

INNOVATIVE TECHNOLOGIES FOR PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE ASH

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ABSTRACT

The scarcity in Europe of phosphate ore along with the constantly growing demand for phosphorus-based products make it essential to find new sources and innovative recovery techniques for phosphorus in all of its forms. In order to avoid phosphate rock reserves exhaustion, its recovery from incineration Sewage Sludge Ash (SSA) might be a solution. Phosphorus concentration in municipal SSA is 9% (Krüger et al., 2014), which is within the range of the currently mined phosphate rock. However, the high amount of metallic elements (especially iron and aluminium) leads to a higher consumption of concentrated sulphuric acid, as it is used for the phosphate mineral treatment. The aim of this preliminary survey is to assess the acid demand and the efficiency of different acids towards the dissolution of the phosphate minerals in ash. Elemental and mineral composition, leachability and further tests were performed using four different SSA samples originated from three different sewage sludge incinerators located in Germany. First results show that the extraction yields with organic acids are higher compared to the ones achieved with mineral acids. Especially for oxalic acid, for which dissolution occurs both due to protonation and reduction, extraction rates close to 100% were achieved using lower amounts of acid.

1. INTRODUCTION

The phosphate rock processing trend shows a steady increase in the last years (Figure 1). In addition, the forecasts concerning the fertilizers demand published by the Food and Agriculture Organization of the United Nations emphasises that the global demand is constantly increasing (Table 1). It is important to associate the fertilizer utilisation with the phosphate rock mining industry, since it is estimated that 82% of the produced phosphorus is used for the production of fertilizers (IFCD, 2010).

Due to growth in phosphate rock extraction and demand, it is legitimate to question when this trend will ultimately be sustainable, since phosphate rock is a non-renewable resource and it cannot be substituted in agriculture (IFCD, 2010). Some authors have previously reported alarming data concerning phosphate rock depletion in the near future:

- 50 - 100 years (Atienza et al., 2014)
- A few decades (Biswas et al., 2014)
- 60 - 125 years (Franz, 2007)
- 370 years (Cooper et al., 2011)

However, it should be noted that these data are only re-

lated to the reserves of phosphates, and not to resources.

According to the United States Geological Survey (USGS), classification for phosphate rock, reserves are a subset of resources that meet specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth. In contrast, resources are classed as the concentrations of materials in a form and quantity that can be extracted currently. Extraction itself might be performed after a detailed evaluation of the deposit with the aim to prove that it satisfies the minimum requirement for its exploitation.

According to the USGS (USGS; 2016), the identified reserves (69 million Gg), which are at the current extraction rate of 224 thousand Gg/a, are expected to be depleted in approximately 300 years. However, considering the resources, which amount to more than 300 million Gg, the depletion time is shifted to more than 1,300 years from now.

Therefore, theoretically the amount of phosphate rock supply is not a global issue in the near future. For Europe, the situation could be different. Evidence of this is the inclusion first of phosphate rock in 2013, and later of phosphorus in 2017 within the Critical Raw Materials (CRMs) list. The issue concerning the choice of the European Com-


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TABLE 1: World demand forecasts for fertilizer nutrients, 2014-2018 (FAO, 2015).

Year	2014	2015	2016	2017	2018
P ₂ O ₅ demand (in thousand Mg)	42,706	43,803	44,740	45,718	46,648

munity to include phosphate rock in the CMRs list resides in the fact that Europe imports this resource almost completely. The main exporters worldwide are three countries (China, United States and Morocco) and actually, there is not a relevant phosphorus recycling process (European Commission, 2014).

Hence, the basis of research should not be the scarcity of raw materials, but rather the opportunity to reduce phosphorus waste whenever it is possible.

2. PHOSPHATE ORE AND SEWAGE SLUDGE ASH

Table 2 shows the average content of the extracted phosphate rock worldwide. The elemental phosphorus content in ore is calculated using the following equation (European Parliament, 2003):

$$\text{Phosphorus (P)} = \text{Phosphorus Pentoxide (P}_2\text{O}_5) * 0.436$$

The first four producer countries (China, United States, Morocco and Russia) share 78% of the global phosphate ore production. Considering only the main producers, the average content is 31.8% P₂O₅, ranging between 28.5-36.8% (average data for the years 2009 – 2013) (USGS, 2016).

Similar values are also reported from the International Fertilizer Development Center (IFDC), where commercial phosphate rock shows a P2O5 content from less than 25% to over 37%, (10.9-16.13% P) (IFDC, 2010).

As a comparison, German municipal sewage sludge ash has a lower phosphorus content (9%, see table 3) than the one of extracted phosphate rock, but still within the world

TABLE 3: Elemental mass fractions in German SSA (Krüger et al., 2014).

Element	Min	Max	Mean	Median	Mass flow [Mg/a]
P	1.5%	13.1%	7.3%	7.9%	18,812
P (Municipal)	3.6%	13.1%	9.0%	9.1%	10,939
P (Mun. / Ind.)	2.8%	7.5%	4.9%	4.8%	7,319
P (Industrial)	1.5%	3.8%	2.3%	2.3%	554
Ca	6.1%	37.8%	13.8%	10.5%	42,669
Si	2.4%	23.7%	12.1%	12.1%	38,637
Fe	1.8%	20.3%	9.9%	9.5%	29,049
Al	0.7%	20.2%	5.2%	4.8%	14,999
S	0.3%	6.9%	1.5%	1.0%	6,028
Mg	0.3%	3.9%	1.4%	1.3%	4,061
Na	0.2%	2.6%	0.7%	0.6%	2,416
K	0.0%	1.7%	0.9%	0.9%	2,227
Ti	0.1%	1.5%	0.4%	0.4%	1,264

TABLE 2: Phosphorus pentoxide and elemental phosphorus content in phosphate ore (USGS, 2013).

Compound	Min	Average	Max
P ₂ O ₅	11.00%	30.41%	46.00%
P (elemental)	4.80%	13.26%	20.06%

range for extracted ore (USGS, 2013).

According to the IFDC report, phosphate ore has to meet specific metal content requirements in order to be processed. For this, two ratios are defined (IFDC, 2010):

$$M_2O_3 = (Fe_2O_3 + Al_2O_3) \div P_2O_5 < 0.10 \quad (1)$$

$$M_2O_3 + (MgO \div P_2O_5) < 0.12 \quad (2)$$

Referring to the values highlighted in the survey performed by Krüger et al. (2014) for Germany, it can be seen that the two ratios for SSA vary in comparison to the indications of the IFDC study, resulting of 1.43 and 1.57 for (1) and (2) respectively.

Another recycling route could be the direct application of SSA in soil as fertilizer. In this case, issues come from the fact that the European Directive 87/278/CEE establishes limit values for the concentration and annual load for specific elements, which often are exceeded in SSA. Moreover, national legislations have stricter limits that hinder the reuse of ash without pretreatment. Table 4 uses the situation in Germany as an example.

Furthermore, it has to be considered that phosphorus contained in SSA is not plant available (BMEL, 2011; Petzet et al., 2012; Ottosen et al., 2013) due to its strong bonds in ash minerals.

3. MATERIALS AND METHODS

3.1 General

The aim of this work is the evaluation of the phosphorus extraction yields from sewage sludge ash via wet processes. In this study, the extraction of phosphorus is performed dissolving ashes from sewage sludge incineration.

The dissolution of the mineral phases present in sewage sludge ash were investigated using different inorganic and organic acids, such as nitric, sulphuric oxalic, citric and lactic acid. Tests were performed on 4 different sewage sludge ash samples obtained by 3 different incineration plants located in Germany.

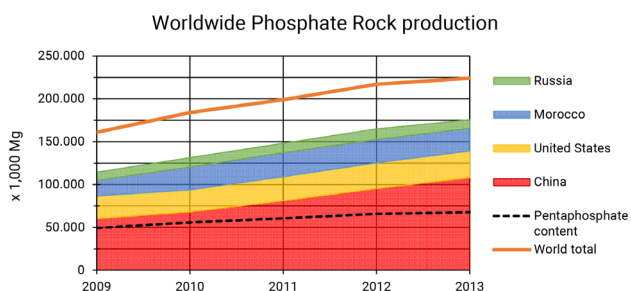


FIGURE 1: Leading producers of phosphate, and the total rate of worldwide production (USGS, 2013).

TABLE 4: Heavy metals concentrations in German SSA (Krüger et al., 2014) and comparison with limits from different German ordinances (BMEL, 2001).

Element	Min [mg/kg]	Max mg/kg]	Mean mg/kg]	Median [mg/kg]	Mass flow [mg/kg]	Limit [mg/kg]	Ordinance
Pb	3.5	1,112	151	117	62	150	AbfKlärV
Cd	0.1	80,3	3.3	2.7	1.4	1,5	BioAbfV
Cr	58	1,502	267	160	107	2	DümV
Cu	162	3,467	916	785	395	100	BioAbfV
Ni	8.2	501	105.8	74.8	58	50	BioAbfV
Hg	0.1	3.6	0.8	0.5	0.3	1	BioAbfV
Zn	552	5,515	2,535	2,534	763	400	BioAbfV
As	4.2	124	17.5	13.6	6.7	40	DümV

First, elemental and mineral composition of the ash were investigated in order to evaluate the extraction yields achieved in the following leaching tests. These tests include aqua regia dissolution of the sample and characterisation via X-rays diffraction technique.

Once the elemental composition of each sample was deciphered, a standardised leaching test with nitric acid was performed at 16 different pH values. The aim of this was to obtain a baseline standard for the acid requirements and to observe indications concerning the operational pH values to perform additional experiments. In particular, further leaching tests with sulphuric, oxalic citric and lactic acid were conducted at values of liquid-to-solid ratios and pH values suggested by the previous analyses.

The overall result obtained pursuing this approach is a preliminary understanding of the parameters affecting the phosphorus extraction yield which will be used as a basis for further research on the topic.

The following paragraphs present the methodology applied in order to evaluate the physical-chemical characterisation of samples, pH-dependency of the sewage sludge ash dissolution and the phosphorus extraction carried out with different inorganic and organic acids.

3.2 Elemental and mineral composition

In order to evaluate the elemental composition of the ash, water content and organic dry matter; samples were oven dried at 105 °C according to DIN EN 13346 and DIN EN 15935 respectively.

Afterwards, 1 g of each sample was treated for 10 min at 175 °C in triplicates via microwave assisted aqua regia digestion (CEM Corporation MARS 6 microwave digestion system) according to DIN EN 16174.

At the end of the digestion, samples were vacuum filtered at 0.45 µm and properly diluted prior to analysis via ICP-OES. (Agilent 5100 ICP-OES) according to DIN EN ISO 11885. Furthermore, in order to recognise the mineral species, X-rays diffraction analysis was performed for each sample to detect the main crystalline phases contained in the ashes. For this purpose, 1 g of milled sample was prepared and analysed with a Siemens D500 XRD system.

3.3 Sequential extraction

The leaching behaviour of sample SSA-1 was tested in order to evaluate the acid requirements for the successive

extractions according to DIN EN 14429 norm. For this, 16 individual experiments were carried out to cover a pH range between 0 and 7.56. Glass bottles of 500 ml volume were used to perform the extraction.

Extracting solutions were prepared by adding correct amounts of pure nitric acid in demineralised water for a total volume of 300 ml. For each bottle, the total amount of extracting solution was added to 30 g of dried sample, in three steps within the first 2 hours of the experiment, for a final L/S ratio of 10 ml/g. The experiment duration was 48 h in order to reach the chemical equilibrium. The pH values were monitored according to the norm identified above.

3.4 Leaching tests

Phosphorus extraction tests were performed for all samples with 0.4 M solutions of sulphuric, oxalic, citric and lactic acid. While sulphuric acid application is justified by its strength and low cost, organic acids were selected for their reduction properties (especially oxalic acid) and for their environment-friendly production (citric and lactic acid).

In order to simulate different conditions, the amount of sample for each test was varied, to keep the molarity of the solutions constant. This translates into a change in the specific amount of acid per mass of ash (or mol H⁺/g ash) allowing the utilisation of limited quantities of chemicals (especially for organic acids). Therefore, the main parameters controlled during the leaching were the L/S ratio and the pH variation of the solution. Liquid-to-solid ratios of 10, 20 and 40 ml/g were obtained through mixing 100 ml solution with 10, 5 and 2.5 grams of ash respectively.

The leaching was performed in sealed, stirred bottles for 1 hour at an ambient temperature. Afterwards, samples were filtered at 0.45 µm and analysed with ICP-OES system.

4. RESULTS AND DISCUSSION

4.1 Elemental and mineral composition

4.1.1 Elemental composition

The water content and the organic dry matter analysis for samples n°1 and 4 is reported in table 5. Samples n°2 and 3 were received in a dry state.

Table 6 shows the results of the ICP-OES analysis. As it can be seen, SSA-1 and SSA-4 clearly arise from incinera-

TABLE 5: Water content and organic dry matter.

	SSA-1	SSA-2	SSA-3	SSA-4
Water content	20.95%	0.00%	0.00%	19.93%
Organic dry matter	0.73%	1.33%	1.89%	4.93%

TABLE 6: Elemental composition of sewage sludge ash.

Element	SSA-1	SSA-2	SSA-3	SSA-4
P Phosphorus	9.31%	4.50%	10.25%	8.99%
Fe Iron	14.38%	6.23%	1.83%	10.14%
Ca Calcium	9.27%	5.88%	9.00%	10.32%
Al Aluminium	3.10%	5.21%	12.67%	4.63%
Mg Magnesium	1.02%	0.82%	0.82%	1.35%
K Potassium	0.91%	1.04%	1.28%	0.80%
S Sulphur	0.59%	0.67%	0.31%	0.62%
Na Sodium	0.37%	0.29%	0.33%	0.32%
Main elements (Total)	38.95%	24.64%	36.49%	37.17%
Balance	61.05%	75.65%	63.51%	62.83%

tion of sludge where iron precipitants are used, while SSA-3 arises from sludge with aluminium salts as precipitants. SSA-2 shows a comparable concentration of iron and aluminium. Furthermore, this sample also showed a total mass of primary elements of 24.7%, compared to 36-39% found in the other samples. This can be explained by less silicon being dissolved by aqua regia and clearly detected via X-ray diffraction analysis.

4.1.2 Mineral phases

Results show that the main crystallised minerals in the sample SSA-1 and SSA-4 are quartz (SiO_2), hematite (Fe_2O_3) and calcium phosphates with substitutions of iron ($\text{Ca}_9\text{Fe}(\text{PO}_4)_7$) and magnesium (whitlockite, $\text{Ca}_{18}\text{Mg}_2\text{H}_2(\text{PO}_4)_{14}$), in line with the findings of Petzet et al. (2012), Donatello and Cheeseman (2013). Analysis on sample SSA-2 detects a predominance of a quartzose component, followed by calcium iron phosphates and aluminium phosphates (AlPO_4).

SSA-3 shows besides quartz, also the presence of aluminium phosphates and whitlockite.

4.2 Sequential extractions

The leaching characteristic is shown in Figure 2. It can be seen that calcium and magnesium are leached simultaneously at a pH close to neutral. Starting from pH below 4.5 it can be observed that Ca and P concentrations increase, whereas calcium phosphates are also dissolved. This can be demonstrated by the increase of the phosphorus concentration in solution. Additionally, it can be observed that aluminium is participating as substitution for magnesium in Ca-Al-P crystals.

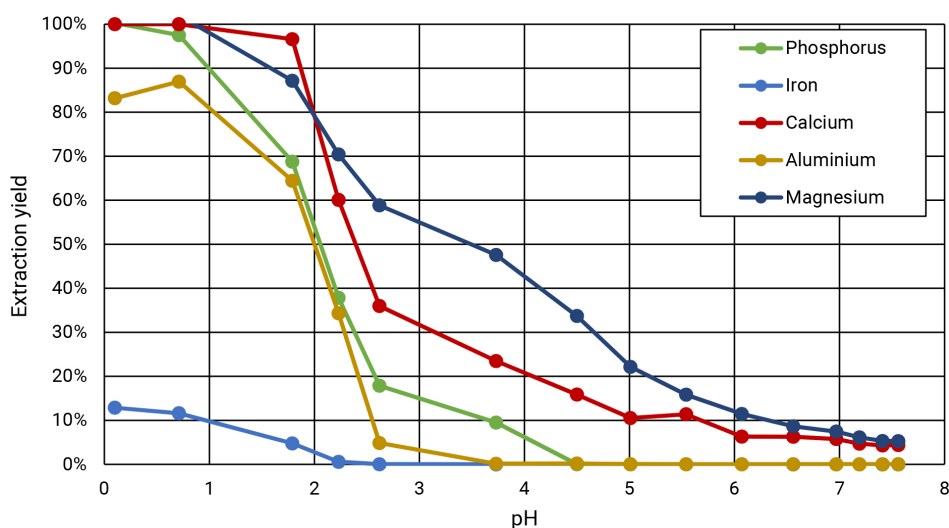
The leaching of iron starts at pH values close to 1.8. Therefore, in order to avoid the dissolution of hematite and other heavy metals (released simultaneously with iron (Franz, 2008)), a pH higher than 1.8 should be used. Under this condition, it is possible to extract 70% of the total phosphorus contained in the ash, limiting the amount of impurities in the leachate. Considering the acid demand, this corresponds to a need of 0.004-0.007 mol H+/g ash for respective phosphorus extraction rates of 68.8-97.5%, which is in line with the acid demand according to Petzet et al., (2012).

4.3 Leaching tests

For all the samples, the higher extraction yields were achieved for oxalic acid, followed by sulphuric acid. The effectiveness of citric acid was proven for high L/S ratios, while due to the limited strength of the solutions lactic acid was least effective.

As displayed in figure 3, extraction yields over 90% were achieved for SSA-1. SSA-2 and SSA-3 using oxalic acid, which shows a higher effectiveness in phosphate solubilisation. On the other hand, SSA-4 showed the lowest extraction yield; this is most likely to be caused by its higher organic dry matter content (4.93%).

For sample SSA-1, values from the different extractions above described and from the sequential extraction performed with nitric acid were compared.

**FIGURE 2:** Leaching behaviour with nitric acid at different pH values for SSA-1.

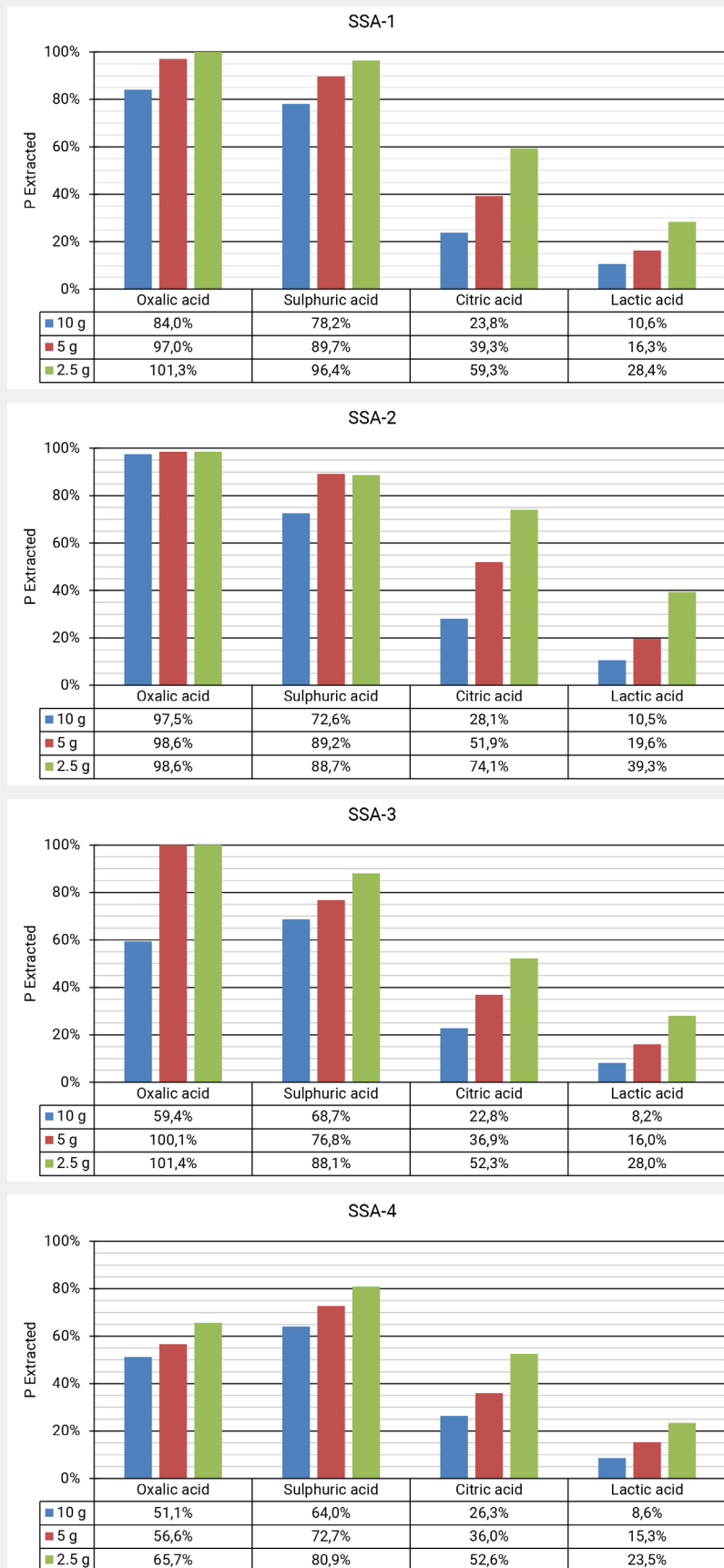


FIGURE 3: Leaching tests performed with different acids at different L/S ratios.

Figure 4 shows the acid demand in mmol H+/g SSA. The amount of protons required for the phosphorus solubilisation for nitric and sulphuric acid is comparable, even if performances of this last one are slightly lower, probably due to a re-precipitation of gypsum in the ash surface (from the reaction of Ca with H₂SO₄ (Ottosen et al., 2013)). Moreover, for oxalic, citric and lactic acid higher extraction rates are achieved in comparison with nitric acid even at low mmol H+/g SSA values. This is caused not only by the low pH of the solution, but also for reduction potential of

organic acids, which promotes the dissolution of Ca-Fe-P/ Ca-Mg-P minerals. This fact can clearly be seen in Ca and Fe concentrations in the lactic and citric acid solutions in Figure 5 and Figure 6.

5. CONCLUSIONS

In this work the wet phosphorus leaching from sewage sludge ash was investigated. The elemental composition of ash evaluated after aqua regia dissolution of samples showed a phosphorus content in the samples investigated

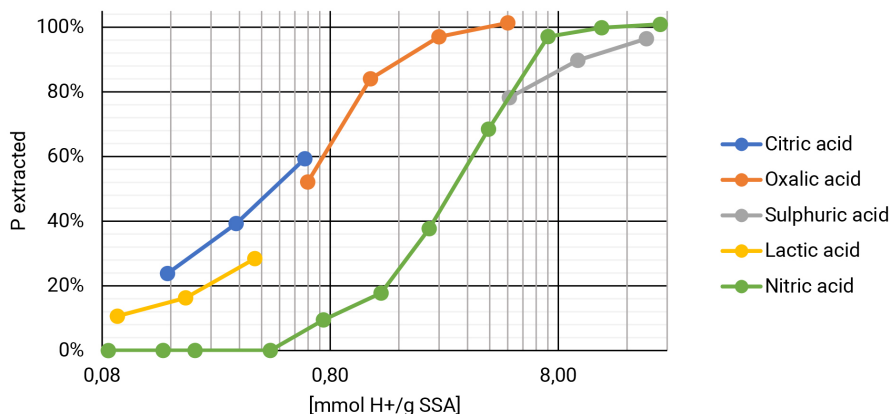


FIGURE 4: Phosphorus extraction yields for SSA-1.

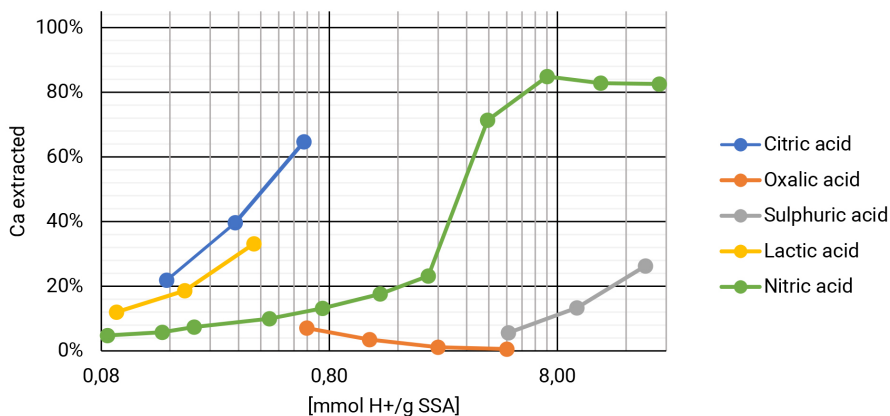


FIGURE 5: Calcium extraction yields for SSA-1.

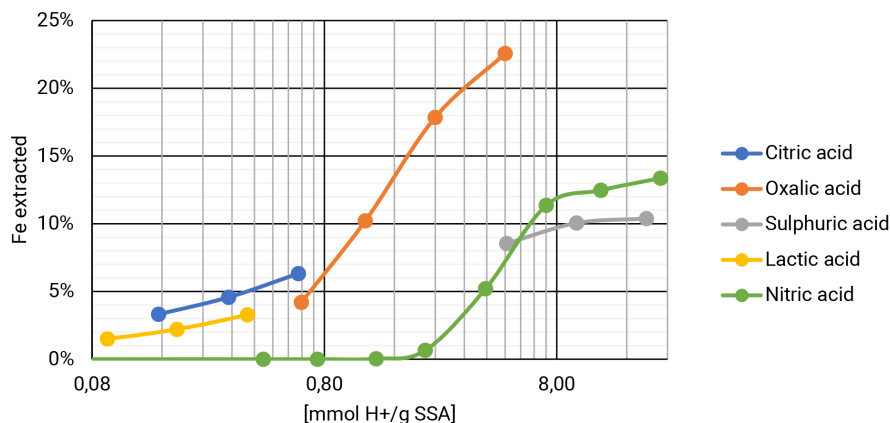


FIGURE 6: Iron extraction yields for SSA-1.

ranging between 4.50% and 10.25%. Other main elements of the ash were iron, calcium, and aluminium, which reflect the mineral composition of the samples. In fact, phosphorus is bonded in calcium phosphates in which iron, magnesium or other minor elements are substitutes in the mineral phases. Aluminium phosphates were found to be the main mineral phase in ash arising from wastewater treatment plants that use aluminium salts as precipitant agents.

The leaching performed under standard conditions using nitric acid showed that in order to achieve phosphorus extraction yields close to 100%, a specific amount of at least 7 mmol H⁺/g SSA is necessary. Furthermore, leaching with nitric acid shows that the extraction of phosphorus closely follows the solubilisation of calcium. This confirms the connection of the two elements already determined via X-rays diffraction. Therefore, the dissolution of calcium phosphates is the main process to consider while recovering phosphorus via wet acid processes.

Using these preliminary information as basis, further leaching tests were performed using different acids. While using sulphuric acid for the leaching, similar phosphorus extraction yields were obtained though performances were slightly lower than if using nitric acid. This could be explained by the successive precipitation of gypsum on the ash surface, which may obstruct further dissolution of phosphorus-containing minerals.

Different conclusions can be drawn concerning the use of organic acids. Oxalic acid achieved the best extraction yields in this work. The use of oxalic acid allows extraction rates close to 100% to be achieved with 1 mmol H⁺/g SSA, compared to values higher than 8 mmol H⁺/g SSA using nitric and sulphuric acid.

The main difference in the leachate obtained using oxalic acid was the lower concentration of calcium. This is probably due to its precipitation as oxalate salt. This information could be useful for the context of further research focused on the precipitation of phosphorus in other forms rather than calcium phosphates. However, an increased solubilisation of iron was also observed, which should be investigated in more detail when assessing successive recovery steps.

The effectiveness of organic acids for the dissolution of SSA was also proven for citric and lactic acid. In these cases, the overall yield was sensibly lower than the one achieved for oxalic and sulfuric acid. Nevertheless, extraction yields for citric and lactic acid were higher than the ones achieved using nitric acid in standard conditions. This was explained by the fact that the extraction with organic

acids is principally given from reduction at even higher pH values, and not from the protonation of the solution. For citric acid in particular, investigations on leaching at higher temperatures might bring an increase in phosphorus extraction yields.

In conclusion, further investigations will be focused on the experimentation through the application of additional leaching conditions. In particular, higher solution molarities with lower L/S ratios may lead to similar extraction yields, but also to an increased overall concentration of phosphorus in solution due to the higher quantity of ash available for leaching.

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