Recovery of phosphorus from incinerated sewage sludge ash by combined two-step extraction and selective precipitation

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Abstract:

The recovery of phosphorus (P) from acid extracts of incinerated sewage sludge ash (ISSA) is invariably complicated by the co-dissolution of metal(loid)s. An extra purification treatment step is thus needed, which reduces the efficiency of P recovery. This study developed a two-step extraction method which can produce highly purified P-extract where ISSA is treated first with ethylenediaminetetraacetatic acid (EDTA) and then with sulphuric acid. The recovery conditions of this two-step extraction method were optimized (pre-extraction by 0.02 mol/L of EDTA at a liquid to solid ratio (L/Kg) of 20:1 during 120 min, then extraction by 0.2 mol/L sulphuric and at a liquid to solid ratio of 20:1 during 120 min). Compared with direct extraction by sulphuric acid (namely, single-step leaching), the two-step extraction method dissolved 2.34 mmol/kg ISSA less of P, but with 5.16 mmol/kg ISSA less of

metal(loid) contamination.

Furthermore, the potential for co-precipitation of P and the metal(loid) contaminates in the extracts (both single-step extraction and the two-step extraction methods) was examined from pH 2 to 12 (adjusted by addition of NaOH and $Ca(OH)_2$). By applying $Ca(OH)_2$ and at the optimal pH of 4, the two-step extraction method could significantly increase Ca-P in the precipitate and notably decreased the metal(loid) contaminants by 50% compared to the single-step method.

Key words: phosphorus recovery, wet-extraction, pH adjusting, incinerated sewage sludge ash, two step extraction.

1. Introduction

The exhaustion of limited natural phosphate rock resources and the one-way flux of phosphate rock from highly concentrated ores to diffuse low level concentrations in the environment stimulate the motivation of recycling P from waste streams and convert a linear consumption of P resources into a partially circular consumption model. Current worldwide available phosphate ore reserves are predicted to be depleted within the next 50-100 years [1-3] while Chinese phosphate ore might be exhausted within 37 years [4]. After mining, only 10% of P is consumed by human activities [5], and then the consumed-P and waste-P are disposed as waste streams [6]. If properly collected, these P-wastes typically end up in the sewage of waste-water treatment plants, where the vast majority of P is removed in the sewage sludge [7]. Although land-spreading remains the dominant form of sewage sludge disposal, during the last 20 years there has been a trend at a global level away from landfilling and sea disposal towards incineration of sewage sludge [8]. Incineration is especially attractive in densely-populated regions and effectively reduces the volume of waste, eliminates odour problems, produces a sterile ash and allows for potential energy recovery from the organic solids in the sludge [9, 10]. Almost all of the P in sewage sludge remains in the inorganic fly ash produced by sewage sludge incineration [3, 11,

12].

Incinerated sewage sludge ash (ISSA) consists of small glassy particles partially sintered together into irregularly shaped porous agglomerates containing Fe, Al, Si and P [13, 14]. The P is preferentially deposited on the surface of particles, thus facilitating ease of recovery [5, 10, 15]. The main crystalline phases containing P in ISSA are whitlockite, beta-tricalcium phosphate mineral and $AlPO_4$ [5, 16, 17]. However, the presence of Mg and Fe can also influence the type of P phases formed.

According to previous studies, either thermal treatment or wet-extraction is used to recover P from ISSA [10, 18, 19]. Thermal methods have limitations due to high energy consumption and unsatisfactory removal results for non-volatile metals (Ni, As, Mo, etc) [20]. Wet-extraction is more common and mineral acids have been shown to be the best recovery agents because they readily dissolve P but the co-dissolution of metal(loid)s is a problem [10] . However, alkaline solutions induce a low P solubility although the co-dissolution of metal(loid)s is also low [20-24]. The presence of metals such as Zn, Cd, Mg and Pb, reduce the quality of phosphate fertilizer [25]. Efforts to eliminate these metal(loid)s have included adsorption by organic and inorganic media (activated carbon, biochar, modified silicate, etc.) [26-29], cation-exchange resins [3], solvent extraction [10] and ion migration in electric fields [30].

Each purification method has specific limitations. For example, removal efficiencies by cation adsorption in a highly acidic solution are impeded by the high concentration of H^+ ions. Organic solvent extraction is not sufficiently efficient and also requires an additional step for P extraction from the solvent and solvent recovery before a phosphoric acid product can be obtained [10, 23]. The removal of metal ions by direct current was found to be limited by high energy consumption and low efficiency [31, 32]. Hence, it is necessary to find new methods which can effectively extract P with high purity through a simple process route.

Our previous study has identified that ethylenediaminetetraacetatic acid (EDTA) and sulphuric acid could effectively leach metal(loid)s and P, respectively [14]. EDTA is applied mostly in soil washing and can remove metal(loid)s effectively [33-35], while sulphuric acid was found to be an optimal P extraction agent [14]. Consequently,

it makes sense to combine the properties of these two extractants in a sequential procedure.

Obtaining a solution with low concentrations of metalloids and a high concentration of P is only part of the challenge. The next step is to convert that solution in a useful P-based product. Previous studies have demonstrated that P co-precipitates with Al, Fe and Ca at pH above 4 [36, 37]. Of the three kinds of P-precipitation, only Ca-P is an effective constituent for fertilizer application and therefore significant efforts have been made to recover Ca-P directly or produce it from other P-phases. However, direct recovering of Ca-P has low efficiency while the complex transforming process would result in P loss [36, 37].

Consequently, this study has assessed the feasibility and efficiency of generating a solid CaP-based product by pH adjustment (by addition of NaOH or $Ca(OH)_2$) of the less contaminated solution obtained from the two-step extraction procedure. The overall aim of the research is to develop a commercially viable process for extrcating P from sewage sludge ash so that P can become part of a circular economy.

2. Materials and methods

The ISSA used in this study was from the Sludge Treatment Facility (T-park) in Hong Kong and it has been characterised in previous studies [14, 15]. The H_2SO_4 (AR, 98%) and EDTA (ACS, 99.5%) were supplied by RCI Labscan limited and Anaqur Chemicals, respectively.

2.1 Extraction process by two-step and single-step methods

The optimized conditions for metal(loid)s removal and P extraction using only EDTA or only sulphuric acid have been investigated in our previous study [14]. However, when considering these extractions in sequence, it is evident that the first step with EDTA influences the mobility of heavy metals in the solids that are fed to the second step [38, 39]. It therefore becomes necessary to reoptimize the conditions for both steps, with the aim of achieving the highest P recovery with the lowest

metal(loid) impurities.

The two-step extraction method is illustrated in Fig. 1. The variables of the EDTA (1st step) single-factor optimization conditions are shown in Table 1, which includes concentration, liquid to solid ratio and reaction time. For extraction experiments, 1.0 g of dried and homogenized ISSA was weighed ($\pm$0.005) and transferred into a 50 ml centrifuge tube. The EDTA reagent (concentration and volume according to Table 1) was added, and the tube placed on an end-over-end mechanical rotator at 30 rpm for continuous mixing (contact times are given in Table 1). After the EDTA extraction, the mixture was centrifuged at 4000 rpm for 10 minutes. The supernatant was withdrawn, filtered using a 0.45-µm mixed cellulose ester membrane filter paper and analysed for metal(loids) by inductively coupled plasma optical emission spectroscopy (ICP-OES, SPECTROBLUE FMX 36) and for P by colorimetry after molybdenum blue complex formation. Prior to the second step, the solid residues were washed with deionized water to remove excess EDTA and then dried at 105 °C overnight.

The second step involved adding sulphuric acid under the optimized conditions (0.2 mol/L, 2 hours, 20:1 of liquid to solid ratio) as identified in a previous research [14]. For comparison, a single step extraction was also carried out, also using 0.2 mol/L H_2SO_4, 2 hours contact time and liquid to solid ratio of 20:1. All the tests were carried out in triplicate and the average results were reported, and the error bars in the respective figures indicate the standard deviations.

The extracted mass of P and metal(loid)s were calculated using the equation:

$$\text{Extracted mass (mg} \cdot g^{-1}) = \frac{c \times T \times V}{M_0} \tag{1}$$

Where, c is the concentration of the metal(loid)s or P in mg/L, *(c)*; T is the dilution factor; V is the volume of extract, *(L)*; and M_0 is the mass of the ISSA before processing, *(g)*.

2.2 pH adjustment for obtaining the P-precipitates

Final extracts were subjected to pH adjustments in order to precipitate P from

solution. A 40 ml aliquot of the extract was added to a beaker with a magnetic stirrer and continuously mixed. The pH was increased incrementally by addition of NaOH or $Ca(OH)_2$ while a pH electrode was used to continuously monitor the pH. When the target pH was reached, the resulting suspension was centrifuged at 4000 rpm for 10 minutes. The supernatant was filtered through a 0.45-µm mixed cellulose ester membrane filter and tested for P and metal(loid)s. The remaining precipitate was dried at 105 °C overnight prior to further analysis.

2.3 P-precipitate analysis

The crystalline-phases in the dried and milled precipitate were analysed by X-ray diffraction (XRD, Rigaku Smartlab, Japan). The CuKα radiation (λ= 1.54059 Å) at 40 kV and 30 mA was used for scanning. Peaks were identified in the range from 5 to 70° 2θ with a scanning increment of 0.02° and a counting time of 2 seconds per step. For qualitative analysis, the Rigaku XRD software (PDXL) was applied for Rietveld refinement phase verification. The elemental composition of the precipitates were analyzed by X-ray fluorescence (XRF, Rigaku Supermini 200). The micro-morphology of the precipitate was observed using scanning electron microscopy (Tescan-vega3) with energy dispersive X-ray spectroscopy (SEM-EDX).

3. Results and discussion

3.1 Optimization of two-step extraction conditions

3.1.1 P extraction

A limited fraction of P in the ISSA can be extracted by EDTA and the majority of the P was extracted by sulphuric acid. Both the extracted mass of P in the 1st step (EDTA pre-treatment) and the 2nd step (sulphuric acid extraction) are shown in the first row of Fig. 2. The mass of extracted P by the single-step extraction is shown in the right column for reference. Besides the low pH of EDTA solution triggered the solubility of P, the EDTA was found to be able to release P by breaking the ligands of Ca-P to form EDTA-Ca (Eq. (2) and (3)) [40].

$$H_4EDTA \leftrightarrow 4H^+ + EDTA^{4-} \tag{2}$$

$$M^{2+} + EDTA^{4-} \leftrightarrow M - EDTA^{2-} \tag{3}$$

$$M^{3+} + EDTA^{4-} \leftrightarrow M - EDTA^- \tag{4}$$

The results in Fig. 2. show that an increase in EDTA concentration (0.01 to 0.05 mol/L) or in liquid to solid ratio (from 5:1 to 40:1) considerably increased undesirable P extraction in the 1st step, resulting in an inevitable decrease in the quantity of P extracted in the 2nd step. Increasing the EDTA concentration or liquid to solid ratio would decrease the molar ratio of P:EDTA significantly in the extracts (by about 20%) over the ranges studied as shown in (Fig. S1) in the supporting information. The molar ratio of P:EDTA was increasing up to 120 minutes but then became constant. For a given quantity of EDTA used, the P recovery in the 2nd step gradually decreased as reaction time increased. To ensure recovery of P > 70% in the 2nd step, the concentration of EDTA in the 1st step should not be higher than 0.02 mol/L and the L/S ratio no higher than 20:1. Lowering the L/S ratio and reducing the reaction time of the 1st step improved P recovery in the 2nd step. However, the optimum conditions must be based on minimizing the co-dissolution of metal(loid)s in the 2nd step.

3.1.2 Co-dissolution of major metal(loid)s

Any soluble metal(loid)s in the ISSA forming multi-valent cations can potentially compete for the complexing sites on EDTA (see Eq. (3) and (4)) and the metal(loid)s removal in the 1st and 2nd step of the two-step extraction method shown in Fig. 2. Additionally, free H^+ from EDTA (see Eq. (1)) would also enhance the dissolution of metal(loid)s by attacking alkaline oxides because the ISSA used in this research was slightly alkaline [14]. If not removed previously, metal(loid)s such as Al, Cu, Fe and Zn can co-precipitate with P when the pH is raised, reducing the purity and potential commercial value of the P precipitate.

These metal(loid)s can be easily dissolved by acids or chelates [15, 41], while the effect of chelates was mainly related to the dissolution of metallic carbonates or sulfides by the chelating effect [42]. When using EDTA to remove undesirable impurities, it is necessary to consider (i) the molar ratios of impurities:EDTA present

in ISSA, (ii) the potential solubilities of these impurities in the pH range studied and (iii) different affinities (chelating coefficients) of different impurities for chelation by EDTA. Due to the importance in analytical chemistry, the relative stabilities of different metal cation-EDTA complexes (under standard conditions) are well known. The general order of preference for the most relevant leachable cations from ISSA is $Fe^{3+}/Fe^{2+}/Mn^{3+} > Cu^{2+}/Ni^{2+}/Pb^{2+} > Zn^{2+}/Al^{3+} >> Ca^{2+} > Mg^{2+} >>> Na^{+} > K^{+}$. Kim and Ong [43] used the much greater affinity of Fe^{3+} than Pb^{2+} to effectively recycle EDTA used to treat Pb contaminated wastewaters. In researches with contaminated soils, the Pb^{2+} removal by EDTA was strongly influenced by pH of solution [44]. Finzgar and Lestan [33] found that Pb^{2+} removal was generally more efficient than Zn^{2+} but that further increases in removal efficiency were hampered by the presence of Fe cations. Similar results were found by Sawai et al. [45] that, under acidic conditions, even though the apparent stability constant of Cu-EDTA was greater than that of the corresponding Zn complex under the same pH conditions, the Zn-EDTA was dominant. In order to ensure the cost-effective use of EDTA, it is important to assess the efficacy of metal(loid) removal under different conditions.

Although (Fig. S1) shows that decreasing the molar ratio of metal(loid):EDTA (either by increasing the EDTA concentration or the L/S ratio at a fixed concentration) had a direct benefit on the removal efficiencies of Al, Cu, Fe and Zn, it was also clear that this came at the cost of undesirable co-dissolution of P in 1st step. In the EDTA concentration ranges studied, the extraction rate of Fe, Cu and Zn fell significantly between 0.01 and 0.02 mol/L indicating the highest efficiency can be obtained using 0.02 mol/L EDTA. Al extraction rate remained constant after 0.02 mol/L EDTA. In considering P extraction, higher concentration has lower removal efficiency while the range of 0.01 to 0.02 mol/L is associated with a decrease in efficiency. The optimal concentration was selected as 0.02 mol/L. Similarly, increasing the volume of EDTA induces more metal(loid)s dissolution resulting in more impurities in the final extract. However, the extraction efficiency of EDTA falls with increased volume applied. Considering that the higher L/S ratio was unfavorable for P recovery nor practical, a L/S of 20:1 was selected as the optimized for EDTA pretreatment. The reaction time

study indicated that taking the balance of P and metal(loid) extraction, the optimal contact time was 120 min. Additionally, residue EDTA in the second step is favorable to purity, the washing by dionized water after 1st in the applied two-step extraction method would be removed in future application.

3.2. Comparison of two-step extraction and single-step extraction

The final extract of the two-step method and the only extract of the single-step method were analyzed respectively under optimized reaction conditions and the results are shown in Fig. 3. According to the total digestion results from previous studies on raw ISSA [14], the extracted mass ratios of major elements are shown in Table 2.

Of the 11 metal(loid)s studied, the two-step method, with the notable exception of Ca, effectively decreased concentrations in the final extracts when compared with the single-step method. The unusual results for Ca can be at least partially attributed to the lower stability of Ca-EDTA complex compared with other EDTA complexes such as Fe^{3+}, Cu^{2+}, Zn^{2+} and Al^{3+}. This effect would explain why Ca is not so effectively removed during the first step. However, the same effect does seem to apply to Mg^{2+}, which could be expected to have an even lower stability than Ca^{2+} in EDTA complexes, yet the two step process succeeded in reducing Mg^{2+} levels in the final extract but not Ca^{2+}. The basic observation is that EDTA has a direct or indirect effect on the (sulphuric) acid solubility of Ca. One logical explanation would be that the residual EDTA from the first step is still present on the surface of dried ISSA particles when they are used in the second step. This residual EDTA then inhibits the formation of gypsum precipitates (from reaction with SO_4^{2-} ions from sulphuric acid) allowing Ca to remain in solution as Ca-EDTA complexes. This results in the higher concentration of soluble Ca when compared to the single step, where no EDTA residues are present and gypsum precipitation is uninhibited.

The presence of metal(loid)s in fertilizers is legally restricted in most countries [46]. In this context, the decreases in Cr (92%), Zn (58%), Cu (49%) and Al (38%) shown in Table 2 are especially helpful in ensuring that the extractant can be used to

generate a fertilizer with low problematic impurities. Arguably of greatest concern is the content of Al due to its proven effects on plant toxicity in acidic soils. The decrease in Mn (50%), Mg (49%) and Fe (23%) are of benefit in terms of permitting a much purer phosphate product to be produced (either as fertilizer or an intermediate for further processing). Interestingly, the EDTA pre-treatment did not significantly affect the extractability of Pb (3%), Ni (1%) or As (1%). The most probable explanation for this observation is that these metals are present only in non-soluble forms in ISSA particles, where they may be immobilized in a glassy matrix.

Overall, by using the two-step method, the purity of the final extracts can be improved. To be specific, 5.16 mmol/kg ISSA of metal(loid)s was removed, although 2.34 mmol/kg ISSA of P was lost at the same time, when compared to the single-step method. These results indicated that the two-step method can produce an extract with a higher application value.

3.3 Precipitation of metals and phosphates by pH adjustment

As the pH of the acidic extract is increased, it causes precipitation of different phosphate, silicate, sulphate and hydroxide solid-phases. The presence of Al, Ca and Fe has a string influence on phosphate precipitation [47]. Graphs of the extract concentrations of Al, Ca and Fe against pH are shown in Fig. 4 and similar plots for As, Cu, Ni and Zn are shown in Fig. 5.

3.3.1 Predicted precipitation reactions

The type of P-precipitates and saturation indexes have been simulated by MINTEQ (as shown in (Fig. S2) and (Table S1) in Supporting information) to predict the main precipitates at specific pH values following the addition of NaOH. Gypsum ($CaSO_4 \cdot 2H_2O$), strengite ($FePO_4 \cdot 2H_2O$), variscite ($AlPO_4 \cdot 2H_2O$) and hematite (Fe_2O_3) are predicted to be the main precipitates. As the pH increases, P would precipitate as predominantly Al or Fe phosphates. However, there is potential for Ca-P formation at high pH and to a much greater extent in the extract from the two-step process. Nevertheless, it is worth highlighting some of the limitations regarding values from

the MINTEQ equilibrium calculations:

(1) The input SO_4^{2-} concentration used was the concentration of extractant (sulphuric acid). However, some of this would precipitate with the metals (with Ca^{2+} $\rightarrow$ gypsum) and not be available in the aqueous phase. Thus, the concentration of SO_4^{2-} in the extract may be overestimated.

(2) Anions like SiO_2^{2-} were released from the ISSA when contacting with sulphuric acid. However, they could not be detected by the ICP and were excluded from the simulation calculation. Silicates were not the focus of this study.

(3) Although the residues were washed using deionized water twice prior to the 2nd step, some EDTA might still be adsorbed onto the residues of the 1st step and these EDTA residues would affect the equilibrium to some extent.

3.3.2 Experimental observations after pH adjustment with NaOH

Fig. 4a shows that only a negligible decrease in Al and P concentrations was observed between pH 1.0 and 2.6. A significant decrease in soluble Al and P began when the pH increased from 2.6 to 3.2 and most of the Al and virtually all of the P had precipitated by pH 4.4, suggesting precipitation of Al-P [37, 47]. In contrast, more than half of the soluble Fe precipitated before pH 2.6, suggesting it was not related to phosphate precipitation as strengite ($FePO_4 \cdot 2H_2O$) but to formation of Goethite (FeO(OH) or hematite (Fe_2O_3). By pH 4.4, almost all Fe had precipitated, which could be due to any combination of these phases because P also begins to precipitate at that point. The possibility of the formation of significant quantities of Ca-P below pH 4.9 is unlikely due to absence of any significant decreases in Ca present in the soluble phase. The same behavior was noted with both extracts (Fig. 4a, b). However, two slight differences are that (i) Fe precipitation was never completed at any pH of the two-step extract and (ii) there was a slight lag in P precipitation after Al precipitation. The first difference could be directly attributed to the continued presence of residual EDTA in the two-step extract, while the second difference could possibly be explained by the increased possibility of Ca (more present) and Fe (more

still available in solution at pH 3.2-4.4) contributing to initial P precipitation. It is interesting to note that in (Fig. 4a, b) P resolubilises at some point between pH 6.5 and 12.8 and that this coincides with almost complete precipitation of Ca. This observation can be explained by the excess OH^- ions from NaOH forming insoluble Ca, Al and Fe hydroxide precipitates and the Na^+ from NaOH forming soluble Na_3PO_4. Changing the alkali from NaOH to $Ca(OH)_2$ prevents this resolubilisation regardless of whether the extract was from the single-step of two-step process (i.e. comparing Fig. 4a with 4c and comparing Fig. 4b with 4d).

The variation in As, Cu, Ni and Zn concentrations with pH adjustment for the single-step and two-step extracts by adding NaOH are shown in the (Fig. 5a) and (Fig. 5b) respectively. The behaviour of Ni and As were relatively consistent in both the single-step and two-step extracts, except for the redissolution of As noted for the single-step extract at pH 11.0. No such behavior was noted in the two-step extract, even when the pH rose to 12.2. The main difference in the two extracts was the behavior of Zn and Cu. In the single-step extract, virtually all Zn and Cu precipitated between pH 2.4 and 5.2 which coincides with P precipitation. However, with the two-step extract, only very limited precipitation of Zn and negligible precipitation of Cu occurred across the entire pH range. The most logical explanation for such a difference must be linked to the continued presence of residual EDTA in the two-step extract. Additionally, the stability constants of metal-EDTA varied with the solution pH, which can be confirmed by a the previous research result that Cu-EDTA complexes was a more dominant species than Zn-EDTA in the alkaline pH region [45]. This is an advantage for the two-step process because it means that incorporation of Cu and Zn into the P-precipitate by isomorphic substitution is greatly reduced [48].

3.3.3 Experimental observations after pH adjustment with $Ca(OH)_2$

To study the feasibility of improving the formation of Ca-P, and minimise the formation of Al-P and Fe-P, $Ca(OH)_2$ was used for pH adjustment of the extracts produced by the two extraction methods and the results are shown in Fig. 4 and Fig. 5.

The close correlation between Al and P precipitation observed in (Fig. 4a) (for

the single-step, NaOH addition) was affected by using the two-step process (i.e. compare to Fig. 4c) and the use of both the two-step process and Ca(OH)$_2$ addition instead of NaOH (i.e. compare to Fig. 4d). Changing to Ca(OH)$_2$ for the single-step extract (Fig. 4c) delayed both the precipitation of Fe and Al with respect to P precipitation. This implies that Ca had a greater, if still relatively minor role in P precipitation, than when NaOH was used.

When considering the two-step extract (Fig. 4d), there is a clear break between Al and Fe precipitation which occurs mostly between pH 1.0 and 3.2, and P precipitation which occurs mostly between pH 3.2 and 3.9. Consequently, the use of Ca(OH)$_2$ with the two-step extract appears to facilitate the production of much purer Ca-P precipitate than with the single-step extract if the pH can be carefully controlled between pH 1.0 and 5.0. Looking at the effect of pH adjustment with Ca(OH)$_2$ on the precipitation behavior of heavy metals, Fig. 5 shows that there was no major effect caused by this change with single-step extracts (i.e. compare Figs. 5a and 5c). With two-step extracts, the major difference was the ability for Ca(OH)$_2$ to precipitate Zn and Cu between pH 6.3 and 9.3. Following on from the previous explanations in this paper, this effect would mean that Ca(OH)$_2$ was somehow able to successfully compete with residual EDTA for the Zn and Cu (i.e. with excess Ca^{2+} ions). Once released, from the EDTA complex, the Zn and Cu precipitates as insoluble hydroxides. This explanation is further supported by the fact that Na$^+$ ions from NaOH have an extremely low affinity for EDTA and, even when present in excess, are unable to compete with Zn and Cu for active sites in EDTA complexes. Precipitation of Zn and Cu should not be a concern for contamination of the Ca-P preciptate because the heavy metals only precipitate above pH 6.3 while all the P will have been recovered below pH 5.0.

3.4 Identification of crystalline phases in P precipitates

The crystalline components of four different precipitates (formed by addition NaOH or Ca(OH)$_2$ to raise the pH of extracts of the single-step and the optimized two-step method) were determined by XRD (Fig. 6). No metal(loid) based crystalline

phases were present in sufficient quantities to be detected by XRD. However, XRF results (expressed as oxides in Table 3) showed consistently detectable levels of Zn and Cu. The precipitates of the two-step method by adding $Ca(OH)_2$ (2-Ca) and the single-step method by adding NaOH (1-Na) were analyzed by SEM-EDX as shown in Fig. 7.

The XRD results show that the main crystalline phases in the precipitates were $Ca_3(PO_4)_2$, $AlPO_4$, $FePO_4$, $MgSiO_4$, gypsum ($CaSO_4$) and kaolinite ($Al_2Si_2O_5(OH)_4$). The peaks of Ca-P were enhanced in 2-Na, 2-Ca and 1-Ca, whereas the peaks of Al-P were reduced in 2-Ca and 2-Na. This indicates that both the two-step method and pH adjusting by $Ca(OH)_2$ could increase the Ca-P formation while the formation of Al-P was averted. The formation of Fe-P precipitate could not be avoided by adding $Ca(OH)_2$ but the peaks were reduced, either due to reduced crystallinity or reduced formation.

The XRF results show that the molar ratio variation of P/Al was related to different P-precipitates. The precipitates from the single-step method using NaOH adjustment had a P/Al of 0.796, while that produced by the two-step method under the same condition was 0.943. This indicates that the two-step method was beneficial to P-precipitation. When using $Ca(OH)_2$, a large amount of $CaSO_4$ was formed which decreased the mass ratio of other components. For the extract of the single-step method, the P/Al was also decreased from 0.804 to 0.796, but it was increased from 0.891 to 0.943 for the two-step method. These observations indicate that the precipitates of the two-step method formed by adding $Ca(OH)_2$ had the highest efficiency of P-recovery.

SEM-EDX was completed on the precipitate of the two-step method formed by adding $Ca(OH)_2$ (precipitate 1) and the single-step method (precipitate 2) formed by adding NaOH (Fig. 7). For precipitate 1, large crystals of $CaSO_4$ were observed (chemical compositions detected by EDX). Discrete smaller particles were Ca-P precipitates according to EDX data. For precipitate 2, there were many agglomerates and small irregular particles. EDX verified these were a combination of Al-P with other metal(loid)s.

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The main oxide compositions of these four kinds of precipitate are shown in Table 3. The mass ratio of MgO, CuO and As_2O_3 were reduced by using the two-step method, indicating improved purity of the P-precipitate. Constituents such as TiO_2 and Y_2O_3 are effective soil restorers [49, 50], and the presence of SrO is also conducive for plant growth [50], thus they provide additional benefits of recovering P precipitates as phosphorus fertilizers. In summary, the two-step extraction method formed Ca-P with improved purity when pH adjustment used NaOH. Using $Ca(OH)_2$ instead of NaOH favours more Ca-P formation but also causes significant precipitation of gypsum. Effective plant grow components including P_2O_5, TiO_2, Y_2O_3, and SrO were enriched in the precipitate of the two-step method which is favorable for valorization of the ISSA for fertilizer applications.

3.5 Secondary environmental impact and economic costs

Recovering of P from the ISSA is increasingly attractive because of the diminishing global P researves and retrenchment of disposal costs for the ISSA. The sequential leaching by EDTA and H_2SO_4 has removed the leachable parts of the ISSA, thus the solid residues mainly consist of immobile glassy phases which pose low risk to the environment. As a result, these residues can be reused as an additive in construction materials, such as concrete, mortar and subbase. However, the liquid extract after P recycling must be treated to meet the local regulation before discharging.

For practical application of this technology, the costs mainly include consumption of EDTA and sulphuric acid. Based on the online quotations afforded by the largest regional supplier in Hong Kong [51], the costs of EDTA and sulphuric acid are approximately USD 2000/tonne and USD 390/tone, respectively. As a result, at the optimal extraction condition, the total cost is about USD 386.48/tonne ISSA. However, the recycled P-fertilizer can be sold at 600 USD/tonne and may provide greater financial return [51].

4. Conclusions

To obtain a high purity P-extract from ISSA a two-step extraction method was developed. This method sequentially leached ISSA with EDTA and then sulphuric acid. The optimal extraction condition was pre-extraction by EDTA (concentration of 0.02 M, L/S ratio of 20:1 and reaction time of 120 min), followed by P extraction with sulphuric acid (concentration of 0.2 M at a 20:1 L/S ratio with a 120-min reaction time). This decreased the final extract concentration of most metal(loids) studied. For example Cr (by 92%), Zn (by 58%), Mn (by 50%), Mg (by 49%), Cu (by 49%), Al (by 37%) and Fe (by 23%). Pre-treatment with EDTA increased the quantity of Ca in the final extract (+22%), which is explained by residual EDTA in ISSA solids restricting the formation of gypsum occurring to the same extent during the single-step extraction. The two-step method produced a precipitate with higher Ca concentration and lower concentrations of Fe and Al impurities. While this favours increased formation of Ca-P, co-precipitation of gypsum makes it difficult to draw a clear conclusion. Detectable levels of desirable minor elements for soil remediation (TiO_2, Y_2O_3 and SrO) were found only in the P-precipitate formed using the two-step method. Therefore, applying the two-step method for P recovery not only produces a P-extract with higher purity but also produce a P-precipitate which is advantageous for fertilizer applications.

Acknowledgements

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Recovery of phosphorus from incinerated sewage sludge ash by combined two-step extraction and selective precipitation

List of Table:

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Table 1 Mix design for single-factor conditions optimization of EDTA pretreatment of two-step extraction

Agents	Condition optimized	Fix quantify	Variate
1st step: EDTA	Concentration	Reaction time: 120 min, liquid to solid ratio 20:1.	0.01, 0.02, 0.03, 0.04 and 0.05 mol/L.
	Liquid to solid ratio	Reaction time: 120 min, concentration 0.02 mol/L.	Liquid to solid ratios of 5:1, 10:1, 20:1, and 40:1.
	Reaction time	Concentration: 0.02 mol/L, liquid to solid ratio 20:1.	10 min, 30 min, 60 min, 120 min, 240 min, 420 min and 1440 min.
2nd step: sulphuric acid	-	Concentration is 0.2 mol/L, 20:1 of liquid to solid ratio and 120 min of reaction time.	-

Table 2 Extracted mass ratio of major elements by single-step extraction and two-step extraction methods

Extraction mass ratio	Cr	Zn	Mn	Mg	Cu	Al	Fe	P	Pb	Ni	As	Ca
						(%)						
Single-step	1.3	32.7	16	35.4	36.1	55.0	4.8	94.0	10.3	15.4	9.8	75.2
Two-step	0.1	13.8	8	17.9	18.5	34.4	3.7	73.3	10.0	15.3	9.9	96.7
Difference	92.3	57.8	50	49.4	48.8	37.5	22.9	22.0	0.3	0.1	0.1	-22.2

Table 3 Chemical compositions of precipitates produced by changing the pH by adding NaOH and $Ca(OH)_2$ into extracts from the single-step method and the two-step method.

Compositions	Raw ISSA	1-Na	2-Na	1-Ca	2-Ca
P_2O_5	9.27	27.154	34.415	9.953	12.907
Al_2O_3	11.88	24.498	26.221	8.893	10.406
SiO_2	31.15	17.431	5.285	8.915	4.918
SO_3	4.08	13.987	19.460	25.321	32.688
Na_2O	2.42	9.484	7.534	ND	ND
Fe_2O_3	23.95	2.836	3.058	1.115	2.294
CaO	9.73	2.310	2.640	43.170	35.384
K_2O	3.50	0.992	0.760	0.377	0.556
MgO	1.66	0.574	0.264	1.905	0.542
ZnO	0.77	0.281	0.056	0.129	0.134
CuO	0.24	0.148	0.021	0.068	0.032
TiO_2	0.55	0.107	0.216	ND	ND
SrO	ND	0.035	0.037	0.038	0.101
Y_2O_3	ND	0.024	0.038	0.012	0.037
As_2O_3	ND	0.008	ND	ND	ND

Ps: '1' is short for 'single-step extraction'; '2' is short for 'two-step extraction'; 'Na' representing adjusted pH with NaOH; 'Ca' representing adjusted pH with $Ca(OH)_2$; 'ND' representing not detected.

Recovery of phosphorus from incinerated sewage sludge ash by combined two-step extraction and selective precipitation
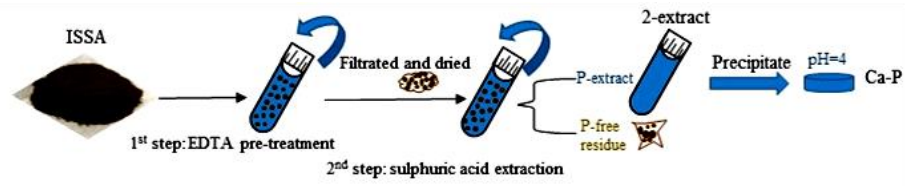
List of Figures:
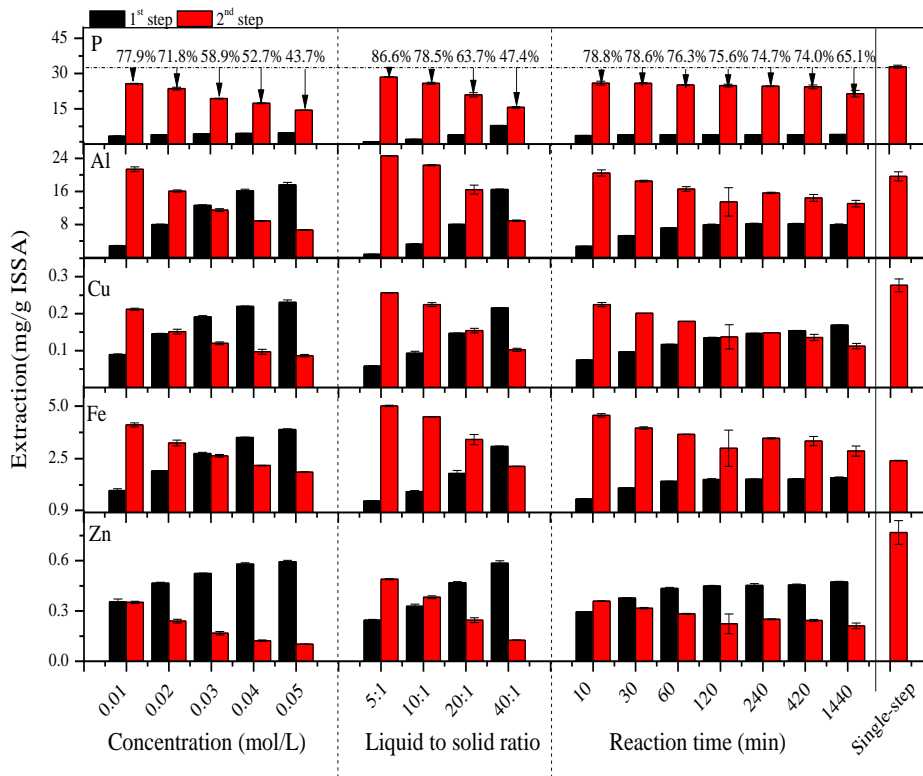
Fig. 1. Process of two-step extraction

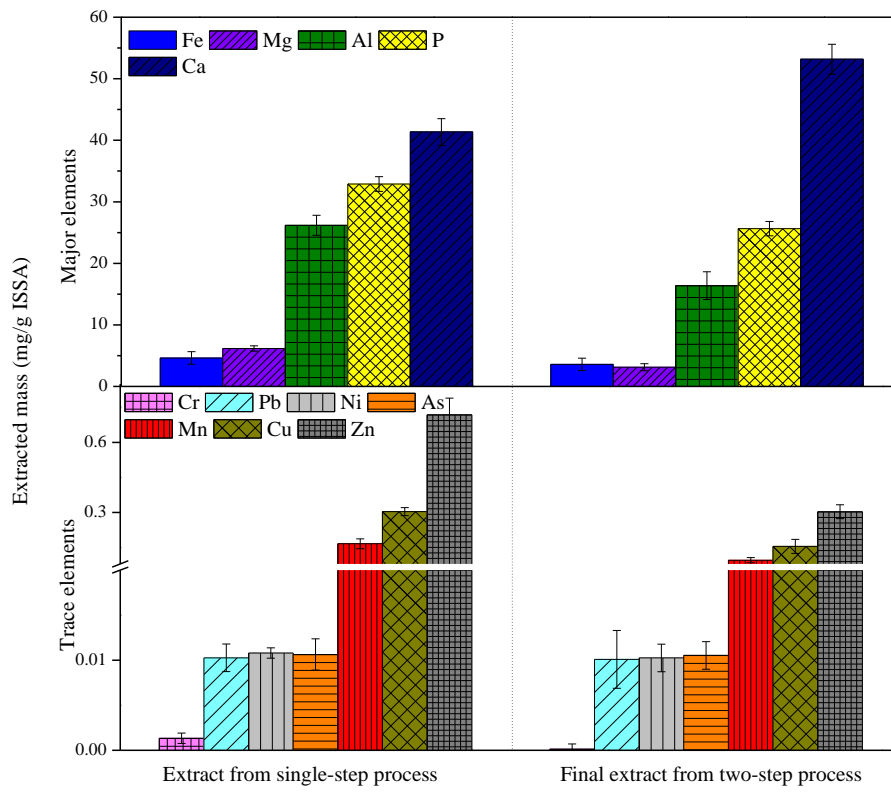**Fig. 2.** Optimization of EDTA pretreatment conditions

Fig. 3. Extracted mass of metal(loid)s and P from ISSA by two-step extraction and single-step extraction
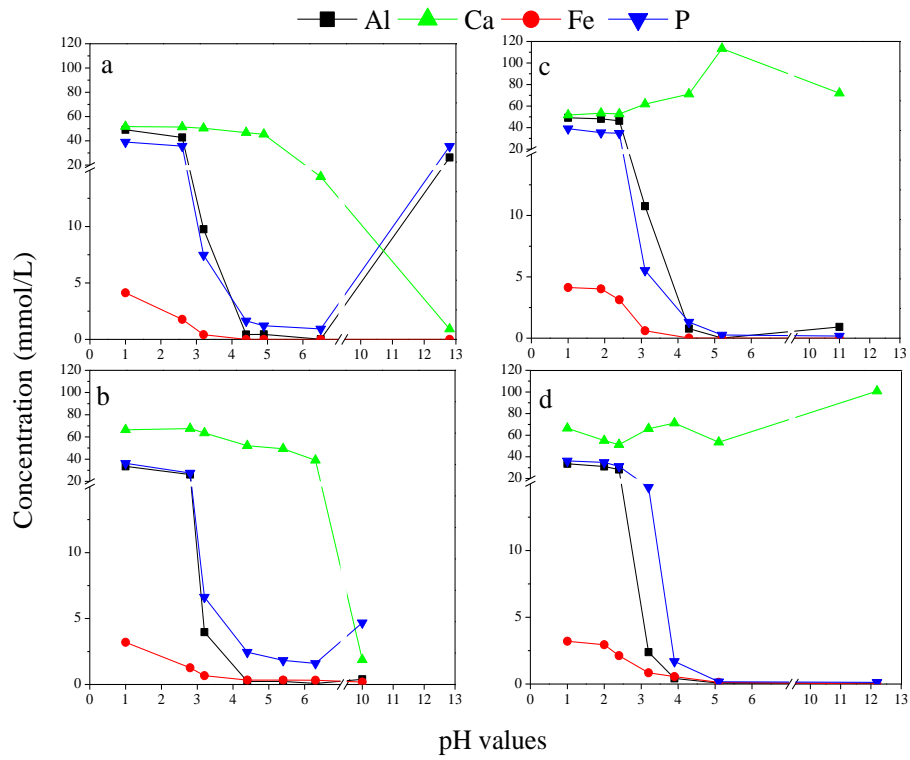
Fig. 4. Variation of main metals (Fe, Al and Ca) and P concentration in extract when pH adjusting: a. extract of single-step method by NaOH; b. extract of two-step method by NaOH; c. extract of single-step method by Ca(OH)$_2$; d. extract of two-step method by Ca(OH)$_2$.
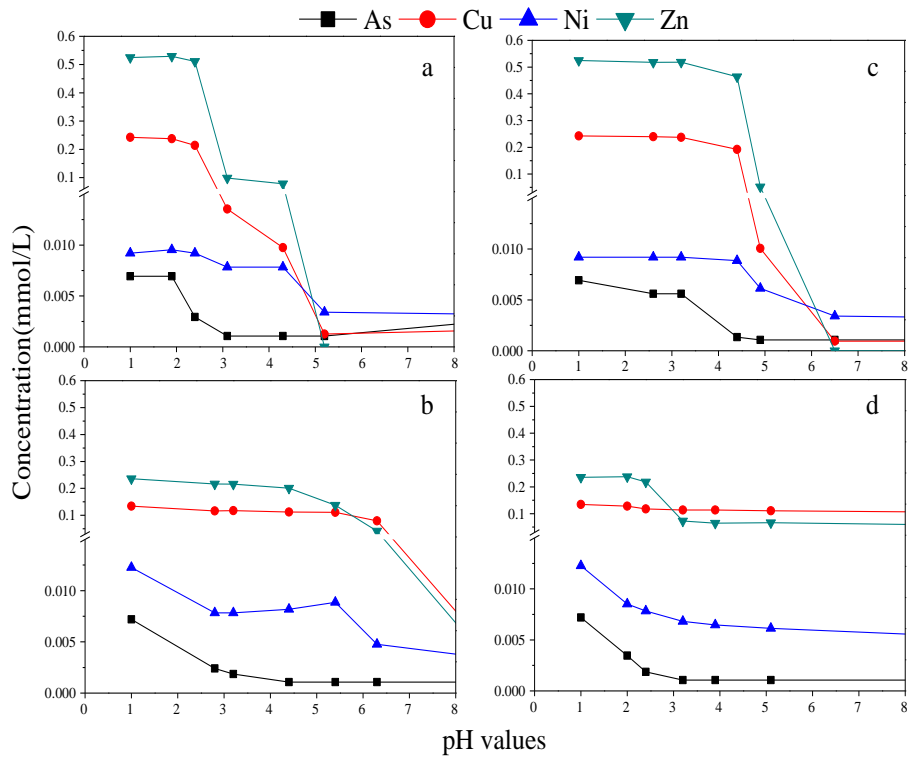
Fig. 5. Variation of trace metals (As, Cu, Ni and Zn) concentration in extract when pH adjusting: a. extract of single-step method by NaOH; b. extract of two-step method by NaOH; c. extract of single-step method by Ca(OH)$_2$; d. extract of two-step method by Ca(OH)$_2$.
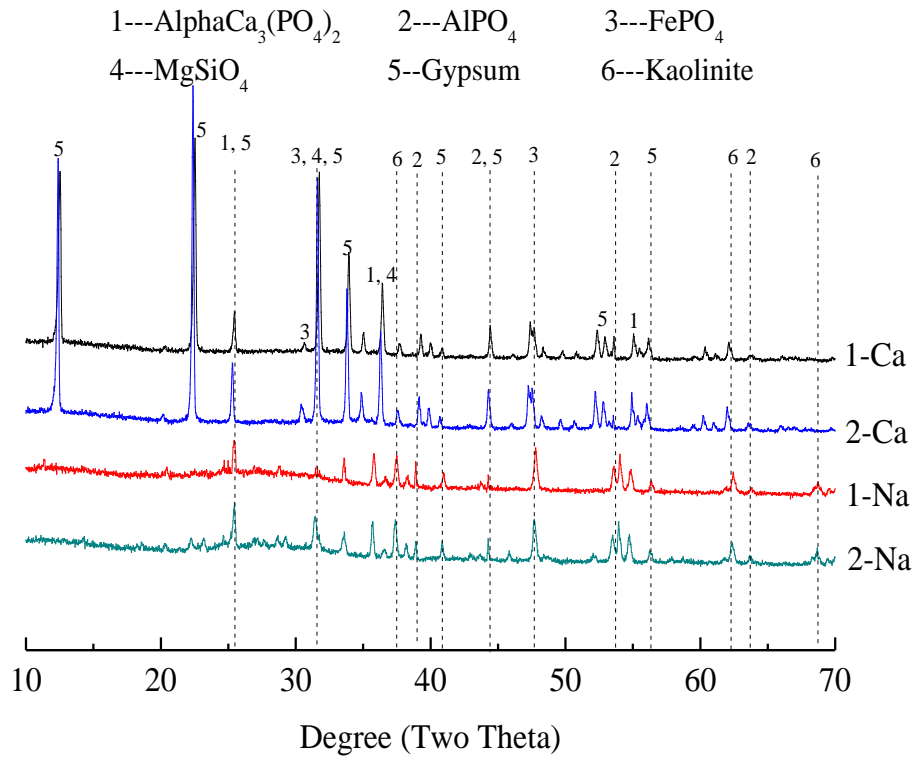
1---AlphaCa$_3$(PO$_4$)$_2$ 2---AlPO$_4$ 3---FePO$_4$
4---MgSiO$_4$ 5--Gypsum   6---Kaolinite

Degree (Two Theta)

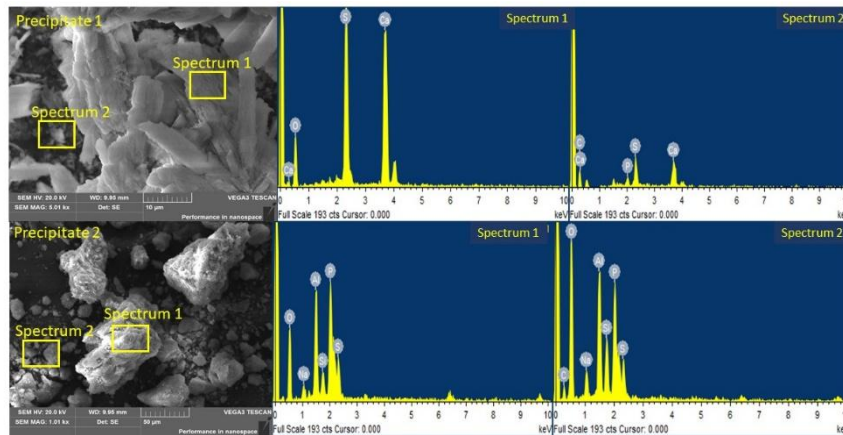**Fig. 6.** XRD patterns of P-precipitate

Fig. 7. SEM-EDX images of precipitates from extract of two-step method by adding Ca(OH)$_2$ (precipitate 1) and extract of single-step method by adding NaOH (precipitate 2) at pH 4

Supplementary Material

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