

Phosphorus recovery from sewage sludge amended with alum and ferric sludges using sequential extraction and pyrolysis

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Introduction

In 2014, European Commission included phosphate rock in its critical raw materials list due to its limited reserves, growing demand, skewed geographic distribution and vital need (European Sustainable Phosphorus Platform). Sewage sludge (SS) has one of the highest phosphorus (P) contents among biomass types and it is a reclaimable P source (Jupp et al., 2021). Among many approaches to P extraction from SS, wet extraction/ leaching is the most prevalent. Sequential extraction (acid→alkali) is an innovative method of P recovery which minimizes the leaching of toxic trace elements (TEs) and enhances P recovery from SS or its ash or char. Acid extraction promotes apatite phosphorus (AP, mainly Ca-P) to non-apatite inorganic phosphorus (NAIP, mainly Al-P and Fe-P) conversion in SS/ash, which is subsequently extracted via alkali extraction (Petzet et al., 2012). However, sequential extraction is not applicable for Al or Fe-deficient SS/ash, in other words, sequential extraction is dependent on the chemical composition of SS (Petzet et al., 2012).

This study presents a novel SS amendment approach for a wider application of sequential extraction for P recovery. Alum sludge (AS) and ferric sludge (FS) were added to two SS samples (S1 and S2) separately as ex-situ sources of Al and Fe ions, respectively. These amended SS samples were subjected to acid extraction at various pH levels and the effects of the addition of AS and FS and pH on P conversion were investigated. This is probably the first study on the application of both, AS and FS for P recovery from SS.

Experimental

Dewatered SS samples (S1 and S2) were mixed with dry powdered AS and FS separately to ensure an Al:P and Fe:P molar ratio of 3:1 (dry basis) in the mixtures. 5 mL of deionized water was added per 1 g of these mixtures to make slurries. The pH of these slurries was reduced to 1, 3, 5 and 7 using 6 M HCl and then leached for 2 h. The pH of the slurries post-acid leaching was recorded (equilibrium pH) and acid leachates were obtained from the slurries using centrifugation. The acid leachate samples were analyzed for major ions such as P, Ca, Al, Fe, Mg and TEs using ICP-OES.

Results and discussion

As shown in Table 1, S2 has a higher inorganic content than S1. However, Ca/P molar ratio in both S1 and S2 is about 1. For a medium to high alkali extraction of P (>50%), Ca/P molar ratio should be less than 0.5 as Ca-P precipitates at high pH (Liu et al., 2021). In acidic conditions, Ca-P dissolves while Al-P and Fe-P precipitate (Levlin and Hultman, 2004), thus selectively eliminating Ca from SS during acid extraction. Consequently, the Ca/P molar ratio in the solid residue reduces after acid extraction making it suitable for alkali P extraction.

Table 1: Physico-chemical characterization of the sludge samples.

Sludge sample	Moisture (%)	Dry density (g/mL)	Al (%)	C (%)	Ca (%)	Fe (%)	Mg (%)	P (%)
S1	87.1±0.1	0.6±0.0	1.1±0.0	38.2±0.4	2.4±0.1	1.4±0.0	0.8±0.0	2.0±0.1
S2	84.9±0.1	0.7±0.0	3.2±0.1	30.3±0.2	3.2±0.1	3.2±0.1	1.0±0.0	2.4±0.2
AS	66.2±0.1	0.6±0.0	19.1±1.6	9.8±0.0	0.5±0.1	1.7±0.0	0.2±0.0	0.1±0.0
FS	60.0±0.5	0.7±0.0	3.3±0.3	10.0±0.0	15.9±1.1	18.8±1.2	1.6±0.1	0.1±0.0

Both S1 and S2 have a higher AP to NAIP conversion (evident from low P leaching) when amended with AS or FS in the pH range ~3-7 (Fig.1). At pH<3, there was a significant dissolution of P, Al and Fe, indicating that low pH is unsuitable for AP to NAIP conversion for both, AS and FS amended samples. TEs such as Mn, Zn

and Cu were also leached at $\text{pH} < 3$. To prevent P loss during the acid extraction, the most suitable pH ranges were ~3-4 and ~5-6 for AS and FS amended samples, respectively. However, to obtain Ca/P molar ratio less than 0.5 in the solid residue after acid extraction, the optimum pH is less than 5 (Fig. 2). At $\text{pH} \sim 7$, samples amended with FS have a high Ca/P molar ratio because FS has high Ca content (comparable to Fe content in it) and at neutral pH, Ca dissolution is insignificant.

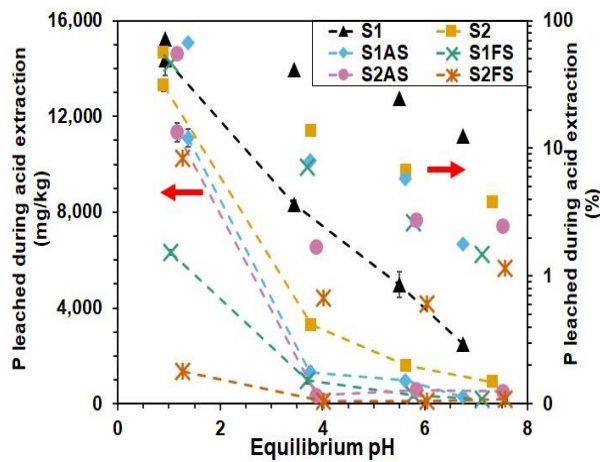


Fig.1: Phosphorus leached during the acid extraction of unamended (S1, S2) and amended (S1AS, S2AS, S1FS, S2FS) sludge samples at different pH levels.

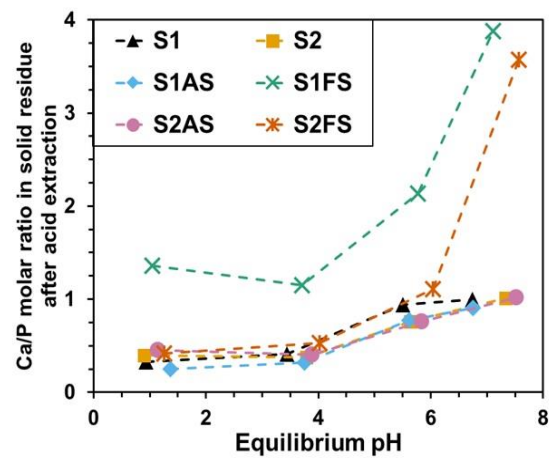


Fig.2: Ca/P molar ratio in the solid residues after the acid extraction of unamended (S1, S2) and amended (S1AS, S2AS, S1FS, S2FS) sludge samples at different pH levels.

The acid consumption at this pH range contributed a minor fraction of the total cost of P extraction using sequential extraction, thus improving the techno-economic feasibility of the proposed process (Semerci et al., 2021). In the subsequent experiment, AS or FS-amended samples will be pyrolyzed and the P extraction efficiency from different pyrochars using alkali extraction will be analyzed. A high P extraction efficiency is expected as NAIP is easily dissolved in alkali conditions.

Conclusion

Amendment of SS with AS and FS and subsequent acid extraction is an effective strategy for AP to NAIP conversion in SS. This conversion is likely to promote the subsequent P extraction using an alkali. Usage of AS and FS for sequential extraction not just promotes resource recovery from waste but offers a dual waste management strategy.

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