Recovery of Biomass Incinerated as Struvite-K Precipitates Followed Aluminium Removal

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Abstract

Phosphorus (P) and potassium (K) are non-renewable materials and widely in many industries such as agricultural sectors. On the other hand, the demand of P and K as fertilizers increases which following global population. The nutrient source of P and K which get from biomass waste *i.e.* incinerated of activated sludge and coffee husk biochar, respectively. The present study was conducted recovery of P and K as struvite-K ($KMgPO_4 \cdot 6H_2O$) precipitates. The results showed that aluminium was released simultaneously with P from incinerated activated sludge with precipitate of Al:P of 1:1, K:P of 0.5, and Mg:P of 3. However, aluminium was inhibited to form struvite-K. Then, we examined cation removal especially for removed Al by dissolved 0.5 M HNO_3 and the solution was mixed with KH_2PO_4 and $MgCl_2 \cdot 6H_2O$ as source of K and Mg, respectively. The results showed aluminium (Al) was removed with precipitate K:P of 0.5, and Mg:P of 0.8. This study was confirmed that recovery of biomass incinerated was successful as struvite-K and can be used as fertilizers.

Keywords

Struvite-K, Recovery of Biomass Waste, Coffee Husk, Sludge Waste, Precipitates

1. Introduction

Current population projections estimate the world population to reach between 9 and 10 billion by 2050 [1] [2]. Among other things, this will mean increases in food production to feed the growing population. Commercial fertilizers play an important role in our food system, and most of our phosphorus and potassium-based fertilizers are derived from mined sources.

Phosphorus (P) is a limited asset, and it is assessed that global reserve of

phosphate rock must be mined economically somewhere between 50 and 100 years that usually is used in industry such as agricultural sectors [3] [4]. On the other hand, potassium is generally used to create fundamental fertilizers, since the contains cannot be replaced as a nutrients source for plants. The reserve is as much as the utilization in many years with current consumption rate. In 2014, 31 million tons of potassium compost (as K_2O) were applied around the world, with request expected to increment by about 3% each year [5]. Moreover, potassium is mined as mineral in limited number of countries, for example, Canada, Russia, Belarus and China [6] [7]. In any case, the cost of the potassium changes as seen in February 2009 due to the supply side issue [8]. Subsequently, potassium recovery should be considered as well as phosphorus to supply and demand K and P as fertilizers.

Based on the above reasons, we should discover alternatives for phosphorus and potassium sources for expanding global food production. Current organic sources of phosphate like bone meal, and animal manure are insufficient so new advancements should be developed for sustainable phosphate recovery from other natural waste sources, such as from sewage solid sludge. The materials are created during wastewater treatment processes and are a source of phosphorus [9]. Approximately, 90% of the P in wastewater is caught in the sewage sludge solids [10].

The sewage sludge solids are the most part organic, so the elemental analysis shows high levels of carbon, oxygen and hydrogen. In any case, the sludge cannot be used directly as a fertilizer, due to the presence of harmful heavy metals and other toxic compounds [11]. Therefore, treatment is required to make the solids safe and make the nutrients recoverable. One option for sludge treatment may be to use its energy content to digest sewage sludge to produce biogas. However, the volume of the residual materials is almost the same as the volume of the original sludge [12]. In addition, this system requires an additional process to separate the phosphorus remaining after digestion. Based on these deliberations, incineration has becoming popular as the final disposal process of sludge. The incineration of municipal solid waste sludge reduces the mass and volume by about 70% to 90%, respectively [13]. However, after incineration, the nutrient constituents not only phosphorus but other heavy metals such as aluminium (Al). On the other hand, this process is not expensive, waste management easier and more efficient [11].

While potassium source is from coffee husk which contains from 0.4% to 3.7% [14], USDA [15] reported production of coffee husk of 380.55 million bags (60 kilogram/bag) since 50% produced 1 kg of coffee bean [14]. So, this is potential issues for utilized this waste as nutrient sources for plants. Moreover, this waste might be contributed to environmental problems such as global warming issues. Global warming indicates a quick temperature increases which have been noticed around the world. This might result from discharge of greenhouse gases into the atmosphere during burning of biofuels and decomposition of organic matter. Because they release carbon dioxide (CO_2) or greenhouse gas. The

scientists around the world have been working to reduce the greenhouse gas productions by storing carbon in the environment [16]. In addition, global warming can be diminished globally through the process of soil carbon sequestration. The pyrolysis of biomass wastes into biochar is a potential strategy of accomplishing carbon sequestration [17]. Biochar can be utilized as a device to alleviate current climatic change and accomplish sustainable development in the world.

The objectives of this experiment were to recover of phosphorus and potassium from activated sludge charcoal and coffee husk biochar, respectively as struvite-K precipitates with the formula $MgKPO_4^{3-} \cdot 6H_2O$. The struvite-K is gained attention in the world because the formula suited to supplying nutrients through soil on crop growth.

2. Materials and Method

2.1. Materials

Sodium hydroxide (NaOH), acetic acid (CH_3COOH) and magnesium chloride ($MgCl_2 \cdot 6H_2O$) were obtained from the Kanto Chemical Co. Inc (Tokyo/Japan). All chemicals and reagents were of analytical grade used with purification by dissolved of distilled water.

2.2. Sample Preparation

Activated sludge is obtained from wastewater treatment plant, Miyoshi city, Hiroshima Prefecture. We collected which have already to become carbonized by factory. Coffee husk was collected from previous of our studied [18]. The dried sample was crushed and passed through 4.75 m/m sieve at 60˚C for 24 h in oven. The muffle furnace (model F0100 Yamato, Japan) is used to make biochar with temperature 600˚C for 2 h. The biochar passes through a sieved < 1 mm and washed with distilled water, oven dry at 60˚C for 24 h and sealed in a beaker for further studies. The characteristics of biochar were presented in **Table 1**.

2.3. Phosphate and Potassium Extraction

Activated sludge charcoal used for phosphate extraction. The concentration was used NaOH with concentration from 0.1, 0.2, 0.3, 0.4 and 0.5 M for 24 hours. The samples were carried out with 1 gram in 50 mL of solution. While for potassium extraction used coffee husk biochar, we used CH_3COOH with concentration from 1, 2, 3, 4 and 5 M for 30 minutes. The sample was carried out with 0.25 gram in 50 mL of solution.

2.4. Procedure of Precipitation

The best results of phosphate and potassium extraction were used. 50 mL of

Table 1. Characteristics of coffee husk biochar.

C-Total (%)	Oxygen (%)	N-Total (%)	CEC (meq/100 g)
57.81	24.40	0.88	52.67

1000 ppm magnesium solution was added to fixed amount of obtained solution. Phosphate and potassium were added 20 and 50 mL, respectively. The detailed of procedure in Figure 1 and Figure 2.

2.5. Analytical Methods

The concentrations of PO_4^{3-} were determined by standard method (Japan Industrial Standard method JIS KO 102). The concentration of potassium was measured using atomic absorption spectrophotometer (AA-6300, Shimadzu Kyoto, Japan). Cation exchange capacity (CEC) was extracted 1 M NH$_4$OAc pH 7. Morphology and chemical composition of crystal was measured by Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) (JED-2300) (Shimadzu, Kyoto, Japan).
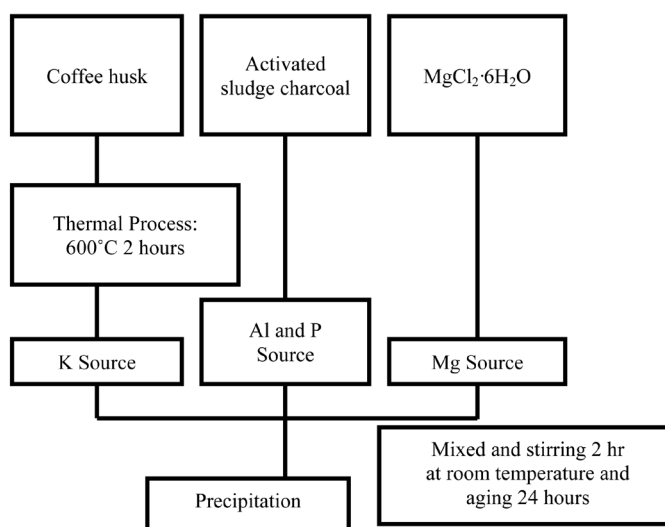
   1) First precipitation

   2) Cation removal for eliminated of aluminium to get struvite-K precipitates

We examined cation removal especially for removed Al to get pure struvite-K by dissolved 0.5 M HNO$_3$ for 1 hour with ratio of 1/100 of solid sample/liquid. 1000 ppm of 50 mL of the potassium and magnesium solution from KH$_2$PO$_4$ and MgCl$_2$·6H$_2$O, respectively. The solution was adjusted to pH 11 by NaOH. The detailed procedure is in Figure 2.

3. Results and Discussion

3.1. Phosphate Extraction

Phosphate recovery from sewade sludge with alkaline conditions has been studied in some authors [19]. Alkaline extraction is a good alternative since it gives a phosphorus product with a lower metal contamination. Most metals are most insoluble in alkaline than in acids, and extraction with alkaline gives a phosphorus product with a lower contamination of metal [20]. However, the process of

Figure 1. First precipitation, Al was released simultaneously with P from activated sludge charcoal.
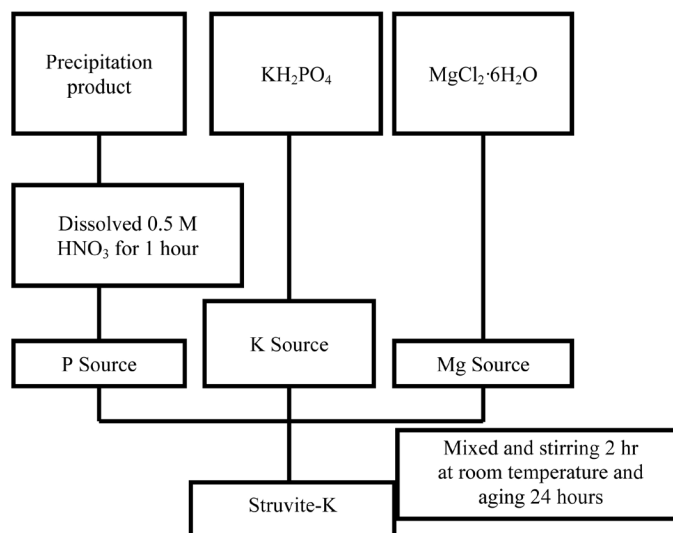
Figure 2. Procedure of cation removal especially Al to get Struvite-K.

extraction, aluminium was released which simultaneously with P. To confirm the release of aluminium, we examined extraction of activated sludge charcoal of 50 mL with pH of 12.8. This pH value is considering low precipitation. However, we must adjust to pH 11 by HCL [21].

To compete aluminium, we added $MgCl_2 \cdot 6H_2O$ as magnesium source to adjusted molar Mg: P of 1:1 with formula in Equation (1), since this value is considering favorable for precipitation in many scientists. Stirring for 2 hours and aging for 24 hours then filtered. The solid precipitate was obtained then oven dried 60°C. The results were obtained in **Figure 3** and composition of precipitation as shown in **Table 2**.

$$2AlPO_4 + 3MgCl_2 \rightarrow Mg_3 \left(PO_4 \right)_2 + 2AlCl_3 \qquad (1)$$

Table 3 presents the results of phosphate recovery under different concentration of NaOH. It is found that the phosphate recovery increased, when concentration of NaOH increased from 0.1 M to 0.3 M. Thereafter, the phosphate recovery decreases from 0.3 M to 0.4 M and slightly increased from 0.4 M to 0.5 M. This is indicated that around this concentration phosphate recovery from activated sludge charcoal was effective. This is agreement with [22] that recovery of sludge in Karlskoga with sodium hydroxide reaches 90% of the phosphorus content.

3.2. Potassium Extraction

Potassium is a chemical element with the symbol K and atomic number 19. Potassium reacts rapidly with oxygen. Carboxylic acid is an organic acid that contains a carboxyl group and contains oxygen with formula (C(=O)OH). The present study, we used acetic acid (AA). Acetic acid is the second simplest carboxylic acid (after formic acid). In the other hand, acetic acid is widely used bulk chemical and it can be used as green solvent that non-toxic in environment [23].
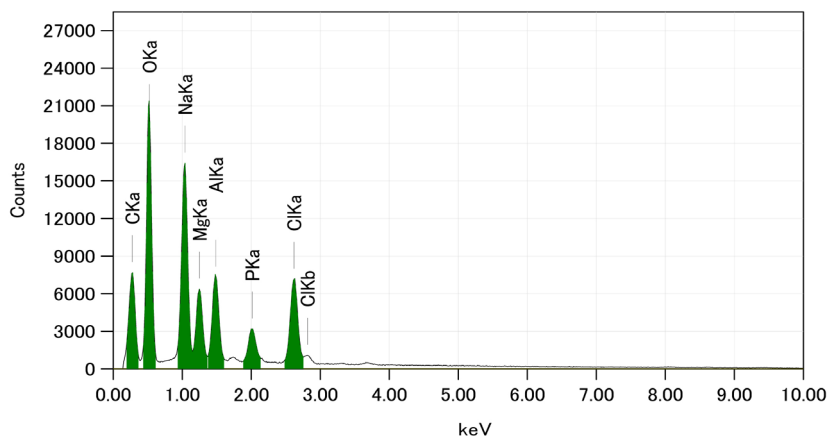
**Figure 3.** EDX results (extracted from activated sludge charcoal).

Table 2. Composition of precipitation (extracted from activated sludge charcoal).

Composition (wt%)						
C	O	Na	Mg	Al	P	Cl
24.90	40.33	13.60	4.97	5.37	2.64	8.19

Table 3. Concentration of different phosphate extraction.

Extractants	Equilibrium time	Equilibrium pH	PO_4^{3-}
0.1 M NaOH	24 hours	11.6	400
0.2 M NaOH	24 hours	12.3	424
0.3 M NaOH	24 hours	12.8	2920
0.4 M NaOH	24 hours	13.1	2620
0.5 M NaOH	24 hours	13.2	2730

Acetic acid is acidic character because release of the proton (H^+). Furthermore, acetic acid is in the carboxyl group (-COOH) can separate from the molecule by ionization in Equation (2) and reacts with cation such as potassium with formula in Equation (3).

$$CH_3COOH \rightarrow CH_3CO_2^- + H^+ \tag{2}$$

$$K_2O + CH_3COOH \rightarrow CH_3COOHK + H_2O \tag{3}$$
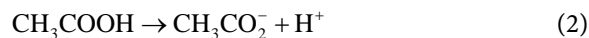
Table 4 presents the recovery of potassium under different concentration of acetic acid (AA). It is found that the potassium recovery fluctuating in all concentrations. The lower results in 4 M CH_3COOH with concentration of 26 mg/L while the higher in 5 M CH_3COOH with concentration of 1891 mg/L. This is indicated that higher concentration of acetic acid can easily react with potassium.

3.3. First Precipitation Process

The present study, we examined the reaction conditions for the first precipitation. Experimental conditions we conducted in glass and stirring for 2 hours. The solution is from 50 mL of 1000 ppm magnesium from $MgCl_2 \cdot 6H_2O$. The

Table 4. Concentration of different potassium extraction.

Extractants	Equilibrium time	Equilibrium pH	K+
1 M CH₃COOH	30 minutes	2.2	122
2 M CH₃COOH	30 minutes	2.1	58
3 M CH₃COOH	30 minutes	2.0	190
4 M CH₃COOH	30 minutes	1.8	26
5 M CH₃COOH	30 minutes	1.7	1891

phosphate solution is added 20 mL from 0.3 M NaOH extractants as shown in Table 3. While for potassium solution is added 50 mL from 5 M CH₃COOH as shown in Table 4. However, the aluminium was released simultaneously with P from activated sludge charcoal which has described in above as shown in Figure 3. While for this precipitation we added potassium to make composition of struvite-K ($MgKPO_4 \cdot 6H_2O$) as shown in Figure 4.

The results show that the aluminium content is 0.85 wt% (Table 5) which lower than Figure 3 is 5.37% (EDX results from activated sludge charcoal). This is indicated that potassium can compete with aluminium in precipitation with precipitate of Al: P of 1, Mg: P of 3 and K: P of 0.5 (in mol/l). Calculated from wt% to mol/l in Equation (4).

$$wt\%/Fw \tag{4}$$

Morphology of precipitation as shown in Figure 5. Seen that needle-like mixed with tetrahedral structure, indicated that aluminium reacts with phosphate to become aluminium phosphate precipitates [24]. However, to get pure of struvite-K we must examine or release of aluminium in solid precipitation. On the other hand, benefit of aluminium is can be used as coagulate of organic matters which occurs of eutrophication [25]. Moreover, if aluminium can directly use in soil as fertilizer, it may have negative effect on plant growth [26].
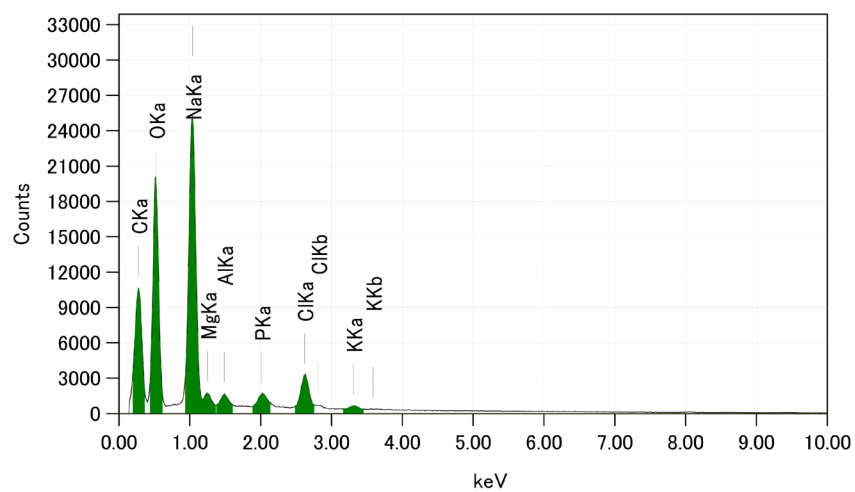
3.4. Cation Removal to Get Struvite-K Precipitates

After the first precipitation, we examined cation removal especially to removed aluminium from precipitation product to get struvite-K by dissolved 0.5 M HNO_3 with reacts with aluminium with formula in Equation (5):

$$Al_2O_3 + 6HNO_3 \rightarrow 2Al(NO_3)_3 + 3H_2O \tag{5}$$
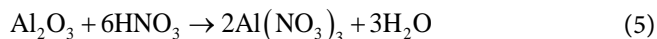
KH_2PO_4 and $MgCl_2 \cdot 6H_2O$ as potassium and magnesium sources, respectively as solution of struvite-K precipitates. The solution was adjusted to pH 11 by NaOH. The results show in Figure 6 with chemical composition in Table 6.

Based on Figure 6, the aluminium was successfully removed from solid precipitation. This is indicated that HNO_3 was effectively used to release of cation especially aluminium with precipitate of K: P of 0.5 and Mg: P of 0.8. Furthermore, struvite-K precipitates during processing which fall to become sediment as shown in Figure 7. And if have dried, struvite-K precipitates can be seen as crystal through SEM images as shown in Figure 8. The shape is needle-like which have reported in some experimental works [27] [28].

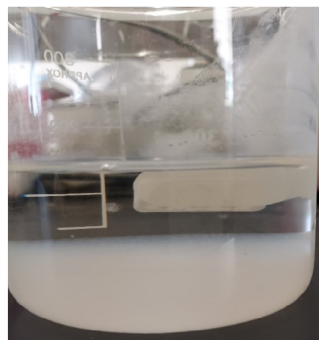**Figure 4.** EDX results, first precipitation.
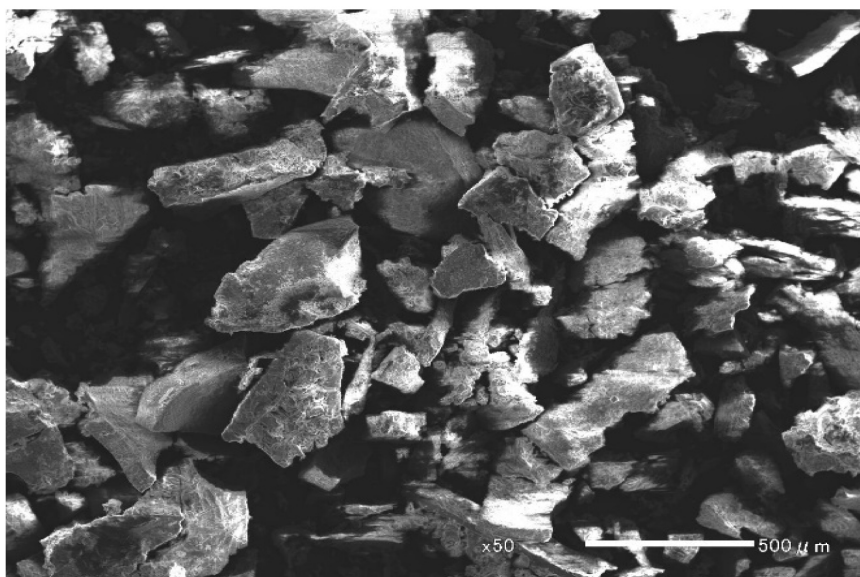
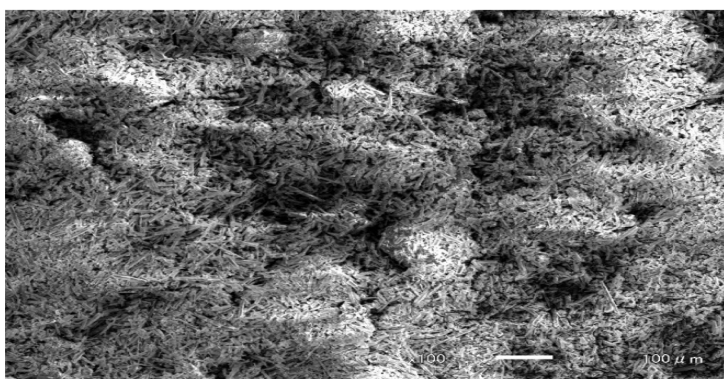

Figure 5. SEM images in first precipitation.
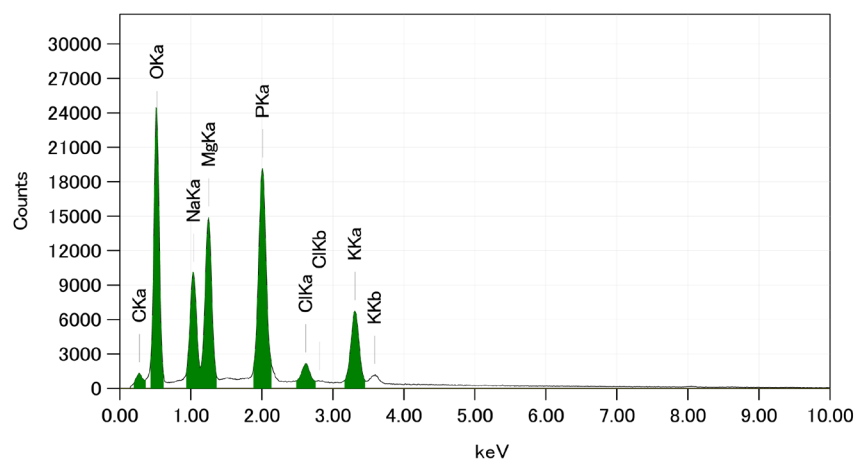
Figure 6. EDX results from cation removal as struvite-K precipitates.

Figure 7. Images of struvite-K precipitate in aging process.

Figure 8. SEM images of struvite-K precipitates.

Table 5. Composition of first precipitation.

Composition (wt%)							
C	O	Na	Mg	Al	P	Cl	K
27.27	40.63	23.42	2.20	0.82	1.02	4.06	0.55

Table 6. EDX results from cation removal as struvite-K precipitates.

Composition (wt%)						
C	O	Na	Mg	P	Cl	K
3.53	45.47	8.83	11.12	18.31	2.03	10.71

4. Conclusion

Recovery of phosphorus and potassium from biomass incinerated was investigated. We found that aluminium was released simultaneously with P from activated sludge charcoal. To eliminate aluminium, we examined by dissolving 0.5 M HNO_3 and the solution was mixed with KH_2PO_4 and $MgCl_2·6H_2O$ as source of potassium and magnesium, respectively as struvite-K precipitates.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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