Technical Note

Extraction of raw sewage sludge containing iron phosphate for phosphorus recovery

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HIGHLIGHTS

\begin{itemize}
  \item Raw sewage sludge is more effective than incinerated ash for phosphorous extraction using alkali.
  \item An unheated method would be superior for FePO\textsubscript{4} containing sewage sludge.
  \item The alkali extraction using FePO\textsubscript{4} containing sewage sludge was allowed to extract phosphorus selectively.
\end{itemize}

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ABSTRACT

The objective of the present study was to establish an alkali extraction technology for FePO\textsubscript{4} containing sewage sludge obtained from a wastewater treatment system that includes phosphorus removal by iron electrolysis. By clarifying the extraction properties of phosphorus, organic matter, and inorganic matter, conditions for alkali extraction were optimized. As a result, it was suggested that unheated phosphorous extraction would be superior for FePO\textsubscript{4} containing sewage sludge. And, extraction methods and sewage sludge properties were also compared, and the noteworthy result that extraction of metals can be suppressed to extremely low amounts with alkali extraction as compared with acid extraction was obtained. A new insight was also gained that, as compared with the use of incinerated ash reported in previous studies, alkali extraction was more efficient when raw sewage sludge was used.

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1. Introduction

The environmental standard for total phosphorous (TP), which is identified as being harmful to the beneficial use of water, has been met in only 67 of 115 designated water areas in Japan (Ministry of the Environment, 2010). Eutrophication in closed water bodies, such as lakes and marshes, has not been resolved. Additionally, removal technologies for phosphorous are still needed in addition to those for organic matter and nitrogen. Although wastewater treatment covers 85% of Japan, available throughout the majority of the population, there is still disparity between urban areas and rural areas. In rural areas, with less than 50,000 people in particular, the coverage has remained at 71% (Ministry of the Environment of Japan, 2006).

As described above, phosphorous is a factor that causes eutrophication in aquatic environments. On the other hand, its economically exploitable reserve is estimated at 16 Gt, and there are some concerns for resource depletion (Vaccari and Strigul, 2011). The consumption of phosphorous is expected to increase with increasing world population and improving living standards of developing countries. Major producer countries are attempting to secure domestic raw materials and have designated phosphorous as a strategic resource (Cordell et al., 2009). In recent years, because the countries that produce phosphorous ore have restricted direct export of the ore or because they are exporting phosphorus in the form of processed and chemical products with added value, the import of phosphorous ore to Japan has declined year by year, dropping by 50% in the last 20 years. With this trend, the import price of phosphorous ore has been increasing. Therefore, it is important to ensure a stable supply of phosphorous through recovery and recycling of phosphorous resources (Ministry of Finance of Japan, 2009).

To cope with this issue, various phosphorous recovery technologies have been developed, including phosphorous removal by adsorption (Ebie et al., 2008), Heatphos method (Hirota et al.,...
phosphorous crystallization as HAp (hydroxylapatite) (Song et al., 2006; Hossni et al., 2008) and MAP (magnesium ammonium phosphate) (Arakane et al., 2006; Song et al., 2007; Gunes et al., 2008). However, the costs of these projects are too high due to their complex processes for phosphorus recovery. The conventional method using HAp crystallization is illustrated in Fig. 1a as a process compared with our study. With respect to the wastewater treatment system that includes phosphorous removal by iron electrolysis, which is relevant to the present study, it has been reported that it has high phosphorous removal capability and can obtain iron phosphate (FePO₄) containing sewage sludge with high phosphorous content (Morizumi et al., 2005; Yang et al., 2005). A phosphorous recovery from FePO₄-containing sewage sludge has been examined in our previous study (Shioiri et al., 2007) by using zirconium in the adsorption method. However, problems concerning practicality and sustainability could not be solved as with the other phosphorous recovery methods.

In the present study, a simple and low-cost method consisting of alkali extraction and HAp crystallization was proposed as shown in Fig. 1b. Alkali extraction was selected in this system because HAp crystallization was operated in alkali condition. Some extraction methods are also being studied as pretreatment for phosphorous crystallization, such as acid extraction (Cohen, 2009), alkali extraction (Yoshida et al., 2002), thermal treatment (Wzorek et al., 2006), and supercritical water oxidation (Stark et al., 2006); however, these methods are for incinerated ash from sewage sludge. A unique feature in this system is that raw sewage sludge, instead of incinerated ash from sewage sludge, are being used directly. This system has merit for reduction of incinerating cost. So, the effects of incineration on extraction characteristics were clarified using raw sludge and the ash. Another feature is the application of FePO₄-containing sewage sludge to phosphorus recovery. In our previous study (Sano et al., 2012), the application of recovery material from solution extracted using raw FePO₄-containing sewage sludge as fertilizer was reported. As a result, fertilization of the recovery material had a positive impact on the yields of plants. Here, clarification of extraction characteristics contributing to HAp crystallization was considered more important. Therefore, the extraction characteristics of FePO₄-containing sewage sludge and standard sewage sludge were compared for the purpose of establishing simple and low-cost method. In addition, extraction methods that require alkali and acid extractions were also compared to ascertain the practicality of the technology. The final goal of the present study was to optimize the alkali extraction for raw FePO₄-containing sewage sludge.

2. Materials and methods

2.1. Sludge materials

FePO₄-containing sludge samples were obtained from a wastewater treatment system with phosphorus removal by iron electrolysis. There were two types of FePO₄-containing sludge samples: one sample collected from wastewater treatment of households (PS 1 and PS 2) and another sample collected from rural sewage treatment facility (PS 3). In addition, a sludge sample (no FePO₄-containing sludge sample) was also collected from a wastewater treatment system without phosphorus removal process (S 1) as a standard sample. All samples were adjusted to suspended solids (SS) concentration of 10000 mg L⁻¹. In order to prevent changes in their properties, all samples were preserved at 278 K.

With the obtained ash samples, the sludge samples were centrifuged at 277 K and 5000 rpm for 10 min, dried at 378 K for 24 h and incinerated at 873 K for 3 h.

2.2. Extraction methods

Alkali extraction tests were performed to determine optimal conditions. 100 mL of sludge sample, or the ash sample obtained from 100 mL of sludge sample, was placed in a 300 mL beaker. Then, ion-exchanged water was added into the beaker until the volume reached 200 mL. NaOH was added at a set concentration (0.5–5%). The pH was about 13–14. Extraction time ranged from 10 to 120 min. Extraction temperature varied between 293 and 353 K by a hot stirrer. The extracted sample was immediately centrifuged at room temperature at 10000 rpm for 3 min in a centrifuge and filtered with a glass filter (GS-25, Advantec, Japan) for analysis.

Acid extraction tests were performed using HNO₃ in order to compare extraction methods. The pH was about 2.

2.3. Analysis

The SS for adjusting initial sludge concentration and COD of extracted sample were measured with standard methods (APHA, 2005). Phosphorous and inorganic matter in sludge and extracted samples were subjected to acid decomposition following a method.
reported by Hou et al. (2006) and were then analyzed with ICP-AES (ICAP-750, Nippon Jarrell-Ash, Japan).

3. Results and discussion

3.1. Effects of extraction time and NaOH concentration on phosphorus extraction

Fig. 2 shows the change in extracted amount of phosphorous with time at different NaOH concentrations. Here, the extracted amount of phosphorous was the ratio of extracted phosphorus to SS in the sample. Alkali extraction of PS 1, PS 2, and PS 3 showed similar trends. So only the result for PS 2 is shown in Fig. 2. The extracted amount of phosphorous increased with increasing time. At a NaOH concentration of 2% and 5%, the differences in the extracted amount remained at about 3 mg g\(^{-1}\) over time. The observed small differences are presumably due to extraction of organic phosphate in biological accumulation. At a NaOH concentration of 1%, an extracted amount equivalent to the case of the 2% NaOH concentration could be obtained by extending the time to 120 min. These results indicate that extracted amount of phosphorous under a low NaOH concentration agrees with that under a high NaOH concentration if sufficiently long reaction time is ensured.

3.2. Effect of temperature on phosphorus extraction and comparison of sludge property

Based on the results reported in Section 3.1, an experiment was conducted under conditions of 2% NaOH concentration and 30 min extraction time, with varying extraction temperatures. Fig. 3a shows a comparison of sludge properties at different temperatures, showing PS 2, PS 3, and S 1, FePO\(_4\)-containing ash sample (PS 2 ash), and standard ash sample (S 1 ash). With regard to PS 2, PS 3, and S 1, some increases were observed in extracted amount of phosphorous with an increase in temperature; however, the increase was about 5 mg g\(^{-1}\) regardless of the types of sludge. On the other hand, an increase in the extracted amount was observed for PS 2 and S 1 ash with an increase in temperature, and a considerable increase of about 17 mg g\(^{-1}\) was observed for PS 2 ash. Furthermore, the extracted amount for S 1 ash reached 23 mg g\(^{-1}\), which is equivalent to the extracted amount of S 1, by heating it to 313 K. Similarly, the extracted amount for PS 2 ash reached 34 mg g\(^{-1}\), which is equivalent to the extracted amount of PS 2, by heating it to 353 K. These results indicate that incinerated ash from sewage sludge needs to be heated when used for phosphorous extraction. This is consistent with the finding in a previous study (Yoshida and Noike, 2004). On the other hand, it was found that the phosphorous extraction from raw sewage sludge is hardly dependent on heating.

Fig. 3b shows the effect of temperature on the extracted amount of organic matter. The extracted amount of COD was larger for S 1 as compared with that of PS 2 and PS 3. This is likely due to the fact that the organic matter content in sludge is lower in the FePO\(_4\)-containing sludge than that in the standard sludge. The extracted
amount of COD linearly increased with an increase in temperature for PS 2 and 3. At 293 K, about 30–40% of COD extracted, and at 353 K, 90–100% of COD extracted. Therefore, it was found that extraction of organic matter was inhibited in an unheated method.

When the energy required for drying and incinerating sewage sludge is taken into consideration in addition to the above results, a new insight evolves that raw sewage sludge is more effective than incinerated ash for phosphorous extraction using alkali. In particular, it was suggested that an unheated method would be superior for FePO₄-containing sewage sludge.

### 3.3. Comparison of extraction methods

Based on the above results, alkali extraction for FePO₄-containing sludge sample was performed under optimal conditions, i.e., a NaOH concentration of 2%, an extraction time of 30 min, and room-temperature extraction. Fig. 4 shows the comparison of extracted phosphorous fraction using different extraction methods. Here, the phosphorous extraction fraction is the ratio of extracted phosphorous to initial phosphorous in the sludge.

For PS 1–3, HNO₃ extraction resulted in an average extracted phosphorous fraction of 70%, whereas the average extracted phosphorous fraction of NaOH extraction was extremely high at 92%. In other words, alkali extraction was superior to acid extraction with regard to FePO₄-containing sludge. For S 1 on the other hand, HNO₃ extraction resulted in the extracted phosphorous fraction of 80%, whereas the extracted phosphorous fraction of NaOH extraction was 66%. In other words, it was found that acid extraction was superior to alkali extraction with regard to standard sewage sludge, showing opposite behaviors from the case of FePO₄-containing sludge. It is assumed that this is because phosphorous in FePO₄-containing sewage sludge exists in the form of iron phosphate; however, much of the phosphorous in standard sewage sludge exists in the form of organic phosphate due to biological accumulation. Additionally, because extracted phosphorous can reform bonds with calcium, the calcium content in sewage sludge shown below is also likely a factor.

The extracted amount of inorganic components compared by extraction methods and the results for FePO₄-containing sludge sample (averages for the three samples) and those for S 1 are shown in Tables 1 and 2, respectively. Here, the inorganic components contained in sludge samples are shown, too. The iron content was the highest in FePO₄-containing sludge sample, at 112 mg g⁻¹, followed by aluminum and calcium, at 12 and 14 mg g⁻¹, respectively. S 1, on the other hand, contained aluminum and calcium in the highest amounts, at 41 and 21 mg g⁻¹, respectively, and the iron content was 7 mg g⁻¹.

For both of the sludge samples, the extracted amounts of inorganic components other than aluminum tended to be extremely low with NaOH extraction as compared with HNO₃ extraction. It is assumed that the extracted amounts of heavy metals were lower with alkali extraction than acid extraction due to coprecipitation of hydroxides employed in the treatment of wastewater containing heavy metals. This is a method of precipitating dissolved metals as hydroxides by adding an alkaline agent, which takes advantage of a phenomenon in which dissolved metal concentration decreases with an increase in hydroxide ion concentration according to the theory of solubility product. In the case of an alkaline solution, it should be possible to remove heavy metals to a minute amount by using an iron salt as a coprecipitating agent (Lefers et al., 1987; Cheng et al., 2009). Because the subject material in this study was FePO₄-containing sludge with high iron content, it is likely that extracted iron brought about a coprecipitating effect on other heavy metals, reducing the extraction of inorganic components. Aluminum and lead, which are amphoteric hydroxide, should dissolve well with alkaline solution. However, lead was barely detected in extracted sample by alkali extraction. With S 1, aluminum contained in the sewage sludge was almost entirely extracted. When utilized as fertilizer in acidic soil, aluminum ions bond with phosphate in the fertilizer, making the fertilizer application less effective; therefore, when utilized as compost, processes to separately recover phosphorous and aluminum need to be implemented because aluminum is shifted to recovery products by crystallization, as reported by Yoshida et al. (2002). Though our crystallization results will be reported in follow-up study, Aluminum concentration in recovery product crystallized from the sample extracted using FePO₄-containing sludge was below levels of compost standard in Japan.

Previous studies (Takahashi et al., 2001a,b) have reported that acid extracts all kinds of heavy metals from incinerated ash from sewage sludge. The previous results corresponded to the results of acid extraction in this study. Therefore, it is noteworthy that the alkali extraction using FePO₄-containing sewage sludge was allowed to extract phosphorus selectively, inhibiting extraction of heavy metals other than aluminum.

### 4. Conclusions

To establish an alkali extraction technology for FePO₄-containing sewage sludge obtained from a wastewater treatment system that includes phosphorous removal by iron electrolysis,
extraction properties of phosphorous, organic matter, and inorganic matter were clarified. Conditions of alkali extraction were optimized to raw FePO4-containing sewage sludge and extraction methods and sewage sludge properties were also compared. Major findings can be summarized as follows: The extracted amount of phosphorus increased with increasing time. At a NaOH concentration of 2% and 5%, the differences in the extracted amount of phosphorus remained at about 3 mg g⁻¹ over time. With regard to PS 2, PS 3, and S 1, some increases were observed in extracted amount of phosphorus with an increase in temperature; however, the increase was about 5 mg g⁻¹ regardless of the kinds of sludge. On the other hand, an increase in the extracted amount was observed for PS 2 ash and PS 1 ash with an increase in temperature, and a considerable increase of about 17 mg g⁻¹ was observed for PS 2 ash. The extracted amount of COD linearly increased with an increase in temperature for PS 2 and 3. At 293 K, about 30–40% of COD extracted, and at 353 K, 90–100% of COD extracted. Acid extraction was superior to alkali extraction with regard to standard sludge, showing opposite behaviors from the case of FePO4-containing sludge. Extracted amounts of inorganic components, other than aluminum, tended to be extremely small in alkali extraction as compared with acid extraction.

A new insight is gained that raw sewage sludge is more effective than incinerated ash for phosphorus extraction using alkali. In particular, it is suggested that an unheated method would be superior for FePO4-containing sewage sludge. It is noteworthy that the alkali extraction using FePO4-containing sewage sludge was allowed to extract phosphorus selectively, inhibiting extraction of heavy metals other than aluminum. Therefore, increasing adoption of wastewater treatment systems including phosphorus removal by iron electrolysis may contribute to enhancing feasibility of phosphorus recovery.

References


