

Recovery of Phosphate Rock Equivalents from Incineration Ash of Chicken Manure by Elution-Precipitation Treatment

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To obtain calcium phosphates - a phosphate rock equivalent - from the incineration ash of chicken manure, which is obtained from power generation systems that use the manure as fuel, the incineration ash was treated with an aqueous solution of nitric acid to elute phosphorus. By using 0.3 M HNO₃, most of the phosphorus could be eluted from 1.0 g of ash within 0.1 h. Unlike in the case of composted chicken manure which was previously examined in our laboratory, the concentration of HNO₃ was increased for elution from the incineration ash. The use of incineration ash of chicken manure enabled the removal of inorganic species at a lower boiling or sublimation temperature, and organic species by calcination in the power generation system. The phosphorus contents of the incineration ash and nitric acid extract were higher than that of composted chicken manure. XRD analysis showed that the treatment of the obtained nitric acid extract with aqueous NH₃ yielded a precipitate of poorly-crystallized calcium hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂), which is one of the main components of phosphate rock. To confirm the formation and purity of calcium phosphate species, precipitation calcination was conducted at 1,078 K for 5 h. XRD analysis revealed that the calcined solid was tricalcium phosphate, and no contamination was evident. These results reveal that a phosphate rock equivalent could be easily obtained from the incineration ash of chicken manure, which implies that approximately 14% of the phosphate rock that is currently being imported into Japan could be replaced by this product.

Introduction

Livestock manure accounts for ca. 20% of industrial waste in Japan (Miyoshi *et al.*, 2011). To reduce and recycle industrial waste, most livestock manure is recycled as fertilizer and the rest is incinerated and landfilled. Such a treatment method merely returns industrial waste to the earth, which is insufficient. Since most livestock manure contains a considerable amount of phosphorus, they are reused as fertilizer. The phosphorus content in chicken manure (6.2% and 4.2% as P₂O₅ in dried hen and broiler manure, respectively) is greater than that in pig (5.6%) and cattle manure (1.8% and 2.6% in dried dairy cattle and meat cattle, respectively) (Ito, 2015). Tokushima Prefecture is home to the largest production area of *Jidori* (free range chickens) in Japan. Chicken farmers are now being forced to process chicken manure. To promote effective utilization of chicken manure beyond recycling as fertilizer, a project involving boiler power generation using chicken manure as fuel was begun in the Tokushima Prefecture in 2015. Although power

generation is conducted smoothly, the incineration ash of chicken manure (IACM) is again reused as a fertilizer. It should be noted that phosphate rock as a raw material for phosphorus will disappear in the near future (Abelson, 1999). Therefore, the United States stopped exporting phosphate rock in 1997, followed by other exporting countries (Yokoyama *et al.*, 2007). Since there is no phosphate rock in Japan, the development of a production method for phosphate rock or its equivalent is an urgent requirement in Japan. Phosphorus derived from phosphate rock is used for manufacturing various phosphorus-containing classic and advanced materials, including biomaterials, pharmaceuticals, chemical products, and food additives as well as fertilizers (Ohtake *et al.*, 2017). Although reusing chicken manure as fertilizer is effective for food production, it is currently impossible to turn it into various classic and advanced materials containing phosphorus. Therefore, studies have been conducted on the elution of phosphorus from chicken manure using acidic solutions (Szögi *et al.*, 2008; Szogi and Vanotti, 2009; Kaikae *et al.*, 2009; Miyoshi *et al.*, 2011), and emphasis is placed on the enhancement of phosphorus concentration in the eluate. Under these circumstances, we focused on the high content of calcium in chicken manure. The calcium content in chicken manure (26% and 8.9% as CaO in dried hen and broiler manure, respectively) is greater than that in pig (8.3%) and cattle

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manure (4.4% and 3.0% in dried dairy cattle and meat cattle manure, respectively) (Ito, 2015). It is widely known that the main component of phosphate rock is calcium phosphates, and that high-purity phosphate rock is formed by the accumulations of sea bird manure. This indicates that phosphate rock equivalents may be formed from chicken manure. Since phosphate rock equivalents are expected to be introduced directly into the currently operating phosphorus production plants, chicken manure, which is now used only as fertilizer, could be used as a raw material for various phosphorus-containing products. The direct use of chicken manure, however, faces problems with legislation. Therefore, in a previous paper (Sugiyama *et al.*, 2016), we reported a combined treatment involving elution with nitric acid and precipitation with ammonia (elution-precipitation treatment) for composted chicken manure (CCM) to recover high-purity calcium phosphate, the main component of phosphate rock. The composting of chicken manure is known to enhance the concentration of phosphorus mainly due to the decomposition of organic compounds (Nakasaka *et al.*, 1999; Nakasaka, 2014), and, therefore, our previous paper reported the possible utilization of chicken manure for generation of phosphate rock.

In the present study, to further utilize chicken manure, we employed the elution-precipitation treatment to obtain phosphate rock equivalent from the incineration ash of chicken manure, which was used as a fuel for power generation.

1. Experimental

IACM (**Figure 1 (A)**) produced by burning chicken manure at 1073 K, was supplied by a power generation plant in the Tokushima Prefecture, in which chicken manure was used as a fuel. Since the moisture content in the incineration ash was quite low (less than 1%), the IACM was used as supplied for the following experiments.

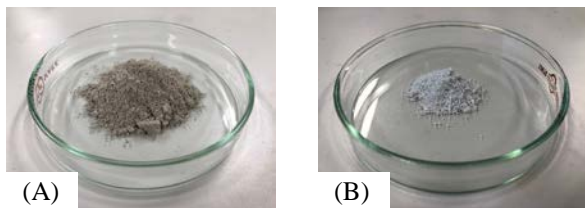


Fig. 1 Photos of (A) incineration ash of chicken manure and (B) recovered solid via elution-precipitation treatment of the incineration ash

A batch method was employed to examine the elution behaviors of phosphate and various cations from the IACM using various concentrations of aq. HNO₃ (Wako Pure Chemical Industries, Ltd.) as an eluate. The composition of IACM was analyzed by X-ray fluorescence (XRF; Supermini 200WD, Rigaku Co.)

spectroscopy and the results are presented in **Table 1**. Phosphate will hereafter be referred to as P. The weight percentages of P and Ca in the manure were approximately estimated as 22.9 and 36.6 wt.%, respectively. The present study was focused mainly on the cations described in Table 1.

Table 1 Composition of incineration ash of chicken manure estimated by XRF spectroscopy

Composition [wt.%]						
Mg	Al	P	K	Ca	Mn	Fe
3.3	0.6	22.9	34.1	36.6	1.2	1.2

Since the XRF data is insufficient for quantitative analysis, the CCM was first treated by dissolving in conc. HNO₃ for approximately 1 month, and then analyzed by ICP-AES (SPS3520UV, SII Nanotechnology Inc.) to determine the elemental composition as well as the amount of substance of each element in 1.0 g of CCM (**Table 2**). The composition of the CCM is presented in Table 2. ICP-AES is an insufficient analytical method for potassium (Sugiyama *et al.*, 2016) nevertheless, the potassium content is presented in Table 2 to compare with the data in Table 1. The phosphorus content of CCM determined by the two methods was found to be similar.

Table 2 Amount of substance and composition of incineration ash of chicken manure estimated by ICP-AES

Mg	Al	P	K	Ca	Mn	Fe
Amount of substance (mmol) / 1g of CCM						
1.21	0.18	4.92	6.29	6.06	0.16	0.14
Composition [wt.%]						
4.2	0.7	22.0	35.5	35.1	1.3	1.1

The batch method began with the addition of 100 mL of an aqueous acidic solution of HNO₃ to a flask (200 mL), followed by the addition of 1.0 or 10 g of IACM with a particle size of less than 355 μm. The mixture was stirred at 130 rpm and 298 K in a constant-temperature bath. The solution was filtered after a scheduled time of stirring using a filter paper (5 μm pore size) and a membrane filter (0.45 μm of pore size), and then analyzed by ICP-AES. In the present study, the amounts of substances except K in Table 2 were used to calculate the elution rate and recovery rate.

To precipitate the solid from the nitric acid extract, the pH of the nitric acid extract was increased using an aq. NH₃ solution. The solid samples thus obtained (**Figure 1 (B)**) were dried and analyzed by X-ray diffraction (XRD; SmartLab/RA/INP/DX, Rigaku Co.) spectroscopy using monochromatized Cu Kα radiation (45 kV, 150 mA) and X-ray fluorescence (XRF; Supermini200WD, Rigaku Co.) spectroscopy.

2. Results and Discussion

2.1 Elution behavior of the incineration ash of chicken manure using various concentrations of HNO₃

Figure 2 shows the XRD spectrum of IACM, which shows that the IACM consists of calcium hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂; PDF 00-055-0592), calcium phosphate (Ca₃(PO₄)₂; PDF 00-056-0064), calcium hydroxide (Ca(OH)₂; PDF 00-044-1481), and calcium hydrogen phosphate (CaHPO₄; PDF 01-070-0359).

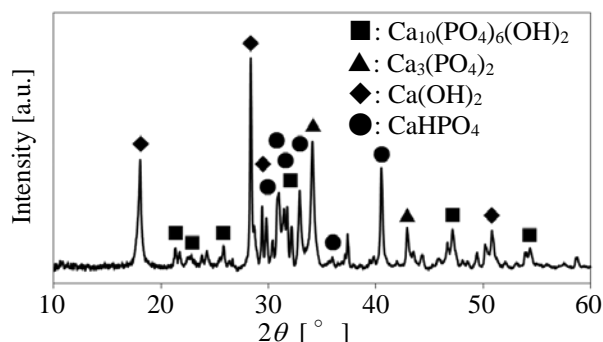


Fig. 2 XRD spectrum of incineration ash of chicken manure

The first two phosphates are the main components of phosphate rock. The presence of calcium hydroxide is because a sufficient calcium source was provided to the chickens to form good egg-shells, which indicates that, even in the presence of an excess amount of amorphous phosphate in IACM, it can convert into calcium phosphate.

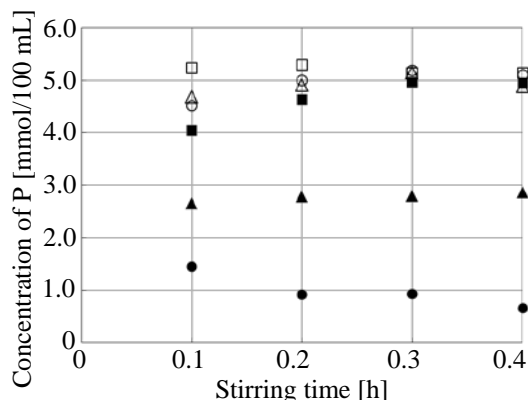


Fig. 3 Elution behaviors of P from incineration ash of chicken manure (1.0 g) using various concentrations of HNO₃

Symbols ●: 0.08 M, ▲: 0.1 M, ■: 0.2 M, ○: 0.3 M, △: 0.4 M, □: 0.5 M.

Figure 3 shows the elution behaviors of P from 1.0 g of IACM using various concentrations of HNO₃ and stirring times of up to 0.4 h. The vertical axis of this figure shows the amount of substance (mmol) of each element eluted from the IACM in the solution (100 mL) used in the experiment. Instead of nitric acid, sulfuric

acid or hydrochloric acid can also be used. However, the use of sulfuric acid increases the possibility of production of calcium sulfate, but not calcium phosphates. Moreover, using hydrochloric acid may eventually yield various chlorides. Therefore, nitric acid was used in this study. As shown in our previous study using CCM (Sugiyama *et al.*, 2016), Ca was favorably eluted as P from CCM. Furthermore, in the present case, an excess amount of calcium is present in the IACM as shown in Table 1. Therefore, in the present study, we focused on the elution behavior of P. Evident eluates of P were detected even after a short stirring time of 0.1 h using all the concentration of HNO₃ solutions, while the elution amount at 0.1 h was similar to that at 0.4 h, which indicated that the elution equilibrium was reached at a shorter stirring time of 0.1 h. Furthermore, the effect of HNO₃ concentration on the elutions of P was evident for a concentration of 0.02 M, and a higher HNO₃ concentration resulted in an increase in the elution amount of P. In contrast, the same amount of P was detected in concentrations greater than 0.3 M. It was evident that a more concentrated HNO₃ (over 0.3 M) and a longer stirring time (over 0.1 h) resulted in better elution of P. However, it may result in a greater consumption of acid and render the process time-consuming. Therefore, HNO₃ concentration of 0.3 M and a stirring time of 0.1 h were considered suitable under the present conditions. Under these conditions, P was eluted from IACM at a rate of 91.8%. It should be noted that elements other than P also eluted, as shown in **Table 3**.

Table 3 Concentration [mmol/100 mL] and elution rate [%] of each element from IACM (1.0 g) after 0.1 h of elution using 0.3 M HNO₃

	Mg	Al	P	Ca	Mn	Fe
Conc.	1.01	0.14	4.51	5.65	0.13	0.12
Elution rate	84.1	76.5	91.8	93.2	80.4	83.5

The elution rate of Ca (93.2%), which was greater than that of P (91.8%), seemed suitable for the formation of calcium phosphates. Comparable elution rates, however, were been detected for Mg, Al, Mn, and Fe. Therefore, the following process (precipitation process) was used to remove elements other than Ca and P.

2.2 Scale-up treatment of incineration ash of chicken manure using various concentrations of HNO₃

Since 1.0 g of IACM could be easily eluted in a short time of 0.1 h under the above conditions, 10 g of ash was treated using the same amount of solution, i.e., 100 mL of an aqueous acidic solution of HNO₃, to examine the possibility of scale-up. Preliminary experiments showed that lower HNO₃ concentrations of 0.01 and 1.0 M were insufficient for treating 1 g of ash. Therefore, HNO₃ concentrations ranging from 1.8 M to 2.2 M were employed to perform elution in a shorter time. As shown in **Figure 4**, the elution behaviors of P

were similar to those detected using 1.0 g of IACM, and the eluates of P were evident even when a stirring time as short as 0.1 h was employed for all the HNO₃ solutions. With increasing pH from 1.8 to 2.0, the elution amount of P increased, while the concentrations of HNO₃ between 1.8 M and 2.2 M afforded essentially the same elution amount of P. Therefore, the suitable HNO₃ concentration and stirring time were 2.0 M and 0.1 h, respectively, for 10 g of IACM. These conditions yielded a 92.5% elution rate of P from the IACM, which was essentially the same as that obtained using 1.0 g of IACM.

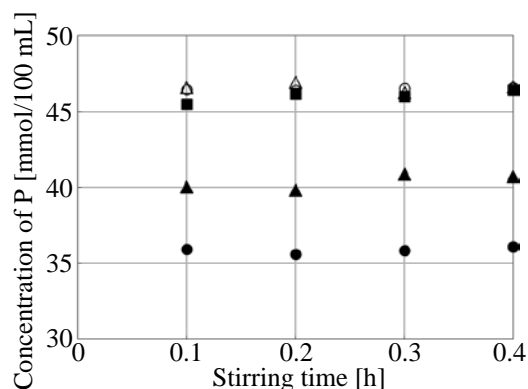


Fig. 4 Elution behaviors of P from incineration ash of chicken manure (10 g) using various concentrations of HNO₃
 Symbols ●: 1.8 M, ▲: 1.9 M, ■: 2.0 M, ○: 2.1 M, △: 2.2 M

2.3 Recovery of phosphate rock equivalents (calcium phosphates) from nitric acid extract

The nitric acid extract of IACM (1.0 g) was treated with NH₃ to obtain precipitates at pH = 6.0, 6.5, 7.0, and 7.5. The precipitations were analyzed by XRD, and broad peaks arising from calcium hydroxyapatite were detected for all the precipitates produced at various values of pH, as shown in **Figure 5 (A)**. The crystallinity of each component of the precipitates was measured to check for byproducts produced via calcination at 1073 K for 5 h. The calcined precipitates consisted mainly of calcium phosphate (**Figure 5 (B)**). Since calcium hydroxyapatite converts to calcium phosphate under high temperatures (Sugiyama *et al.*, 1998), the amounts of calcium hydroxyapatite and calcium phosphate produced before and after calcination were reasonable. It should be noted that both the phosphate species are the main components of phosphate rock, which indicates that the elution-precipitation treatment of IACM using aqueous HNO₃ and NH₃ results in the formation of phosphate rock equivalents. Ammonia is contained in the feces and urine of chickens (Kobayashi, 1997). Although the use of other alkaline reagents besides ammonia was possible, considering the future utilization of unused wastes, ammonia was used in the present study.

Table 4 presents the weights of the precipitates, formed at various pH values before and after calcination at 1,073 K for 5 h. Under all pH conditions, the weights decreased after calcination due to the conversion of calcium hydroxyapatite to calcium phosphate. Regardless of the calcination, the weight of the precipitate formed at pH = 6.0 was the smallest, while the weights of precipitates formed at pH = 6.5 and above were almost the same. A small recovery at pH = 6.0 indicated insufficient precipitation at a lower pH. It should be noted, however, that an excessive high pH resulted in an increase in the usage of aqueous NH₃, followed by an additional precipitation of elements other than calcium and phosphorus. Therefore, in the present study, the pH of 6.5 is considered optimal.

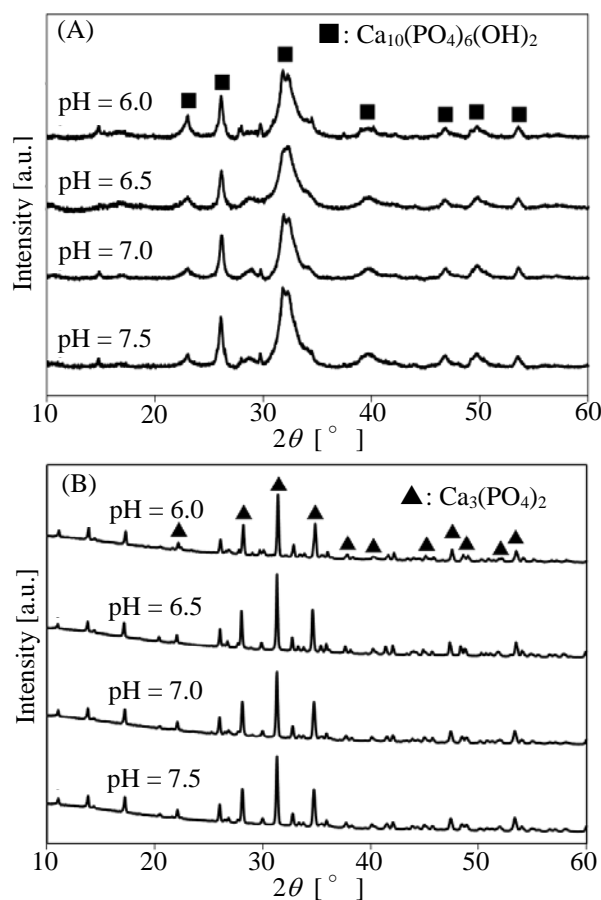


Fig. 5 XRD spectra of the precipitates obtained at various pH from elution-precipitation treatment of IACM before (A) and after (B) calcination

Table 4 Weights [g] of precipitates recovered at various pH

pH	6.0	6.5	7.0	7.5
Before calcination	0.368	0.443	0.451	0.449
After calcination	0.272	0.351	0.359	0.360

The precipitate obtained at pH = 6.5 from the elution-precipitation treatment of IACM before and after calcination was further analyzed by XRF spectroscopy. As shown in **Table 5**, the composition of the precipitate is the same irrespective of calcination. As shown in Figure 4, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ was mainly present before calcination. In this case, the atomic ratio of Ca/P was 1.67, however, it was determined as 1.99 by XRF spectroscopy. XRD analysis showed that the main component after calcination was $\text{Ca}_3(\text{PO}_4)_2$, having a Ca/P atomic ratio of 1.50. However, XRF spectroscopy yielded a ratio of 1.97. These results show that a calcium-rich phosphate rock equivalent could be obtained from the IACM due to the excess amount of calcium in IACM.

Table 5 Composition of precipitate at pH = 6.5 before (A) and after (B) calcination

	Composition [wt.%]						
	Mg	Al	P	K	Ca	Mn	Fe
(A)	0.5	0.6	26.0	1.6	66.9	1.8	2.7
(B)	0.6	0.6	26.1	1.1	66.7	2.0	2.9

2.4 Comparison of phosphorus recovery rates from incineration ash of chicken manure and composted chicken manure

Finally, the phosphorus recovery rates from the IACM and CCM (Sugiyama *et al.*, 2016) via dissolution and precipitation processes followed by calcination from calcium hydroxyapatite to calcium phosphate were compared. As shown in **Table 6**, the phosphorus recovery rates (elution rate) from CCM and IACM obtained by the dissolution process are different. This was possibly because of an enhancement in the phosphorus content of IACM due to the removal of inorganic species with either a lower boiling or a lower sublimation temperature and organic species by the power generation system. Furthermore, it is possible that the difference in the morphologies of the P species in CCM and IACM contributed to the enhancement. Therefore, the total phosphorus recovery rate (45.9%) from IACM was greater than that (17.1%) from CCM. However, it should be noted that approximately half of the phosphorus in the nitric acid extract cannot be precipitated in the precipitation process. In the precipitation step, the precipitate rapidly formed just after the addition of aqueous NH_3 , and was immediately filtered. According to the solubility product of calcium hydroxyapatite ($\text{pK}_{\text{sp}} = 58.5$ at 298 K) (Chow, 1991; Monma, 1996), more precipitate should be obtained in the precipitation process when a longer precipitation time is employed. A longer precipitation time, however, will result in the mixing of other elements rather than Ca and P. If the final precipitate contains low amount of Mg and K, it will not be suitable for phosphorus production. To obtain high-purity calcium

hydroxyapatite, an easy method for the removal of elements other than Ca and P should be developed.

Chicken farmers around the world are struggling with large amounts of chicken manure. For example, in Japan, approximately 13,900,000 tons of chicken manure will be discharged annually based on 2016 data. It is estimated that even now approximately 100,000 tons of phosphate rock equivalent could be produced from chicken manure using the present method. This would be approximately 14% of Japan's annual consumption of phosphorus (Ministry of Agriculture, Forestry and Fisheries of Japan, 2016; Tsuiki and Harada, 1997). Further work to improve the efficiency of the method is in progress.

Table 6 Recovery rates of phosphorus via dissolution, precipitation, and calcination processes

	After dissolution	After precipitation	After calcination
CCM	58.6%	19.8%	17.1%
IACM	91.8%	50.0%	45.9%

Conclusions

The present study showed that the IACM can be used for the recovery of phosphate rock equivalent via a simple and easy method that involves an elution-precipitation treatment using aqueous HNO_3 and NH_3 . By further improving this method, it might be possible to produce a large amount of calcium phosphate equivalent to phosphate rock even in a country that does not have a natural resource of phosphate rock.

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