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Recovery of phosphorus as struvite from sewage sludge ash

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Abstract

Phosphorus (P) is an element vital for all living organisms, yet the world's reserves of phosphate rock are becoming depleted. This study investigated an effective P recovery method from sludge ash via struvite precipitation. Results showed that more than 95% of the total P content was extracted from sludge ash by applying 0.5 mol/L HCl at a liquid/solid ratio of 50 mL/g. Although heavy metal leaching also occurred during P extraction, cation exchange resin efficiently removed the heavy metals from the P-rich solution. Orthogonal tests showed that the optimal parameters for P precipitation as struvite would be a Mg:N:P molar ratio of 1.6:1.6:1 at pH 10.0. X-ray diffraction analysis validated the formation of struvite. Further investigations revealed that the harvested precipitate had a high struvite content (97%), high P bioavailability (94%), and low heavy metal content, which could be considered a high quality fertilizer.

Key words: phosphorus recovery; heavy metal; sewage sludge ash; struvite; X-ray diffraction

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Introduction

Phosphorus (P) is an element vital for all living organisms and cannot be replaced by other elements (Seyhan, 2009). It is estimated that 7000 million tons of phosphate rock exists as P_2O_5 in reserves that could be economically mined, and about 80% of phosphate produced is currently used for fertilizers (Shu et al., 2006). However, P is a finite resource and it is estimated that currently minable P resources (apatite) will only last another 50–100 years (Driver et al., 1999; Liu et al., 2007). Thus, it is of great importance to develop a sustainable method to recycle and conserve P from any P-rich residues.

Sewage sludge ash from incineration is characterized by a typically high P_2O_5 content of about 13.7%–25.7% (Adam et al., 2009), which can be considered a potential P resource. However, sludge ash is also inevitably enriched in heavy metals, hindering its direct utilization as P fertilizer (Adam et al., 2009; Franz, 2008). Heavy metals in sludge ash are of great concern due to their non-biodegradability, toxicity, and persistence (Chaves et al., 2009). Sewage sludge ash could be a high quality P resource, but only after the removal of heavy metals.

Some methods aimed to extract and/or recover P from sewage sludge ash have been widely reported. Hong et al. (2005) studied the effect of acid concentration on P release from ash at a set liquid/solid (L/S) ratio. Cohen (2009) investigated the effects of acid volumes and concentrations on P extraction from sewage sludge and animal carcass

ashes. Franz (2008) recovered P as fertilizer by adding lime water to precipitate calcium phosphates and other calcium compounds, while the precipitates were characterized with a low P_2O_5 content (< 40%).

Compared with traditional fertilizers, struvite ($MgNH_4PO_4 \cdot 6H_2O$) has a high P_2O_5 content (58%), and is an excellent slow release fertilizer that does not “burn” roots when over applied due to its low solubility in pH neutral solutions (Hu et al., 1996; Shu et al., 2006). Struvite use for P recovery has been applied to urine (Ronteltap et al., 2007; Wilsenach et al., 2007), wastewater (Pastor et al., 2008), and anaerobic supernatants (Moerman et al., 2009). Although struvite has been proven technically feasible and economically beneficial (Shu et al., 2006), no information is available concerning P recovery from sewage sludge ash by this method.

The present study focused on P recovery as struvite from sewage sludge ash. Effects of acid and base on P extraction were firstly compared, and the heavy metals were removed from the P-rich solution by a cation exchange resin (CER) to obtain a heavy metal free solution. The P was then recovered from the heavy metal free solution via struvite precipitation. Increasing knowledge of this issue would deepen the understanding of sewage sludge ash as a P resource, and help to develop an effective method to recover P from sewage sludge ash.

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1 Materials and methods

1.1 Sewage sludge ash samples

Dewatered sludge was sampled from two local wastewater treatment plants (WWTPs), named WWTP1 and WWTP2. The influent composition of WWTP1 consisted of 93% domestic wastewater and 7% industrial wastewater, and the WWTP2 influent consisted of 60% domestic wastewater and 40% industrial wastewater. The sewage treatment processes of WWTP1 and WWTP2 were conventional activated sludge and anaerobic-anoxic-oxic processes, respectively. The dewatered sludge was dried at 105°C for 24 hr, followed by incineration at 850°C for 4 hr at the laboratory. Afterwards, the ash was milled using a ball-mill (Retsch MM 400, Germany) and stored in a desiccator. The sewage sludge ashes obtained from WWTP1 and WWTP2 were named ash A and ash B, respectively.

1.2 Ash extraction experiment

The extraction experiments were carried out at room temperature. Before analysis, all glassware were treated in a 5% nitric acid solution for 24 hr and washed with de-ionized water. The ash samples were extracted using different types of solvents such as hydrochloric acid (HCl) and sodium hydroxide (NaOH) at varying concentrations (0.01–0.8 mol/L) and L/S ratios (25–150 mL/g). A measured amount of the ash sample (500 mg) was mixed with the solvent in a conical flask and shaken at 120 r/min for 2 hr. The slurry was then immediately filtered and analyzed for the concentrations of P and heavy metals. Factors affecting the extraction process, such as HCl and NaOH concentrations, extraction times, and L/S ratios were thoroughly examined. All measurements were carried out in duplicate and the average values were presented.

1.3 Removal of heavy metals from P-rich solution

Heavy metal leaching inevitably occurred during P extraction (Adam et al., 2009; Franz, 2008). CER 732 (Sinopharm Chemical Reagent Co., Ltd., China) was used to remove heavy metals from the P-rich solution. Different amounts of resin were added to a 25 mL solution, with L/S ratios ranging from 0.04 to 0.2 g/mL. The solution was then shaken at 200 r/min for 30 min and the heavy metal concentrations were measured before and after the application of CER to determine the removal efficiency.

1.4 Recovery of P as struvite precipitation

For struvite precipitation, magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and ammonium chloride (NH_4Cl) were used as the magnesium and nitrogen source, respectively, and pH adjustment was achieved by a 5 mol/L NaOH solution. A 3×3 orthogonal test was applied to investigate the joint effects of pH, Mg:P, and N:P on the P recovery as struvite. To further confirm the optimal parameters, a magnesium source was firstly poured into the heavy metal free solution, followed by the addition of NaOH solution for pH adjustment, and finally the nitrogen source for struvite precipitation. Afterwards, the mixture

was immediately stirred with a magnetic stirrer (85-1A, Shanghai, China) for 15 min, and the suspension was filtered to obtain the struvite precipitates.

1.5 Analytical methods

Phosphorus was determined by the molybdenum blue/stannous chloride method (Pettersson et al., 2008). Heavy metals were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-optima 2001DV, PerkinElmer, USA). Extraction efficiencies of P and heavy metals were defined as the ratios of each element's content in the extraction solvent to its original total content (Biswas et al., 2009).

The chemical composition of sludge ash was determined by X-ray fluorescence (XRF) (SRS 3400, Bruker, Germany). To check the formation of struvite crystals, the obtained precipitates were dried at 35°C for 72 hr and then analyzed by X-ray diffraction (XRD). The XRD analysis was carried out on the D/max 2550 VB3 system (Rigaku, Japan) with a Cu anode operating at 40 kV and 100 mA. Step-scanned data were collected between angles of 5°C and 90°C at a rate of 2°C/min using a computer automated diffractometer. The purity of the harvested precipitates was determined by the dissolution-precipitation method (Hao et al., 2009). The P-bioavailability was denoted by the solubility of P compounds in 2% citric acid (Gericke, 1968).

2 Results and discussion

2.1 Characterization of sludge ash

The main components of sewage sludge ash were phosphorous, silicon, iron, aluminum, and calcium (Table 1). The P_2O_5 contents of ash A and ash B were 15.2% and 27.4%, respectively, which were comparable with the results of Franz (2008) and Mattenberger et al. (2008). Notably, the higher P_2O_5 content in ash B were attributed to the higher domestic wastewater percentage (93%) in the WWTP2 influent and the efficient P removal for the anaerobic-anoxic-oxic process. Comparing with conventional P fertilizers, like single super phosphate and multi-nutrient fertilizers, which generally contain a P_2O_5 content of 18%–20% and 5%–12%, respectively, sewage sludge ash would be considered an ideal P resource for fertilizer production.

As listed in Table 1, considerable amounts of heavy metals were also contained in sewage sludge ash, such as zinc (1930–3318 mg/kg), copper (465.2–787.4 mg/kg), nickel (44.6–53.8 mg/kg), and lead (118.3–199.4 mg/kg), which partially exceed the limits of fertilizer ordinances. Therefore, heavy metals in sewage sludge ash must be removed prior to agricultural application.

2.2 Phosphorus extraction from sewage sludge ash

Acid (HCl) and base (NaOH) were used to investigate P extraction from sewage sludge ash, and the effects of L/S ratios and extraction solvent concentrations were thus studied. Sulfuric acid (H_2SO_4) was not selected as the

Table 1 Chemical composition and heavy metal contents of ash samples

Parameter	Ash A	Ash B	Adam et al., 2009	Franz, 2008	Limit value of fertilizer ordinances			
					Austria	China	Switzerland	Turkey
Na ₂ O (%)	1.52	1.51	0.30–1.12	4.80–5.50				
MgO (%)	2.72	3.94	1.79–3.63	2.30–3.10				
Al ₂ O ₃ (%)	15.1	9.89	8.9–24.9	6.50–9.10				
SiO ₂ (%)	49.1	43.1	19.6–43.4	18.2–20.0				
P ₂ O ₅ (%)	15.2	27.4	13.7–25.7	8.9–21.0				
K ₂ O (%)	2.83	3.38	0.95–2.77	0.50–0.60				
CaO (%)	7.77	10.3	12.5–18.5	22.7–22.8				
Fe ₂ O ₃ (%)	6.44	5.70	3.2–22.6	15.6–20.0				
Cd (mg/kg)	ND	ND	2.23–4.71	1.9–3.0	15	10	3	–
Pb (mg/kg)	118.3	199.4	89.9–264	109–158	100	150	200	–
Cr (mg/kg)	124	89	70.0–130	102–200	667	500	200	270
Hg (mg/kg)	0.22	0.23	0.1–0.23	–	1	5	–	–
Cu (mg/kg)	465.2	787.4	470–1267	400–625	778	–	400	–
Zn (mg/kg)	1930	3318	1540–2181	1300–1850	3333	–	1300	1100
Ni (mg/kg)	44.6	53.8	39.5–80.2	49.6–40	–	–	50	120

–: not contained.

extraction solvent in this study due to its inherently low extraction efficiency (Cohen, 2009). The extraction percentage of P increased with increasing extraction solvent concentrations and L/S ratios (Fig. 1). Specifically, P extraction at an L/S ratio of 25 mL/g and HCl concentration of 0.2 mol/L was 86%. Increasing the L/S ratio to 50 mL/g resulted in 98% P extraction, but increasing the L/S ratio beyond this amount did not significantly improve P extraction. Considering the cost-effective acid consumption and

complete P extraction, 0.2 mol/L HCl with an L/S ratio of 50 mL/g was considered the most suitable conditions for extracting ash A. Ash B had a similar extraction pattern as ash A (Fig. 2b), with the optimum conditions at 0.5 mol/L HCl and L/S ratio 50 mL/g. Most efficient extraction not occurred at higher acid concentration and L/S ratios, due to the fact that the remaining fractions not extracted may be formed as nucleation particles in the center matrix of sludge ashes (Hong et al., 2005). In addition, it should be

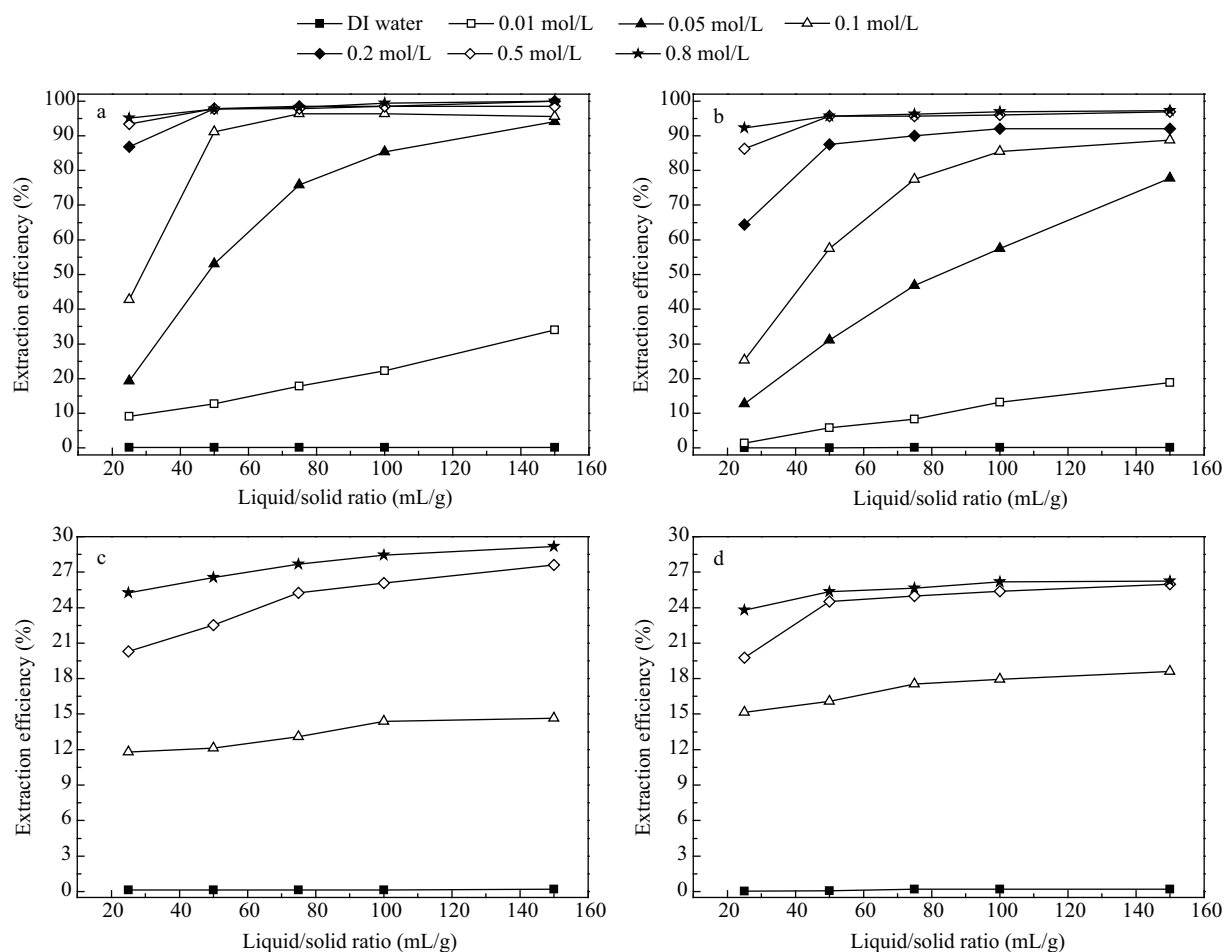


Fig. 1 Effects of extraction concentrations and liquid/solid ratios on P extraction from sewage sludge ash. (a) HCl extraction for ash A; (b) HCl extraction for ash B; (c) NaOH extraction for ash A; (d) NaOH extraction for ash B. Extraction time: 120 min.

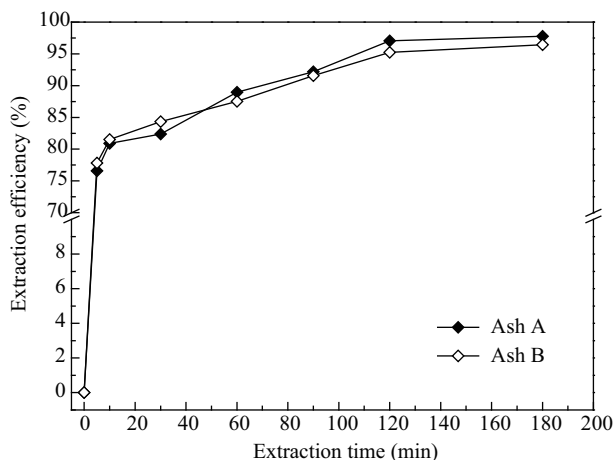


Fig. 2 Effect of extraction time on P extraction from sewage sludge ash.

noted that the residue after acid extraction is corrodible and needs safe disposal, such as landfill.

As shown in Fig. 1, P extraction efficiency of ash A by HCl was much higher than that by NaOH (< 30%), clearly showing that base extraction was not effective. Other researchers also reported that NaOH was not an effective extraction solvent for P extraction from sewage sludge or sludge ashes (Biswas et al., 2009; Stark et al., 2006). In addition, P extraction by de-ionized water was minimal (< 0.2%), regardless of the types of ash and L/S ratios, indicating that P in the sewage sludge ash was present in the form of insoluble salts (Adam et al., 2009).

Extraction efficiency was highly influenced by the extraction time (Biswas et al., 2009; Cohen, 2009). As depicted in Fig. 2, the extraction efficiency rapidly increased up to 15 min, and then slowly increased afterwards, with more than 95% extraction efficiency achieved after 120 min of reaction. Therefore, an extraction time of 120 min was selected as the optimum condition for P extraction from ash A and ash B. The fast P extraction rate may be attributed to the acid soluble nature of the ash material as well as the small particle size (Biswas et al., 2009).

2.3 Removal of heavy metals from P-rich solution

In acid extraction solution, the dissolved P as well as heavy metals (Cohen, 2009; Stark et al., 2006), such as

zinc, copper, nickel, lead, and chromium were the principal elements limiting agricultural applications (Stylianou et al., 2007). Figure 3 depicts the leaching of heavy metals during P extraction. Leaching efficiency increased with increasing acid concentrations, which can be explained by the fact that an increase in acid concentration resulted in an increase in offered energy for breaking the metal chemical bonds (Naoum et al., 2001). It was notable that the leaching percentage of heavy metals in the two ashes was much lower than that of P. The relatively low leaching percentage was due to the fact that parts of metals were present as nucleation particles in the center matrix of the ashes (Biswas et al., 2009; Naoum et al., 2001; Stark et al., 2006). A similar phenomenon was also reported by Hong et al. (2005) for waste activated sludge.

Moreover, Cu in the two ashes had almost the same leaching efficiencies, with a rapid increase to about 50% at 0.1 mol/L HCl, and a slow increase to about 70% at 0.8 mol/L HCl. The leaching patterns of Zn and Cr for ash A were similar to those for ash B, despite the fact that ash B had a 2–6 times higher leaching percentage than ash A. The leaching patterns of Pb in the two ashes were both characterized by gradual increasing curves, with a leaching efficiency of about 50%–70% at 0.8 mol/L HCl. No Ni leaching was observed for ash A, while its leaching for ash B reached about 70% at 0.8 mol/L. The different leaching efficiencies were due to the dissimilar chemical bonds in ashes (Naoum et al., 2001), which needs further investigation.

The leached heavy metals inevitably co-precipitated with P and further contaminated the recovered precipitates (Franz, 2008), thus the P-rich solutions required purification before P recovery. Figure 4 depicts the removal of heavy metals from the P-rich solution by CER. Phosphorus was not removed by CER addition, while high removal efficiencies of heavy metals were obtained, indicating that CER was appropriate for purifying the P-rich acid leach solutions. Specifically, the concentrations of heavy metals rapidly decreased with increasing CER dosage (< 0.04 g/mL), but remained relatively constant when the dosage was increased further. Thus a CER dosage of 0.04 g/mL was optimal for heavy metal removal.

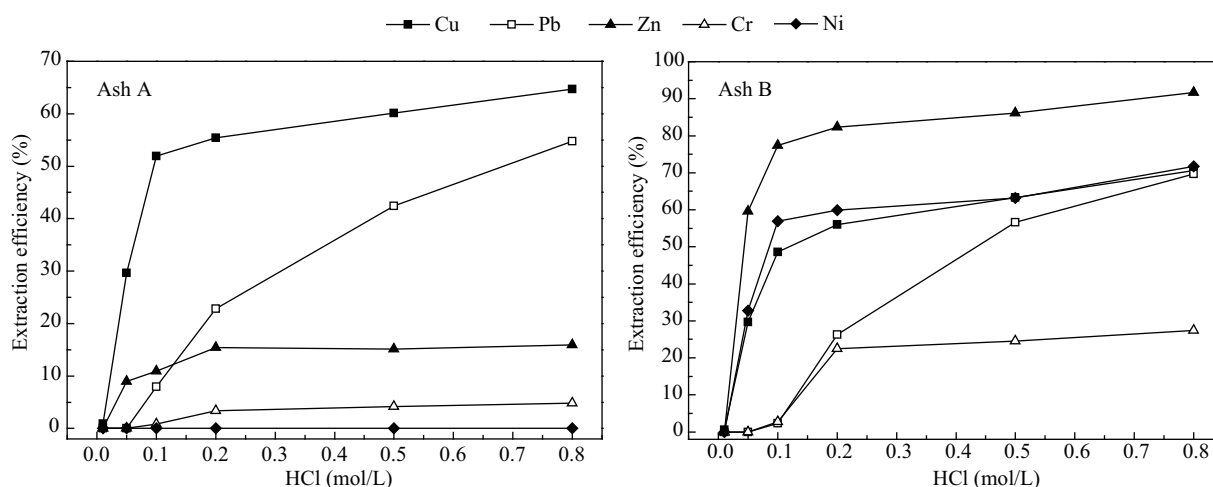


Fig. 3 Effect of acid concentrations on the leaching of heavy metals. L/S ratio 50, extraction time 120 min.

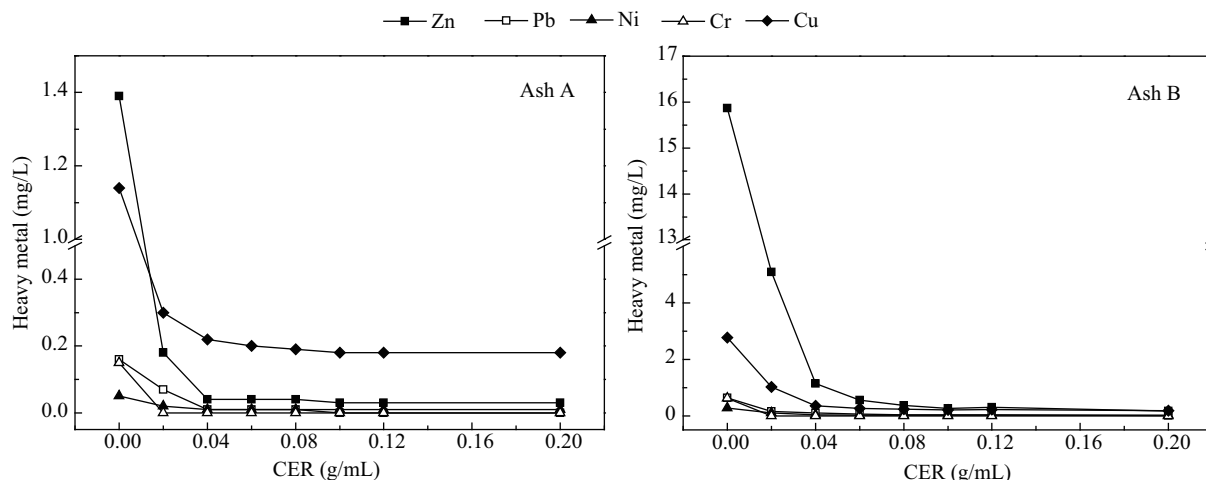


Fig. 4 Effect of cation exchange resin (CER) dosage on the removal of heavy metals.

2.4 Recovery of P as formation of struvite

The P recovery in this study was based on the formation of struvite, which was highly associated with pH and the molar ratio of Mg:N:P in the solution. To investigate the joint effects of these parameters on struvite formation and further confirm the optimal parameters, an orthogonal test was applied, as shown in Table 2. The reduction ratio of Mg:N:P during struvite formation was applied as the index for parameters optimization. Based on the results of the orthogonal test, when the Mg source and N source were 1.6 times higher than the P source at pH 10.0, the reduction ratio of Mg:N:P was 1.05:0.98:1, indicating the possible formation of struvite. The highest P recovery of 97.2% was also achieved under these conditions. In addition, the parameters influencing the struvite formation were ranked as: pH > N:P > Mg:P.

Previous research has also investigated the influencing factors for struvite formation. Ryu et al. (2008) demonstrated that struvite precipitation was highly pH dependent and the optimum reaction for P removal was observed at pH 10.0. Martí et al. (2010) and Uysal et al. (2010) obtained a high purity of struvite precipitate with Mg:P in the range of 0.78–1.78, which was similar to the results obtained in this study. However, Jaffer et al. (2002) found that a higher Mg:P ratio of 3:1 was required to guarantee P removal as struvite. The lower ratio necessary for struvite

Table 2 Results of orthogonal experiment

	pH	Mg:P	N:P	P recovery	Reduction ratio of Mg:N:P
1	9.0	1.2	1.0	75.6%	1.11:1.03:1
2	9.0	1.6	1.3	87.1%	1.30:0.92:1
3	9.0	2.0	1.6	93.6%	1.27:0.91:1
4	10.0	1.2	1.3	92.1%	1.12:0.92:1
5	10.0	1.6	1.6	97.2%	1.05:0.98:1
6	10.0	2.0	1.0	94.9%	3.26:0.44:1
7	11.0	1.2	1.6	84.1%	1.88:0.69:1
8	11.0	1.6	1.0	89.6%	5.16:0.31:1
9	11.0	2.0	1.3	94.3%	4.06:0.39:1
\bar{k}_1	1.30	1.67	8.38		
\bar{k}_2	3.23	6.38	4.35		
\bar{k}_3	9.93	6.41	1.73		
Range	8.63	4.74	6.65		

precipitation in this study was attributed to the lack of any competing reactions (Moerman et al., 2009).

2.5 Evaluation of harvested struvite precipitates

The structure composition of the harvested precipitates was evaluated using XRD as shown in Fig. 5. Good correlation between the peaks of the precipitates harvested in this test and those of the standard struvite pattern confirmed that the precipitates formed were mainly struvite. Purity analysis further demonstrated that the precipitates had a high struvite purity of about 97%.

To assess the possible agricultural application of the harvested struvite precipitates, the heavy metal contents were analyzed. The results showed that only 150–800 mg/kg of Zn and 260–350 mg/kg of Cu were observed in the harvested struvite precipitates, not exceeding the limit values (Table 1). The P-bioavailability of harvested struvite precipitates was about 94%, higher than that of conventional single super phosphate (87%). Heavy metal and P-bioavailability analysis demonstrated that the harvested struvite precipitate was a high quality agricultural fertilizer.

Lastly the economic evaluation of P recovery as struvite from sludge ashes was applied. Based on the obtained results, the HCl consumption for ash A and ash B were 10 and 25 mol/kg, respectively, and CER consumption was 2 kg/kg for both ashes. The struvite production from ash A and ash B were 0.23 and 0.43 kg/kg, respectively.

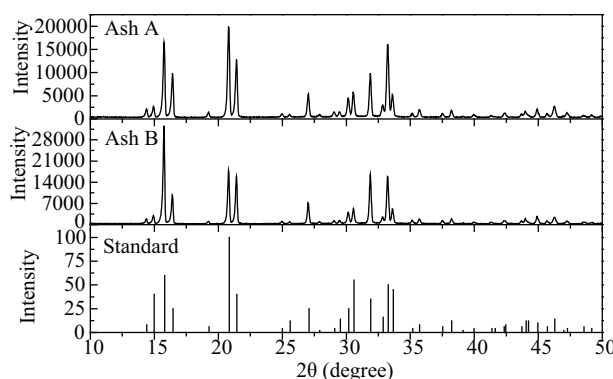


Fig. 5 XRD diffraction patterns of precipitates from ash A, ash B and the standard struvite.

The profit would exceed 5 USD/kg sludge ash based on the struvite value. The technology developed in this study could provide a sustainable method for P recovery from sludge ashes.

3 Conclusions

Sewage sludge ash was a suitable secondary raw material for P fertilizer production, but also contained considerable amounts of heavy metals. Acid was more effective than base removal for P extraction. Heavy metals were simultaneously leached during P extraction, whilst their leaching percentages were much lower than that of P. Heavy metals were removed from the P-rich solutions by applying 0.04 g/mL CER. Struvite precipitation could recover more than 97% of P in sludge ashes. Heavy metal and P-bioavailability analysis showed a high quality of struvite precipitate harvested in this study.

Acknowledgments

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