Development of a high-efficiency phosphorus recovery method using a fluidized-bed crystallized phosphorus removal system

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Abstract The authors have been engaged in the research and development concerning the recovery of MAP (Magnesium Ammonium Phosphate) using a fluidized-bed crystallized phosphorus removal system. In the reactor of the fluidized-bed crystallized phosphorus removal system, seed crystals (of MAP) are fluidized previously and new MAP crystals are produced on the seed crystal surfaces. Conventionally, the reactor consisted of one reaction tank only, but this practice had the problem that as the crystallization progresses, the seed crystal is grown excessively and as a result, the effective reaction surface areas are decreased and the fluidization effect is degraded, causing the recovery ratio to be decreased. Recently, the authors have devised a two-tank type reactor by adding a sub reaction tank to the reactor (now the main reaction tank) so that the MAP particle size in the main reaction tank may be kept constant making the recovery ratio stable. They conducted a demonstration test with a pilot experimental system of the 2-tank type reactor. For raw water T-P 111 to 507 mg/L, the main reaction tank treated water T-P 14.0 to 79.5 mg/L and phosphorus recovery ratios 84 to 92% were obtained. Because the mean MAP particle size in the main reaction tank could be kept constant, the phosphorus recovery ratio could always be above 80%, realizing stable treatment.

Keywords Crystallization; fluidized-bed; magnesium ammonium phosphate

Introduction

Phosphorus is a limited resource which is anticipated to be exhausted in the 21st century. Japan is short of the phosphorus resource and imports it mostly as fertilizers, industrial chemicals, foods and feeds. On the other hand, in the living environmental system, much phosphorus is discharged and red tides and other eutrophication phenomena have become a serious problem in closed waters, such as lakes and ponds, inland bays, etc. (Matsumiya et al., 2000) The authors have considered it important to recover phosphorus in an easily usable form in spite of mere removal from wastewaters and they have been investigating recovering phosphorus by the crystallization method. The phosphorus recovery using the crystallization method has the following advantages.

1. Phosphorus can be recovered in an easily reusable form.
2. The sludge generation resulting from coagulants in the wastewater treatment plant is reduced.

Recently in Japan, MAP (magnesium ammonium phosphate: struvite) recovery facilities making use of fluidized-bed reactors have been in operation and the recovered MAP has been reused as fertilizer (Ishizuka et al., 1998; Tomoda, 1999; Ueno and Fujii, 2001). However, with the conventional fluidized-bed reactors, as the crystallization progresses, the particle sizes of MAP in the reactor become large and it is difficult to keep them constant. Moreover, excessive growth of MAP crystals has such problems that the fluidization effect is degraded, the MAP surface areas necessary for reactions are reduced and as a
result, the MAP recovery ratio is decreased (Shimamura et al., 2001). Then, this time, the authors added a sub reaction tank and used this two-tank type reactor in our MAP recovery experiment. This system has such features that the seed crystals of relatively small particle sizes prepared in the sub reaction tank are added from time to time into the main reaction tank so that the particle sizes of MAP in the main reaction tank may be adjusted not to become too large. The purposes of this experiment are to realize stable treatment with high phosphorus recovery ratios and also to obtain the recovered products that are easy to reuse and having stable properties. In this paper, the influence of the phosphorus concentration in the raw water influent portion and the phosphorus surface area loading on the phosphorus recovery ratio is investigated and the treatment performance of the two-tank type reactor is confirmed.

**Methods**

**Experimental apparatus**

MAP is formed when phosphate ions, ammonium ions and magnesium ions exist in the solution in excess of the solubility products. The reaction for MAP formation is shown by Eq. (1).

\[
\text{HPO}_4^{2-} + \text{NH}_4^+ + \text{Mg}^{2+} + \text{OH}^- + 5\text{H}_2\text{O}^- \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}
\]  

Figure 1 shows the experimental apparatus used in this experiment. This apparatus consists of a main reaction tank and a sub reaction tank, and each reaction tank has the following roles.

**Main reaction tank.** Relatively large MAP particles (mean particle size 0.5 to 1.5 mm) are fluidized in this tank, and new MAP particles are precipitated on the surfaces of MAP particles already fluidized in the main reaction tank, and through this process, phosphorus is recovered. MAP in the main reaction tank is withdrawn from time to time through the bottom of the main reaction tank. The mean particle sizes of MAP in the main reaction tank are kept constant by supplying the seed crystal (mean particle size about 0.3 mm) at a frequency of once in 3 to 4 days from the sub reaction tank.

**Sub reaction tank.** Fine MAP particles (mean particle size 0.05 to 0.25 mm) floating in the upper portion of the main reaction tank are transferred at a frequency of once in 3 to 4 days.
into the sub reaction tank where they are grown up to about 0.3 mm. These grown MAP particles are returned entirely into the main reaction tank where they are used as the seed crystals.

The raw water and the circulated water are applied in up-flows through the raw water influent portion of the reaction tank bottom in both the main reaction tank and the sub reaction tank. The water application ratio of the raw water is about 9:1 between the main reaction tank and the sub reaction tank. Magnesium was supplied in the circulated water. As the source of magnesium, magnesium chloride was used. The ratio of magnesium addition was 1.3 to 1.9 in Mg/P ratio by weight. To each reaction tank, air for MAP agitation and alkali for pH adjustment were supplied. As the raw water for this experiment, the actual wastewater, anaerobically treated, was used. The mean particle size in this report is shown on a weight basis.

Investigation on the fundamental operating conditions

Before conducting a continuous experiment with the two-tank type reactor, the fundamental operating conditions were investigated separately.

Relation between the raw water influent portion phosphorus concentration and the phosphorus recovery ratio

In general, crystallization reactions produce fine crystals when the degree of supersaturation is high. The fine crystals settle slowly and therefore, flow out easily with the treated water and when the degree of crystallization is large, the recovery ratio is degraded. In the case of this reactor, the degree of supersaturation is highest in the raw water influent portion of the reactor bottom where the raw water is mixed with magnesium and alkali. Then, in order to grasp the conditions of phosphorus concentration under which the formation of fine MAP particles is minimum, the phosphorus recovery ratio was compared by changing the PO$_4$-P concentration in the raw water influent portion. The raw water flow rate was 4.4 m$^3$/d and the raw water PO$_4$-P was about 150 mg/L. The PO$_4$-P concentration in the raw water influent portion was adjusted to 150 to 50 mg/L by returning the circulated water to the raw water influent portion at a circulation ratio of 0 to 2 without changing the raw water flow rate. The mean MAP particle size used was 0.3 to 0.8 mm.

Relation between the phosphorus surface area loading and the phosphorus recovery ratio and the MAP growth rate

The phosphorus surface area loading (L$_{sur}$) means the amount of phosphorus supplied per unit MAP surface area (NOTE 1). The relation of the phosphorus recovery ratio and the crystallization ratio to the L$_{sur}$ was investigated. Moreover, because the L$_{sur}$ gives a large influence on the MAP growth rate, the relation between the L$_{sur}$ and the MAP growth rate was also investigated. By changing the raw water flow rate to 0.3 to 0.8 m$^3$/d and the charged MAP mean particle size to 0.2 to 0.4 mm while keeping raw water T-P 100 mg/L and charged MAP amount 120 g constant, respectively, L$_{sur}$ 5 to 30 g-P/m$^2$·d was obtained. Here, the phosphorus recovery ratio means the T-P recovered in proportion to the raw water T-P (NOTE 2), and the crystallization ratio shows the PO$_4$-P crystallized in proportion to the raw water PO$_4$-P (NOTE 3).

NOTE 1: $L_{sur} = \frac{W_P}{S_{MAP}}$

NOTE 2: Recovery ratio = \( \left\{ \frac{(T-P)_{Rw} - (T-P)_{Tw}}{(T-P)_{Rw}} \right\} \times 100 \)

NOTE 3: Crystallization ratio = \( \left\{ \frac{(PO_4-P)_{Rw} - (PO_4-P)_{Tw}}{(PO_4-P)_{Rw}} \right\} \times 100 \)
Fine MAP particle growth rate. In order to determine the retention time for the fine MAP particles in the sub reaction tank transferred from the main reaction tank, the fine MAP particle growth rate was measured. The retention time was set at a value at which the mean fine MAP particle size was above 0.3 mm. The conditions of water application were raw water T-P about 300 mg/L, raw water flow rate 0.13 m³/d and circulated water flow rate 0.87 m³/d.

Continuous water application experiment
The treatment performance of the two-tank type reactor was confirmed. The items investigated include the treated water quality and, in addition, the stability of the mean MAP particle size in the main reaction tank and the changes of the phosphorus recovery ratio when the mean MAP particle size in the main reaction tank was changed. The continuous water application experiment was conducted under four experimental conditions, Test 1, Test 2, Test 3 and Test 4. Table 1 shows these experimental conditions. In any of the four Tests, the PO₄-P concentration in the raw water influent portion was adjusted to about 50 mg/L by circulating the treated water. The phosphorus concentration of the raw water was 100 mg/L in Test 1, 300 mg/L in Test 2 and Test 3, and 500 mg/L in Test 4. The mean particle size of MAP in the main reaction tank was 1 mm in Test 1 and Test 2 and 0.5 mm in Test 3 and Test 4.

Results and discussion
Investigation on the fundamental operating conditions
Relation between the raw water influent portion phosphorus concentration and the phosphorus recovery ratio. Figure 2 shows the relation between the PO₄-P concentration in the raw water influent portion and the phosphorus recovery ratio. The phosphorus recovery ratio was 92% and 66% when the PO₄-P concentration in the raw water influent portion was PO₄-P 50 mg/L and 150 mg/L, respectively; that is, there was a tendency that the phosphorus recovery ratio decreased when the phosphorus concentration in the raw water influent portion increased. In the raw water influent portion, the condition of supersaturation occurred
locally because of the high PO$_4$-P concentration, and fine MAP particles were precipitated in large numbers. Based on the results of this experiment, the PO$_4$-P concentration in the raw water influent portion was lowered by diluting with the circulated water in the continuous water-application experiment using a two-tank type reactor.

\textit{Relation between the L$_{sur}$ and the MAP growth rate and the phosphorus recovery ratio.} Figure 3 shows the relation between the L$_{sur}$ and the crystallization ratio and the phosphorus recovery ratio. The phosphorus recovery ratio was 80\%, 75\% and 60\% when the L$_{sur}$ was 10 g-P/m$^2$·d, 20 g-P/m$^2$·d and 30 g-P/m$^2$·d, respectively; that is, there was a tendency that the phosphorus recovery ratio decreased when the L$_{sur}$ increased. The crystallization ratio was about 90\% with almost no change at any value of the L$_{sur}$. Based on the fact that the difference between the crystallization ratio and the recovery ratio increased with increasing L$_{sur}$, it is considered that as the loading increased, fine MAP particles were precipitated in larger numbers and flowed away with the treated water. It was found that, in order to raise the phosphorus recovery ratio, it was necessary to lower the L$_{sur}$. In the continuous water application experiment using the two-tank type reactor, the recovery ratio was compared when the L$_{sur}$ was changed by changing the mean particle size of MAP to be charged. Figure 4 shows the relation between the L$_{sur}$ and the MAP growth rate. The MAP growth rate was 0.05 mm/d, 0.11 mm/d and 0.19 mm/d when the L$_{sur}$ was 10 g-P/m$^2$·d, 20 g-P/m$^2$·d and 30 g-P/m$^2$·d, respectively; that is, there was a tendency that the MAP growth rate increased when the L$_{sur}$ increased. As the L$_{sur}$ was increased, the phosphorus recovery ratio was lowered because the MAP growth rate was increased and fine MAP particles were precipitated in larger numbers.
Fine MAP particle growth rate. Figure 5 shows the increase of the mean fine MAP particle size. The mean particle size of fine MAP particles transferred from the main reaction tank was 0.17 to 0.26 mm. The growth rate of fine MAP particles was 0.025 to 0.057 mm/d and the mean growth rate was 0.046 mm/d. When the retention time was longer than 3 days, the mean particle size of fine MAP particles was mostly larger than 0.3 mm. In the continuous water application experiment, the retention time of fine MAP particles in the sub reaction tank was 3 to 4 days.

Continuous water application experiment
Figure 6 shows the changes with the passage of time (d) of the treated water quality in the continuous treatment experiment and the changes with the passage of time (d) of the mean MAP particle size in the main reaction tank.
**Particle size of MAP in the main reaction tank.** When the water was applied under the same conditions as in Test 1 in the reactor of the conventional one-tank type, the mean particle size was 1.5 mm, 1.8 mm and 2.1 mm after 3 days, 7 days and 14 days, respectively, when the mean seed crystal particle size (at the beginning of the experiment) was 0.79 mm; that is, the mean particle size increased by 1.3 mm for 2 weeks. When the two-tank type reactor was operated this time, the MAP mean particle size was 0.85 to 1.43 mm in Test 1 and Test 2, and 0.41 to 0.68 in Test 3 and Test 4, respectively, as seen in the changes with the passage of time (d) of the mean MAP particle size in Figure 6; that is, the mean MAP particle size in the reactor was stable. It was confirmed that the MAP particles in the main reaction tank could be kept approximately constant without excessive growth by supplying the seed crystal from time to time from the sub reaction tank.

**Treated water quality.** Table 2 shows the average water quality of the raw water, the main reaction tank treated water and the sub reaction tank treated water.

When the raw water had T-P 111 to 507 mg/L, the main reaction tank treated water had T-P 14.0 to 79.5 mg/L and PO₄-P 7.1 to 18.5 mg/L. The treated water T-P increased with increasing raw water T-P, but the treated water PO₄-P hardly changed irrespective of the raw water T-P. The phosphorus recovery ratio was 84 to 92%. The sub reaction tank treated water had T-P 27.8 to 128 mg/L and PO₄-P 4.0 to 12.1 mg/L. Similarly to the case of the main reaction tank, the treated water T-P increased with increasing raw water T-P, but the treated water PO₄-P hardly changed irrespective of the raw water T-P. The phosphorus recovery ratio was 71 to 91%, and it was lower than in the main reaction tank in any Test. In the case of the main reaction tank, the mean MAP particle size in this tank was stable, and therefore, the phosphorus recovery ratio was above 80% at all times; that is, high recovery ratios can be maintained.

**Mean MAP particle size and phosphorus recovery ratio.** In Figure 3, it was confirmed that, as the Lₘₐₓ was decreased, the phosphorus recovery ratio increased. Then, in Test 2 and Test 3, the Lₘₐₓ was changed by changing the mean MAP particle size in the main reaction tank

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Experimental results</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction pH (–)</strong></td>
<td>Test 1</td>
</tr>
<tr>
<td>SS</td>
<td></td>
</tr>
<tr>
<td>Raw water (mg/L)</td>
<td>66.0</td>
</tr>
<tr>
<td>Sub reaction tank (mg/L)</td>
<td>112.0</td>
</tr>
<tr>
<td>Main reaction tank (mg/L)</td>
<td>53.0</td>
</tr>
<tr>
<td>T-P</td>
<td></td>
</tr>
<tr>
<td>Raw water (mg/L)</td>
<td>111</td>
</tr>
<tr>
<td>Sub reaction tank (mg/L)</td>
<td>32.5</td>
</tr>
<tr>
<td>Main reaction tank (mg/L)</td>
<td>14.0</td>
</tr>
<tr>
<td>PO₄-P</td>
<td></td>
</tr>
<tr>
<td>Raw water (mg/L)</td>
<td>90.1</td>
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<tr>
<td>Sub reaction tank (mg/L)</td>
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<tr>
<td>Main reaction tank (mg/L)</td>
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<tr>
<td>NH₄-N</td>
<td></td>
</tr>
<tr>
<td>Raw water (mg/L)</td>
<td>177</td>
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<tr>
<td>Sub reaction tank (mg/L)</td>
<td>153</td>
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<tr>
<td>Main reaction tank (mg/L)</td>
<td>154</td>
</tr>
<tr>
<td>Mg</td>
<td></td>
</tr>
<tr>
<td>Raw water (mg/L)</td>
<td>5.3</td>
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<tr>
<td>Raw water* (mg/L)</td>
<td>140</td>
</tr>
<tr>
<td>Sub reaction tank (mg/L)</td>
<td>32.1</td>
</tr>
<tr>
<td>Main reaction tank (mg/L)</td>
<td>50.3</td>
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<tr>
<td>Recovery ratio</td>
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<tr>
<td>Sub reaction tank (%)</td>
<td>71</td>
</tr>
<tr>
<td>Main reaction tank (%)</td>
<td>87</td>
</tr>
</tbody>
</table>

* After MgCl₂ addition (calculated)
while keeping the amount of MAP charged constant. In Test 2, the mean particle size was
0.94 to 1.43 mm and the $L_{\text{sur}}$ was 4.8 g-P/m²·d and in Test 3, the mean particle size was 0.41
to 0.67 mm and the $L_{\text{sur}}$ was 3.3 g-P/m²·d. As seen in Table 2, the treated water T-P of the
main reaction tank was 49.2 mg/L and 23.2 mg/L in Test 2 and Test 3, respectively, when
the raw water T-P was about 300 mg/L; that is, the concentration in Test 3 was about half
that in Test 2. The phosphorus recovery ratio was 85% and 92% in Test 2 and Test 3, respec-
tively; that is, the value in Test 3 was 7 points higher. It was confirmed that the $L_{\text{sur}}$ was
lowered and the phosphorus recovery ratio was raised by reducing the mean particle size
without changing the amount of MAP charged.

Mass balance for P, N and Mg

The mass balance for P, N and Mg in Test 1 was investigated by comparing the decrease in
PO$_4$-P, NH$_4$-N and Mg concentrations in the raw water with the composition of recovered
MAP. The composition of recovered MAP was measured by XRF. While the raw water quality
is PO$_4$-P 90.1 mg/L, NH$_4$-N 177 mg/L and Mg 140 mg/L (after MgCl$_2$ addition), the treated
water quality is PO$_4$-P 7.5 mg/L, NH$_4$-N 154 mg/L and Mg 50.3 mg/L. The decrease ratios of
component concentrations, P:N:Mg, were 1.0:0.28:1.1. On the other hand, XRF indicates that
the composition of recovered MAP is P-16 wt%, N 4.8 wt% and Mg 16 wt% and therefore, the
composition ratios, P:N:Mg, were 1.0:0.30:1.0. Since the decrease ratios of raw water concen-
trations and the composition ratios of recovered MAP approximately agree with each other, it
could be confirmed that, by the growth of MAP, the raw water concentrations were decreased.

Conclusions

With the conventional fluidized-bed reactors, as the crystallization progressed, the particle
sizes of MAP in the reactor became large and it was difficult to keep them constant.
Moreover, excessive growth of MAP crystals had such problems that the fluidization effect
was degraded, the MAP surface areas necessary for reactions were reduced and as a result,
the MAP recovery ratio was decreased. This time, the authors constructed a two-tank type
reactor consisting of a main reaction tank and a sub reaction tank and operated it in such a
manner that the mean particle size of MAP in the main reaction tank might not be changed. It
was confirmed that stable treatment with high recovery ratios was possible. Moreover, the
MAP could be recovered in a form easy to reuse because of the uniform mean particle sizes.
It is considered that, in addition to phosphorus recovery by MAP formation, this system can
be applied to phosphorus recovery by calcium phosphate formation, water softening by cal-
cium carbonate formation, fluorine recovery by calcium fluoride formation, etc.

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