedure based on ISO/TS-14256-1.

E1306 own method based on ISO/DIS-17586.

E1417 own method based on NEN-EN-ISO-11732, NEN-EN-ISO-13395, and NEN-EN-ISO-15681-2 (measurement of N and P with segmented flow analyser (SFA)).

⁶ From pig slurry 2 a thick fraction obtained by a screw press was available. However in this experiment we standardised the method of production of a thick fraction by using the low tech separation method of centrifugation at 300 rpm.

⁷ Separated solid particles are called pellet in the laboratory studies.

⁸ Samples of pig slurry and its separation products differ in their times in which equilibrium was reached in pH after acid addition. The evolution of CO₂ delayed this equilibrium. The procedure therefore was adapted. After acid addition, samples were shaking vigorously. After controlled release of the produced CO₂ the pH was measured. Lower pH required more acid additions, thus repeated shaking was required leading to a range of reaction times of acid with samples of pig slurry or its separation products.

3 Results

3.1 Composition of pig slurries

Table 1 shows the chemical and physical characteristics of the pig slurries. Pig slurry 3 contains less total P (1.64 g P kg^{-1} ; $3.8 \text{ kg P}_2\text{O}_5 \text{ ton}^{-1}$) than pig slurry 1 (1.44 g P kg^{-1} ; $3.3 \text{ kg P}_2\text{O}_5 \text{ ton}^{-1}$) and pig slurry 2 has the highest P-content (1.92 P kg^{-1} ; $4.4 \text{ kg P}_2\text{O}_5 \text{ ton}^{-1}$). The separation efficiency of the solid fraction of the three pig slurries are 48.5, approx. 5 and 11.3, respectively. The highest P-contents in the liquid fraction are obtained by the screw press (pig slurry 2). Centrifuging at 3500 rpm gives a liquid fraction with a relatively low P-content (0.5 g P kg^{-1}), which is about 13% of the total P content (P-separation efficiency).

Table 1

Composition and separation efficiencies for three pig slurries of fattening pigs.

Product	Dry matter	Organic matter	P	N	Separation efficiency			
					product		component	
					Total matter in solid fraction	P	N	DM
	%	%	g P kg^{-1}	g N kg^{-1}	%	%	%	%
Pig slurry 1	9.65	79.70	1.44	3.23				
Pig slurry 1 solid fraction 1000 rpm	13.40	81.23	1.3*	3.8*	48.5	45	58	67
Pig slurry 1 liquid fraction 1000 rpm	6.10	70.76	0.91	6.78		33	111	33
Pig slurry 2	10.41	76.50	1.92	5.89				
Pig slurry 2 solid	37.32	89.60	1.11	3.15	5**	11**		
Pig slurry 2 liquid	8.44	72.90	2.28	7.81		92**		
Pig slurry 3	6.20	66.80	1.64	7.54				
Pig slurry 3 solid 300 rpm	11.98	73.70	2.66	5.32	11.3	35.5	15.4	21.8
Pig slurry 3 liquid 300 rpm	4.96	67.00	1.51	8.36		65.4	78.7	70.9
Pig slurry 3 solid 3500 rpm	16.34	72.70	2.92	5.53	18.0	91	37.4	50.5
Pig slurry 3 liquid 3500 rpm	3.36	63.70	0.50	9.74		13.4	56.4	43.7

* Sample size possibly too small for accurate measurement.

** Separation efficiencies are estimated from the P measurements taking into account that the sum of P (and N) in the liquid and solid phase should be approx. 100%; volume of solid fraction and liquid fraction were not measured.

It was difficult to separate the liquid fraction of pig slurry 1 at low centrifugation rates ($< 600 \text{ rpm}$; coagulants were not used), therefore a higher centrifuge speed was used (1000 rpm). Pig slurry 2 (screw press on fresh pig slurry) is more rich of fibres than pig slurry 3 which has been stored in a manure pit for a while (old pig slurry). The separation efficiency of the solid fraction of pig slurry 2 was estimated by the contractor at 35-38%. This is highly overestimated and should be approx. 5% because then the sum of P (and N) in the liquid and solid phase will be approx. 100%. The separation efficiency of the liquid fraction of pig slurry 3 determined at 3500 rpm is 82%. The separation efficiency of the solid fraction of pig slurry 3 was relatively low and therefore different centrifugation rates were used to determine the impact of centrifugation rate on the separation efficiency (Figure 5). The maximum separation efficiency of the solid fraction of pig slurry 3 is 18%. The particles in the liquid phase of pig slurry 3 are very small and also the mass of these particles is low. Many particles are still in the liquid fraction obtained at 10,000 rpm (in practice ultra-centrifuge takes place at 4000 rpm). The sum of the measured separation efficiencies of the fractions of pig slurry 3 are between 101-104% for P and about 94% for N.

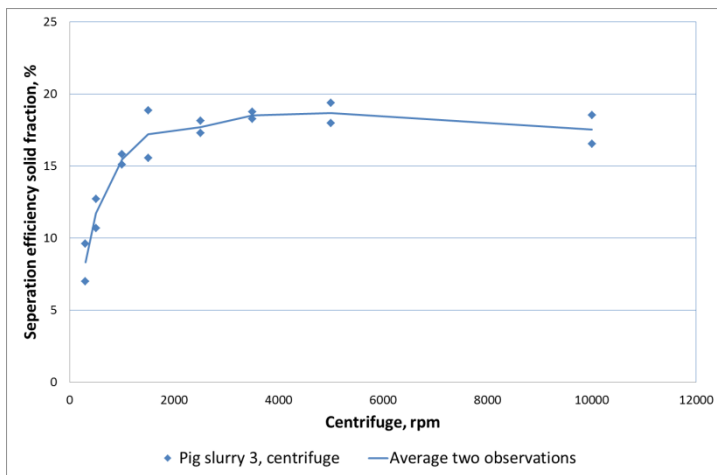


Figure 5 Separation efficiency (solid fraction) of pig slurry 3 (approx. three month old).

3.2 P-recovery after lowering the pH of manure or manure fractions by acidification

3.2.1 Pig slurry

The buffer capacity of the three pig slurries was determined by measuring the pH after adding H_2SO_4 until a pH of 3 is reached. The results are presented in Figure 6, expressed as meq H^+ /L slurry (top), and as meq H^+ /kg DM in (bottom). The backward titration with NaOH was only carried out for pig slurry 1 (Figure 7).

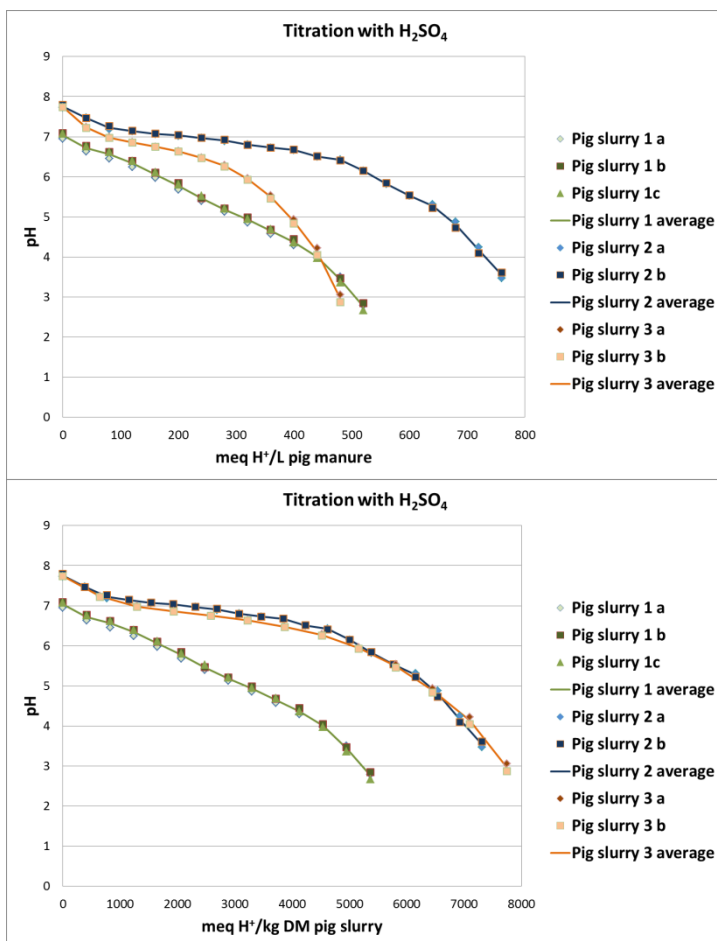


Figure 6 Titration of the pig slurries with H_2SO_4 . Top: expressed as meq H^+ per liter manure and bottom: meq H^+ per kg dry matter (DM).

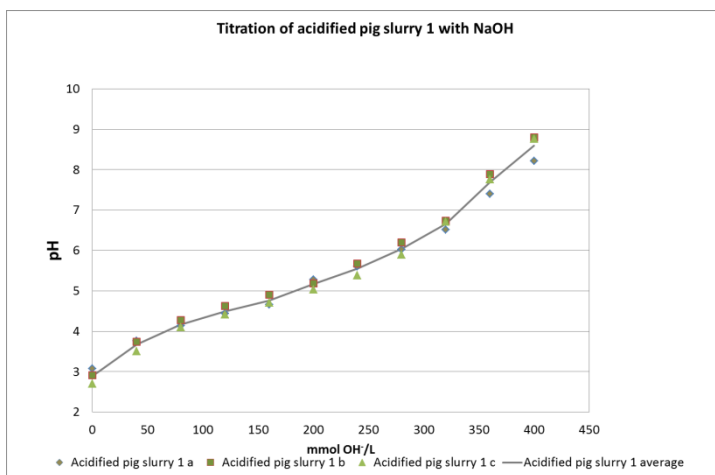


Figure 7 Backward titration of the acidified pig slurry 1.

For reducing the pH of the whole original pig slurry 1 from pH 7 to pH 3 about 520 meq $H^+ L^{-1}$ is required (see Figure 6). At pH 5 the soluble P-concentration in the separated liquid phase from the acidified manure has increased to 1200 mg $P L^{-1}$ (Figure 8). This experiment shows that the soluble P-concentration will increase to a maximum value in the separated liquid phase if the pH is decreased (Figure 8). The maximum value is obtained at pH = 5. However, at a pH value of 5.5 already 80% of this maximum value is obtained. At pH = 6 about 70 to 75% of this maximum value is obtained.

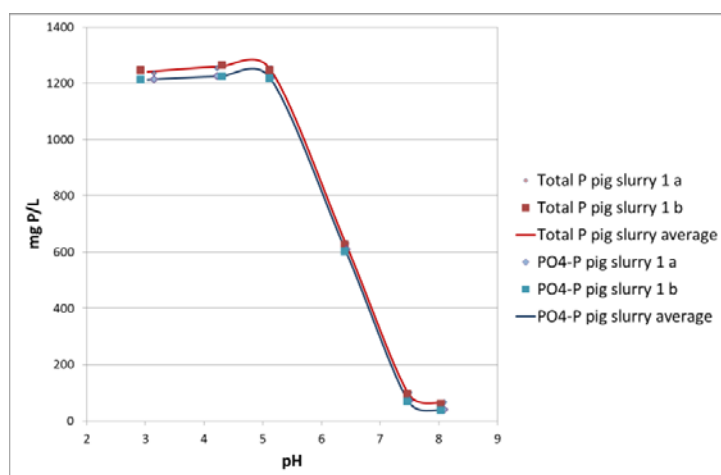


Figure 8 P-concentrations (Total P (ICP) and PO_4 -P (SFA)) in the separated liquid phase (3000 rpm) as a function of the pH of acidified pig slurry. Affixes a and b are duplicates.

In the laboratory a first exploration of the precipitation reaction (P-recovery) was done. A suspension of calcium hydroxide (1 g $Ca(OH)_2$ in 4 ml H_2O) was added to the separated (centrifuged at 3000 rpm) liquid phase of acidified pig slurry to a final pH of 8. A precipitate was formed and filtered. Based on the decrease of the P-concentration in solution the amount of precipitated P-material was calculated (Figure 9; duplicate of experiments). In Figure 9 also the starting P-concentrations are shown again (green lines; which are equal to Figure 8).

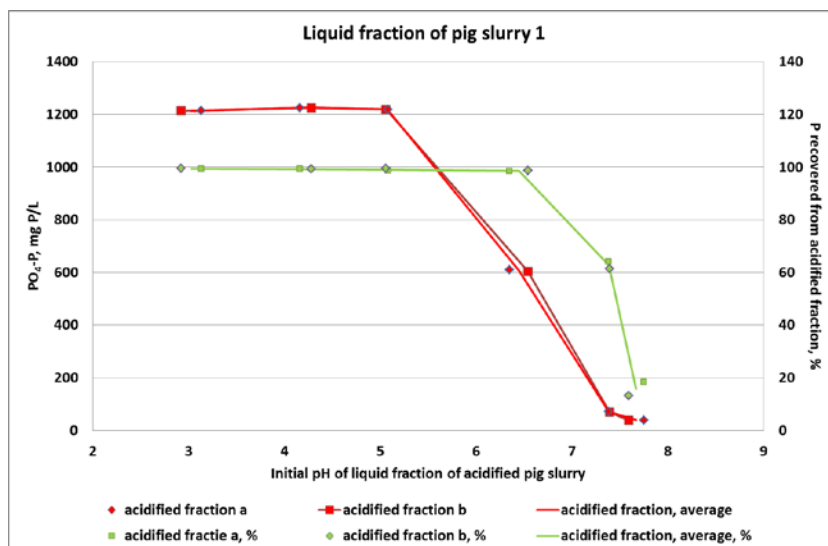


Figure 9 Ortho-P concentration ($PO_4\text{-P}$) in the liquid phase (left Y-axis, green lines) and percentage P-recovery from the liquid phase after addition of $Ca(OH)_2$ to the solution up to pH 8 (right Y-axis; red lines). Affixes a and b are duplicates.

Addition of $Ca(OH)_2$ to the acidified treated liquid fractions with a pH of 6.5 and lower values gives almost a complete recovery of the soluble amount of P (Figure 9; green line). At higher initial pH the recovery is lower than 100%. To recover 25% of the P from pig slurry 1, just a slight decrease of the pH (to pH 6.75) is needed (Figure 9), followed by separation of the liquid phase and addition of $Ca(OH)_2$ to the liquid phase. To recover 50% and 75% of the amount of P from pig slurry 1 the pH has to drop to pH 6 and 5, respectively, before the separation process.

Based on the titration curve of pig slurry 1 (Figure 6) it is calculated that about 120 meq H^+ /L is required to reach pH 6.5 with 100% P-recovery of P from the liquid fraction, while 320 meq H^+ /L is needed to obtain a pH of 5. To recover 25% of the P-content of pig slurry 1 about 40 meq H^+ /L pig slurry is necessary which equals to 2.0 kg H_2SO_4 per ton pig slurry. To increase the pH to the original pH again, approximately 25 meq OH^- per liter pig slurry is needed (Figure 7), but to be safe, it is assumed that the same amount of OH^- is necessary to increase the pH as used for H^+ to decrease pH. Table 2 shows that the total costs for chemicals varies between 0.33 and 2.96 € per ton pig slurry to recover 25% of the P in the slurry. Both average and high market prices of chemicals have been used. If a higher P recovery is required (about 50% at pH 6 and 75% at pH 5), the chemical costs of these three samples will vary respectively between 1.32 and 8.88 € per ton pig slurry (Table 2 bottom) or 2.47 – 10.85 € per ton pig slurry (Table not presented). If the market prices for chemicals are high the chemical treatment of the whole pig slurry becomes rather expensive.

Acidification of the whole pig slurry is rather costly as the buffer capacity is relative high due to sorption of H^+ on organic matter (including volatile fatty acids), reaction with minerals (e.g. $CaCO_3$) and high concentrations of soluble HCO_3^- and NH_3/NH_4 . All these components consume H^+ -ions and H_2CO_3 (CO_2^1) en NH_4^+ are produced. We explored which particle size fraction requires least acidification to meet at least a 25% P-recovery aim. Therefore, as a next step, the P-recovery from different particle size fractions of pig slurry was determined.

Table 2

Indication of the costs to recover **25%** of P from pig slurry.

Parameter	Unit	Pig slurry 1	Pig slurry 2	Pig slurry 3
DM pig slurry	%	9.7	10.4	6.2
initial pH pig slurry	-	7	8	7.7
P-content pig slurry	g P/kg	1.4	1.9	1.6
required amounts of acid	meq H ⁺ /l	40	340	180
	g H ₂ SO ₄ /l	1.96	16.66	8.82
	kg H ₂ SO ₄ /m ³	2.0	16.7	8.8
pH decreased to	(-)	6.75	6.75	6.75
required amounts of base	meq OH ⁻ /l	40	340	180
	g Ca(OH) ₂ /l	1.48	12.58	6.66
	kg Ca(OH) ₂ /m ³	1.5	12.6	6.7
final pH	(-)	7	7.25	7.25
reduction in P content pig slurry	%	25%	25%	25%
average costs H ₂ SO ₄ : 130 €/ton	€/ton pig slurry	€ 0.25	€ 2.17	€ 1.15
high costs H ₂ SO ₄ : 260 €/ton	€/ton pig slurry	€ 0.51	€ 4.33	€ 2.29
average costs Ca(OH) ₂ : 50 €/ton	€/ton pig slurry	€ 0.07	€ 0.63	€ 0.33
high costs Ca(OH) ₂ : 100 €/ton	€/ton pig slurry	€ 0.15	€ 1.26	€ 0.67
Total acid + base (average)	€/ton pig slurry	€ 0.33	€ 2.79	€ 1.48
Total acid + base high	€/ton pig slurry	€ 0.66	€ 5.59	€ 2.96

Indication of the costs to recover **50%** of P from pig slurry.

Parameter	Unit	Pig slurry 1	Pig slurry 2	Pig slurry 3
DM pig slurry	%	9.7	10.4	6.2
initial pH pig slurry	-	7	8	7.7
P-content pig slurry	g P/kg	1.4	1.9	1.6
required amounts of acid	meq H ⁺ /l	160	540	320
	g H ₂ SO ₄ /l	7.84	26.46	15.68
	kg H ₂ SO ₄ /m ³	7.8	26.5	15.7
end pH	(-)	6	6	6
required amounts of base	meq OH ⁻ /l	160	540	320
	g Ca(OH) ₂ /l	5.92	19.98	11.84
	kg Ca(OH) ₂ /m ³	5.9	20.0	11.8
end pH	(-)	7	8	7.7
reduction in P-content pig slurry	%	50%	50%	50%
average costs H ₂ SO ₄ : 130 €/ton	€/ton pig slurry	€ 1.02	€ 3.44	€ 2.04
high costs H ₂ SO ₄ : 260 €/ton	€/ton pig slurry	€ 2.04	€ 6.88	€ 4.08
average costs Ca(OH) ₂ : 50 €/ton	€/ton pig slurry	€ 0.30	€ 1.00	€ 0.59
high costs Ca(OH) ₂ : 100 €/ton	€/ton pig slurry	€ 0.59	€ 2.00	€ 1.18
Total acid + base (average)	€/ton pig slurry	€ 1.32	€ 4.44	€ 2.63
Total acid + base high	€/ton pig slurry	€ 2.63	€ 8.88	€ 5.26

3.2.2 P-recovery from solid fraction and from different particle size fractions of pig slurry

3.2.2.1 Solid fraction and second solid fraction of liquid fraction

P-recovery from the solid fraction was studied to answer the following questions:

1. Does the solid fraction require less acid than pig slurry to solubilize P.
2. Can the use of acid be further reduced to solubilize P solely from the finest solid particles retained in the liquid fraction obtained after a mechanical separation process ?

The solid fraction and the fine solids in the liquid fraction, obtained after a mechanical separation process of the pig slurry, were tested on their perspective to solubilise P. For this the solid fraction, obtained after centrifuging at 300 rpm (low tech separation), and the pellet obtained by centrifuging

the liquid fraction at 10,000 rpm respectively, were treated with different quantities of H₂SO₄ (2.3.4.). The P-content of the pellet was not known and difficult to determine. The quantities of acid needed were derived from titration curves of the original pig slurries. It has to be noticed that the solid fraction and the pellet of the liquid fraction had a higher initial pH than the original pig slurries and their liquid fractions (Figure 10). In the first steps of the titration more acid was needed than calculated from the titration curve of the whole pig slurry. At pH values less than 7, less acid was needed to lower the pH (Figure 10). The solid fraction of the (fresh) pig slurry 2 () showed poorer buffering of pH than the solid fraction of the (aged) pig slurry 3, for unknown reasons.

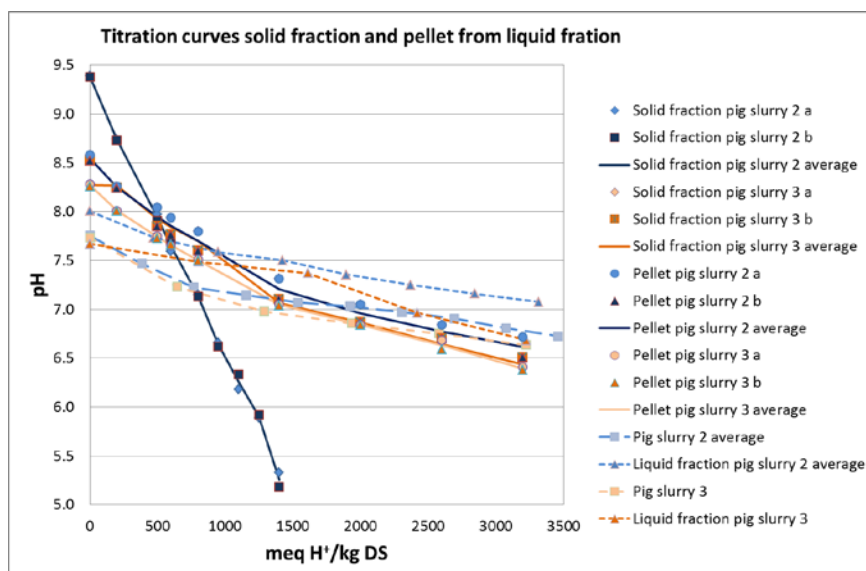


Figure 10 Titration curves for the solid fractions and pellets of centrifuging the liquid fraction of two pig slurries. For comparison the average values of the titration curves for the original pig slurries and their liquid fractions are given.

Acidification did enhance the total P-solubilisation from both the solid fraction and from the pellet of the second separation (Figure 11). Solubilisation was poorest for the solid fraction of pig slurry 2. The solid fraction of pig slurry 3 and the pellets of the liquid fractions of pig slurries 2 and 3 showed a similar trend (Figure 11).

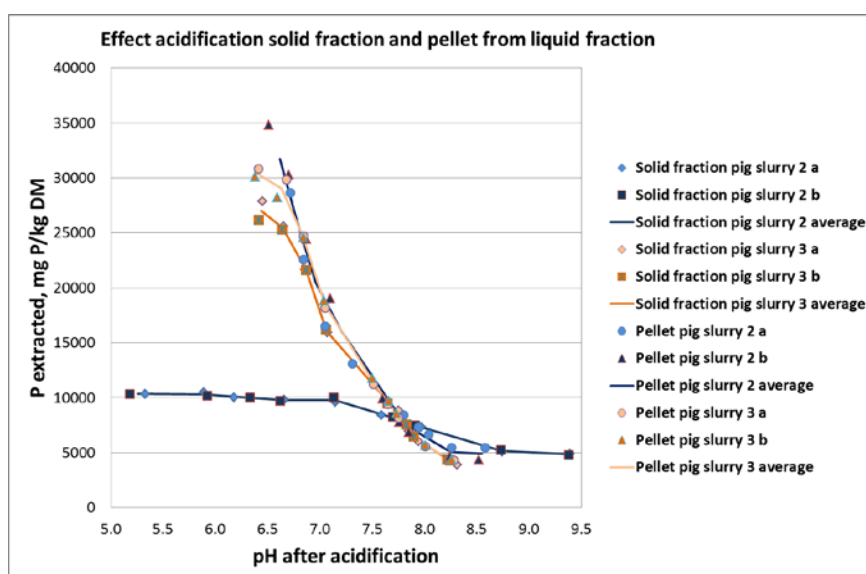


Figure 11 Total P-solubilisation from the solid fraction and from the pellet of the second separation of fine particles from liquid fraction in mg P/kg DM as a function of the pH during extraction.

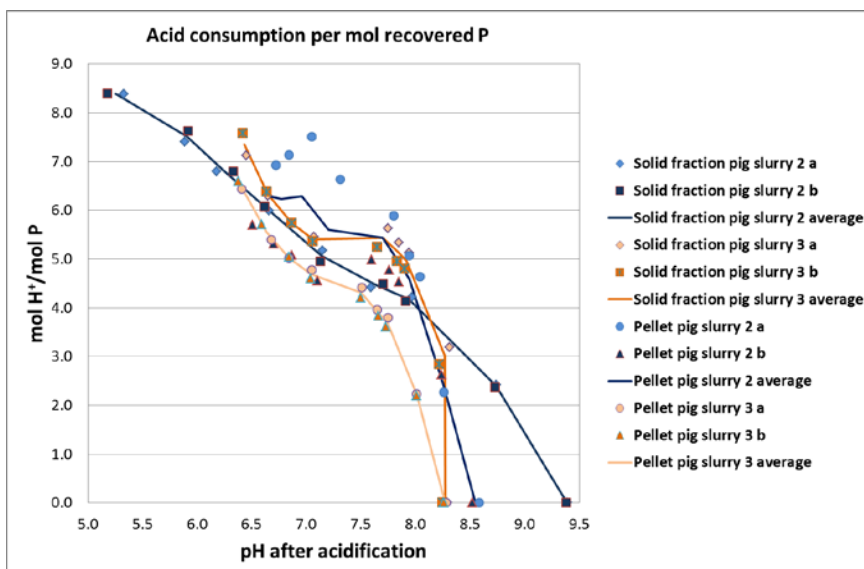


Figure 12 Acid requirement in mol H⁺ per mol P for solid fraction and pellet of the second separation of fine particles from liquid fraction.

The solubilisation of P-increases as pH is lowered (Figure 11). At lower pH more acid is needed to solubilise P (Figure 12). Variation was found between the different pig slurries and pellets. The solid fraction of pig slurry 2 starts at a higher pH (caused by the dilution with water, see 2.3.4) but at lower pH less acid is required than for the pellet. The solid fraction of pig slurry 3 requires more acid than the pellet of its liquid fraction. However, the differences are relatively small. To lower the pH to 7.0 about 5.5 mol H⁺/mol P is needed, for pH 6.5 about 7 mol H⁺/mol P is needed.

In this experiment relatively small quantities of acid are needed to solubilise P compared to the quantity needed for recovery of P from the liquid fraction of the pig slurries (see 3.2.3). Also the use of acid can be reduced to extract solely P from the fine particles of the liquid fraction. However, separation of this fine fraction requires quite an effort (10,000 rpm).

3.2.2.2 Different particle size fractions obtained by sieving the pig manure

The exploratory study on the effect of particle size on the efficiency of P-recovery has been carried out with pig slurry 2 (fresh pig slurry). Different particle size fractions were obtained by sieving the pig slurry over 106 µm, 250 µm and 500 µm. Particle size fractions obtained were ≤ 106 µm, 107-250 µm, 251-500 µm and > 500 µm (Figure 2). Separations started with 1 L pig slurry that was sieved over 500 µm to obtain a solid fraction and a liquid fraction. The solid fraction was brought into suspension with distilled water back to 1 L and then different pHs were created by adding H₂SO₄. Small samples were taken after each addition of acid. Subsequently, the liquid fraction (of known volume) was passed over a finer sieve (250 µm). This produced again a second thick and a second thin fraction. This new solid fraction was re-suspended in the original volume of the thin fraction from which it was produced, after which the process creating different pH-levels and subsampling was carried out. This process was repeated to obtain the sieve fraction of < 106 µm and > 107 µm and ≤ 250 µm. About 37% (mass based; solid material, water present in the wet particle cake) of the material in pig slurry (nr. 2) is larger than 500 µm, 51% is smaller than 106 µm (Table 3). The fraction between 107-500 µm is limited to 12%. The dry matter content was not determined (not enough material).

Table 3

Weights of sieve fractions P-contents.

Sieve fraction	Weight, g
>500 μm	391.1
>250 μm and $\leq 500 \mu\text{m}$	71.4
>107 μm and $\leq 250 \mu\text{m}$	53.8
$\leq 106 \mu\text{m}$ (including liquid fraction)	543.4
Total	1059.8

Size fractions differ in their acid requirement for reaching an intended pH. The finest separation fraction requires most acid, followed by the largest fraction. The fraction 106-250 μm requires the smallest amount of acid (Figure 13), but also the particle mass was low. The amount of acid that is required to achieve a certain pH depends on the buffer capacity of the liquid material, the buffer capacity of the solids and the amount of solids as presented in Table 3. The latter was not determined. Acidification of the fractions obtained from sieving the pig slurry causes two effects:

1. The P-recovery after solubilization of the P present in the particles by acidification increases at lower pHs (Figure 14).
2. An increase of P-PO_4 at low pH (not presented).

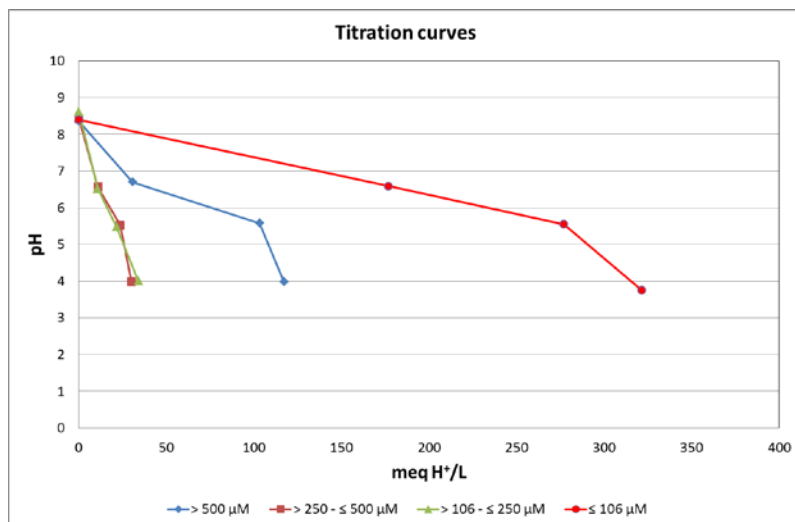


Figure 13 Titration curves of four size fractions of pig slurry.

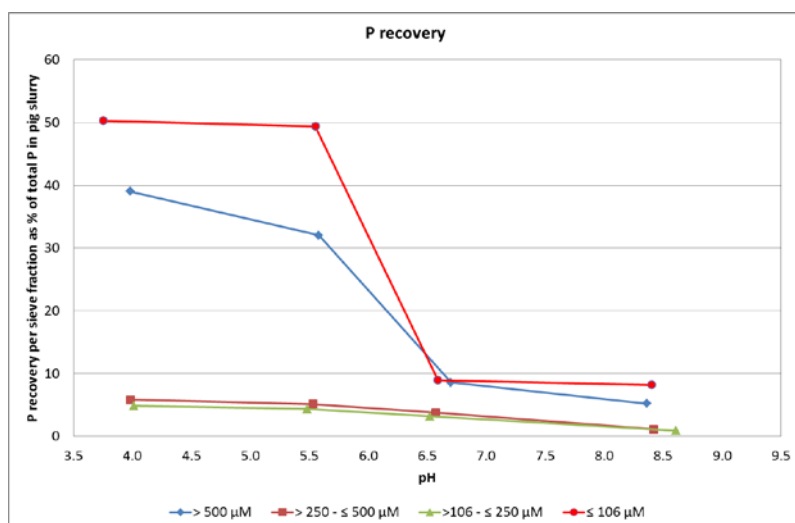


Figure 14 P-recovery in per cent of four size fractions of pig slurry as a function of the pH.

Increasing acidity enhances P-recovery (Figure 14). The effect of increasing acidity for the separated fraction between 106-205 μm is small, the effect for the finest (<106 μm) and largest (>500 μm) separated fraction is the largest.

In size fractions not treated with acid 90-95% of the phosphorus is present as $\text{PO}_4\text{-P}$ (SFA). By acidifying these size fraction almost all P is measured as $\text{PO}_4\text{-P}$. Size fractions require different amounts of acid for P-solubilization and recovery. Figure 12 shows the acid requirement per mol P recovered ($\text{mol H}^+/\text{mol P}$). The size fraction with the smallest particles requires more acid than other fractions. The size fraction with the largest particles consumes more acid per mol P than the size fractions 106-250 and 250-500 μm .

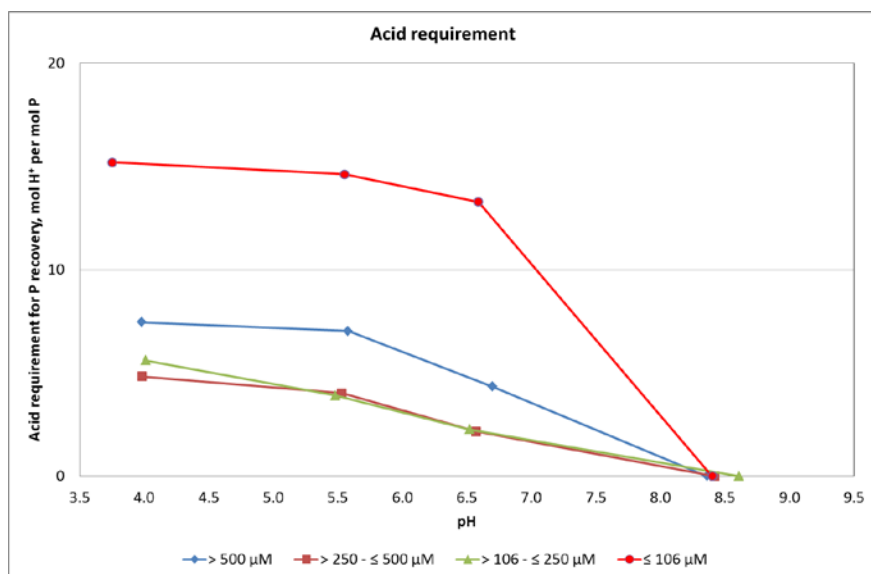


Figure 15 Acid requirement for P-recovery for four size fractions of pig slurry.

It can be concluded that P in the pig slurry that has been investigated is dominantly present in the finest (< 106 μm including the liquid fraction) and largest (>500 μm) particle size fraction. A target of 25% P-recovery can be met by slight acidification to pH 6.15 (finest fraction) and pH 5.90 (coarsest fraction) but not by the fractions between 106-205 μm , mainly because the size of this fraction is too small (Table 3) and therefore the potential P-recovery is too low to meet the target of 25% (Figure 14). The smallest size fraction including the residual liquid fraction (< 106 μm) requires more acid per mol P-recovery than the other fractions due to the residual high amount of liquid causing a higher buffering capacity. The costs have been calculated to recover P from the largest (> 500 μm) and finest size fraction (< 106 μm) after decreasing the pH to 6.25 of these fractions (P-recovery 25%; Figure 14). The costs of to recover P from these two fraction varies between 0.34 and 2.12 € (Table 4 top), which can still be substantial. These results show that the best suitable approach is to treat the largest fraction, which can be retrieved quite easily and less chemicals have to be used if this fraction is diluted. To recover 50% of P from pig slurry either the whole solid fraction has to be treated or the finest fraction (< 106 μm) Figure 14). In order to recover 50% of P via the finest fraction, the pH has to decrease to 5.5 (Figure 14) and the cost will vary between 1.14 and 2.28 € (Table 4 bottom). With the coarse solid fraction (> 500 μm) a maximum of 40% can be recovered at pH 4 (Figure 14) and the cost will vary from 0.73 to 1.46 (Table 4 bottom).

Table 4

Indication of the costs to recover 25% (TOP) or 40-50% (BOTTOM) of P from pig slurry by means of the treatment of a particle size fractions of pig slurry that contains sufficient P.

Parameter	Unit	> 500 μm	< 106 μm
Weight	g/L	391	543
P-content in fraction	g P/kg	0.94	1.97
Required acid	meq H^+ /l	113	296
	g H_2SO_4 /l	5.5	14.5
	kg H_2SO_4 per m^3 pig slurry	2.0	7.4
End ph	(-)	5.9	6.15
Required base	meq OH/l	113.0	296.0
	g $\text{Ca}(\text{OH})_2$ /l	4.2	3.7
	kg $\text{Ca}(\text{OH})_2$ per m^3 pig slurry	1.5	1.9
End ph	(-)	8	8
Reduction in P-content pig slurry	%	25%	25%
Average costs H_2SO_4 : 130 €/ton	€/ton pig slurry	€ 0.27	€ 0.97
High costs H_2SO_4 : 260 €/ton	€/ton pig slurry	€ 0.53	€ 1.93
Average costs $\text{Ca}(\text{OH})_2$: 50 €/ton	€/ton pig slurry	€ 0.08	€ 0.09
High costs $\text{Ca}(\text{OH})_2$: 100 €/ton	€/ton pig slurry	€ 0.15	€ 0.19
Total acid + base (average)	€/ton pig slurry	€ 0.34	€ 1.06
Total acid + base high	€/ton pig slurry	€ 0.69	€ 2.12

Parameter	Unit	> 500 μm	< 106 μm
Weight	g/L	391	543
P-content in fraction	g P/kg	0.94	1.97
Required acid	meq H^+ /l	240	320
	g H_2SO_4 /l	11.8	15.7
	kg H_2SO_4 per m^3 pig slurry	4.3	8.0
End ph	(-)	5.9	6.15
Required base	meq OH/l	240.0	320.0
	g $\text{Ca}(\text{OH})_2$ /l	8.9	3.7
	kg $\text{Ca}(\text{OH})_2$ per m^3 pig slurry	3.3	1.9
End ph	(-)	8	8
Reduction in P-content pig slurry	%	40%	50%
Average costs H_2SO_4 : 130 €/ton	€/ton pig slurry	€ 0.56	€ 1.04
High costs H_2SO_4 : 260 €/ton	€/ton pig slurry	€ 1.13	€ 2.09
Average costs $\text{Ca}(\text{OH})_2$: 50 €/ton	€/ton pig slurry	€ 0.16	€ 0.09
High costs $\text{Ca}(\text{OH})_2$: 100 €/ton	€/ton pig slurry	€ 0.33	€ 0.19
Total acid + base (average)	€/ton pig slurry	€ 0.73	€ 1.14
Total acid + base high	€/ton pig slurry	€ 1.46	€ 2.28

Our further research focused on the liquid fraction (see Section 3.2.3), because this fraction has not to be diluted to adjust the pH in order to release P into solution. The main question was if sufficient P can be recovered from this fraction at low costs.

3.2.3 P-recovery from liquid pig slurry

The hypothesis is that after using low-tech separation techniques a considerable amount of P of the total P-content in pig slurry is still present in the liquid fraction and that the buffer capacity of the separated liquid fraction is lower than pig slurry (e.g. because it contains less CaCO_3). The approach of P-recovery is the same as with the non-separated pig slurry: after reducing the pH of the liquid

fraction, the liquid fraction is filtrated / centrifuged and thereafter $\text{Ca}(\text{OH})_2$ is added to precipitate the soluble P.

Three samples of pig slurry liquid were used for this experiment: the liquid fraction of pig slurry 1 (centrifuged at 1000 rpm), pig slurry 2 (obtained via a screw press) and the liquid fraction of pig slurry 3 (separated at 300 rpm). The P-content of the liquid fractions is 0.91, 2 and 0.8 g P per liter liquid, respectively (Table 1). The pH titration curves were determined first and thereafter the samples were brought to a fixed pH between 8 and 4 (steps 0.5) with 20 ml of adjusted concentrated acid. Samples were centrifuged (at 3000 rpm during 10 minutes) and subsamples of the separated liquid were taken to determine the concentrations o-P, t-P, NH_4 and total N in this liquid. $\text{Ca}(\text{OH})_2$ was added to the remaining separated liquid for increasing the pH to 8 in order to precipitate P. The precipitate was recovered by centrifugation and analysed for dry matter content and total P.

Figure 13 shows the titration curve of the liquid fraction of all three slurries. The buffer capacity of the liquid fractions of the pig slurries decreased in the order: slurry 2 > slurry 3 > slurry 1 (Figure 16). However, the dry matter content differs between the slurries. The dry matter content in the liquid fraction of pig slurry 2 (screw press) is 8.4%, in the liquid fraction of pig slurry 3 (330 rpm) is 5% and in the liquid fraction of pig slurry 1 is 6.1%. The titration curves per kg dry matter of pig slurries 2 and 3 are quite similar (Figure 17).

The titration curves were used to calculate the amount of acid needed to bring the liquid fraction of the pig slurry samples at the required pH (steps of 0.5). The observed pHs were 0.2 – 0.4 units higher than based on the observed titration curve. This is probably caused by the longer contact time of the acid with the liquid (one hour) to reach the required pH compared to the time to derive a stable pHs during the titration curve. A pH lower than 5 does not increase the P-concentration in the liquids much further (Figure 8).

After acidification, samples were taken and separated in a supernatant and pellet via centrifugation. This provides information on the effect of acidification on the quantity of soluble P. In Figure 18 the total amount of P in the supernatant is given as the percentage of total P in the liquid fraction (supernatant plus pellet), as a function of the final pH. At lower pH the phosphate is dominantly found in the supernatant (Figure 18): at pH < 5.5 this is more than 90%.

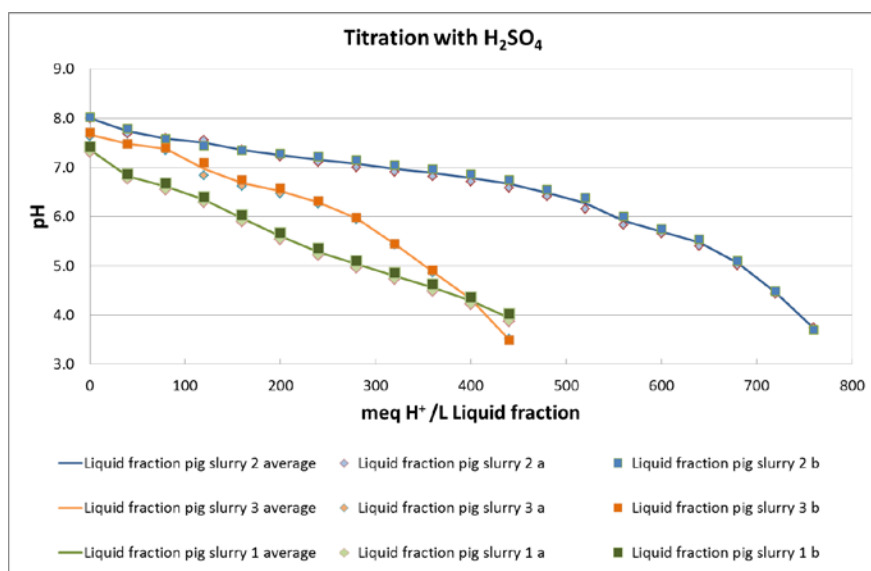


Figure 16 Titration with H_2SO_4 of the liquid fraction of pig slurry 2 (screw press; blue), pig slurry 3 (centrifuged at 300 rpm; orange) and pig slurry 1 (centrifuged at 1000 rpm; green). Amount of acid expressed per liter liquid fraction.

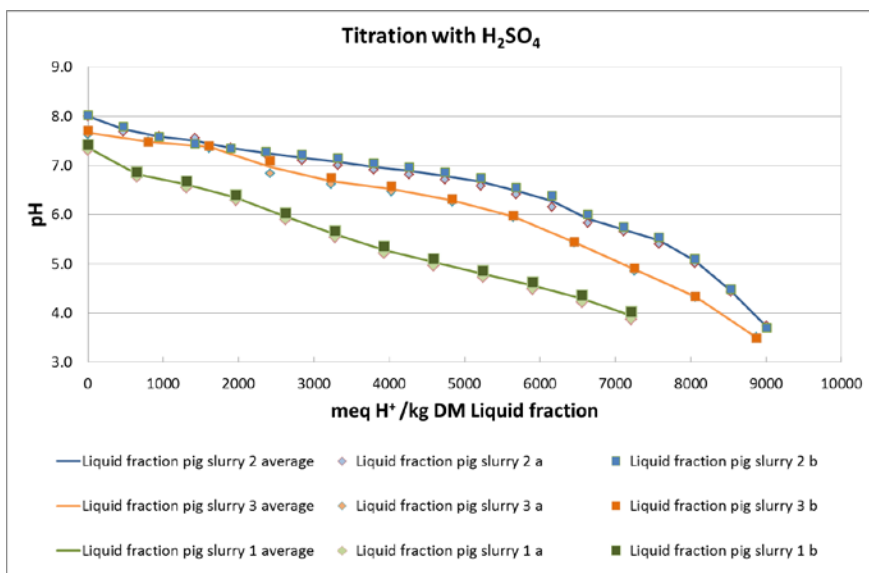


Figure 17 Titration with H_2SO_4 of the liquid fraction of pig slurry 2 (screw press; blue), pig slurry 3 (centrifuged at 300 rpm; orange) and pig slurry 1 (centrifuged at 1000 rpm; green). Amount of acid expressed per kg dry matter in liquid fraction.

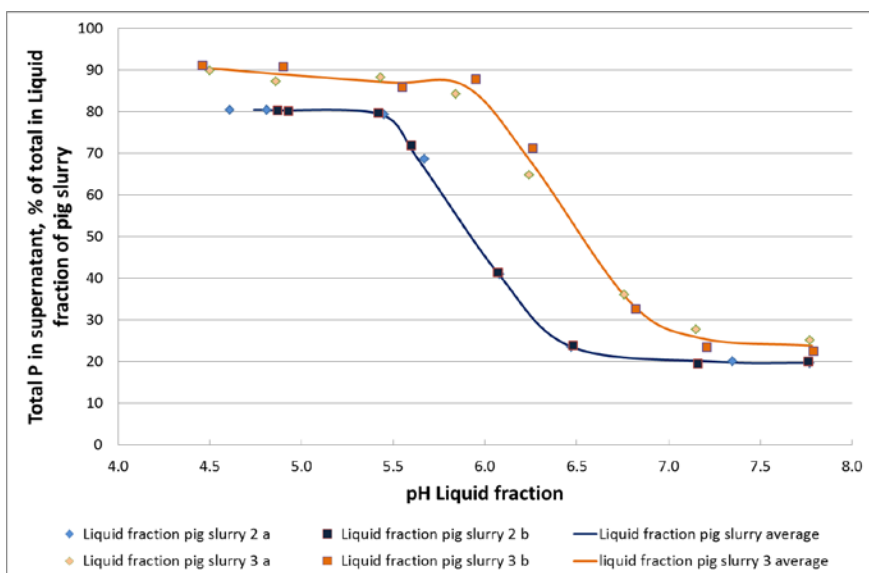


Figure 18 Percentage of P precipitated from solution compared to total P present in the liquid fraction for two pig slurries, as a function of the pH.

The acid requirement compared to the derived amount of soluble P is shown in Figure 19. The acid requirement of the liquid fraction of pig slurries to lower the pH is higher than those for the solid fractions, but lower than for the whole pig slurry.

Next the contents of N (NH_4 -N, Nts (SFA) and N-total after destruction) and the contents of P (P (ICP), ortho-P (SFA) and P-total after destruction) were measured and the effect of the pH was evaluated. Lowering the pH does not change the measured N-fractions (Table 5). Most of the N (Nts) in solution is measured by SFA (segmented flow analysis) but not all: 7-17% is locked in organic matter and is only released after destruction. Thus destruction of the organic matter results in higher values of N-fractions.

At lower pH more P is released and has a significant effect on the solubility of P. Acidification leads to virtually only ortho-P. At high pH ortho-P (SFA) or P-ICP are significant lower than total P determined after destruction (Table 5). At high pH 50-70% of the P is particulate P (Table 5).

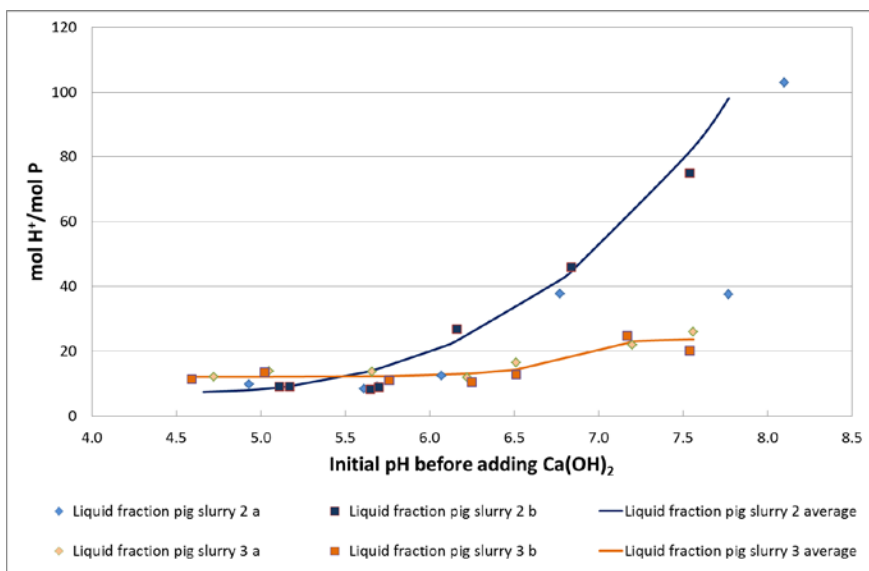


Figure 19 Ratio between the amount of H^+ (mol) and the amount of soluble P (mol) at different pH for liquid fractions of pig slurries 2 and 3.

Table 5

Ratios (expressed in %) between ammonium nitrogen (NH_4-N) and total N measured with the ICP (Nts) and after destruction (N-total) and the percentage ratio of ortho-P (not filtered) and total P (P-total ICP) and total P after destruction (P-total).

pH	NH_4-N / Nts	Nts/ Ntotal	$N-NH_4$ / N-total	ortho-P/ P-total ICP	P-total-ICP/ P-total	OrthoP/ P-total
8.13	83	92	77	97	58	56
7.66	85	91	77	97	57	55
6.81	85	93	79	100	64	64
6.12	86	88	75	103	72	74
5.7	87	90	78	103	87	90
5.63	87	88	76	102	92	94
5.05	87	90	79	103	94	97
4.89	88	88	78	104	94	98
7.93	87	83	73	87	39	34
7.55	87	85	74	90	43	39
7.19	88	85	75	94	43	40
6.51	88	84	75	98	65	63
6.24	89	87	77	100	96	96
5.71	89	86	76	100	93	92
5.04	90	85	77	100	94	93
4.66	91	84	77	100	93	93

The separated acid liquid fractions were treated with $Ca(OH)_2$ to pH 8.1 and thereafter the solution was centrifuged for ten minutes at 3000 rpm. The separation of the pellet was very difficult.

The fraction P remaining in the liquid fraction after increasing the pH is shown in fFigure 20. The variation between the duplicate samples is substantial. The P remaining in the liquid fraction of fresh pig slurry 2 (screw press) is higher than in the liquid fraction of pig slurry 3 (manure pit) obtained by 300 rpm centrifugation. The fraction P that can be recovered from the liquid phase is presented in Figure 21. More than 80% of the P can be recovered from the liquid phase at pH values below 5.5. At pH levels between 6 and 6.5 the P recovery varies between 40 and 70%.

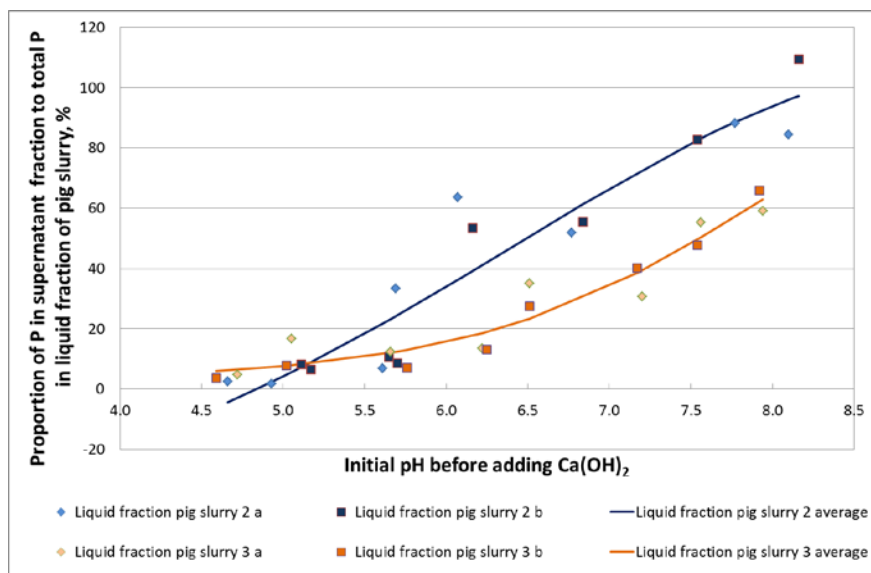


Figure 20 Percentage of P that remains in liquid phase (supernatant) after increasing the pH to about 8 for a range of initial pH values before adding Ca(OH)_2 .

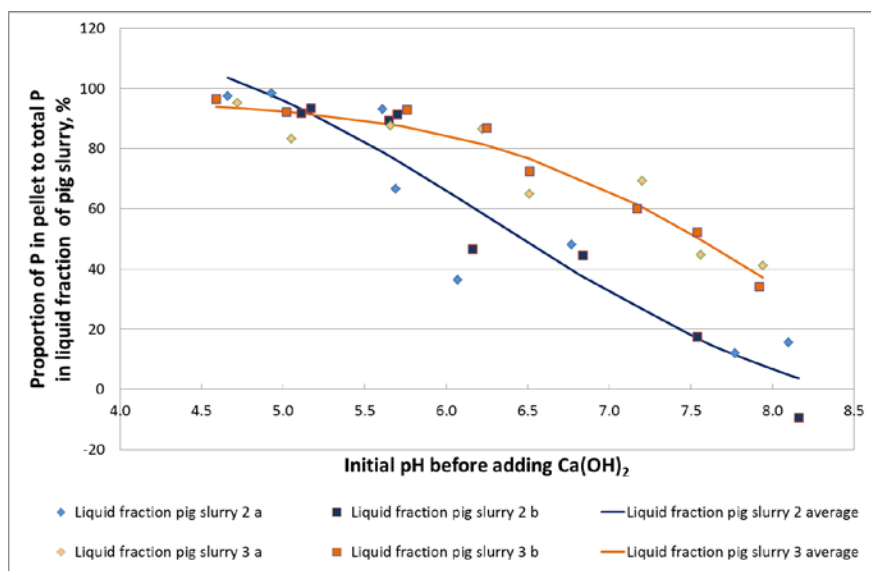


Figure 21 P-recovery from the liquid fraction after increasing the pH to about 8. Percentage of the total amount of P in the liquid fraction of pig slurry, shown for a range of initial pH values before adding Ca(OH)_2 .

The P-separation efficiency of the liquid fraction obtained by the screw press (pig slurry 2) is appr. 92% and the P-separation efficiency of the liquid fraction of pig slurry 3 at 300 rpm is 65.4% (Table 1). The quantity of P that needs to be recovered from the liquid fraction to reach 25% P-recovery of the total amount of P in pig slurry is 27,2% for pig slurry 2 ($25/(0.01 \cdot 92) = 27.2\%$) and 38.2% for pig slurry 3 ($25/(0.01 \cdot 65.4) = 38.2\%$). These recoveries are met at pH 7.27 and 7.85 respectively (Figure 21) and require 200 meq H^+/L and no acidification respectively (Figure 16).

An indication of the costs of this treatment process is calculated for the condition that 25% of the total P in pig slurry can be recovered by P-precipitation from the liquid phase. The results of the cost calculation are presented in Table 6.

The cost of chemicals to recover P (Table 6) can be high in case of relatively high market prices for H_2SO_4 and the need to reduce the pH to retrieve sufficient soluble P in the liquid fraction

(solid fraction 2; up to almost 7 € per ton slurry). Therefore, we investigated if the acidification step can be omitted by direct alkalisation of the liquid fraction.

Table 6

Indication of the costs of treatment of the liquid fraction of pig slurry 2 and 3 to recover 25% of the total amount of P in the pig slurry.

parameter	unit	pig slurry 2	pig slurry 3
DM pig slurry	%	10.41	6.20
P content pig slurry	g P/kg	1.92	1.64
volume liquid fraction	m ³	0.95	0.89
DM liquid fraction	%	8.44	4.96
P content liquid fraction	g P/kg	2.28	1.51
required acid	meq H ⁺ /l	430.00	0.00
	g H ₂ SO ₄ /l	21.07	0.00
	kg H ₂ SO ₄	20.02	0.00
end pH	(-)	6.00	8.00
required base	meq OH/l	430.00	10.00
	g Ca(OH) ₂ /l	15.91	3.70
	kg Ca(OH) ₂	15.11	3.33
end pH	(-)	6.75	7.85
P recovery from liquid fraction	%	41.50	38.20
average costs H ₂ SO ₄ : 130 €/ton	€/ton pig slurry	2.60	0.00
high costs H ₂ SO ₄ : 260 €/ton	€/ton pig slurry	5.20	0.00
average costs Ca(OH) ₂ : 50 €/ton	€/ton pig slurry	0.76	0.17
high costs Ca(OH) ₂ : 100 €/ton	€/ton pig slurry	1.51	0.33
Total acid + base (average)	€/ton pig slurry	3.36	0.17
Total acid + base high	€/ton pig slurry	6.72	0.33

3.3 Phosphorus recovery options from liquid fractions with Mg with and without addition of NaOH

This experiment was set up to produce Mg–P precipitates, which can be formed at high pH (>8). The precipitate was filtered (together with colloids and suspended material). The experimental design comprised two factors: pH (ambient and pH 9.5) and Mg-sources (Mg(OH)₂, MgCl₂ and MgO). Figure 22 shows the titration curve of the liquid fraction of the studied pig slurries with NaOH. The liquid fraction of pig slurry 1 has the lowest buffer capacity, so a relatively small amount of NaOH is needed to increase the pH. The liquid fraction of pig slurry 2 has the highest buffer capacity.

Liquid fractions of pig slurries 1, 2 and 3 were treated and P-recovery was measured by collecting the pellets (3000 rpm, ten minutes) which consist of particles and precipitates. Table 7 gives the P-recovery from the liquid phase for two pHs and three Mg-sources, expressed as percentage of the total amount of collected P in the pellet (after centrifugation) compared to the initial amount of P in the liquid fraction before centrifugation (Table 7a). The P-recovery is also expressed in terms of the total amount of P in the pig slurry (Table 7b). The amount of precipitated P is calculated based on the reduction in P-concentration before and after centrifugation.

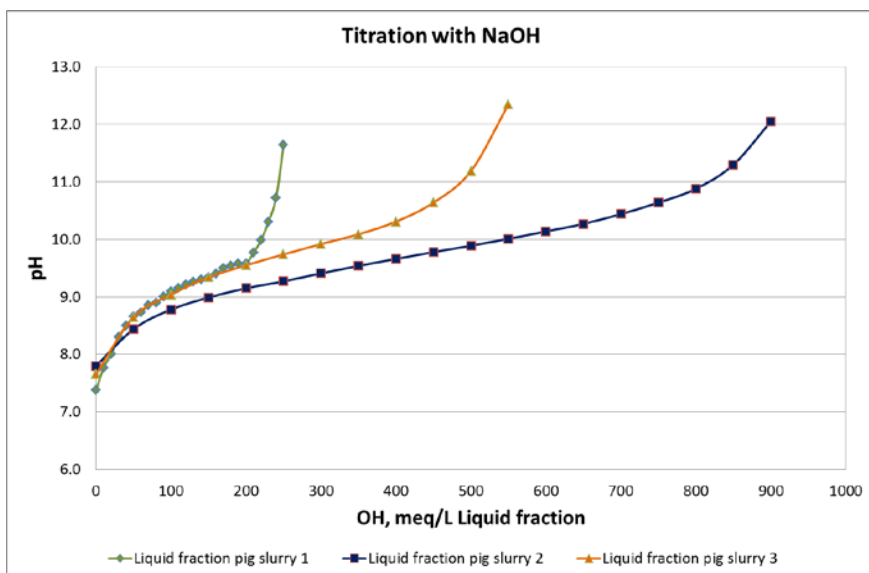


Figure 22 Titration of the liquid fraction of three pig slurries with NaOH.

Table 7a

P-recovery from the liquid fraction of pig slurries, expressed as percentage of the total P-content of the liquid fraction.

Liquid fraction	Slurry P g P kg ⁻¹	Without NaOH (pH ~8)			With NaOH (pH ~ 9.5)		
		Mg(OH) ₂	MgCl ₂	MgO	Mg(OH) ₂	MgCl ₂	MgO
Pig slurry 1 (1000 rpm)	0.91	67	74	73	70	70	76
Pig slurry 2 (screw press)	2.28	94	92	93	92	92	93
Pig slurry 3 (300 rpm)	1.51	90	92	93	90	91	91

Table 7b

P-recovery from the liquid fraction of pig slurries, expressed as percentage of the total P-content of the pig slurry (estimated product separation efficiencies).

Liquid fraction	Slurry P g P kg ⁻¹	Without NaOH (pH ~8)			With NaOH (pH ~ 9.5)		
		Mg(OH) ₂	MgCl ₂	MgO	Mg(OH) ₂	MgCl ₂	MgO
Pig slurry 1 (1000 rpm)	1.44	34	38	38	36	36	39
Pig slurry 2 (screw press)	1.92	89	87	89	87	88	88
Pig slurry 3 (300 rpm)	1.64	80	81	82	80	81	81

These results confirm the hypothesis that by addition of Mg, substantial amounts of P can be recovered. The recovery of P from the liquid phase of pig slurry 1, 2 and 3 is 74%, 92% and 92%, respectively (addition of MgCl₂ at pH 8). Calculated as percentage of the total amount of P in the pig slurry the results are: 38%, 87% en 81% (MgCl₂ at pH 8).

The aim to recover 25% of the P, can be met in these samples and an increase of the pH to 9.5 is not necessary to meet the goal. In addition, the P-recovery does not change much between pH 8 and 9.5. However, it is not known if an increase in pH has an impact on the stability of the formed product and its quality. From the liquid fraction of pig slurry 1 up to 35-40% of P can be recovered in the flotated and precipitated material. The costs of chemicals to extract 25% of the P from the liquid fraction at pH

8 varies between 0.23 and 1.29 €/ton pig slurry (Table 8). The costs at pH 9.5 are not mentioned since no extra effect of P-recovery was achieved. It has to be noticed that the recovered P precipitate will also contain some colloids and suspended material (e.g. organic matter).

Table 8

Indication of the costs of treatment of the liquid fraction of pig slurry at high pH to recover 25% of the total amount of P in the pig slurry.

Parameter	Unit	Ph 8 (ambient)		
		Pig slurry 1	Pig slurry 2	Pig slurry 3
P-content pig slurry	g P/kg	1.44	1.92	1.64
Liquid fraction	m ³ liquid per m ³ pig slurry	0.52	0.95	0.89
P-content liquid fraction	g P/kg	0.91	2.28	1.51
Required amount of Mg(OH) ₂	kg product/m ³ pig slurry	1.1	5.2	3.2
Required amount of MgCl ₂	kg product/m ³ pig slurry	1.4	6.4	4.0
Required amount of mgo	kg product/m ³ pig slurry	1.1	5.1	3.2
Average costs Mg(OH) ₂ : 200 €/ton	€/ton pig slurry	€ 0.23	€ 1.04	€ 0.64
High costs Mg(OH) ₂ : 400 €/ton	€/ton pig slurry	€ 0.45	€ 2.08	€ 1.29

3.4 P-recovery from low and high tech separated liquid fraction

P was recovered by Mg-precipitation without additional alkalisation of liquid fractions, separated by centrifuging at 300 rpm (~ low tech separation technique) or 3500 rpm (~ high tech separation technique). The experiment followed the procedures given in Paragraphs 2.1 and 2.3.4 (see Figure 4, left). MgCl₂ was used as magnesium source. Precipitates were collected by centrifuging at 3500 rpm. Two pig slurries were used, i.e. pig slurry 2 and a new received sample of digestate (50% pig slurry and 50% other substrates). Figures 23 and 24 give the yield of P as percentage of the original content of P in the pig slurry and digestate respectively. Annexes 1 and 2 summarise the composition of input and fractions obtained directly after separation (dry matter, P) and after treatment with MgCl₂ (dry matter, organic C, pH, N-total, NH₄-N, P-total, K-total, Ca-total, Mg-total, Na-total). Table 9 gives the composition of the collected P-precipitate.

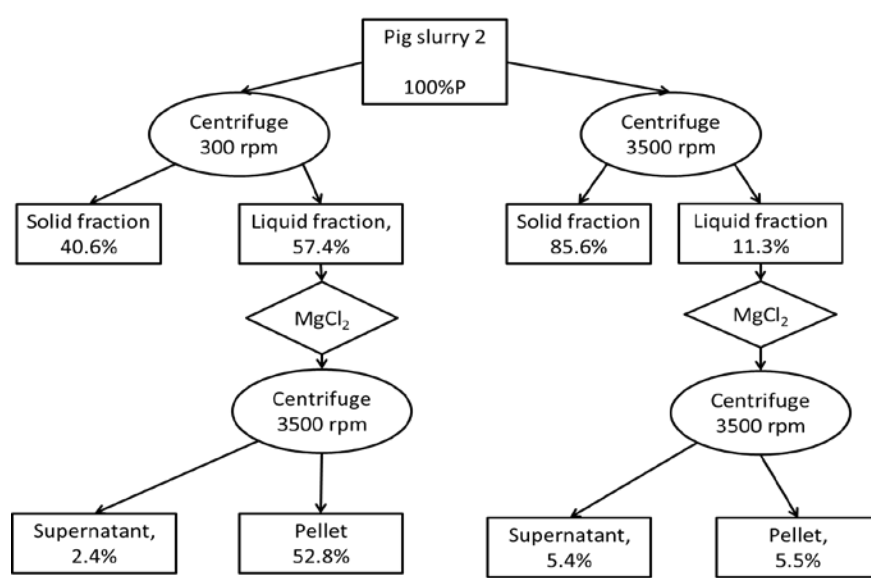


Figure 23 P-recovery in percent of total P in pig slurry 2 with a low tech separation technique (300 rpm) and a high tech separation technique (3500 rpm).

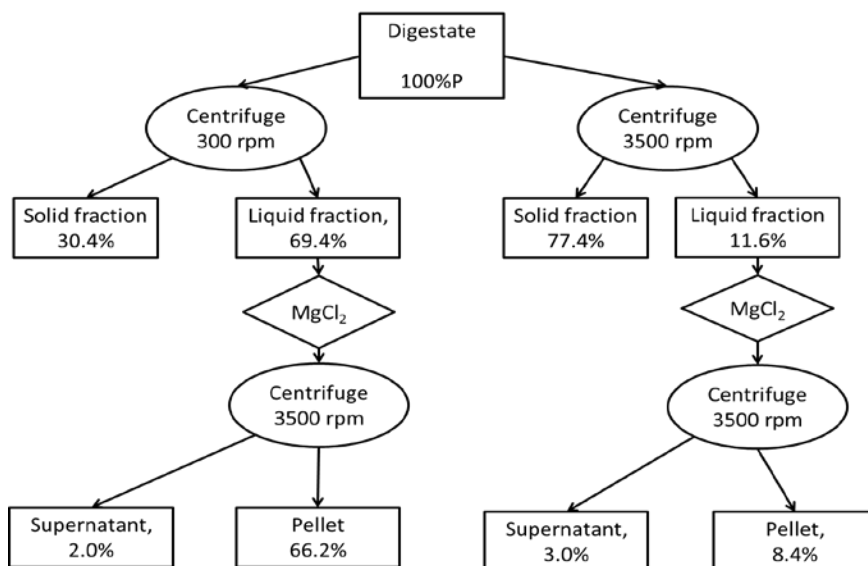


Figure 24 P-recovery in percent of total P in digestate with a low tech separation technique (300 rpm) and a high tech separation technique (3500 rpm).

Separation of pig slurry 2 or digestate at 300 rpm (low tech) yielded less P in the solid fraction than at 3500 rpm. Not all P was recovered within the solid and liquid fraction at 3500 rpm. It is not clear which factor has caused a loss of P. Most of the P remained in the LF at 300 rpm while at 3500 rpm most P was found in the solid fraction.

Treatment of the liquid fraction with MgCl_2 recovered 52.8% of the P originally present in the digestate at 300 rpm while only 5.5% was recovered from the liquid fraction obtained with the 3500 rpm separation method (Figure 23).

Treatment of the liquid fraction with MgCl_2 recovered 66.2% of the P originally present in the digestate at 300 rpm while only 8.4% was recovered from the liquid fraction obtained with the 3500 rpm separation method (Figure 24).

Although the quantity of P recovered at 300 rpm was much higher than with separation at 3500 rpm, the concentration of P and other nutrients was higher in the dry matter in materials recovered by separation at 3500 rpm. However the concentration of organic C in the dry matter was similar.

At high centrifuges rates (3500 rpm) the P content of the pellets (P precipitate) are 62 and 69 g P/kg DM for the digestate and pig slurry 2, respectively (Table 9), which equals to 14.1% and 15.8% P_2O_5 of DM or 4.5 and 6.2% P_2O_5 per kg wet pellet. At low centrifugation speed (300 rpm) the P-content is approximately two times lower. In the pellet the molar Mg:P ratio is about 1:1, but the N-content is approximately four times higher (struvite has a NH_4 :Mg:P ratio of 1:1:1). This is caused by the fact that the water content of the pellet is 60-70% and relative high concentrations NH_4 are still present in the solution. If this is taken into account the ratio will be much more in line with struvite.

Table 9

Composition of the P-precipitates of digestate and pig slurry 2 obtained from MgCl_2 addition to liquid fractions after separation at 300 rpm (low tech) and 3500 rpm (high tech). In italics the concentration in mol per kg dry matter (DM) is given.

Product	Material	C % DM	N g/kg DM	P g/kg DM	K g/kg DM	Mg g/kg DM	Ca g/kg DM	Na g/kg DM
Digestate	Pellet from LF of 300 rpm	31.9	61.6	37.0	52.5	30.2	30.2	6.1
			4.4	1.2	1.3	1.2	0.8	0.3
	Pellet from LF of 3500 rpm	29.8	110.5	62.0	101.6	52.0	17.3	11.1
Pig slurry 2	Pellet from LF of 300 rpm	39.0	7.9	2.0	2.6	2.1	0.4	0.5
			62.0	30.6	32.9	27.5	16.3	5.4
	Pellet from LF of 3500 rpm	33.6	151.2	69.0	85.4	58.6	21.7	10.1
			10.8	2.2	2.2	2.4	0.5	0.4

4 Discussion

The laboratory experiments show that there are technical options to recover at least 25% of the P from pig slurries in a rather simple way. Through the recovery, the P-content of pig slurry can be reduced. The aim of this study was to explore techniques that are able to reduce the P-content of pig slurry with at least 25%, because this is the percentage of the total manure phosphate production in The Netherlands that has to be processed and exported.

At present, most of the manure phosphate surplus is exported (as dried poultry manure and pasteurized pig slurry) or incinerated (dried poultry manure). However, both the export of pasteurized pig slurry and the incineration of poultry manure are debatable; these disposal pathways are no guarantee for a long-term solution of the manure phosphate surplus in The Netherlands. Moreover, phosphate application limits for agricultural land in The Netherlands tend to become stricter, while the manure production may tend to increase due to the abolishment of the milk quota and the expiration of the pig and poultry production rights by 2015. Hence, the need to process and export more manure is urgent. As manures and slurries from cattle are largely reused on grassland and on silage maize of the farms where they are produced, and poultry manure is already exported as dried pellets and partly incinerated and the P-rich ash exported, solutions have to be found for pig slurries. At the short term (2015) 50% of the phosphate manure surplus has to be processed, which equals to 20 - 25 million kg P_2O_5 of pig slurry. It is expected that by lowering the P content in feed the P-surplus in pig slurry can be reduced with about 10 to 15 million kg P_2O_5 . This means that approximately 25% of the P in pig slurry has to be processed and recovered. This study therefore focusses on technical opportunities for recovering P from pig slurries. For our experiments, we used a tentative target of a recovery of at least 25% of P from manure.

Main findings

Phosphorus release

By decreasing the pH of pig slurry or fractions of pig slurry, phosphorus is released from the solids and is solubilized in the liquid phase, mainly as inorganic P (ortho-P). This phenomenon is well known (see e.g. studies on struvite precipitation and studies on speciation (Bril and Salomons, 1990; Daumer *et al.*, 2007; Daumer *et al.*, 2010; Shen *et al.*, 2012; Szogi and Vanotti, 2009; Tasistro *et al.*, 2004; Tasistro *et al.*, 2007; Zhang *et al.*, 2010). After filtration or centrifugation a liquid fraction with soluble P is obtained which requires further treatment to recover P (by means of a precipitation reaction). The precipitated P can be filtered as wet solid material with a relative high P-content. Depending on the further processing steps of this material (resource for P consuming industries, fertiliser, and export) additional steps are necessary to meet with the conditions of the (end)users. Our study was targeted on P-recovery. Further tailor-made designs and steps have to be made to satisfy the requirements of the end-users.

In order to decrease the pH of slurries and to solubilise manure P, substantial amounts of acid are needed; these quantities differ between the three pig slurries studied. The amount of H_2SO_4 needed varied between 4 and 25 kg H_2SO_4 per ton pig slurry (80-500 meq H^+ per liter pig slurry). This range is comparable with other studies reported in literature. Research with poultry manure showed that approx. 100 meq H per liter manure is needed to reduce the pH to 4 (Alitalo *et al.*, 2012), which is equal to 3.6 kg HCl or 4.9 kg H_2SO_4 per ton manure ($M_{HCl} = 36.46$ en $M_{H_2SO_4} = 98.08$). For the titration of dairy cattle slurry with HNO_3 about 550 meq H^+ per kg manure was needed (Oenema and Velthof, 1993) which is 5.5 times higher than for poultry manure. Danish research with pig slurry showed that about 7 kg H_2SO_4 per ton pig slurry was needed to reduce the pH to 5.5 – 6 (142 meq H^+ per kg manure). Thus, the amount of acid needed to reduce the pH differs for the different types of manure. It is well known that animal type, feed and duration of manure storing influence the composition of manure and, as a result, the buffer capacity of the manure.

Our study shows that the variation in amount of acid needed to reduce the pH is mainly caused by the difference in the dry matter content (Figures 6 and 10) and the buffer capacity. This buffer capacity is for a significant part determined by the presence of ammonium and bicarbonate. Most fractions react similar but probably also other factors are important, like the age of the pig slurry, because due to decomposition of organic matter the bicarbonate and NH_3 -content can increase which causes a higher buffer capacity. Acidification of pig slurry can be accomplished by a chemical treatment (addition of acid) and by biological processes such as biological acidification. The release of P by decreasing the pH by an acid is a relative fast reaction process (minutes) compared to e.g. biological treatment (hours to days). The main reason for this is that the major part of the P in the solid fraction of pig slurry is highly soluble at low pH and that mainly the pH determines the solubility.

Phosphorus in manure is present both in particles and in soluble form. Not only by acid treatment of the whole pig slurry can phosphorus be released, but also through separation of the solid fraction or by treatment of the separated liquid fraction of pig slurry. The distribution of particle size fractions in pig slurries has been studied for one pig slurry. The largest quantity was found in the particle size fraction $> 500 \mu\text{m}$ (37%) and the finest particles $< 106 \mu\text{m}$ (51%), so the mass fraction between 106 and $500 \mu\text{m}$ is small ($< 12\%$). So, treatment of part of the largest fraction with simple separation techniques is also an option and the amount of acid needed will be less compared to treatment of the whole pig slurry in order to recover 25% of P. To reduce the pH and recover P from the large and fine particle size fractions about 2.3 kg H_2SO_4 (pH 6.25) and 7 kg H_2SO_4 (pH 6) were needed, respectively. However, an additional separation step is needed to collect this material for further treatment, as is the case for treatment of the liquid fraction. Treatment of the liquid fraction showed that for one of the pig slurries there was no need to decrease the pH to solubilize sufficient P (pH 8) and for the other liquid fraction a huge amount was needed: 24 kg H_2SO_4 (pH 6).

P-recovery approaches

Phosphate was recovered from P solubilized from solid materials after acidification, by means of separating the soluble P-fraction and addition of $\text{Ca}(\text{OH})_2$ and is called the 'acid-base approach'. The liquid fraction of pig slurries were also treated with another technique: the addition of Mg sources with and without increasing the pH to 9.5 (with NaOH) which is called the 'Mg-approach'. The P-recovery in the Mg-approach was not higher if the pH was increased from pH 8 to pH 9.5. Consequently, the addition of base (NaOH) can be omitted. Also, there is no preference for a specific Mg-source, all sources tested gave comparable results. However this Mg-approach is only successful if enough P is present in the liquid phase, and if this can be obtained via low-tech separation techniques.

Cost of chemicals for P-recovery

'Acid-base approach': the overall costs of the chemicals needed to recover 25% of the P-content of pig slurry, by means of decreasing the pH – filtering – increasing the pH ('acid – base approach'), are presented in Table 9. The cheapest method seems to be the treatment of the solid fraction with a particle size fraction $> 500 \mu\text{m}$. However, a simple additional sieving step (about 1 €/ton; (Schröder *et al.*, 2009) to retrieve this fraction has to be included. Treatment of the liquid fraction can also be cheap, especially if after separation already sufficient phosphate is present in the suspended solution (like with pig slurry 3 at 300 rpm). In that case only $\text{Ca}(\text{OH})_2$ has to be applied. Such sufficient high P-concentrations will rarely occur at pH 8 and due to the high buffer capacity of the liquid fraction substantial amounts of acid are needed to decrease the pH in order to release sufficient P from the suspended particles in the liquid fraction (liquid fraction pig slurry 2; screw press). The costs of chemicals for the treatment of the whole pig slurry varies between 0.33 and 2.80 € m^{-3} at average prices of the chemicals, and will be a factor 2 higher if higher prices of chemicals are used (up to 5.59 € m^{-3}). Based on the results of these laboratory experiments and the average price of the chemicals, it is expected that the costs of chemicals for recovering 25% of total P in pig slurry via acid-base-treatment will be around 3 euro per ton pig slurry (range 1 to 7 €/ton). More samples of pig slurry need to be tested for a more reliable estimate. Furthermore, special attention is needed for the treatment of only the coarse material ($> 500 \mu\text{m}$), because this fraction can be easily gathered by simple separation techniques, the buffer capacity was much lower compared to the whole pig slurry or the liquid fraction of pig slurry, and also 25% of the total P content in pig slurry can be recovered.

'Mg approach': besides the P-recovery experiments based on the treatment of pig slurry with an 'acid-base-approach', also a second approach has been tested by adding Mg-salts at high pH to induce both flotation of suspended particles and precipitation of Mg-P-precipitates. Laboratory experiments by adding Ca-salts after increasing the pH to 11 (with NaOH to increase the CO_3^{2-} concentration to initiate a $\text{CaCO}_3 \sim \text{P}$ type of precipitation) did not lead to a successful and feasible perspective. Therefore, the experiment was focussed on the addition of Mg. About 67-94% of the P in the liquid fraction could be recovered at pH 8, which equals to 34-82% of the total P-content in slurry. There was no significant effect of pH (pH 8 compared to pH 9). A pH of 8 is preferred, because less NH_3 will be lost by emissions to the air. The cost of chemicals for such a treatment are relative low (0.23 to 2.08 € per ton pig slurry; Table 9). However, with this Mg-approach the recovered P-product contains much more particles (mainly organic material) compared to the acid-base approach where mainly soluble inorganic P is precipitated.

Table 9

Cost of chemicals (range based on average and high market prices) to recover 25% of total P from pig slurry by means of the 'Acid-base approach' or 'Mg-approach' at pH 8.

Acid - Base approach (Ca ~ P)		
	€ / ton pig slurry	€ / kg P
Pig slurry	0.33 - 5.59	0.92 - 11.64
Pig slurry 3 coarse fraction (>500 µM)	0.34 - 0.69	
Pig slurry liquid fraction	0.17 - 6.72	1.36 - 11.79

Base - Mg approach (Mg ~ P)		
	€ / ton pig slurry	€ / kg P
Pig slurry liquid fraction (pH 8)	0.23 - 2.08	1.01 - 3.65

Implications

Technical opportunities

This study shows that there are technical possibilities to recover P from manure as secondary source and to produce manure with a lower P-content. This was shown for only three pig slurries. There is variation between results from these three pig slurries and it is not clear yet which factor(s) attribute(s) to this variation. To clarify factors involved additional tests with different types of pig slurries and digested pig slurries (or other types of slurry like dairy slurry) are needed to give a more reliable assessment of the P-recovery under laboratory conditions and more reliable indications of the variation in costs. A second step is needed also, to scale up to pilot scale. Treatment units of the pilot scale (Figure 1) have to be designed, built and tested in order to determine a more practical estimate of the effectiveness of P recovery and the associated costs. This design of the pilot scale will bring up more realistic information on the experimental conditions at the pilot scale and next on a full scale installation.

The focus of this study was on P-recovery to meet an ambitious target of at least 25% of the P-surplus of pig slurry in The Netherlands, taking into account that also the P-content in manure will be reduced due to a lowering of the P-content in feed. The proof of principle was given. However the recovered phosphorus will be used for other purposes, which will set requirements to the recovered P. This study has not dealt with these requirements. The specific criteria on purity with respect to contamination with organic matter, physical stability (water content and pH) and chemical quality need to be further developed depending on the requirements of the end users (e.g. secondary resource for industries, direct export as fertiliser etc.). Optimisation experiments are needed in collaboration with producers as well with users of the recovered P. There are several options to tailor the quality of the end product, e.g. type of separators (see also Figure 1 for design; low versus high tech), flotation, pH conditions, drying and pelleting options. Good quality products on the market of calcium phosphate contain (mass based) 18 - 22% of P ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$) and phosphate rock contains 8.5 - 13% of P. The quality of the produced wet Ca~P precipitate was not determined yet, but it is expected that the P-content will be below 9% (theoretically 7-9% when similar calcium phosphates are produced and the product contains 60% water and 2% organic material). After drying to a 10%

water content, the P-content can increase to theoretical values of 16-20%, making this a potential valuable secondary resource for industries.

The composition of the precipitated Mg~P products, after addition of MgCl₂ to a low tech separated liquid fraction, showed that a relative high P content can be achieved: 2.0 and 2.7% P per kg wet product which equals to 6.1-7.0% P per kg DM. In fact, 53 – 66% of the amount of P in the original manure was recovered.

Besides the recovered P-product also pig slurries are produced with a lower P content (at least 25% lower). In theory, this P depleted pig slurry can be applied on agricultural land, taking into account the current phosphate use standards. However, this P-depleted pig slurry has to be accepted by arable farmers and it is not clear if this will happen. The lower P content will be beneficial because of better N:P ratio and also the fact that more organic matter can be applied on land compared to manure with a higher P content. But the degree of acceptance will also depend on the market value of this pig slurry compared to other manure. The setup of the chosen design (Figure 1) including the type of separators, pH conditions etc. can influence the P-content (and therefore N/P-ratio) of the treated manure, so in principle a product 'tailored to requirement of (mainly) farmers on arable land' can be produced. Especially if also N-stripping will be part of the treatment, even more options will become available. If the products will be better in line with the requirements of the crop as well as phosphate use standards, more pig slurry and less fertiliser can and will probably be applied (Schoumans *et al.*, 2012).

Perspective

This explorative study of phosphorus recovery from pig slurry shows that the P-content in pig slurry can be relative easily lowered with at least 25% (up to approximately 50%) by treatment of the solid fraction or treatment of the liquid fraction, while the cost for chemicals are expected to be less than 5 €/ton pig slurry. This seems to be practical feasible. A major advance will be that more pig slurry can be applied on agricultural land in The Netherlands and less pig slurry has to be exported to neighbouring countries. Furthermore, the valuable organic matter remains in The Netherlands and there are more options to maintain the organic matter content of arable land. The treatment approach can be applied in the region, at regional processing centres like threshing contractors, at farms with large scale digestion installations, or as manure treatment units at, or in combination with, waste water treatment plants (WWTP). The expected investments needed are probably too expensive for individual pig farms. Another advantage of a regional approach is a relative short transport distance between the farm and the treatment centre. Furthermore, the treated manure can probably be applied at arable land of nearby crop farms, but the composition of the treated manure (organic matter, N- and P-content) should meet the applications standards of the arable crops in the nearby arable region.

It is expected that the volume of the produced phosphate precipitate is small compared to the treated amount of pig slurry. Yet, it is not clear if the concentrated phosphate precipitate can be used directly as secondary phosphate for the industry. Probably the physical-chemical treatment has to be further improved to optimize the composition as secondary source, or the concentrated phosphate precipitate has to be incinerated at e.g. sludge incineration biomass plant (SNB) or poultry biomass incineration plant (BMC), since P ash is already used as secondary P resource by industries. Due to the relative small amounts of precipitate the costs per ton pig slurry will be a fraction of the costs of treatment of the pig slurry itself, but still needs to be investigated.

Although the perspectives of the explorative laboratory experiments seem good, more evidence and experience is necessary, both on laboratory scale (more samples) and pilot scale, to prove the practical perspectives of the treatment of the solid or the liquid fraction, and to collect practical information on investment needed and on maintenance costs.

5 Conclusions and recommendations

Laboratory experiments were designed and carried out to test and quantify the options of P-recovery from pig slurry or from liquid and solid fractions of pig slurry. The main objective was to recover at least 25% of the total P-content of pig slurry by means of simple chemical and physical treatment techniques. The following conclusions are drawn:

- P-recovery from pig slurry or from the solid or liquid fraction of pig slurry in amounts of at least 25% is technically feasible. The proof of principle was successful. Two main strategies can be derived from our studies:
 - P-solubilization by means of acid addition, separation and precipitation / recovery of P from the liquid manure fraction by means of a base (acid-base-approach). This approach can be applied on the entire pig slurry as well as on solid manure fractions.
 - P-recovery by means of addition of MgO , $\text{Mg}(\text{OH})_2$ or MgCl_2 to a liquid fraction (Mg approach). For a successful application of this technique, the liquid fraction should contain enough dissolved P or P-containing particles. Therefore not all liquid fractions from separated pig slurries can meet this requirement. The way of separation of the manure into a liquid fraction and a wet solid manure cake is very important for the feasibility of this approach. Moreover the concentrated phosphate product will contain, beside the phosphate precipitates, also organic material and particles.
- The cost of chemicals of the Mg approach at pH 8 was lower compared to the acid-base approach. For the tested approaches the chemical costs are expected to be less than 5 € per ton pig slurry.
- The techniques are relatively simple and are expected to be feasible at small industrial scale ('loonbedrijven') and at larger innovative livestock farms.
- The treated pig slurry still has a high organic matter content, but a lower P-content and is therefore suited for use within the system of strict phosphorus application standards for soils with moderate to high phosphorus status.
- Compared to a situation in which the solid fraction is exported, containing both phosphate and organic matter, our approach has the advantage that only phosphate is exported or used as secondary P-resource.
- The recovered P-precipitates can be used as secondary raw material by chemical industries. But specific requirements of end users), regarding inorganic impurities, physical characteristics and chemical composition (other co-precipitated minerals) still require additional studies. There are several options available to tune the quality of recovered phosphates to the specification of industries. Compared to pig slurry, P-precipitates have a small volume and can be easily transported to other industries at relatively low costs. At present, P-recovered from sewage sludge is transported to Germany and Belgium where it is used for fertiliser production. This renewed use proves economically viable.

Recommendations

- The proof of principle has been delivered with three pig slurry samples. These tests show variation in P-recoveries between the pig slurries. Since the variation of pig slurry is high, additional tests with different types of pig slurry and digested pig slurry (or other types of slurry like dairy slurry) are needed to give a more reliable assessment of the P-recovery under laboratory conditions.
- Tests are needed to regulate the amount and quality of recovered P. The quality has to meet standards of the end-users of recovered P.
- Tests with larger units of each treatment step are needed, followed by tests on pilot scale to demonstrate the practical feasibility and to determine the practical costs of the treatment strategies.

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Annex 1 Composition of digestate and pig slurry of MgCl₂ experiment and separation efficiencies.

Slurry	Description material	Parameter	Dry Matter	N-total	P-total	Volumetric mass density	Separation Efficiency (SE)			
			%	g N/kg fresh	g P/kg fresh		Fresh	Dry matter	N	P
						kg/L	%	%	%	%
Digestate	Starting material	Mean	9.47	8196	2662		100	100	100	100
		std	0.01	50	9.75		*	*	*	*
	Thick fraction of 300 rpm	Mean	13.25	8631	3533		23.0	32.1	24.1	30.4
		std	0.01	109.99	84.89		0.43	0.59	1.00	1.44
	LF of 300 rpm	Mean	8.46	8162	2401	1.026	77.0	68.8	76.6	69.4
		std	0.09	113.49	24.91	0.004	0.40	0.37	1.42	0.68
	Thick fraction of 3500 rpm	Mean	18.13	8961	5288		38.9	74.6	42.6	77.4
		std	0.10	149.16	126.41		0.15	0.17	0.49	1.81
	LF of 3500 rpm	Mean	4.47	6701	507	1.022	61.1	28.8	50.0	11.6
		std	0.05	42.78	2.54	0.001	0.16	0.20	0.25	0.01

LF: liquid fraction, SM: starting material.

Slurry	Description material	Parameter	Dry Matter	N-total	P-total	volumetric mass density	Separation efficiency			
			%	g N/kg fresh	g P/kg fresh		Fresh	Dry matter	N	P
						kg/L	%	%	%	%
Pig slurry 2	Starting material	Mean	10.45	9064	2697		100	100	100	100
		std	0.02	165.59	42.37		*	*	*	*
	Thick fraction of 300 rpm	Mean	13.06	9429	3090		35.0	43.7	36.8	40.6
		std	0.06	24.91	39.79		1.31	1.36	0.63	1.63
	LF of 300 rpm	Mean	8.84	9243	2359	1.014	64.8	54.8	66.7	57.4
		std	0.02	87.06	6.63	0.002	1.17	1.19	1.76	1.78
	Thick fraction of 3500 rpm	Mean	18.61	10929	5261		44.4	79.1	53.0	85.6
		std	0.30	88.55	18.91		0.51	1.95	0.03	0.37
	LF of 3500 rpm	Mean	4.07	7833	555	1.002	55.6	21.7	47.6	11.3
		std	0.03	83.33	2.95	0.002	0.53	0.44	0.85	0.29

LF: liquid fraction, SM: starting material.

Annex 2 Composition of pellet and supernatant after MgCl2 addition and P-recoveries.

Slurry	Description	Para- meter	Dry matter	C	Total N	N-NH ₄	Total P	K	Mg	Ca	Na	CaCO ₃	Ratio pellet to input LF ¹	P Reco- very from LF	P Reco- very from SM ¹
			%	g/kg fresh	mg/kg fresh							g/kg fresh	%	%	%
Digestate	Pellet from LF of 300 rpm	Mean	17.30	55.18	10652	4836	6405	9081	5230	5224	1059	16.4	34.10	95.5	66.2
		std	0.17	1.63	169	361	0.7	69	39	71	4.0	2.2	0.01	1.03	0.07
	Supernatant remaining LF of 300 rpm	Mean	4.04	10.22	6271	4820	97	9938	723	173	1078	12.3		2.81	1.95
		std	0.15	0.07	136	61	0.9	124	53	5.0	38	4.0		0.05	0.02
	Pellet from LF of 3500 rpm	Mean	9.56	28.45	10568	4978	5925	9711	4974	1657	1063	4.7	5.87	71.9	8.4
		std	0.42	1.74	23	131	115	23	115	41	1.6	2.3	0.02	2.12	0.25
	Supernatant remaining LF of 3500 rpm	Mean	4.05	10.75	6393	5006	131	10123	203	172	1107	12.0		25.6	3.0
		std	0.02	0.03	11	78	5.5	48	3	0.5	8.4	0.39		0.95	0.11
Pig slurry 2	Pellet from LF of 300 rpm	Mean	17.69	68.97	10970	5452	5420	5819	4865	2881	961	6.7	38.11	92.0	52.8
		std	0.29	3.07	98	4	67	47	14	203	30	0.15	0.04	1.00	2.21
	Supernatant remaining LF of 300 rpm	Mean	3.84	12.8	7320	5944	153	6346	809	204	1007	1.8		4.2	2.4
		std	0.01	0.07	12	80	3.5	104	1.2	7.0	31	0.06		0.08	0.12
	Pellet from LF of 3500 rpm	Mean	7.16	24.04	10829	5820	4945	6118	4195	1552	726	3.3	5.21	48.7	5.5
		std	0.82	2.59	136	160	261	143	328	8.5	36	*	0.60	3.32	0.24
	Supernatant remaining LF of 3500 rpm	Mean	3.68	12.47	7403	5791	266	6386	362	221	968	6.0		47.8	5.4
		std	0.00	0.02	138	69	19	87	21	7.9	2.9	5.7		3.37	0.52

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The mission of Wageningen UR (University & Research centre) is 'To explore the potential of nature to improve the quality of life'. Within Wageningen UR, nine specialised research institutes of the DLO Foundation have joined forces with Wageningen University to help answer the most important questions in the domain of healthy food and living environment. With approximately 30 locations, 6,000 members of staff and 9,000 students, Wageningen UR is one of the leading organisations in its domain worldwide. The integral approach to problems and the cooperation between the various disciplines are at the heart of the unique Wageningen Approach.

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