Research on MAP Recovery Conditions using a Fluidized-bed Crystallized Phosphorous Removal System

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Abstract

A research was made on phosphorus recovery conditions using a MAP (Magnesium Ammonium Phosphate) method and anaerobically digested desorption liquor (containing ammonia and phosphorus). A fluidized-bed phosphorus removal system was used as the reactor. The main objective of the research was to study the treatment performance, influent phosphorus load and MAP microcrystallization, and phosphorus recovery. One typical result of treatment performance was a treated water T-P of 26.6 mg/L and a phosphorus recovery of 81%, versus a raw water T-P of 142 mg/L. It was found that MAP microcrystallization increased and phosphorus recovery declined along higher influent phosphorus loads. In a case where the mean MAP particle size was 1.5 mm, the recovery was about 80% under an influent phosphorus load of 25 kg-P/m^3/d, 60% under 40 kg-P/m^3/d, and reaching a constant recovery rate of about 70 kg-P/m^3/d at loads exceeding 100 kg-P/m^3/d. The constant recovery rate was assumed as due to the limit in the growth rate of MAP particles. Study results indicated that effective phosphorus recovery using the fluidized-bed system could be achieved by maintaining the MAP particles in the reactor to be small (1 - 2 mm) so that they could be easily handled.

KEYWORDS

crystallization; growth rate; fluidized-bed; Magnesium Ammonium Phosphate; phosphorus; recovery

INTRODUCTION

Japan has a very little phosphorus resource and most of its phosphorus is imported as ore from countries such as Morocco. About 25% to 30% of the imported phosphorus ends up flowing into sewage treatment facilities. Phosphorus flowing into closed water bodies such as lakes, swamps, and inland bays causes red tides and eutrophication. There is also a predicament that the supply of phosphorus ore in the world may become exhausted by mid-21 Century. It is therefore meaningful to remove phosphorus, from sewage or return water of sludge treatment processes, and reuse it as a recovered resource.

As for phosphorus recovery making use of crystallization, two methods have been under study. One is the MAP method (Ishiduka et al (1998)) and the other is the HAP (hydroxyapatite) method (Hirasawa et al (1998)). By the MAP method, phosphorus in the wastewater is crystallized using ammonium and magnesium, and then recovered. This method is used for desorption liquor and reject water from anaerobic digestion processes as such wastewater contains phosphorus with excess amounts of ammonia. By the HAP method, the phosphorus in wastewater becomes crystallized by calcium, and then recovered. As the solubility product is lower by the HAP method than that by the MAP method, it is possible to reduce the concentration of phosphorus. The HAP method is therefore used for secondary treatment of sewage and such.

The wastewater used for this research was ammonia and phosphorus containing desorption liquor from an anaerobic digestion process. Studies on phosphorus recovery conditions were made using the MAP method. A fluidized-bed phosphorus removal system was used as the reactor. Studies were made on the treatment performance, influent phosphorus load and MAP microcrystallization, and phosphorus recovery. The following outlines the study results.
EXPERIMENTAL METHOD

The reaction by which MAP is formed can be expressed in the following equation.

\[ \text{Mg}^{2+} + \text{NH}_4^+ + \text{HPO}_4^{2-} + \text{OH}^- + 5\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \ldots (1) \]

The raw water used was artificially prepared wastewater with an ammonium concentration of about 200 mg/L and phosphorus concentration of about 100 mg/L. MAP was formed by adding magnesium and adjusting the pH.

The experimental apparatus (see Figure 1) comprised a fluidized-bed reactor (inner diameter of 150 mm and a height of 4000 mm), a settling tank (inner diameter of 300 mm and a height of 2500 mm), and a treated water tank. The raw water and part of the treated water in the treated water tank was made to flow upward (LV: 60 m/hr) from the bottom section of the reactor. MAP particles were made to be in a fluidized state (to a height of 2000 mm) in the reactor beforehand. A supersaturated condition was made by adding magnesium and adjusting the pH, and new MAP was made to form on the surface of the MAP particles already in the reactor. The interior of the reactor was aerated using air to enhance the fluidizing of MAP particles. MAP particles were extracted from the bottom of the reactor.

EXPERIMENTAL CONDITIONS

Continuous experiments were carried out. The inflow of raw water was started after charging 250 mm of MAP particles into the reactor. The quality of the treated water became stable after 10 days. Experiments were then split into 3, namely Test 1, 2, and 3. Table 1 shows the experimental conditions of each test. In each test, the raw water flow rate and the raw water phosphorus concentration were adjusted to study the influent phosphorus load (hereinafter referred to as the volumetric phosphorus load ; \( L_{\text{vol}} \) (kg-P/m³/d)). The influent phosphorus load versus overall surface area of MAP particles (hereinafter referred to as the phosphorus surface load ; \( L_{\text{sur}} \) (kg-P/m²/d)) was also changed and the treated water compared. The phosphorus volumetric load and the phosphorus surface load were calculated using the following equations.

\[ L_{\text{vol}} = \frac{W_p}{V_{\text{MAP}}} \ldots (2) \]
\[ L_{\text{sur}} = \frac{W_p}{S_{\text{MAP}}} \ldots (3) \]

Where, \( W_p \) is Amount of influent phosphorus load (kg-P/d), \( V_{\text{MAP}} \) is Volume of MAP particle layer (m³), \( S_{\text{MAP}} \) is Overall MAP surface of MAP particle layer (m²). Overall MAP surface was calculated using the following assumption.

a) MAP particles were completely circular
b) Regardless of particle size, 1040 kg (measured) MAP particles were charged per 1 m³ of reactor space
c) The specific gravity of MAP particles was 1.74 g/cm³
EXPERIMENTAL RESULTS

Results of continuous treatment tests

Figure 2 shows the treatment conditions versus changes in the quality of treated water along the elapse of days, while Table 2 shows the mean quality of raw water and treated water.

In Test 1, the volumetric phosphorus load was set at 22.8 kg-P/m³/d. Compared to a T-P concentration of 81.9 mg/L and solubility of PO₄-P of 64.2 mg/L (hereinafter simply referred to as PO₄-P) as for the raw water, the same for treated water were 26.8 mg/L and 6.7 mg/L, respectively, indicating a phosphorus recovery of 67%. The T-P concentration in the treated water increased when the mean MAP particle size exceeded 3 mm (Height of MAP particle layer being about 2000 mm). Moreover, the fluidizing performance of the MAP particles deteriorated. On the 35th day of treatment, enlarged MAP particles were crushed in a mixer (a mean particle size of 1.13 mm) and an amount equivalent to 25% of the MAP particle layer height was charged back into the reactor. This worked to reduce the T-P concentration in the treated water.

In Test 2, the volumetric phosphorus load was adjusted to be 54 kg-P/m³/d by increasing the T-P concentration in the raw water. Compared to a T-P concentration of 168 mg/L and a PO₄-P of 149 mg/L in the raw water, the same for treated water were 64 mg/L and 5.7 mg/L, respectively, indicating a phosphorus recovery of 62%. As will be discussed later on, the rise in the T-P of treated water was due to effluent MAP microcrystallization.

In Test 3, the T-P concentration in the raw water was the same as that in Test 2. The volumetric phosphorus load was adjusted to be 35.6 kg-P/m³/d by decreasing the raw water flow rate. Compared to a T-P concentration of 142 mg/L and a PO₄-P of 130 mg/L in the raw water, the same for treated water were 26.6 mg/L and 9.3 mg/L, respectively, indicating an increased phosphorus recovery of 81%. This was attributed...
to the decreased outflow of MAP microcrystallization, consequent to the reduced phosphorous volumetric load.

**Relationship between the influent phosphorus load and MAP microcrystallization**

Continuous test results indicated a decrease in the effective reaction surface area due to enlarged MAP particle size. Also indicated was an increase in the T-P concentration in the treated water due to an increase in the influent phosphorus load. The phosphorus surface load and the forms of phosphorus in the treated water were then studied (see Figure 3). The mean MAP particle size here was 2.1 - 3.2 mm. A significant finding here was that the amount of recovered phosphorus became almost a constant, with an increase in MAP microcrystallization, at higher ranges of phosphorus surface loads. For example, at a phosphorus surface load of 26.2 g-P/m²/d, the amount of recovered phosphorus was 21.2 g-P/m²/d; recovery of 81%, while the MAP microcrystallization in the raw water phosphorus was 4%. In contrast, at a higher phosphorus surface load of 36.9 g-P/m²/d, the amount of recovered phosphorus reached 22.9 g-P/m²/d; recovery of 62%, indicating there was almost no change in the amount of recovered phosphorus. However, the MAP microcrystallization in the raw water phosphorus increased to 23% in this case.

Next, the relationship between the volumetric phosphorus load and the amount of recovered phosphorus was studied. The mean particle size of the MAP in the reactor was adjusted to be a constant at about 1.5 mm. Results are shown in Figure 4. It is shown that although there was an increase in the recovered amount along an increase in the volumetric phosphorus load, there was a tendency for phosphorus recovery ratio to decrease. For example, at a volumetric phosphorus load of 25 kg-P/m³/d, the amount of recovered phosphorus was about 20 kg-P/m³/d (recovery of about 80%), while at a volumetric phosphorus load of 65 kg-
P/m³/d, the amount of recovered phosphorus was about 40 kg-P/m³/d (recovery of about 60%). When the volumetric phosphorus load exceeded 100 kg-P/m³/d, the amount of recovered phosphorus became a constant at about 70 kg-P/m³/d.

**Relationship between MAP particle size and maximum recovery**

The amount of recovered phosphorus reached a constant at 70 kg-P/m³/d in the case where the mean MAP particle size was 1.5 mm. This constant amount was regarded as the maximum recovered amount. Figure 5 shows the maximum recovered amount versus mean MAP particle sizes set at 1.5 mm, 2.3 mm, and 3 mm.

There was a tendency for the maximum recovered amount to decrease along greater particle sizes. The maximum recovered amount was about 40 kg-P/m³/d at a mean particle size of 2.3 mm, about 20 kg-P/m³/d at mean particle size of 3 mm.

**CONSIDERATION**

**Optimal MAP particle size**

Putting together the test results discussed so far, phosphorus recovery can be illustrated as shown in Figure 6. Phosphorus in the raw water can be roughly divided into two categories, namely phosphorus that takes part in the reaction and phosphorus that does not. As for the former, there is phosphorus that becomes used in MAP particle growth and phosphorus that microcrystallizes MAP. Under low influent phosphorus loads, most of the phosphorus in the raw water was found to be used up in MAP particle growth. Accordingly, the influent phosphorus load and the growth rate of MAP particles increase proportionally. Under high influent phosphorus loads, however, MAP microcrystallization increases and MAP microcrystallization becomes discharged along with the effluent. This results in low recovery. Moreover, further increases in the influent phosphorus load leads to a constant growth rate of MAP particles and a residual supersaturated condition becomes dominantly directed to microcrystallization. Consequently, the recovered amount is constant and recovery ratio drops further.

It can be gathered from the above that optimal phosphorus recovery using a fluidized-bed crystallized phosphorus removal system can be achieved by using small particle size MAP particles and making adjustment so that the surface load remains small. Faster settling of MAP particles also speeds up treatment. Considering the balance between these two factors, it can be determined that efficient phosphorous recovery can be achieved by setting the MAP particle size to 1 - 2 mm.

![Figure 5 The maximum recovered amount versus mean MAP particle sizes](image)

![Figure 6 The outline of phosphorus recovery](image)
CONCLUSION

Ammonia and phosphorus contained in wastewater was crystallized using a fluidized-bed crystallized phosphorus removal system. The following are conclusions.

a) Continuous tests indicated that compared to a T-P concentration of 142 mg/L and a PO₄-P of 130 mg/L in the raw water, the same for treated water were 26.6 mg/L and 9.3 mg/L, respectively, indicating a phosphorus recovery of 81%.

b) There is phosphorus that becomes used in MAP particle growth (recovered) and phosphorus that microcrystallizes MAP (discharged). Phosphorus recovery using MAP with a particle size of 1.5 mm indicated that under a volumetric phosphorus load of 25 kg-P/m³/d, the amount of recovered phosphorus was about 20 kg-P/m³/d (recovery of about 80%), while at a volumetric phosphorus load of 65 kg-P/m³/d, the amount of recovered phosphorus was about 40 kg-P/m³/d (recovery of about 60%). Although amount of recovery increased along an increase in the influent phosphorus load, the recovery ratio decreased.

c) In the same operation as the above, the amount of recovered phosphorus became a constant at about 70 kg-P/m³/d when the volumetric phosphorus load exceeded 100 kg-P/m³/d. An assumption can be made that a limit in the growth rate of MAP particle had been reached.

d) The maximum recovered amount for the cases of mean MAP particle sizes of 1.5 mm, 2.3 mm, and 3 mm were about 70 kg-P/m³/d, 40 kg-P/m³/d, and 20 kg-P/m³/d, respectively, indicating that the larger the particle size, the less the maximum recovered amount.

e) An optimal phosphorus recovery using a fluidized-bed crystallized phosphorus removal system can be achieved by setting the particle size of the MAP charged into the reactor to 1 - 2 mm.

REFERENCES

