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

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Abstract

In order 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 for fuel, incineration ash was treated with an aqueous solution of nitric acid to elute phosphorus. By using 0.3 M of HNO_3, most of the phosphorus could be eluted from 1.0 g of ash within 0.1 h. Compared with the composted chicken manure that was previously examined in our laboratory, the concentration of HNO_3 was increased for this session of elution. Using the incineration ash of chicken manure made it possible to remove inorganic species at a lower boiling or sublimation temperature, and organic species by calcination in the power generation system. Compared with composted chicken manure, the concentrations of phosphorus contained in the incineration ash and the nitric acid extract were higher in the incineration ash. XRD analysis showed that the obtained nitric acid extract could be treated with aqueous NH_3 to form a precipitation of poorly-crystallized calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which is one of main components in phosphate rock. In order to confirm the formation and purity of calcium phosphate species, the precipitation calcination was conducted at 1,078 K for 5 h. XRD 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 means 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 percent of industrial waste in Japan (Miyoshi *et al*., 2011). In reducing and recycling 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 is reused as fertilizer, it contains a considerable amount of phosphorus. Phosphorus content in chicken manure (6.2 and 4.2% as P_2O_5 in dried hens and broilers, respectively) is relatively greater than that from pigs (5.6%) and cattle (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. In order to promote effective uses beyond recycling chicken manure as fertilizer, a project that involves boiler power generation using chicken manure as fuel was begun in the Tokushima Prefecture in 2015. Although the power generation is conducted smoothly, the incineration ash of chicken manure is again being reused as 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 to export phosphate rock in 1997, followed by other exporting countries (Yokoyama *et al*., 2007). Since there is no phosphate rock in Japan, the development of production method of phosphate rock or the corresponding equivalent is an urgent issues in Japan. Phosphorus derived from phosphate rock is used for manufacturing various phosphorus-containing classic and advanced materials that include biomaterials, pharmaceuticals, chemical products, and food additives together with fertilizer (Ohtake *et al*., 2017). Although reuse as fertilizer is effective for food production, it is currently impossible to turn it into various classic and advanced materials containing phosphorus. Therefore, studies are now reporting 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

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8.9% as CaO basis in dried hens and broilers, respectively) is relatively greater than that from pigs (8.3%) and cattle (4.4 and 3.0% in dried dairy cattle and meat cattle, 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 in 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 currently operating phosphorus production plants, chicken manure which is now used only as fertilizer could be used as raw material for various phosphorus-containing products. Direct use of chicken manure, however, faces problems with legislation. Therefore, in a previous paper (Sugiyama *et al*., 2016), we reported that a combination of the treatment of elution with nitric acid and precipitation with ammonia for composted chicken manure (CCM) was carried out to reveal that high-purity calcium phosphate - a main component of phosphate rock - could be recovered (elution-precipitation treatment). The composting of chicken manure is known to enhance the concentration of phosphorus mainly due to the decomposition of organic compounds (Nakasaki *et al*., 1999; Nakasaki, 2014), and, therefore, our previous paper revealed the possible utility of chicken manure for generation of phosphate rock.

In the present study, in order to further effectively utilize chicken manure, we attempted to employ elution-precipitation treatment to obtain phosphate rock equivalent from the incineration ash of chicken manure (IACM) that had been used as fuel for power generation.

1. Experimental

IACM (**Fig. 1 (A)**) produced from burning chicken manure at 1073 K, was supplied from power generation plant in 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%, IACM was used as supplied for the following experiments.

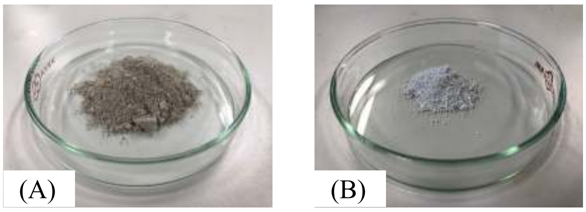

Fig. 1 Photos of (A) incineration ash of chicken manure and (B) recovered solid via elution-precipitation treatment of the incineration ash

A batch method was employed to examine the elution behaviors of phosphate and various cations from IACM using various concentrations of aq. HNO_3 (Wako Pure Chemical Industries, Ltd.) as an eluate. The composition of IACM was analyzed using X-ray fluorescence (XRF; Supermini 200WD, Rigaku Co.), as described in **Table 1**. Phosphate will hereafter be referred to as P. The weight percentages of P and Ca in the manure were approximately estimated at 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 using XRF

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

Since XRF data is insufficient for a quantitative analysis, CCM was treated dissolved using conc. HNO_3 for approximately 1 month, followed by the analysis using ICP-AES (SPS3520UV, SII Nanotechnology Inc.) to obtain amount of substance of each element in 1.0 g CCM (**Table 2**). Furthermore the composition obtained from those amounts of substances was also described in Table 2. Although ICP-AES is insufficient analysis method for potassium (Sugiyama *et al*., 2016), the amount of substance for potassium was described in Table 2 in order to compare the data in Table 1. It was evident from the comparison of Tables 1 and 2 that almost the same tendency was detected.

Table 2 Amount of substance and composition of incineration ach of chicken manure estimated using 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 HNO_3 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 filter paper (5 μm pore size) and a membrane filter (0.45 μm of pore size), then it was analyzed by ICP-AES. In the present study, the amounts of substances except K in Table 2 were used for the calculation of the elution rate and recovery rate.

In order to precipitate the solid from the nitric acid extract, the pH of the nitric acid extract was increased using an aq. NH_3 solution. The solid samples thus obtained (**Fig. 1 (B)**) were dried and analyzed via X-ray diffraction (XRD; SmartLab/RA/INP/DX, Rigaku Co.) using monochromatized Cu Kα radiation (45 kV, 150 mA) and X-ray fluorescence (XRF; Supermini200WD, Rigaku Co.).

2. Results and Discussion

2.1 Elution behavior of the incineration ash of chicken manure using various concentrations of HNO_3

Fig. 2 shows the XRD pattern of IACM. It was evident that IACM consisted of calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; PDF 00-055-0592), calcium phosphate ($Ca_3(PO_4)_2$; PDF 00-056-0064), calcium hydroxide ($Ca(OH)_2$; PDF 00-044-1481) and calcium hydrogen phosphate ($CaHPO_4$; PDF 01-070-0359).

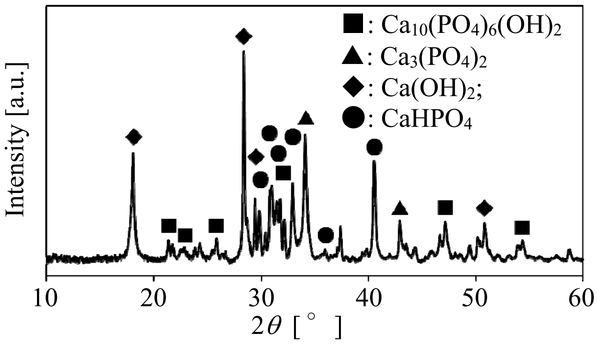

Fig. 2 XRD of incineration ash of chicken manure

The former two phosphates are the main component of phosphate rock. The evident presence of calcium hydroxide was due to the sufficient provision of a calcium source to chickens in order to form good egg-shells, which indicates that, even in the presence of an excess amount of amorphous phosphate species in IACM, it can be converted to a calcium phosphate species.

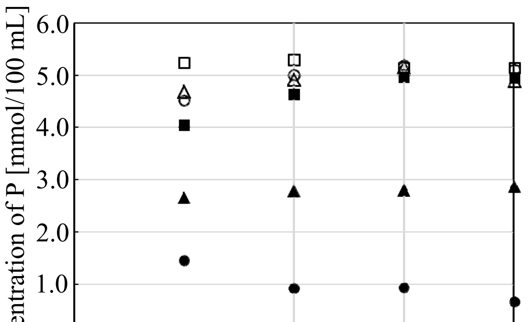

Fig. 3 Elution behaviors of P from incineration ash of chicken manure (1.0 g) using various concentrations of HNO_3
Symbols ●: 0.08 M, ▲: 0.1 M, ■: 0.2 M,
○: 0.3 M, △: 0.4 M, □: 0.5 M.

Fig. 3 shows the elution behaviors of P from 1.0 g of IACM using various concentrations of HNO_3 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 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. Also, using hydrochloric acid may eventually yield various chlorides. Therefore, nitric acid was used in this study. As shown in our previous study using composted chicken manure (CCM) (Sugiyama *et al.*, 2016), Ca was also favorably eluted as P from CCM. Furthermore, in the present case, an excess amount of calcium in the incineration ash of chicken manure was evident 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 HNO_3 solutions, while the elution amount at 0.1 h was similar to that at 0.4 h, indicating that the equilibrium of the elution was reached at the shorter stirring time of 0.1 h. Furthermore, the effect of the concentration of HNO_3 on the elutions of P was evident in a concentration of 0.02 M, and a greater concentration of HNO_3 resulted in an increase in the elution amount of P. By contrast, the same elution of P was detected in concentrations greater than 0.3 M. It was evident that more concentrated HNO_3 and longer stirring time than 0.3 M and 0.1 h, respectively, resulted in the better elution of P. However they may also result in the loss of usage of the acid and the stirring time. Therefore it was concluded that a concentration of HNO_3 of 0.3 M and a stirring time of 0.1 h were suitable under the present conditions. Under these conditions, P was eluted from IACM at a rate of 91.8%. It should be noted that elution of elements other than P was evident, as shown in **Table 3**.

Table 3 Concentration [mmol/100 mL] and elution rate [%] of each element from IACM (1.0 g) after elution for 0.1 h using 0.3 M HNO_3

	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 rates, however, have 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 the incineration ash of chicken manure using various concentrations of HNO_3

Since 1.0 g of IACM could be easily eluted in a time as short as 0.1 h under the above conditions, 10 g of ash was treated using the same solution scale, which involved 100 mL of an aqueous acidic solution of HNO_3 in a 200 mL flask, in order to examine the possibility of scale-up. Preliminary experiments showed that lower concentrations of 0.01 and 1.0 M HNO_3 were insufficient when used to treat 1 g of ash. Therefore, concentrations of HNO_3 that ranged from 1.8 to 2.2 M of HNO_3 were employed to perform elution in a shorter amount of time. As shown in **Fig. 4**, the elution behaviors of P were similar to those detected using 1.0 g of IACM, and eluates of P were evident even when employing stirring times as short as 0.1 h using all HNO_3 solutions. By increasing the pH from 1.8 to 2.0, the elution amount of P increased, while concentrations of HNO_3 of between 1.8 and 2.2 afforded an essentially identical elution amount of P. Therefore, the suitable concentration of HNO_3 and the stirred time were 2.0 M and 0.1 h, respectively, under the employment of 10 g IACM. These conditions achieved a 92.5% elution rate of P from IACM, which was essentially identical to using 1.0 g IACM.

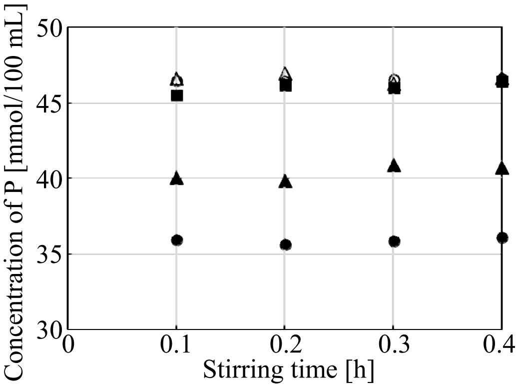

Fig. 4 Elution behaviors of P from incineration ash of chicken manure (10 g) using various concentrations of HNO_3
Symbols ●: 1.8 M, ▲: 1.9 M, ■: 2.0 M, ○: 2.1 M, △: 2.2 M.

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

In treating nitric acid extract from IACM (1.0 g) using aqueous NH_3, precipitation was easily produced at pH = 6.0, 6.5, 7.0 and 7.5. In analyzing this precipitation using XRD, broad peaks due to calcium hydroxyapatite were detected in all precipitation produced at various values of pH, as shown in **Fig. 5 (A)**. The growth of crystallinity in each component in the precipitation was measured to check for by-products via calcination at 1,073 K for 5 h. The calcined precipitations consisted mainly of calcium phosphate (**Fig. 5 (B)**). Since calcium hydroxyapatite is well known to be converted to calcium phosphate under high temperatures (Sugiyama *et al.*, 1998), the levels of calcium hydroxyapatite and calcium phosphate produced before and after calcination were reasonable, respectively. It should be noted that both phosphate species are main component in phosphate rock, which indicates that the elution-precipitation treatment of IACM using aqueous HNO_3 and NH_3 results in the formation of phosphate rock equivalents. Ammonia is contained in the feces and urine from chickens (Kobayashi, 1997). Although the use of other alkaline reagents besides ammonia would also be possible, in view of the future utilization of unused wastes, ammonia was used in the present study.

In **Table 4**, weights before and after calcination at 1,073 K for 5 h of the precipitation formed at pH = 6.0, 6.5, 7.0, and 7.5 are described. Under all pH conditions, weights decreased after calcination due to the conversion of calcium hydroxyapatite to calcium phosphate. Regardless of the calcination, the weight of precipitation formed at pH = 6.0 was the smallest while the weights of precipitation formed at pH = 6.5 and higher were essentially identical. A small recovery at pH = 6.0 indicated insufficient precipitation at lower pH. It should be noted, however, that a pH that was too high resulted in an increase in the usage of aqueous NH_3, followed by an additional precipitation of elements other than calcium and phosphorus. Therefore, in the present study, it was concluded that a pH = 6.5 is optimal.

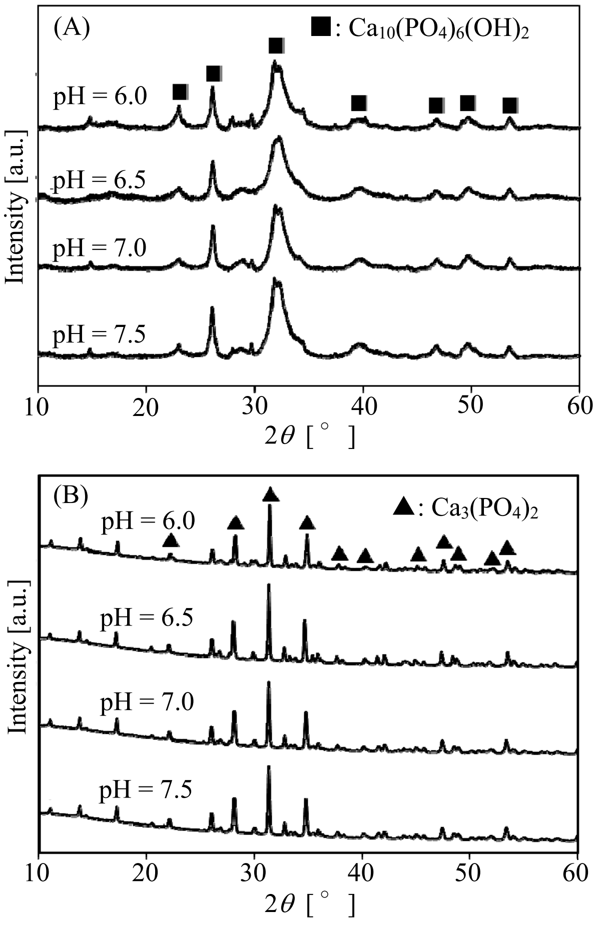

Fig. 5 XRD of the precipitation obtained at various pH from elution-precipitation treatment of IACM before (A) and after (B) the calcination

Table 4 Weight [g] 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 precipitation obtained at pH = 6.5 from the elution-precipitation treatment of IACM before and after calcination was further analyzed using XRF. As shown in **Table 5**, the composition of the precipitation was essentially identical irrespective of calcination. As shown in Fig. 4, $Ca_{10}(PO_4)_6(OH)_2$ was mainly present before the calcination. In this case, the atomic ratio of Ca/P was 1.67, but XRF determined it was 1.99. After calcination, XRD showed that the main component was $Ca_3(PO_4)_2$, resulting in an atomic ratio of 1.50 for Ca/P. However, XRF returned a ratio of 1.97. Therefore, results of the present study show that calcium-rich phosphate rock equivalent could be obtained from IACM due to the excess amount of calcium in IACM.

Table 5 Composition of precipitation 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 the incineration ash of chicken manure and from composted chicken manure

Finally, the phosphorus recovery rates from the incineration ash of chicken manure and from composted chicken manure (CCM) (Sugiyama *et al.*, 2016) were compared using a dissolution process, a precipitation process, and a calcination process from calcium hydroxyapatite to calcium phosphate. As shown in **Table 6**, the phosphorus recovery rates (elution rate) differed between CCM and IACM in the dissolution process. This was likely due to an enhancement of the phosphorus concentration in IACM via the removal of inorganic species with either lower boiling or a lower sublimation temperature and organic species by the power generation system. Furthermore it is possible that the difference in the morphology of P species in CCM and IACM contributed to the enhancement. Therefore, the total phosphorus recovery rate (45.9%) using IACM became greater than that (17.1%) using CCM. It should be noted, however, that approximately half the phosphorus in nitric acid extract cannot be precipitated in the precipitation process. In the precipitation step in the present study, precipitation rapidly formed just after the addition of NH_3 aq, followed by immediate filtration. Based on the solubility product for calcium hydroxyapatite (pKsp = 58.5 at 298 K) (Chow, 1991; Monma, 1996), more precipitation 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 a low % of Mg and K is contained in the final precipitation, it will not be suitable for phosphorus production. In order to obtain a higher purity of 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 even now that approximately 100,000 tons of phosphate rock equivalent could be produced from chicken manure in 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 improvement on the efficiency is now on progress.

Table 6 Recovery rate of phosphorus in 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 incineration ash from chicken manure can be used for the recovery of phosphate rock equivalent via a simple and easy method that involves elution-precipitation treatment with aqueous HNO_3 and NH_3. By further improving this method, there is a possibility that a large amount of calcium phosphate equivalent to phosphate rock can be produced even in a country not producing phosphate rock.

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