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To incinerate or not? –Effects of incineration on leaching and heavy metal concentrations of post-precipitated sewage sludge (RAVITA™)

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Abstract

The major element and heavy metal concentrations of post-precipitated sewage sludge (PPS) and its ash residue (PPA) were determined using microwave digestion followed by inductively coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS). To the best of our knowledge, this has not been previously done. Compared to average heavy metal concentrations in sewage sludge in Europe the obtained concentrations resulted in notably lower in both PPS and PPA. The leaching efficiency of the metal (Al/ Fe) used as a precipitation agent from post-precipitated sludge and its ash residue with phosphoric acid was also investigated. Tests resulted in leaching efficiencies for Al of 85 ± 1 % and 99.5 ± 0.7 % for PPS and PPA, respectively which were produced with aluminum as precipitation agent for phosphorus. Sludge, which was produced using iron as a precipitation agent, had a leaching efficiency of Fe 36.6 ± 0.9 % and 68.0 ± 1.1 %, for PPS and PPA, respectively. The leaching efficiency for P was 94 ± 3 % and 96 ± 5 % for Al-PPA and Fe-PPA, respectively.

1 Introduction

Since the European Commission listed phosphate rock as a critical raw material in 2014, the development of methods to recover phosphorus (P) from secondary sources has been increasing steadily (European Commission, 2014; Scopus, 2019). One of the main secondary sources can be the sewage sludge produced in wastewater treatment plants. It is estimated that 90 % of the P in wastewater end up in sewage sludge (SS) (Liang et al., 2019).

Currently, the three main applications for SS are landfilling, use in agriculture, and incineration (Kacprzak et al., 2017). In 2016, 35 percent of sewage sludge was incinerated in the European countries producing thousands of tonnes of ash (EUROSTAT, 2019). For that reason, many of the wet chemical methods developed for phosphorus recovery utilize the incinerated sewage sludge ash (ISSA). The problem is that incineration concentrates the harmful heavy metals in ash causing challenges in the development of the phosphorus recovery processes (Franz, 2008).

The usual first step in P recovery is the leaching of ISSA with either inorganic or organic acids. This extracts P from the ash along with metals and metalloids (Fang et al., 2018). The purification process for heavy metal separation can be done with solvent extraction, ion exchange resins or membranes before the leachate is utilized for the recovery of P (Biswas et al., 2009; Donatello et al., 2010; Guedes et al., 2014; Paltrinieri et al., 2019; Shiba and Ntuli, 2017). Another method for separation of P from heavy metals is the pretreatment of ISSA. For instance, a chelating agent EDTA (ethylenediaminetetraacetic acid) has been successfully tested as a pre-leaching agent for reducing the metals before P leaching (Fang et al., 2018). This however produces a waste faction containing EDTA and leached metals, which must be processed. Several studies have also investigated the possibilities to directly transform P from the acidic leachate into a plant-available form. Biochars derived from waste materials (peanut shells, sewage sludge) have been successfully used for P-adsorption and then used as fertilizer (Fang et al., 2020a, 2020b). Direct precipitation with calcium silicate hydrates has also been implemented resulting in a leaching efficiency of 55 % for P (Lee et al., 2018).

One way to prevent heavy metals from contaminating the phosphorus-rich sludge, without extra process steps, is so-called post-precipitation (PP) (Eklund et al., 1991). In PP the precipitation agent, typically aluminum or iron salt, is added into effluent wastewater after other wastewater treatment procedures, such as primary treatment and biological treatment.

Post-precipitation of P is utilized by RAVITA™ -process. It is a process developed and patented by the Helsinki Region Environmental Services Authority to recover phosphorus and nitrogen from municipal wastewater (Fred et al., 2019, 2018; Rossi et al., 2018). In RAVITA™ the PP produces a chemical sludge that mainly consists of aluminum or iron phosphate depending on the used precipitation agent. The chemical sludge is separated from effluent wastewater by disc filtration. This results in an extremely low total P concentration of 0.1 mg L^{-1} in effluent wastewater (Rossi, 2014). Formed chemical sludge is leached with dilute phosphoric acid. Next, the leach solution is processed to separate the precipitation metal and phosphorus from each other. Currently, the purification of phosphoric acid with solvent extraction is researched. The purified phosphoric acid solution is partly used in nitrogen recovery to produce ammonium phosphate and the excess phosphoric acid can be utilized in the fertilizer industry. The separated metal is recycled back to the wastewater treatment process to be used as a precipitation agent again. The recycling of the precipitation agent is not utilized in any other P recovery process.

RAVITA™ will utilize only the chemical sludge formed in PP. The biosludge that is formed during biological treatment will contain an estimated 30-35 % of the P that comes with incoming wastewater and it is digested (FCG Suunnittelu ja Tekniikka, 2015). Because of the lower P content, the biological sludge has a better nutrient ratio and greater amounts can be used in agriculture. Also, when P is not chemically bound with iron or aluminum its bioavailability for plants increases. The heavy metal concentrations of the biological sludge depend on industries that produce wastewater (Persson et al., 2015). However, the concentration levels of heavy metals in biological sludge are controlled at the EU level by The Sewage Sludge Directive 86/278/EEC (The Council of the European Communities, 1986). The final treatment for biological sludge varies between the EU member states (Raheem et al., 2018). After digestion and composting the sludge can be utilized in green building or it can be incinerated.

Previously for RAVITA^{TM} -process, we have optimized the leaching procedure for aluminum-based post-precipitated sewage sludge (Al-PPS) with dilute phosphoric acid (Reuna and Väisänen, 2018). The optimized leaching conditions for iron-based post-precipitated sewage sludge (Fe-PPS) have not been previously published. Phosphoric acid was chosen as a leaching solution instead of sulfuric acid or hydrochloric acid in order to avoid the removal of sulfate or chloride ions from the leachate. (Ottosen et al., 2013). In this study, we have studied if the incineration of PPS enhances the leaching process and determined the concentrations of heavy metals (HMs) in the sludge (PPS) and ash residue (PPA). To our knowledge, the HM concentrations have not been previously determined from PPS and PPA. Nor has the leaching of PPA from the post-precipitation of P with dilute phosphoric acid previously been tested.

2 Experimental

2.1 *Materials and chemicals*

The standard stock solutions of the elements (1000 mg L^{-1}, analytical grade) were supplied by PerkinElmer. Boric acid (H_3BO_3, 99.99 %, AlfaAesar) and phosphoric acid (85 wt. %) were obtained from VWR International. Analytical grade nitric acid (65-68 wt. %) and hydrochloric acid (37-39 wt. %) were purchased from Merck. Analytical grade hydrofluoric acid (40 %) was procured from Merck. Ultra-pure hydrochloric and nitric acid were purchased from ANALYTIKA, spol. s.r.o. (34-37 %, Prague, Czech Republic). Certified reference materials CRM029 *Heavy Metals – Sewage Sludge 2* (Lot LRAB1332) and SRM 1663c *Heavy Metals in Coal Fly Ash* were used for method validation. All the chemicals were used as obtained without further purification. High-purity water produced by the Elga Purelab Ultra water purification system was used throughout the experiments.

The batch of post-precipitated aluminum phosphate (Al-PPS) and iron phosphate sludge (Fe-PPS) were received from the RAVITA^{TM} pilot plant located in the Viikinmäki wastewater treatment plant, Helsinki. Post-precipitated sewage sludge (PPS) batches were dried in a fume cupboard for 72 h and ground manually before sample treatment. Parts of the batches were incinerated (550 °C, 2 h) to produce post-precipitated sewage sludge ash (PPA).

2.2 *The procedure of sample treatment*

2.2.1 *Dry matter determination, incineration, and particle size determination*

The dry matter content of sludge samples and reference materials were determined according to the Finnish Standards Association's standard SFS 3008 (SYKE, 2011). Samples of 500 mg were weighed and kept 16 hours at 120°C. After cooling the weight was measured and dry weight and moisture content were calculated. The particle size range was determined with the Retch AS200 sample sieve. The results are presented in supplementary data Table S1.

2.2.2 *Microwave-assisted digestion*

Sewage sludge samples (200 mg, dry weight content 81.8 % for aluminum-based sludge and 70.1 % for iron-based sludge) and ash residue samples (200 mg) were weighed in digestion vessels and 9 mL nitric acid (HNO_3, 65 %), 3 mL hydrochloric acid (HCl, 35 %) and 1 mL hydrofluoric acid (HF, 40 %) was added. Vessels were closed and a digestion program based on EPA 3052 method was performed with CEM Mars6 –microwave oven. After cool down 10 milliliters of boric acid (H_3BO_3, 5 wt.-%) was added and the HF neutralization program was executed. Temperature profiles of digestion programs are presented in supplementary data (Table S2). Digested samples were filtered (filter paper Whatman 41) and diluted to a volume of 40 milliliters with high-purity water. Also, samples from certified reference materials *Heavy metals-Sewage sludge* CRM029-50G (250 mg, dry weight content 89.8 %), SRM 1663c *Heavy Metals in Coal Fly Ash* (200 mg, dry weight content 99.73 %) were digested similarly.

2.2.3 *Leaching*

Leaching of Al-PPS and Al-PPA was done according to optimized leaching conditions (Reuna and Väisänen, 2018): solid to liquid ratio S/L of 15.9 g dry weight (d.w) L^{-1}, the phosphoric acid concentration of 0.5 M and leaching time of 360 minutes. The Fe-PPS and Fe-PPA were leached in the following matter: S/L 121 g (d.w.) L^{-1}, the phosphoric acid concentration of 2 M and leaching time of 60 minutes. The PPS was used in the leaching test as received. The properties of PPS and PPA are listed in Table S1 in the supplementary data.

The specific compounds of metals in the solution after leaching with phosphoric acid is discussed in the supplementary data.

2.3 ICP-OES measurements

The concentrations of the major elements Al, Ca, Fe, and Mg were determined with PerkinElmer ICP-OES Avio 500 –spectrometer for Fe-PPS and Fe-PPS and with PerkinElmer Optima 8300 for Al-PPS and Al-PPA. The GemCone low flow –nebulizer with Tracey spray chamber (HF resistant) was used for sample introduction. The parameters for all measurements are presented in supplementary data (Table S3). The wavelengths, calibration ranges, and the limits of quantification (LOQ) are presented for each element in supplementary data (Table S4).

2.4 ICP-MS measurements

The heavy metals analyzed were As, Cd, Cr, Cu, Ni, Pb, Sb, Se, Sn, Te, and Zn. The element concentrations were determined with PerkinElmer NexION 350D inductively coupled plasma mass spectrometer (ICP-MS). The ICP-MS operating conditions are shown in supplementary data (Table S5). Before measurement, the samples were diluted by a factor of 200 or 50 with ESI Prep-Fast. Method detection limits (MDL) were determined from method blanks (n=9) for each element according to US EPA Method 200.7 (U. S. Environmental Protection Agency, 2001) and are presented along with calibration ranges and internal standards used for analytes in supplementary data (Table S6). Validation of ICP -OES and ICP-MS measurements is presented in the supplementary data.

3 Results and discussion

3.1 Determination of element concentrations of PPS and PPA

Table 1 presents the major and heavy metal concentrations by weight percentages (w-%) for main elements and mg kg^{-1} for heavy metals in PPS and PPA. Concentrations for As, Se, and Cr are not presented since they resulted in concentrations lower than MDLs in all sample types. To see if the heavy metal concentrations are lower in the PPS than in traditionally produced sewage sludge the values were compared to existing literature. Liang et al., (2019) determined the elemental concentrations of raw waste activated sludge and ISSA and the results are presented in Table 1 along with data from this study. Liang et al, (2019) determined that the concentrations of P in raw sludge and ISSA were 29.4 g kg^{-1} and 52.1 g kg^{-1}, respectively. From Table 1 we can see that PPS and PPA contain higher concentrations of phosphorus regardless of the metal used in post-precipitation. The same trend applies to all concentrations of the main elements. For instance, aluminum is present almost thrice as high in concentration in Al-PPA than in ISSA (109.7 g kg^{-1}) that Liang et al., (2019) have researched. This is expected since the precipitation in PP happens after the removal of biological solids, hence increasing the concentrations of main elements.

In both sludge types, the heavy metal concentration is increased by a factor of 1.3 after incineration. However, even after incineration, most heavy metal concentrations are considerably below the average heavy metal content of the sewage sludge in the EU and Finland (Helsinki Region Environmental Services Authority, 2018; Inglezakis et al., 2014). Likewise, Finland's limit values for heavy metals in sludge for use in agriculture are straightforwardly passed (Ministry of the Environment, 1994). This is illustrated in Figure 1a for Al-PPS/PPA and Figure 1b for Fe-PPS/PPA. The only exception is cadmium which average concentration in Fe-PPS is the same as Finland's limit value for Cd in sludge for use in agriculture. However, the cadmium will not concentrate on PPA, since it volatilizes at elevated temperature (Shi et al., 2014; Zhang et al., 2008). Instead, at a full-scale process of incineration, Cd would concentrate on combustion residues (CRs) such as fly ash (Xiao et al., 2015). This could affect the end-use of the CRs, which have been reported to be utilized in construction material production and for agricultural land (Ning et al., 2013). Xiao et al., 2015 studied the mobility and phyto-accessibility of some heavy metal from SS after combustion. They concluded that Cd in fly ash had little bioavailability or eco-toxicity for plants. Thus, incineration could be a viable step in RAVITA™ -process despite the Cd content in Fe-PPS.

ypically, the high concentration of Zn is the reason, which prevents the usage of ash in landfilling or other purposes (Franz, 2008). This will not be the issue with PPA since the concentrations of Zn are 2 times lower than the mean value in Europe. These HM concentrations determined in this study indicate that in a full-scale process most of the HMs in wastewater will be bound in the biological sludge. However, since this has not been piloted, it is too soon to evaluate the possible concentrations in the biological sludge. The obtained results confirm the fact that by using the post-precipitation of phosphorus the heavy metal concentrations are significantly lower in the produced sewage sludge. This simplifies the recovery process of P and the precipitation agent since there is no longer a need to purify the phosphorus product from heavy metals.

3.2 The effect of incineration on leaching of Al, Fe, and P

Table 2 presents the determined concentrations of Al, Fe, and P from the leachates and the pH of the solution after leaching. The concentration of P in the leachate for PPA was determined by subtracting the theoretical P concentration of the phosphoric acid from the measured value. When leaching the PPS, due to the water content, it is not possible to accurately determine the extra P content in leachate. For that reason, those values are not presented.

Figure 2 portrays the effect of incineration on leaching efficiency when dilute phosphoric acid is used. Since the leaching efficiency for Al and Fe seems to be higher with PPA, the Student's t-test (one-tail) was performed to determine if there is a statistically significant difference between the main metal concentration in leach solution after leaching with either PPS or PPA. Table 3 presents the t-test results for both types of sludge. In both cases, the absolute value for t_{Stat} exceeds the critical t-value. This indicates that the leaching efficiency of the main metal from PPA is higher than from PPS.

There are two reasons for the higher leaching efficiency of ash. First, the organic material does not anymore compete with metals. Hence, the ratio of H^+ /metal increases even though metal concentrations rise in 1.5-fold after incineration. The higher H^+/ metal ratio enhances the leaching efficiency. The second reason is the smaller particle size in PPA (see Table S1) resulting in higher surface area, which makes the metals easier to be leached (Hong et al., 2005; Stark et al., 2006).

Even though the leaching efficiency of metal is higher with ash, the effect of increasing concentration must be considered on the whole recovery process. The aluminum concentration (4.60 ± 0.03 g L^{-1}) in leach solution after leaching with Al-PPA seems reasonable, but the leach solution containing iron (36 ± 2 g L^{-1}) could be problematic. For instance, if the solvent extraction (SX) is contemplated as a purification method for leach solution it should be taken into account that aluminum and iron are the main components to cause the formation of crud in SX-settlers (Ritcey, 1980). Thus too high iron concentration in the leachate would increase the possibility of crud formation during solvent extraction. A higher concentration of iron in the aqueous phase also means that the SX-process requires more steps and steeper aqueous to organic phase ratios. Besides, the predominant compound of the Fe in the leaching solution is $FeH_2PO_4^{2+}$ (see Figure S1). Since the goal is to recover both P and the precipitation agent (Al/Fe) in different fractions, it is not possible to achieve if iron forms a compound with phosphate anion. For these reasons, other purification methods for leach solutions that are produced from Fe-PPS/PPA need to be investigated.

For P, high recovery in leaching is achieved after incineration, 94 ± 3 %, and 96 ± 5 % for Al-PPA and Fe-PPA, respectively. These results are consistent with the results Donatello et al.

(2010) obtained when leaching ISSA with sulfuric acid. Their investigation resulted in P recoveries between 72 – 91 %. This supports incineration as a pretreatment method before leaching with H_3PO_4 as it removes the organic matter, thus improving the leaching of the main metal. Lee et al. (2018) achieved 55 % P recovery when leaching SS with sulfuric acid, but due to the water content in PPS, it is not possible to accurately determine the excess P amount in phosphoric acid solution. However, since the pH remains below 2 after leaching it can be estimated that most of the P will be leached from PPS (Monea et al., 2020).

4 Conclusions

The major element and heavy metal concentrations of PPS and PPA were determined. Also, the effect of incineration on the leaching efficiency of the metal used in the P post-precipitation was investigated. A 1.5-fold increase in element concentrations can be observed when comparing the PPA to the PPS. Nevertheless, all heavy metal concentrations were clearly below the average of heavy metal concentrations in sewage sludge in the European Union. This indicates that PP is a valid method to prevent heavy metals to accumulate in sewage sludge hence easing the development of recovery processes for phosphorus.

The leaching efficiency was discovered to increase when PPA was used as raw material instead of PPS. With Al-PPS and PPA, this resulted in a leaching efficiency of 84.0 ± 1.1 % and 99.5 ± 0.7 %, respectively. However, the concentrations in leach solution after leaching of Fe-PPS or PPA are significantly higher but the efficiency is lower, resulting in a leaching efficiency of 45 ± 4 % for Fe-PPS and 68.0 ± 1.1 % for Fe-PPA. Because of the predominant compound of the Fe in the leaching solution is $FeH_2PO_4^{2+}$ other purification methods than solvent extraction needs to be studied for leach solution produced from Fe-PPA. With both sludge types incineration yields high P recovery, 94 ± 3 %, and 96 ± 5 % for Al-PPA and Fe-

PPA, respectively. Hence, it can be concluded that incineration is a viable pretreatment method before leaching with dilute H_3PO_4. In further work the purification method for separation of P and Al/Fe in investigated. The choice of purification method will greatly influence the overall recovery value of P.

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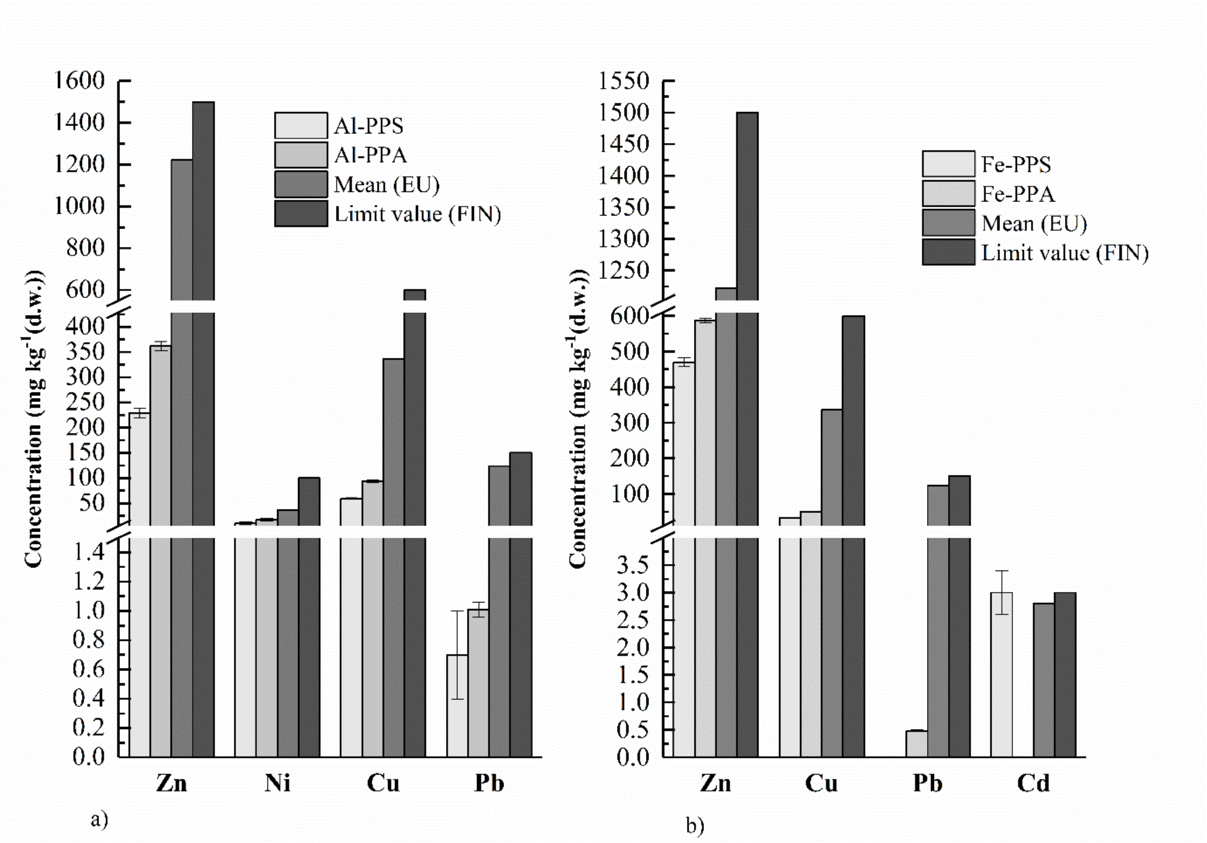

Figure 1. Heavy metal concentrations for PPS and PPA (mean ± standard error of the mean (s.e.m)), average EU concentrations and sludge limit values for agricultural use in Finland, a) Al-PPS and Al-PPA, b) Fe-PPS and Fe-PPA

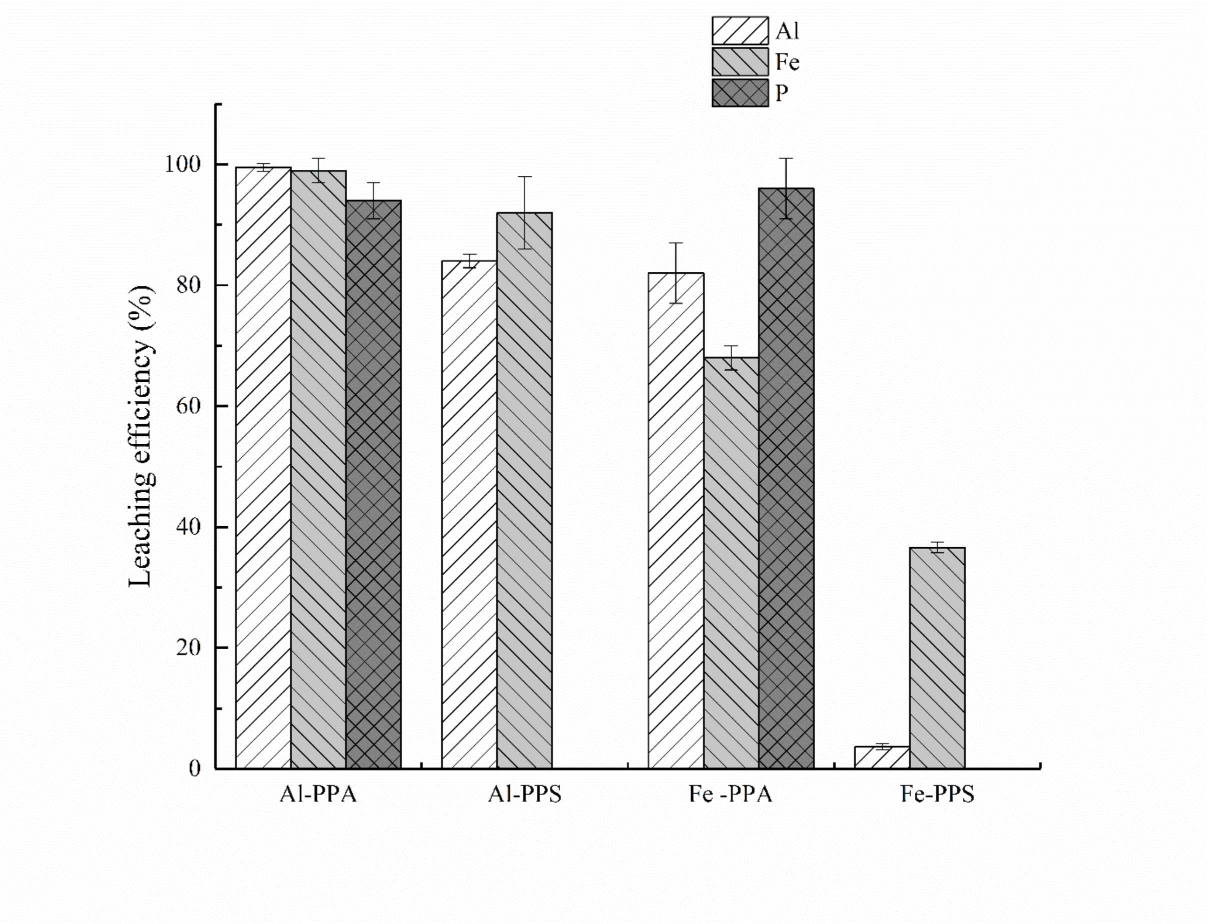

Figure 2. Leaching efficiency of Al, Fe, and P after leaching Al-PPS/PPA and Fe-PPS/PPA with dilute phosphoric acid (n=3, mean ± s.d.).

Table 1. Major and heavy metal concentrations of PPS and PPA (mean ± standard error of the mean (s.e.m)) determined with ICP-OES/MS. Sample size: n(Al/Fe-PPS)=6, n(Fe-PPA)= 5 and n(Al-PPA)=9. Elemental concentrations of waste activated sludge (WAS) and ISSA incinerated at 600 °C determined by Liang et al. (2019).

			Al		Fe		Liang et al. 2019	
			PPS	PPA	PPS	PPA	WAS	ISSA
	Unit	n	6	9	6	5		
Al	(w-%)		18.3 ± 0.3	29.1 ± 0.3	0.221 ± 0.01	0.351 ± 0.009	5.43 ± 0.03	10.97 ± 0.02
Ca	(w-%)		1.14 ± 0.01	1.53 ± 0.03	1.97 ± 0.02	2.39 ± 0.02	1.69 ± 0.05	3.19 ± 0.05
Fe	(w-%)		1.03 ± 0.01	1.62 ± 0.02	36.8 ± 0.2	43.5 ± 0.4	2.64 ± 0.09	5.14 ± 0.06
Mg	(w-%)		0.075 ± 0.002	0.114 ± 0.01	—	0.144 ± 0.002	0.67 ± 0.03	1.3 ± 0.02
P	(w-%)		10.0 ± 0.2	14.85 ± 0.15	8.1 ± 0.08	9.52 ± 0.12	2.84 ± 0.09	5.5 ± 0.07
Cu	(mg kg^{-1})		52.6 ± 0.8	85 ± 3	37.7 ± 0.9	49.8 ± 0.5[a]	90 ± 1	423 ± 10
Zn	(mg kg^{-1})		219 ± 4	360 ± 7	470 ± 13	587 ± 7[a]	225 ± 12	895 ± 49
Sn	(mg kg^{-1})		1.87 ± 0.09	3.1 ± 0.2	1.512 ± 0.014	1.79 ± 0.03[a]	nd[b]	nd
Pb	(mg kg^{-1})		0.66 ± 0.04	1.01 ± 0.05	—	0.481 ± 0.015[a]	nd	460 ± 5
Ni	(mg kg^{-1})		10.6 ± 0.6	18 ± 3	—	—	nd	209 ± 1
Sb	(mg kg^{-1})		—	—	1.09 ± 0.04	1.31 ± 0.02[a]	nd	nd
Cd	(mg kg^{-1})		—	—	3 ± 0.4	—	nd	126 ± 3

— Below LOQ/MDL; [a] n= 6; [b]not detected

Table 2. The determined concentrations of Al, Fe, and P (mean ± s.d, n= 3.) from the leachate, when the leaching solution is 0.5 M H_3PO_4 for Al-PPS/PPA and 2 M H_3PO_4 for Fe-PPS/PPA.

	Al		Fe	
	PPS	PPA	PPS	PPA
Al (g L^{-1})	2.46 ± 0.05	4.60 ± 0.03	0.08 ± 0.01	0.40 ± 0.05
Fe (g L^{-1})	0.151 ± 0.008	0.25 ± 0.1	16.4 ± 0.3	36 ± 2
P[a] (g L^{-1})	—	2.24 ± 0.03	—	11.1 ± 0.6
$pH_{after\ leaching}$	1.5	1.9	1.6	1.2

[a] P concentration determined by subtracting the theoretical P concentration of H_3PO_4 from the measured value.

Table 3. Student's t-test values for Fe-PPS/PPA and Al-PPS/PPA to determine if there is a statistically significant difference between the metal concentration in leach solution after leaching with either PPA or PPS

	Fe		**Al**	
	PPA	PPS	PPA	PPS
Mean	67.963	36.634	99.547	84.653
Variance	9.588	0.807	0.460	1.128
Observations	3	3	4	3
Pooled Variance	5.197		0.73	
Hypothesized Mean Difference	0		0	
df	4		5	
t_{Stat}	16.831		22.873	
P one-tail	< 0.0001		< 0.0001	
$t_{Critical}$ one-tail	2.132		2.015	