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Dissolution of phosphate from pig manure ash using organic and mineral acids

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ABSTRACT

Phosphate fertilizer production from renewable resources like sewage sludge and livestock waste helps to ensure future phosphate supply, while also solving waste management issues. After combustion, the resulting ash contains heavy metals at a restrictively high level, preventing its direct use as fertilizer. In this study, several organic acids and sulfuric acid are used to dissolve phosphates from ash. Acetic, maleic and citric acids perform as expected, but oxalic acid outperforms all, including sulfuric acid. All phosphate is dissolved at pH 4 when using oxalic acid, while pH 2 is needed in the case of sulfuric acid. Furthermore, less of the heavy metals end up in the resulting solution when using oxalic acid. Nearly all calcium is retrieved in the solid residue when oxalic acid is used, pointing towards formation of calcium oxalate, not chelating complexes as often assumed, as the cause of oxalic acid outperforming the other acids in this study.

1. Introduction

Artificial fertilizer plays an important role in today's agriculture, and the combined increase of the world's population, general living standards, and production of biofuels from biomass, mean that a further intensification is needed in order to be able to meet the growing demand for food and energy (Pate et al., 2011; United_Nations, 2017). This in turn is expected to further increase the demand for phosphate containing artificial fertilizer, of which production has been rapidly growing in the last decades. At present, phosphate containing fertilizer is almost exclusively produced from phosphate rock, mostly mined in China, the US, Morocco, and Russia (Walan et al., 2014). In total, approximately 20–24 million tonnes (Mt) of phosphorus (P), or 200 Mt of phosphate rock, is mined every year, and peak production may occur as early as 2033. Close to – and more so after – the production peak, supply is expected to no longer be able to meet the increasing demand, and since phosphorus cannot be replaced by another element for fertilizer application, this can cause serious problems for global agriculture (Cordell et al., 2009; Cordell and White, 2015; IFA, 2018; Reijnders, 2014). In order to ensure the world's future food supply, it is clearly of the utmost importance to maximize the production of phosphate containing fertilizer from alternative – preferably renewable – resources, such as sewage sludge and livestock manure.

Sewage sludge and manure are relatively high in phosphates (Azuara et al., 2013; CBS, 2018; Franz, 2008), and in areas of high population density and/or intensive livestock farming, management of these large organic waste streams is often problematic. There are limits to the amount of manure that can be dispersed on nearby farm land, as over-application can lead to eutrophication of surface water and increased costs for purification of phosphate containing water for human consumption (Magara and Kunikane, 1986; Schoen et al., 2017; Withers et al., 2001). As most manure is high in moisture – over 90% (w/w) –, transportation of the growing surplus out from the regions where it originates to where there is a demand is increasingly expensive and energetically undesirable. Using sewage sludge and livestock manure as renewable resources for the production of phosphate containing fertilizers therefore offers solutions for two problems; it helps ensuring future supply of phosphates, while also solving waste management issues.

Several strategies can be applied to turn manure or sewage sludge into a more manageable and valuable fertilizer. These can include production of struvite, or of pellets from dried dewatered material, but also thermochemical conversion processes such as incineration, pyrolysis, and others. Combusting this material or the pyrolysis char leads to ash with a phosphorus content of around 3.9–7.0% (w/w) (8.9–16% P_2O_5) for sewage sludge ash

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(Franz, 2008), and around 10–11% (w/w) (23–25% P_2O_5) for ash from pig manure (Azuara et al., 2013). These types of ash are usually also relatively high in heavy metals, which can be problematic as may build up in the soil. This has led to fertilizer products generally having to meet demands regarding maximum levels of these contaminants (Carbonell et al., 2011; Franz, 2008; Sabiha et al., 2009). Therefore, a phosphorus recovery process able to reduce the heavy metal content of the resulting product would enhance its application possibilities.

Acidic dissolution of phosphate from sewage sludge ash and pig manure ash has been studied, mostly using sulfuric acid, but also using oxalic acid (Acelas et al., 2014; Atienza–Martínez et al., 2014; Franz, 2008; Kuligowski and Poulsen, 2010). It is interesting to see if organic acids could also be used for phosphate recovery purposes, as most organic acids can be produced sustainably, which is not the case for sulfuric acid. Various plants and fungi are known to excrete organic acids to the soil, hereby locally increasing the soil's acidity and consequently the solubility and uptake of otherwise poorly soluble phosphate sources present (Moghimi et al., 1978; Ström et al., 2005). It has been suggested that organic acids facilitate the dissolution of phosphate from solid phosphate rock particles by on the one hand supplying protons (H^+) to the dissolution reaction (Equation (1)) while on the other hand forming a chelation complex with the released Ca^{2+} ions, enabling the dissolution reaction to continue (Bolan et al., 1994).

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4{}^- + 2F^- \quad (1)$$

With chelation being associated with the number and placement of carboxyl and hydroxyl functional groups in the acids, the capacity for dissolving phosphate rock has been experimentally ordered as tricarboxylic > dicarboxylic > monocarboxylic acid (Bolan et al., 1994).

The dicarboxylic oxalic acid is an interesting option, as it is the strongest naturally occurring organic acid. Another reason to choose oxalic acid for this study is its ability to form insoluble salts with many of the heavy metal contaminants in the ash. Therefore, apart from its application to dissolve phosphate, an additional advantage of the use of oxalic acid lies with reducing downstream processing costs, as less – if any – heavy metals need to be removed in the production of artificial fertilizer.

The work described in this study was performed parallel to that of two other studies on the recovery of phosphate from sewage sludge (Acelas et al., 2014; Atienza–Martínez et al., 2014). The goal of this study is to further investigate dissolution of phosphate from manure ash using organic and mineral acid as a function of pH, with the focus on a product that is high in phosphate, but low in heavy metals. For this purpose, phosphate dissolution from pig manure ash is measured under varying acidic conditions.

2. Materials and methods

2.1. Raw material and ash production

The pig manure used for this study was also used for a former study on pyrolysis and the resulting char and originated from the south of the Netherlands. It was provided by the company Houbraken (Bergeijk, the Netherlands). The manure was collected from a large number of pig farms that house sows as well as slaughter pigs, and the feed consisted of mainly wheat and barley, with by-product streams from the food industry, e.g. whey (Azuara et al., 2013). At the collection facility, the manure was kept in mixed storage until separation into a liquid and a solid fraction in a ratio of 4.8 parts to 1, respectively. The separation procedure consisted of flocculation, aeration, flotation and belt pressing, resulting in a solid fraction containing 32% (w/w) dry matter. This fraction was dried (105 °C, until no change in weight) and stored in an airtight container until used. Ash production consisted of heating a 3 L crucible with approximately 1 kg of dried material in a muffle furnace to 575 °C. The followed procedure was similar to the appropriate NREL LAP method (Sluiter et al., 2008), with extended holding times at 250 °C and at 575 °C (24 h). A small airflow was applied to the bottom of the crucible to ensure presence of oxygen, facilitating complete combustion. The ash content of the dried material was 22.9% (w/w) and the ash composition (measured by X-ray fluorescence spectrometry (XRF); see below) is shown in Table 1.

2.2. Experimental procedure

For the dissolution experiments, 1 g of ash was suspended in 100 mL demineralized water. Using a titrator (Titrino 785 DMP, Metrohm) equipped with a stirrer and a calibrated pH electrode, solutions of demineralized water with sulfuric acid (1.0 mol/L; item code 258105), oxalic acid (0.8 mol/L; item code 194131), citric acid (2.5 mol/L; item code C0759), maleic acid (1.0 mol/L; item code M0375), or acetic acid (2.5 mol/L; item code 695092) were automatically added, in order to reach the next integer pH value. The concentration for 0.8 mol/L was chosen as 1.0 mol/L was too close to oxalic acid's solubility, and 2.5 mol/L was chosen for the weakest two organic acids in order to lessen the volume increase when setting the pH. To study the influence of oxalate anions and sodium kations on the dissolution reaction, an experiment was performed in which 0.80 g sodium oxalate (item code 71800) – based on the amount of oxalic acid needed to reach pH 2.5 in the oxalic acid experiment – or sodium sulfate (item code 238597) was mixed with the 1 g ash before sulfuric acid was added.

On average, each pH step took 45 min, with the first minute needed for main acid addition and the remaining time for automatic fine tuning to constant pH, defined as reached when no dosing occurred for 120 s. 2 mL samples were taken for orthophosphate measurement, also before acid addition.

In a different set of dissolution experiments, the focus is on the residue after dissolution. Sulfuric and oxalic acid were used at pH 2 and pH 4, and citric acid only at pH 4. Reaction time – after pH was set – was set at 4 h. Dissolution residues were obtained by centrifugation (7232 × g, 5 mins), after which the solid fraction was dried (48 h; 105 °C). The dry residues were then combusted (7 h; 575 °C).

All chemicals were obtained from Sigma Aldrich (Schnelldorf, Germany) – unless stated otherwise –, of laboratory grade, and used as received.

2.3. Ash composition

Elemental composition of the ash from solid fraction manure and from the dissolution residues was determined using X-ray fluorescence spectrometry (XRF). Ash samples were dissolved in lithium tetraborate ($Li_2B_4O_7$, flux) to make fused beads. These were measured together with standards of known composition containing the same elements in the appropriate concentration on a Panalytical PW 1480 using the SuperQ software. Results were not normalized for loss on ignition.

2.4. Phosphorus in aqueous samples

For the determination of phosphorus (orthophosphate and total phosphorus) in aqueous samples, Hach Lange kit LCK-349 was used on appropriate dilutions, with a LT-200 heater and a DR5000 spectrophotometer. Results were corrected both for volume gained by acid addition as well as for volume lost by sampling

Table 1
Ash mineral composition (% w/w) of the dried solid phase pig manure used in this study.

Ca	16.6	(0.20)	Al	0.57	(0.022)
P	11.0	(0.13)	Zn	0.54	(0.008)
Mg	7.6	(0.08)	Mn	0.24	(0.008)
Si	6.5	(0.09)	Cu	0.24	(0.014)
K	5.0	(0.04)	Sr	0.05	(0.001)
S	1.6	(0.28)	Ti	0.05	(0.002)
Fe	1.3	(0.01)	Ba	0.02	(0.004)
Na	1.2	(0.03)	Ni	0.02	(0.017)

Determined by XRF. Results 'as is', not normalized for loss on ignition (LOI). Average values, n = 3. Standard deviation is between brackets.

(see experimental procedure), and expressed as yield percentage of the total phosphorus present in the ash as determined by XRF.

2.5. Statistical analysis

Population means were calculated for the phosphate dissolution yields, obtained from all acidic dissolution experiments. Subsequently, Welch's *t*-test was used to find whether each two populations have equal means. The statistical numbers, i.e. p-values and h-values, were determined by using Matlab 2017a inbuilt function ttest2. A Matlab script was written to determine these statistical numbers for all combinations of two acid types (including acid-salt), at each pH value. The p-values were averaged over the range pH 7 to pH 4. An h-value of 1 means that the difference is statistically significant.

3. Results and discussion

3.1. Acidic dissolution yields of phosphate from pig manure ash

When considering the phosphate yield results described below, the results of the statistical analysis (Welch's *t*-test) of all dissolution experiments should be taken into account. Tables 2 and 3 show the statistical analysis results, for the result range from pH 7 to pH 4, with a 95% confidence interval, p = 0.05, and with h = 1 representing a statistically significant difference.

When comparing acetic, maleic, and citric acid – at pH 5, 4, and 3 –, the phosphate dissolution capacity of these organic acids can be arranged as tricarboxylic > dicarboxylic > monocarboxylic acid; the same order mentioned in literature when applied on phosphate rock (Bolan et al., 1994) (Fig. 1). However, the differences are mostly rather small, with only acetic and citric acid trials being significantly different from each other, and not from maleic acid, when focusing on pH 7 to pH 4 (Tables 2 and 3). Of these three organic acids, citric acid seems to result in soluble phosphate yields that are comparable to when sulfuric acid is used (Fig. 2). Apparently, any chelating capacity of acetic, maleic, and citric acid is not resulting in more dissolution of phosphates from the ash, compared to sulfuric acid.

Interestingly, oxalic acid does result in increased dissolution of phosphates from ash, markedly more than sulfuric acid and the other organic acids tested. Dissolution with sulfuric acid as well as with oxalic acid leads to 100% orthophosphate yield (Fig. 2). Oxalic acid however, reaches near 100% yield at pH 4, while sulfuric acid yields over 30% less at that pH and needs pH 2 to reach complete dissolution. Already at pH 6, close to 40% of all phosphate present in the ash is dissolved in presence of oxalic acid, significantly more than the 20% and 10% to 15% in the case of sulfuric and the other three organic acids, respectively. Oxalic acid is the only of the tested organic acids to show this behavior, with the other three showing results comparable to sulfuric acid, or trailing somewhat behind. Citric acid reaches yields very comparable to when sulfuric acid is used, not being able to reach pH 2 because of its lower acidity, but it reaches 100% yield at pH 2.5. Maleic acid reaches 100% yield at pH 2, but is a little less efficient than sulfuric acid at pH 5 and 4. Acetic acid trails behind even more and never reaches more than the 75% orthophosphate yield at pH 3, not being able to reach a lower pH. These positive oxalic acid results with manure ash do not concur with Bolan et al. (1994) on the dissolution of phosphate rock, where using oxalic acid resulted in similar results as other dicarboxylic acids, and partially with Ström et al. (2005) on phosphate dissolution from soils where oxalic acid outperformed citric acid at pH 7.5, but performed much less effectively at pH < 3.5. The exact reasons for the differences in oxalic acid performance are unknown, but possibly in the latter case have to do with pH adjustment and buffering in the applied soils. The current results comparing oxalic and sulfuric acid do concur with former studies on similar raw materials, such as char from manure pyrolysis, and sewage sludge ash that results from combustion and supercritical water gasification, to which the authors contributed (Acelas et al., 2014; Atienza-Martínez et al., 2014; Azuara et al., 2013).

In the presence of added sodium oxalate, the resulting dissolution is similar to when oxalic acid was used, but it is even more efficient at pH 7 to pH 5, as can be seen in Fig. 2. The results show that, firstly, the oxalate anion is key to the improved dissolution caused by oxalic acid compared to sulfuric acid. Secondly, an acidic environment is still needed, seeing as at pH values over 7 the presence of oxalate ions alone does not lead to dissolution of phosphate. Compared to the experiments with sulfuric acid alone, only a minimal amount of extra acid needed to be added to reach the desired pH in the sulfuric acid & sodium oxalate experiments, making it unlikely that the observed effect was caused by an increase in sulfate anion concentration. Furthermore, when sodium sulfate is mixed in with the ash before addition of sulfuric acid, the resulting phosphate dissolution curve is almost exactly the same as when sulfuric acid alone is used, indicating no influence of the sodium ions in the sodium oxalate. The fact that the phosphate yields are higher at around neutral pH when sulfuric acid is used on ash in presence of sodium oxalate compared to when only oxalic acid is used may be explained by the abundance of oxalate ions being available from the start in the former case, possibly combined with local acidity when sulfuric acid is added.

Table 2
Welch's *t*-test p-values calculated for dissolution trials, pH 7 to pH 4, 95% confidence interval.

p-values	Oxalic acid	Sulfuric acid	Acetic acid	Maleic acid	Citric acid	Sulfuric acid + sodium oxalate	Sulfuric acid + sodium sulfate
Oxalic acid	1	0.0065	0.0015	0.0005	0.0005	0.0272	0.0014
Sulfuric acid		1	0.1446	0.2122	0.4122	0.0246	0.2728
Acetic acid			1	0.2950	0.0345	0.0223	0.1220
Maleic acid				1	0.3561	0.0310	0.4819
Citric acid					1	0.0247	0.1488
Sulfuric acid + sodium oxalate						1	0.0012
Sulfuric acid + sodium sulfate							1

Table 3
Welch's *t*-test h-values indicating significant difference between dissolution trials, pH 7 to pH 4, 95% confidence interval, $p \leq 0.05$.

***h*-values**	Oxalic acid	Sulfuric acid	Acetic acid	Maleic acid	Citric acid	Sulfuric acid + sodium oxalate	Sulfuric acid + sodium sulfate
Oxalic acid	0	1	1	1	1	1	1
Sulfuric acid		0	0	0	0	1	0
Acetic acid			0	0	1	1	0
Maleic acid				0	0	1	0
Citric acid					0	1	0
Sulfuric acid + sodium oxalate						0	1
Sulfuric acid + sodium sulfate							0

1 = significantly different; 0 = not significantly different.

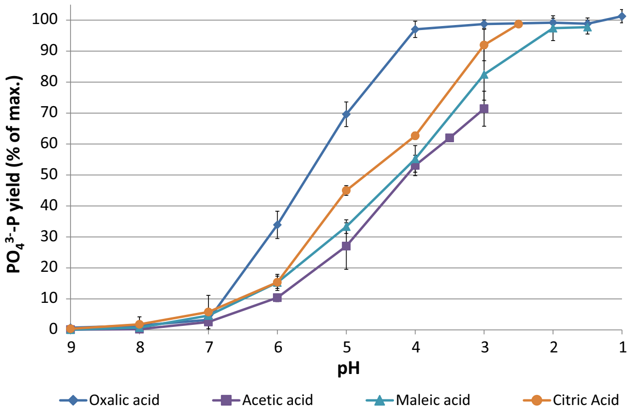

Fig. 1. Orthophosphate yield (% of max.) from pig manure ash (10 g/L) as a function of pH; comparing oxalic, acetic, maleic and citric acid. Average values from three experiments; error bars represent standard deviation.

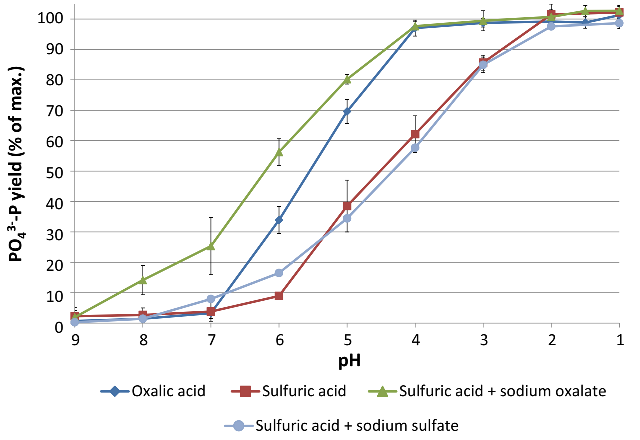

Fig. 2. Orthophosphate yield (% of max.) from pig manure ash (10 g/L) as a function of pH; comparing oxalic acid to sulfuric acid, the latter with and without addition of sodium oxalate or sodium sulfate. Average values from three experiments; error bars represent standard deviation.

These results are in accordance with the idea that manure ash acts similarly to phosphate rock in that when the reaction products are taken away, the dissolution can continue, when protons are supplied to the reaction. Therefore, if the resulting Ca^{2+} ions – but also other metal ions such as Cu^{2+} and Zn^{2+} in the case of manure ash – are taken away from the reaction by precipitation with oxalate ions, this would explain the high degree of dissolution at pH 6 and 5. Furthermore, it seems apparent from these experiments that when using oxalic acid, the precipitation of insoluble oxalate salts plays a more important role than complex formation with this dicarboxylic acid, such as mentioned for maleic acid.

In short, it seems that in addition to supplying the required acidity, oxalic acid's capability of facilitating phosphate dissolution from manure ash, can be explained by the formation and precipitation of insoluble oxalate salts.

To rule out the possibility that the results and apparent differences in Figs. 1 and 2 are influenced by a time effect in the dissolution reaction, a 24-hour dissolution experiment was performed. In this experiment, pH was adjusted from ~11 to 5 in one step of approximately 30 min using either sulfuric or oxalic acid. It is clear (Fig. 3) that equilibrium – approximately 50% and 70% yield for sulfuric and oxalic acid, respectively – is reached quickly, after which no change in the amount of dissolved phosphate occurs. Taking into account the pH adjustment steps of one unit for the data presented in Figs. 1 and 2, meaning that it took 4 to 5 h before dissolution from pH 6 to pH 5 occurred, it is assumed that the results shown in Figs. 1 and 2 are not influenced by a time effect.

While the results displayed in this study are all orthophosphate, 'Total Phosphorus' concentrations –orthophosphate plus other phosphorus present– were also determined and were usually only 1–2% higher than the orthophosphate values (results not shown). It is clear that the phosphorus recovered from the ash is almost exclusively present in the orthophosphate form.

3.2. Selective dissolution at pH 2 and pH 4

The results (Table 4) of this set of experiments concur very well with those of the acidification experiments, and enable a view on the behavior of all ash minerals – albeit indirectly – instead of on phosphorus alone. Using oxalic acid, phosphates almost entirely dissolve at pH 4, while sulfuric acid leaves about 40% undissolved and seems to require pH 2 for complete dissolution of phosphate.

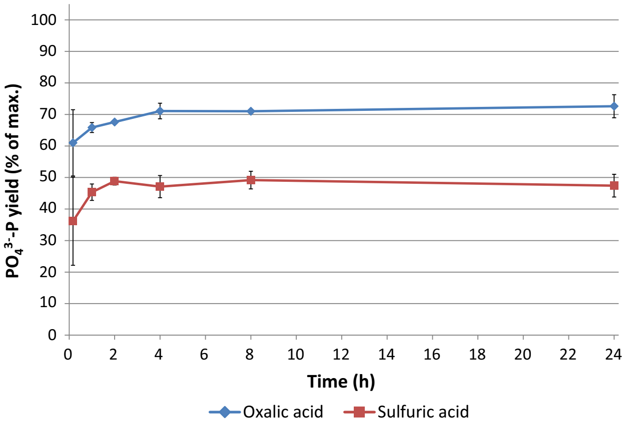

Fig. 3. Dissolution of phosphate (% of max) from pig manure ash (10 g/L) at pH 5 as a function of time (h), comparing sulfuric and oxalic acid. Average values (n = 2); error bars represent standard deviation.

Table 4
Minerals present in dissolution residues, expressed as percentage (%) of originally present in ash.

	Citric acid pH 4	Sulfuric acid pH 4	Oxalic acid pH 4	Sulfuric acid pH 2	Oxalic acid pH 2
Ca	43.1 (0.81)	50.9 (0.07)	96.0 (0.62)	61.4 (1.82)	97.2 (1.48)
P	35.4 (0.45)	43.8 (0.11)	3.5 (0.15)	0.6 (0.004)	2.4 (0.03)
Mg	9.9 (0.01)	12.0 (0.27)	9.6 (0.31)	4.6 (0.003)	6.1 (0.06)
Si	71.0 (1.34)	83.2 (0.07)	82.9 (4.90)	69.6 (1.10)	68.3 (0.95)
K	8.3 (0.02)	9.5 (0.19)	6.5 (0.24)	4.1 (0.03)	5.1 (0.02)
S	9.7 (0.52)	22.8 (2.81)	3.1 (1.59)	374.5 (2.90)	3.9 (0.03)
Fe	77.4 (1.64)	97.3 (0.81)	76.2 (1.80)	76.3 (0.15)	47.8 (1.67)
Na	20.0 (1.40)	28.0 (0.60)	19.5 (1.79)	7.6 (0.04)	11.3 (1.36)
Al	71.7 (0.52)	104.2 (0.20)	88.8 (13.35)	61.3 (0.87)	60.4 (0.61)
Zn	26.3 (0.30)	45.7 (0.28)	47.9 (0.17)	18.9 (0.20)	37.4 (0.26)
Mn	33.7 (0.41)	61.6 (0.53)	62.5 (0.74)	28.8 (0.49)	35.7 (0.28)
Cu	25.1 (0.31)	60.8 (0.35)	19.9 (2.08)	14.1 (0.14)	17.9 (0.15)
Sr	45.5 (2.10)	49.6 (0.26)	97.0 (0.35)	35.0 (1.41)	97.2 (1.23)
Ti	80.1 (0.57)	98.5 (1.19)	94.9 (2.23)	84.9 (0.72)	103.7 (24.99)
Ba	51.5 (0.80)	82.5 (1.19)	86.0 (0.75)	88.2 (1.43)	81.9 (0.27)

Determined by XRF. XRF results used 'as is', not normalized for loss on ignition (LOI). Percentages are corrected for dissolved ash minerals present in the liquid fraction of the wet residue. Average values from two experiments. Standard deviation is between brackets. Traces of nickel were found, but the results were erratic and are left out of this table. It seems the trace of nickel found in the original ash was too small for a comparison with the residues.

With respect to phosphate, citric acid at pH 4 behaves similarly to sulfuric acid in both sets of experiments.

As expected, for sulfuric acid as well as oxalic acid, when comparing results at pH 4 to those at pH 2, more of each mineral dissolves and therefore less remains in the residue. Sulfur is an obvious exception, but as sulfur in the residue may originate from insoluble sulfur salts, but also from the added soluble sulfuric acid, which subsequently got incorporated in to the dry residue, it is to be expected that sulfur results get distorted.

The other exception is calcium. It seems that lowering the pH from 4 to 2 does not result in more dissolution. The type of acid does seem to have a large influence on the dissolution of calcium from the ash. In the case of oxalic acid, almost no calcium ends up in solution; compared to about half when sulfuric acid is used. This points towards the formation of insoluble calcium oxalate salts, as opposed to the formation of a chelating action, which would have resulted in more calcium in solution, and less in the residue. When citric acid is used – at pH 4 –, about half of the calcium remains in the residue, similar to sulfuric acid. Citrate may act as a chelator, but this still means that calcium ions for a large part end up in the aqueous phase, albeit in a less available chelated form.

When comparing dissolution at pH 2 and 4, it is also interesting to look at the behavior of heavy metals such as iron (Fe), zinc (Zn), copper (Cu), and manganese (Mn), in presence of sulfuric acid or oxalic acid. At pH 4, more iron and copper seems to dissolve when using oxalic acid, while about half of all zinc and manganese remains in the residue. But when oxalic acid at pH 4 is compared to sulfuric acid at pH 2 – assuming that full phosphorus dissolution is the key driver of the process –, a different picture emerges. While both treatments cause all of the phosphorus to dissolve, more zinc, more manganese, and possibly more copper is dissolved when using sulfuric acid at pH 2. Also, more sodium (Na), aluminium (Al), and strontium (Sr) are dissolved when using sulfuric acid at pH 2. Only Fe dissolution seems to remain the same. In short, when using oxalic acid at pH 4, almost all phosphate can be dissolved, while dissolving less of the heavy metals and other ash compounds than with sulfuric acid.

3.3. Dissolution of phosphate from ash and the economics of oxalic vs sulfuric acid

In general, 100% dissolution of phosphate from 1 g ash in 100 mL aqueous phase described above means that 0.1 g phosphorus (P), or 0.3 g orthophosphate is in solution. A solution containing 0.3% soluble orthophosphate by weight, or around 35% on dry matter basis may already be economically interesting, especially with reduced levels of contaminants compared to manure. Preliminary tests with higher ash concentrations (results not shown) seem to suggest similar dissolution results. For the trials presented in this study, in order to reach close to 100% phosphate yield, 4.5 kg oxalic acid per kg phosphorus (P) is needed at pH 4, while 7.0 kg sulfuric acid at pH 2 is needed per kg P to dissolve all of the phosphate. This means that 55% more sulfuric acid is needed, compared to oxalic acid (Fig. 4).

When taking into account current market prices for these acids, 200 €/t for sulfuric and 800 €/t for oxalic acid (prices on 28 January 2019, 'Free On Board') (Chembid, 2019), it is clear that a phosphate dissolution process using oxalic acid is not economically preferable to one using sulfuric acid when only taking acid costs into account. It may be that advantages can be achieved concerning the lower amount of dissolved contaminants such as Zn, Mn, Cu, Na, Al, and Sr when using oxalic acid, in the form of lower downstream process costs needed remove these compounds. The fact that a higher level of process sustainability can be claimed when using oxalic acid instead of sulfuric acid may also result the former being preferred over the latter. Of course, possibilities for improving the economics exist. For example, an organic acid cheaper than oxalic acid can likely be used for the first neutralizing additions to the ash, after which oxalic acid can be applied. The current study does

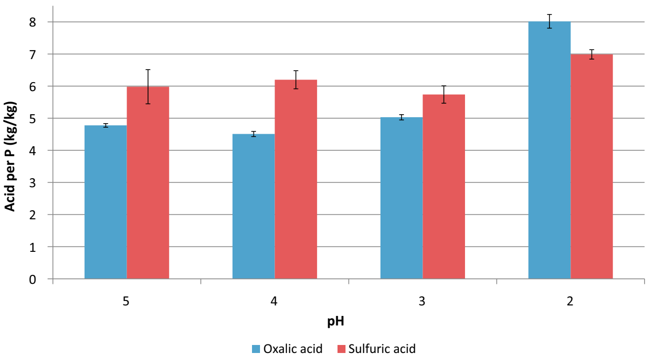

Fig. 4. Acid to phosphorus ratio (kg/kg) for oxalic and sulfuric acid at different dissolution pH. Average values from three experiments; error bars represent standard deviation.

not suggest a major effect on phosphate dissolution using this strategy. Or, cheaper acid can possibly be used to lower the pH further, and oxalate salt can be added in order to induce precipitation. One step further removed is the question of the potential use of carbonates instead of oxalic acid or oxalate salts. The economic specifics of the final process should also entail the question how to apply the resulting phosphate containing solutions. While this certainly warrants further study, it falls outside of the scope of the described research.

4. Conclusions

Oxalic acid outperforms sulfuric, acetic, maleic, and citric acid in dissolving phosphorus from manure ash. Furthermore, when leaching manure ash with acid as described in this study, pH 4 suffices for 100% phosphorus yield when using oxalic acid, while pH 2 is needed to reach this point when using sulfuric acid. Less of the heavy metals from the ash are dissolved when using oxalic acid. The fact that nearly all calcium after leaching is retrieved in the solid residue, points towards the formation of calcium oxalate, not that of chelating complexes, as being the mechanism that causes oxalic acid to outperform the other acids in this study.

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Declarations of interest

None.

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