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## Identification of phosphorus forms in sewage sludge ash during acid pre-treatment for phosphorus recovery by chemical fractionation and spectroscopy

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### ABSTRACT

Identification of phosphorus (P) forms is critical for the recovery of P from sewage sludge ash (SSA). During the HCl treatment of SSA Ca was selectively eluted while P mostly remained in the SSA. Chemical P fractionation of the SSA before and after HCl treatment showed that Al-P increased from 46.6% to 79.2% of total P while Ca-P decreased from 28.9% to 4.4% at pH 2.5. HCl treatment also changed chemical structure of Al-P since no crystalline Al-P was found in the SSA after the treatment, only amorphous Al-P was found from the analyses of XRD and ATR-FTIR.

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### Introduction

Phosphorus (P) is an irreplaceable essential element for all living organisms, especially for agriculture. Agricultural products heavily depend on the supply of P containing chemical fertilizers. Phosphate rock reservoir is mostly the only source for chemical P fertilizer and it is estimated about 100 years of economical mining [1]. Since there are no substitutes for P, recycling of P from waste is critical for the sustainability of human beings.

A significant portion of P flows into food chains and a large part of the P in the food chain is discharged as sewage inevitably. About 80–90% of the P in the sewage is removed and accumulated in the sewage sludge while the others are remained in the sewage and discharged into receiving water bodies. Therefore, sewage sludge is an important P source and many research efforts have been carried out for P recovery from sewage sludge [2,3]. Sewage sludge ash (SSA) is produced from sewage sludge incineration plant and it is much more attractive source for P recovery since P is concentrated during sludge incineration. In average P content in the SSA is about 10% which is comparable to that of phosphate rock.

There are two technical problems to overcome in P recovery from SSA. Heavy metals need to be properly removed from the

recovered P to meet the guidelines of chemical fertilizer [4]. The other issue is a bioavailability of the recovered P as a fertilizer. Bioavailability depends on the solubility of P at neutral pH condition. Chemical P fertilizer needs to be sufficiently soluble in soils at neutral pH and the solubility depends on P bearing compounds. Chemical solubility database showed that P bearing calcium compounds (Ca-P) are more soluble than P bearing aluminum compounds (Al-P) and iron compounds (Fe-P) at neutral pH [5]. Ca-P is highly soluble in acidic condition and insoluble in alkaline condition. Al-P and Fe-P are soluble in both acidic and alkaline condition (amphoteric) whereas they are almost insoluble in neutral condition. Therefore, Ca-P is a preferred chemical P fertilizer to Al-P and Fe-P.

Wet chemical methods using acid/alkali have been used to recover P from SSA. Detailed wet chemical method for P recovery whether to use acid [6] and acid–base leaching with subsequent precipitation [7] depends on the composition of the P bearing compounds in the SSA. Al, Ca, and Fe are the most abundant metal elements in the SSA which combine with P followed by Mg and K. However, their accurate chemical composition of P bearing compounds in the SSA is still mostly unknown.

P can be recovered as Ca-P by adding Ca into the SSA leachate in alkaline condition to form precipitate. For the purpose, Ca in the SSA needs to be removed before the alkali treatment in order to remove heavy metals as hydroxide precipitates and increase P recovery yield since Ca-P is insoluble in alkali. During the acid pre-

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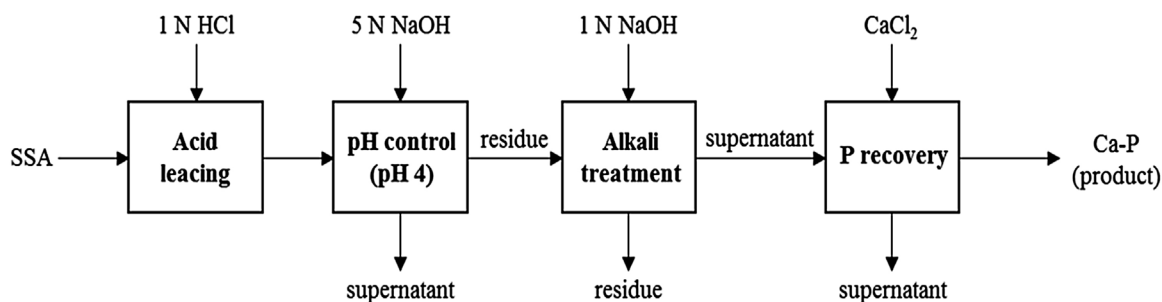


Fig. 1. Schematic procedure of P recovery from SSA by HCl pre-treatment followed by NaOH treatment.

treatment, most of the P bearing compounds (Al-P, Ca-P, Fe-P) are dissociated and solubilized in strong acid solution (pH 1–2). However, most of the elements of the P bearing compounds were disappeared in the liquid phase except Ca as the pH increased to 4 [8]. Analysis showed that the dissociated P from Ca-P and other P and P bearing elements (Al and Fe) were solidified into residual solid. It is speculated that Al-P (or Fe-P) were the main P bearing compounds in the residual solid after acid pre-treatment based on the solubility of Ca-P, Al-P, and Fe-P. However, the detailed bonding or combination of P and Al (or Fe) compounds in the acid pre-treated residual solid has not been investigated yet.

For the purpose chemical fractionation and spectroscopic (XRD, ATR-FTIR) analysis can be applicable. ATR-FTIR can identify specific P bearing compounds in the SSA and monitor the transformation the P compounds during the acid pre-treatment. Specifically, FTIR can provide information on the P–O bond in specific regions (wave number,  $\text{cm}^{-1}$ ) regardless whether they have crystal structure or not. These tools have been used to study the behavior or dynamics of P in soils such as agricultural land and sediment of water reservoir. However, these techniques have never been used to characterize the behavior of P during the pre-treatment of SSA and it is the first report as far as the authors understand. The purpose of this study is to identify the P bearing compounds and the chemical structure in the SSA and the residual solid after acid pre-treatment by chemical fractionation and spectroscopy (XRD, ATR-FTIR) for the enhancement of P recovery.

## Materials and methods

### Sewage sludge ash and selective elution of Ca by HCl pre-treatment

SSA used in this study was collected from a municipal sewage sludge incineration plant in Pocheon city, Korea. Waste activated sludge and the sludge from chemical P removal unit from Pocheon municipal wastewater treatment plant were dewatered and incinerated. Fly ash captured in a bag filter was transported to the laboratory for the experiment. All the SSA samples were dried overnight in a convection oven at  $105^\circ\text{C}$  before the experiment.

Schematic procedure of wet chemical treatment of SSA for P recovery is shown in Fig. 1. Acid pre-treatment removed acid-soluble compounds including Ca from the SSA. After the solid/liquid separation, the residual solid was further treated by alkali to solubilize P and remove heavy metals by forming insoluble hydroxides. After removing the solids, Ca (as  $\text{CaCl}_2$ ) was added to the alkaline supernatant to recover P as Ca-P precipitate. Ca elution of the SSA was investigated with 1 N HCl and 5 N NaOH for pH control. In most cases, 100 g of SSA was eluted with 1 L solution (Liquid (mL)/Solid (g) = 10) for 24 h in a magnetic stirred mixer. For the pH control of the SSA leachate, 5 N NaOH was immediately pumped into the solution after HCl injection to control the pH to  $4.0 \pm 0.1$ . All the experiments were carried out in triplicates ( $n = 3$ )

and the average values and the standard deviation were used for the analysis.

### Fractionation of SSA

A sequential chemical P fractionation procedure was used to discriminate between water soluble P (WSP), iron bound P (Fe-P), aluminum bound P (Al-P), and calcium bound P (Ca-P) as shown in Fig. 2 [9,10]. For the fractionation, 2 g of the SSA and 50 mL of each extraction solvent were used. After extraction, the samples were centrifuged for liquid-solid separation (Mega 17R, Hanil, Korea) and rinsed with the same solution and DI water after each step. Sequentially, the SSA or the residual solid was extracted with DI water, bicarbonate buffered dithionite solution (BD-reagent, 0.11 M  $\text{Na}_2\text{S}_2\text{O}_4 + 0.11 \text{ M NaHCO}_3$ ), 1 N NaOH, and 1 N HCl to extract WSP, Fe-P, Al-P, and Ca-P, respectively. Phosphorus in the residual solid after 1 N HCl step was the residual-P and it was calculated by the difference of total P and the sum of all the extracted P fractions of the SSA.

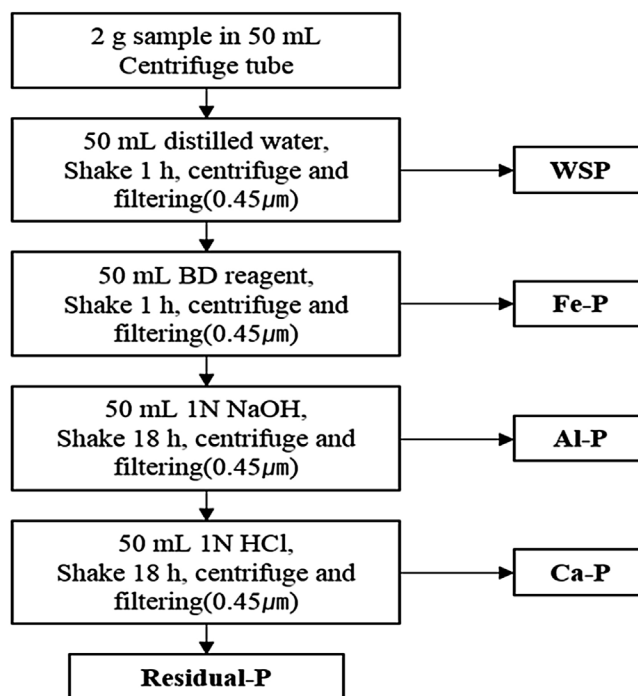


Fig. 2. Chemical fractionation scheme used in this study for the extraction of P from the SSA. (WSP: water soluble phosphorus, Fe-P: phosphorus bound to Fe, Al-P: phosphorus bound to Al, Ca-P: phosphorus bound to Ca, residual-P: phosphorus remained in the SSA after the extractions).

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