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Selective acidic elution of Ca from sewage sludge ash for phosphorus recovery under pH control

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ABSTRACT

Phosphorus (P) is recovered from sewage sludge ash (SSA) by selective HCl elution of Ca. Leaching and rearrangement of P were very fast and the amounts of leaching and recombination of P depend strongly on pH. pH control at 4.0 obtained selective elution ratio (Ca(%)/P(%)) of 20 by recombination of P to Al in SSA residue while it was 5.6 without pH control. XRD and element mass balance showed that Ca–P in the raw SSA was converted to Al–P complex during the acid pretreatment.

Introduction

Phosphorus (P) is an essential fertilizer for the production of agricultural crops. The reservoir of phosphate rock deposit is finite and it is estimated that the resource remains only around 100 years of economical mining [1]. Much research has been carried out to solve the problem, especially on the recycle of P from wastewater and waste [2,3]. P needs to be removed from wastewater to prevent eutrophication by chemical [4] and biological means [2]. Wastewater sludge is considered as a critical sink for P in wastewater and it is regarded as a potential P fertilizer [5]. However, direct application of the sludge to agricultural land is technically infeasible due to low P content and hazardous materials (pathogens, heavy metals and other potential hazardous chemicals) in the sludge.

Wastewater sludge can be stabilized and reduced in volume by incineration. Sewage sludge ash (SSA) after incineration has high P content (about 10%). Therefore, recovery and recycle of P from a SSA has drawn many attentions since it has many potential advantages than other P sources [6,7]. Wet chemical treatment with acid or alkali is the most commonly used P recovery method from a SSA [5,8,9]. Use of acid or alkali depends on the elemental composition of the SSA [9]. Sequential acid and alkali treatment of SSA can also be applied to recover P [5,8]. Acid pretreatment followed by alkali treatment of SSA is used to recover P as Ca–P by the addition of $CaCl_2$ after alkali treatment. In detail, acid pretreatment of SSA selectively dissolves and elutes Ca and the residual SSA is further treated with alkali to dissolve P in the residual SSA after removing the acid solution by liquid/solid separation. Heavy metals in the SSA are precipitated as hydroxides and removed with the residual SSA during the alkali treatment. $CaCl_2$ is added to the P containing alkaline solution to recover P as Ca–P. If Ca was not removed from the SSA in the acid pretreatment, Ca combines with P to form insoluble Ca–P in the following alkali treatment which makes it impossible to separate P by alkali leaching from the SSA.

During the pretreatment of SSA acid concentration (or pH) needs to be optimized to selectively elute Ca while the majority of the P remain in the SSA to minimize P loss. It has been reported that P is dissociated from the original chemical structure and transformed into a new chemical structure with metals during the acidic pretreatment [10,11]. However, the detailed mechanisms behind the P transformation have not been reported yet. Petzet et al. [5] reported that 0.4 N HCl was the optimum condition for selective Ca elution with P rearrangement in the SSA.

During the acid pretreatment pH slowly increased with time and the elutions of P and Ca heavily depended on pH [5]. It took about 24 h for pH stabilization and weak acid needs longer time. Even though strong acid is preferred for the fast dissolution of Ca and P, it cannot be used since large amount of P is also eluted with Ca and lost. Therefore, a new pretreatment technology is needed to elute Ca selectively, effectively and quickly from a SSA while most of the P remaining in the SSA residue. In this study, we propose a novel pretreatment method that uses strong acid (HCl) for

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immediate dissolution of Ca and P from the SSA followed by rearrangement of P by controlling the pH. In a weak acid condition (pH 3–5), P is hardly soluble when combined to Al and Fe [12]. The pretreatment can remove more Ca and less P and recover more P from the SSA.

The objective of this study is to investigate the chemical kinetics of P and metals of a SSA during the acid pretreatment. Specifically, dissolution of Ca, P and other metals was investigated at various pretreatment conditions. For the purpose SSA was treated with various concentrations of HCl and pH control to determine the dynamics and chemical interactions of P with metals. P recovery yield from the SSA was also compared with and without the pH control.

Materials and methods

Pretreatment of SSA by acid and alkali for selective elution of Ca

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 °C before the experiment. Ca elution of the SSA was investigated with various concentrations of acids (H_2SO_4, HCl) and alkali (NaOH). In most cases, 100 g of SSA was eluted with 1 L acid/alkali solution (Liquid (mL)/Solid (g) = 10) for 24 h in a magnetic stirred mixer unless stated otherwise. For the pH control of the SSA leachate after HCl treatment, 5 N NaOH was immediately pumped into the solution after the acid injection to control the pH to 4.0 ± 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.

Analytical methods

Particle size of the SSA was measured by particle size analyzer (Mastersizer 2000, Malvern Ins., England). X-ray fluorescence spectrometer (XRF, ZSX-100e, Rigaku, Japan) and X-ray powder diffraction (XRD, D/Max-2500V, Rigaku, Japan) were used to determine the contents of the elements and the crystalline compounds in the SSA [8]. All the elution samples of the SSA were analyzed with ICP-OES (iCAP 6300, Thermo, USA) after centrifugation and filtration by GFC disc filters [13].

Results and discussion

Particle size analysis showed that the SSA had a mean diameter of 25.8 μm ($d_{0.1} = 4.1\ \mu$m, $d_{0.9} = 121.1\ \mu$m). Elemental composition of the SSA was determined by X-ray fluorescence (XRF) spectroscopy and the analysis showed that Si (11.9%), Al (9.79%), P (9.78%) and Ca (8.99%) were the major elements followed by Mg (2.53%) and Fe (2.21%) (Table 1). Relatively high Al content in the SSA was due to the use of alum ($Al_2(SO_4)_3$) or polyaluminum chlorides (PAC) as the precipitant for P removal. Ca in the SSA was also originated from the incineration plant to remove acid gas emission from the stack by injecting CaO or $Ca(OH)_2$ [14]. Since the contents of Ca and Al were high in the SSA, it is thought that a significant amount of P is combined with Ca and Al. The molar ratio of P/Ca and P/Al was 1.4 and 0.87, respectively. Heavy metals in the SSA was analyzed by ICP-OES after digestion with 7 N HNO_3 [4].

Dissolution of P from SSA by HCl and NaOH

SSA was treated by acid and alkali for P dissolution and Fig. 1 shows the leaching characteristics of P from the SSA with the treatment of HCl (A) and NaOH (B). P leaching was very fast at all the HCl concentrations (Fig. 1[A]). HCl concentration higher than 0.8 N leached most of the P in the SSA immediately. Interestingly, P in the leachate decreased gradually with time in 0.4–0.6 N HCl while other concentrations of HCl (lower or higher than 0.4–0.6 N) maintained almost the same P level. It is likely that P disappeared in the leachate recombined to the residual SSA with 0.4–0.6 N HCl and it will be discussed in detail in the following section.

Contrary to the HCl treatment, NaOH increased P leaching slowly with time (Fig. 1[B]). In addition, NaOH could leach much less P than HCl at the same molar concentration. Only 55% of the total P in the SSA could be leached in 12 h with 2 N NaOH. It is thought that P in the SSA is mainly combined with Al and Ca. XRF analysis of the residual SSA after NaOH (2 N) treatment showed that most of the Ca was still remained in the SSA (data not shown). When P is combined with Ca ($Ca_3(PO_4)_2$, $Ca_5(PO_4)_3(OH)$), it is hardly soluble in alkaline condition whereas Al–P is relatively soluble [12]. The percentage of alkali leachable P to the total P of the SSA depends on the mole ratio of P/Ca. The SSA had a P/Ca mole ratio of 1.4, and it can be assumed that about 52–57% of total P can be extracted by alkali treatment if all the Ca was bound to P with the form of $Ca_3(PO_4)_2$ (P/Ca = 0.67) and $Ca_5(PO_4)_3(OH)$ (P/Ca = 0.6). In this study alkali (2 N NaOH) treatment of the SSA leached up to 55% of the total P, and it is very close to the above assumption and calculation. The result indicates that most of the Ca in the SSA was bound to P. The remaining P in the SSA is thought to be combined with other metals (mostly Al).

Selective Ca elution from SSA by acid treatment

Sequential acid and alkali treatment is an effective way to recover P from the SSA when the SSA contains high amount of Ca. It has been reported that acid pretreatment dissociates Ca–P and elutes Ca selectively from the SSA while the dissociated P combines to other metals in the SSA, like Al and Fe in an appropriate acidic condition [3,8]. During the acid pretreatment, the pH should be adjusted to maximize Ca–P dissociation while minimizing the dissociation of other metal–P complexes (like Al–P and Fe–P) and the elution of dissociated P from Ca-P. After removing the liquid phase of the acidic pretreatment, the residual SSA is further treated by alkali for the dissolution of P. Then, Ca is added to the P containing alkaline solution for precipitation after removing the residual solids including the heavy metals. Most of the heavy metals form insoluble hydroxides in alkaline condition.

Fig. 2 shows the dynamics of P, Al, Ca, and pH during the acidic pretreatment with different concentrations of H_2SO_4 (Fig. 2[A]) and HCl (Fig. 2[B]) for 24 h at the L/S ratio of 10. Both Al and P

Table 1
Elemental composition of the sewage sludge ash based on the XRF (data in mass %) and heavy metals based on the ICP-MS (mg/kg SSA).

Element	Si	Al	Ca	P	Mg	Fe	K	Na	S	Cl
%	11.9	9.79	8.99	9.78	2.53	2.21	1.99	0.75	0.78	0.08

Heavy metals	As	Cd	Cr	Cu	Ni	Pb	Zn
mg/kg SSA	29.84	12.54	86.82	837.00	86.93	823.88	429.70

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