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Enhanced phosphorus bioavailability and heavy metal removal from sewage sludge ash through thermochemical treatment with chlorine donors

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ABSTRACT

Direct application of sewage sludge ash (SSA) to agriculture is mostly prohibited due to its heavy metals and limited bioavailability. Thermochemical treatment of SSA with Cl-donors were carried out to remove heavy metals and enhance P bioavailability. $MgCl_2$ and $CaCl_2$ removed more heavy metal than other Cl-donors. Pb was completely removed followed by Cd, Zn, Cu. They also increased P bioavailability by the conversion of Al–P to Ca/Mg–P which was confirmed by chemical fractionation. XRD confirmed the conversion of $AlPO_4$ to $Ca_5(PO_4)_3Cl$, $Ca_3(PO_4)_2$, and $Mg_3(PO_4)_2$ by the thermochemical treatment.

Introduction

Phosphorus (P) is an essential element for all the living organisms and a major element of a fertilizer. Most of the P is obtained from phosphate rock and its economical mining is estimated about 100 years [1]. Therefore, P recovery from wastewater and waste has drawn much attention due to its limited resource and irreplaceability. Wastewater sludge, which composed of excess activated sludge and chemical sludge from P removal process by coagulation, contains concentrated P [2,3]. Therefore, wastewater sludge is regarded as a potential source for P recovery. However, the sludge has high water content including organics, pathogens, and heavy metals which prohibit direct application of wastewater sludge to agricultural land. Sewage sludge ash (SSA) from sludge incineration plant is another source for P recovery because SSA has much higher P content than wastewater sludge [4,5]. Nonetheless, direct application of SSA as a fertilizer is very rare since it still contains significant amount of heavy metals above the guidelines. Low bioavailability of P is also a limiting factor for direct use of SSA as a fertilizer [5]. Thermochemical treatment of SSA with chlorine (Cl) donor has been reported to enhance heavy metal removal [6–8]. Vogel and Adam (2011) added $CaCl_2$ and $MgCl_2$ to SSA for thermochemical treatment and confirmed the formation of new P containing compound by XRD [9]. They also found that bioavailability of the SSA was improved by the thermochemical treatment with $CaCl_2$ and $MgCl_2$.

Thermochemical treatment of SSA with Cl-donor has been carried out around 1000 °C by chlorination to remove heavy metals and recover P. Chlorination reaction steps between heavy metals and Cl are suggested as follows [6,7]:

$$MO + X\text{–}Cl_2 \rightarrow MCl_2 + X\text{–}O \quad (1)$$

$$X\text{–}Cl_2 + \tfrac{1}{2}O_2 \rightarrow X\text{–}O + Cl_2 \quad (2)$$

$$M\text{–}O + Cl_2 \rightarrow M\text{–}Cl_2 + \tfrac{1}{2}O_2 \quad (3)$$

$$X\text{–}Cl_2 + H_2O \rightarrow X\text{–}O + 2HCl \quad (4)$$

$$MO + 2HCl \rightarrow MCl_2 + H_2O \quad (5)$$

where M: heavy metals, MO: heavy metal oxides, X: metals, $X\text{–}Cl_2$: Cl-donors, MCl_2: chlorinated heavy metals, X–O: metal oxides.

Heavy metals in SSA mostly exist as heavy metal oxides and they are difficult to remove by thermal treatment alone because they have high boiling points and low vapor pressures. On the

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other hand, heavy metals can be easily removed by thermochemical treatment after converting heavy metal oxides to heavy metal chlorides due to their lower boiling points and higher vapor pressures. Heavy metals react with Cl either directly ('direct chlorination' as shown in Eq. (1)) or indirectly as Cl-donor reacts to O_2 or H_2O to produce Cl_2 and HCl which react to heavy metals for removal ('indirect chlorination' as shown in Eqs. (2)–(5)) [8,9]. In case of indirect chlorination, formation of Cl_2 or HCl effects volatilization of heavy metals significantly. If the formation rate is slow, it reduces or limits heavy metal removal rate due to decreased conversion rate of heavy metal chlorides [7].

On the other hand, it is thought that P in SSA is thought to be transformed to new compounds through the thermochemical treatment and the bioavailability of the produced P compounds depends on the type of Cl-donor [8]. However, the reason of the enhanced P bioavailability was not clearly identified yet. It is speculated that non-bioavailable Al–P is transformed to readily bioavailable P compounds, like Ca–P or Mg–P, during the thermochemical treatment with $CaCl_2$ or $MgCl_2$ as the Cl-donor. In this study chemical P fractionation was adopted for the first time to characterize P compounds in the SSA before and after the thermochemical treatment. The fractionation can separate and quantify different P compounds (water soluble P, Fe–P, Ca/Mg–P, and insoluble residual P). It provides valuable information to determine P transformation during the thermochemical treatment.

The objectives of this study were to systematically investigate the effect of Cl-donors including $MgCl_2$ and $CaCl_2$ on heavy metal removal and enhanced P bioavailability of SSA through thermochemical treatment. The cause of P bioavailability enhancement of SSA by thermochemical treatment was also thoroughly studied by determining newly formed P containing minerals and chemical P fractionation of the SSA.

Materials and methods

Thermochemical treatment of SSA and analysis

SSA used in this experiment was a fly ash collected from a sewage sludge incineration plant in Pocheon city, Korea. The SSA was dried in an oven at 105 °C for 24 h before the experiment. For the thermochemical treatment, dried SSA (10 g) and Cl-donor (100 g Cl/kg SSA) were mixed in a crucible and treated for 30 min at 950 °C in a muffle furnace. After the treatment SSA was cooled down to ambient temperature for analysis. For the element analysis of the SSA the sample was digested with *aqua regia* according to the protocols of EN13346 method and the supernatant was used [10]. Total P (TP) was measured by the Standard Methods [11]. Other elements including heavy metals were analyzed by ICP-OES (iCAP 6300, Thermo, USA) after filtration. P mass loss (%) during the thermochemical treatment was calculated based on the lost P mass divided by the initial P mass in the SSA. Heavy metal removal (%) was also calculated by the difference of initial and final masses of the heavy metals. Crystalline structure of P containing compounds in the SSA was examined by X-ray diffraction spectroscopy (XRD, D/Max-2500 V, Riagku, Japan) before and after the thermochemical treatment. All the analytical experiments were carried out in triplicates and the average values were used for the data analysis.

Bioavailability of P

Bioavailability of P in the SSA sample was measured according to the protocols given in the Directive 77/535/EES method 3.1.3 [12]. For the bioavailability analysis, 1 g sample was mixed with 100 mL of citric acid (2%) in a flask and agitated for 30 min at the speed of 40 rpm. The suspension was separated by 0.22 μm cellulose acetate membrane filter (CHMLab Group, Spain) and the TP in the filtrate was measured. Bioavailability was calculated based on Eq. (6).

$$\text{Bioavailability}(\%) = \frac{TP\ dissolved\ in\ citric\ acid}{TP\ in\ sample} \times 100 \quad (6)$$

Chemical P fractionation

P exists in SSA bound with various minerals and the minerals characterize the properties of P compounds. P compounds in SSA are changed during the thermochemical treatment and their P leaching characteristics were investigated with chemical fractionation before and after the treatment. P fractionation was consecutively carried out with distilled water (DW), BD reagent (0.11 M $NaHCO_3$ + 0.11 M $Na_2S_2O_4$), 1 M NaOH, and 1 M HCl [13]. P dissolved in DW is a water soluble P (WSP) and it represents easily available P in water. P dissolved in the BD reagent is a reducible P which bound to Fe/Mn (Fe–P and Mn–P). P dissolved in 1 M NaOH represents Al bound P (Al–P), and P dissolved in 1 M HCl represents Ca/Mg bound P (Ca/Mg–P). The remaining P, the difference of TP of the SSA and the sum of the fractionated P in the four steps, is called as the residual P which exists in very stable form and assumed to have very limited reactivity and bioavailability.

Results and discussion

Transformation of SSA during the thermochemical treatment

The contents of the major elements and heavy metals in the SSA were analyzed by ICP-OES (Table 1). Ca, P, and Al were the most abundant elements followed by Fe, K, and Mg. In case of heavy metals, Cu and Pb were higher than 800 mg/kg SSA followed by Zn, Ni, Cr, As, and Cd.

Mass change of the SSA during the thermochemical treatment was monitored. Mass loss was negligible (about 0.6%) with the thermal treatment without Cl-donor (control) since most of the volatile compounds were already removed during the sewage sludge incineration. Mass loss was also insignificant when Cl-donor was provided to the SSA during the thermochemical treatment. SSA with $MgCl_2$ gave the highest mass loss (2.5%) followed by $CaCl_2$, $AlCl_3$, NaCl, and KCl (data not shown). It is thought that mass loss is mainly caused by the vaporization of Cl_2 or HCl from the Cl-donors as shown in Eqs. (1)–(5).

P mass change in the SSA during the thermochemical treatment was also measured (Fig. 1). Most of the P remained in the SSA when the SSA was thermally treated without Cl-donors (control) and thermochemical treatment with $MgCl_2$ and $AlCl_3$. When the SSA was treated with $CaCl_2$, NaCl, and KCl, about 5, 8, and 10% of the TP were disappeared, respectively. Since most of the P containing compounds in the SSA are non-volatile, therefore, P loss by vaporization during the thermochemical treatment is negligible. Other possibility is that clod formed by melting of the sample during the thermochemical treatment made P extraction difficult and it might be regarded as disappeared P [14].

Table 1
Major elements and heavy metal contents of the SSA used in this study (by ICP-OES).

Element	Na	Mg	Al	Ca	P	K	Fe
g/kg SSA	0.4	15.2	86.2	91.5	86.2	21.3	58.7
Heavy metals	As	Cd	Cr	Cu	Ni	Pb	Zn
mg/kg SSA	29.8	12.5	86.8	837.0	86.9	823.8	429.7

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