Recovery of high purity phosphorus from municipal wastewater secondary effluent by a high-speed adsorbent

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ABSTRACT

High purity phosphorus was recovered from municipal wastewater secondary effluent as phosphate, using a newly developed phosphorus adsorption and recovery system. A high-speed adsorbent having a unique porous structure was used in this system. The secondary effluent, showing total phosphorus (TP) of 0.1–2.1 mg P/L, was passed through an adsorbent packed column at high space velocity (SV) of 15 h^{-1}. The TP of the treated water was as low as 0.02–0.04 mg P/L, indicating that 97% of phosphorus in the secondary effluent was removed. The removed phosphorus was desorbed from the adsorbent by passing a sodium hydroxide aqueous solution through the column. Calcium hydroxide was added to this solution to precipitate the phosphorus as calcium phosphate. This precipitate was neutralized with hydrochloric acid aqueous solution, washed with water, and then solid–liquid separation was performed for the phosphorus recovery. The main constituent of the recovered phosphorus was apatite-type calcium phosphate, with 16% phosphorus content, which matched that of high-grade phosphorus ore. The hazardous elements content of the recovered phosphorus was exceedingly low. Therefore the recovered phosphorus can be applied to an alternative for phosphorus ore, or to a phosphate fertilizer.

Key words | calcium phosphate, high purity phosphorus, high-speed adsorbent, phosphorous removal, phosphorus resource recovery

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INTRODUCTION

Phosphorus is an essential element to life, but depletion of phosphorus resources has become a matter of global concern (Steen 1998). On the other hand, phosphorus in wastewater discharged promotes eutrophication of enclosed water bodies such as lakes or harbors. (Sharpley *et al.* 1994; Barnard 2006; Drury *et al.* 2006). Therefore, technological development is required to remove the phosphorus contained in wastewater to low concentrations and to recover the removed phosphorus as a phosphorus resource.

Currently, there are two widely used methods to remove phosphorus in wastewater, namely, the biological phosphorus removal method (Chan 2002; Barnard 2003;

Barnard & Steichen 2006) and the precipitation method (Luedecke 1989). However, the phosphorus removed using these methods may contain a large number of impurities, or it may be a compound form that is difficult to use as a phosphorus resource (such as aluminium phosphate or ferric phosphate).

In order to resolve these problems, we developed a high-speed adsorbent having a unique porous structure, and a phosphorus adsorption and recovery system using this adsorbent. (Omori *et al.* 2007). In this study, we attempted to demonstrate in field tests, that it is possible for this system to recover high purity phosphorus as calcium phosphate from municipal wastewater secondary effluent.

METHODS

Phosphorus adsorption and recovery system

Figure 1 shows diagram of the phosphorus adsorption and recovery system used in this study. This system consists of following processes; an adsorption process to remove the phosphorus from the municipal wastewater secondary effluent by an adsorbent, a desorption process to desorb the phosphorus adsorbed on the adsorbent by an alkaline aqueous solution, and a recovery process to recover the desorbed phosphorus as calcium phosphate. The adsorbent can be used repeatedly in the phosphorus removal after the desorption process. Also, the alkaline solution after the recovery of the phosphorus can be used again as the desorption solution thereafter.

Materials

Adsorbent

A high-speed adsorbent having a unique porous structure we developed, was used. This adsorbent is spheral with an average diameter of 0.55 mm, and it has the following characteristics (Omori *et al.* 2007).

- Even when raw water is passed through at high flow rate, this adsorbent can remove the phosphorus in the water to very low concentration, and has a high capacity of the phosphorus adsorption.
- The selectivity for phosphorus is high; $PO_4^{3-} > F^- > SO_4^{2-} > Br^-, Cl^-, NO^{2-}, NO^{3-}$
- The adsorbed phosphorus can be desorbed by an alkaline aqueous solution, so it is possible to repeatedly use the adsorbent in the phosphorus removal.

Raw water

Municipal wastewater secondary effluent treated by the conventional activated sludge method was used as the raw water. The qualities of the raw water were as follows; total phosphorus (TP): 0.1–3.2 mg P/L, ortho-phosphate (OP): 0.05–3.0 mg P/L, BOD_5: 9.9–49 mg/L, and COD_{Cr}: 15–47 mg/L.

Analysis

Phosphorus concentration

TP was measured with the persulfate digestion-ascorbic acid method, and OP was measured with the ascorbic acid method (*Standard Methods for the Examination of Water and Wastewater* 2005).
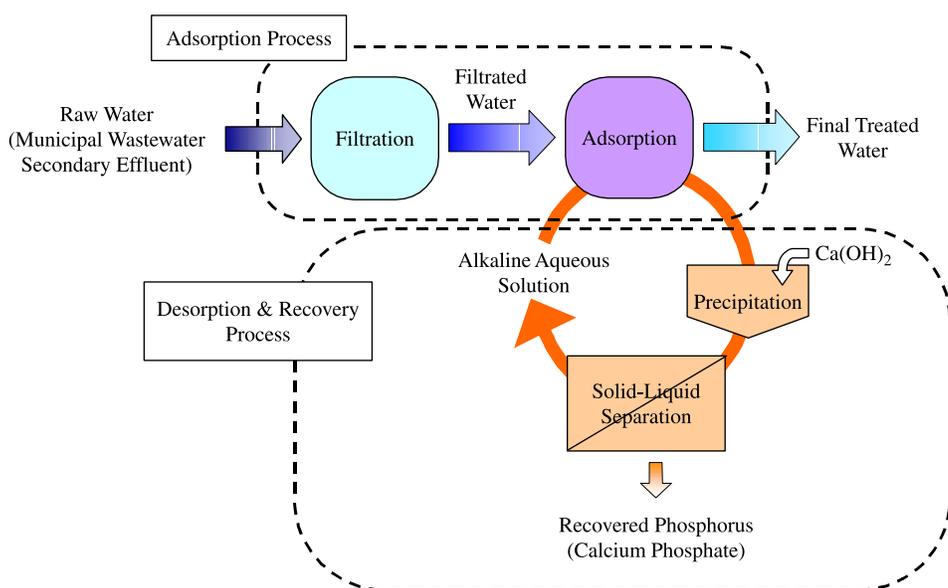

Figure 1 │ Diagram of the phosphorus adsorption and recovery system.

Phosphorus content in the adsorbent

The phosphorus content was measured with X-ray fluorescence analysis (XRF) after drying the adsorbent at 70°C. A calibration curve was determined by analyzing the absorbent, in which a specified amount of phosphorus had been adsorbed.

Composition of the recovered phosphorus

After drying at 105°C, the constituents were determined with X-ray diffraction analysis (XRD). After the recovered phosphorus was dissolved with nitric acid, the contents of calcium, phosphorus, sodium and hazardous elements were determined by inductively coupled plasma optical emission spectrometry analysis (ICP-OES).

RESULTS AND DISCUSSION

Adsorption process

Phosphorus concentration of the treated water

The filtration was performed by passing the municipal wastewater secondary effluent through a column packed with activated carbon with a grain diameter of 0.850–0.355 mm at space velocity (SV) $5\,h^{-1}$ and a linear velocity (LV) of 2.65 m/h. The phosphorus removal was performed by passing the filtrated water through an adsorbent packed column. Two columns were connected in series for phosphorus removal (Figure 2). Each column was packed
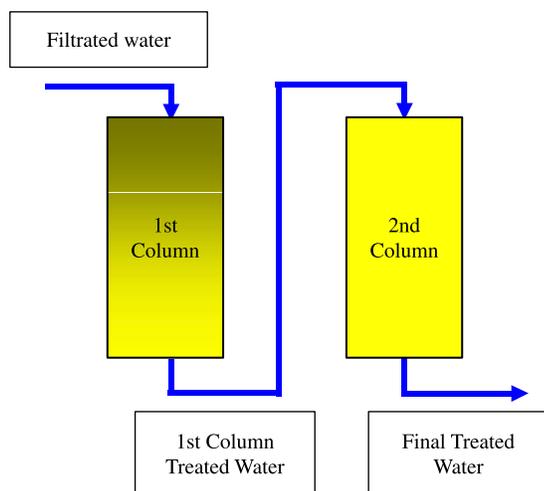

Figure 2 │ Diagram of column connection for phosphorus removal.

with 3L adsorbent, and the flow rate was SV $15\,h^{-1}$ (the value calculated on the total amount of adsorbent packed into the two columns). Therefore, the treated water flow was $2.2\,m^3/day$. The breakthrough for the adsorption was defined as the point at which TP of the final treated water (effluent from the second column) reached 0.05 mg-P/L. The merry-go-round method was used for the adsorption. Concretely, after breakthrough, the flow to the first column was finished, the second column was used as new first column instead, and a fresh column was used as new second column.

Figure 3 shows a time course of TP in the filtrated water, the first column treated water, and the final treated water. Figure 4 shows an expansion of the vertical axis in Figure 3. While the TP of the filtrated water varied significantly within the range of 0.1–2.1 mg P/L, the TP of the final treated water remained in the range of 0.02–0.04 mg P/L until breakthrough.

Figure 5 shows a time course of OP in the first column treated water and the final treated water. The OP of the final treated water was very low as 0.003 mg P/L or less until breakthrough.

These results indicate that, even if the phosphorus concentration of the raw water varies significantly, this phosphorus adsorption and recovery system can constantly remove phosphorus to very low concentration.

Phosphorus removal ratio

The TP removal ratio was calculated as follows. First, the "inflow TP amount" was calculated by integrating the TP concentration of the filtrated water until breakthrough. Also, the "outflow TP amount" was calculated by integrating the TP concentration of the final treated water until breakthrough. Then, the TP removal ratio was calculated using Equation (1).

$$\text{TP removal ratio } (\%) = \{(\text{inflow TP amount} - \text{outflow TP amount})/\text{inflow TP amount}\} \times 100 \tag{1}$$

Similarly, the OP removal ratio was calculated as follows. The "inflow OP amount" was calculated by integrating the OP concentration of the filtrated water until breakthrough, and the "outflow OP amount" was calculated by integrating the OP concentration of the final treated water until
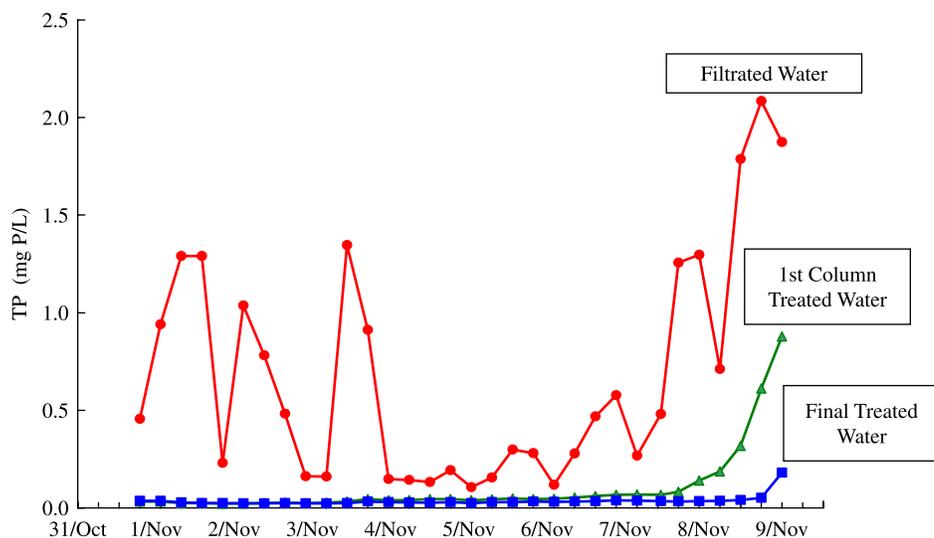
Figure 3 │ TP in the adsorption process. Condition: SV 15 h^{-1}.

breakthrough. Then, the OP removal ratio was calculated using Equation (2).

$$OP\ removal\ ratio\ (\%) = \{(inflow\ OP\ amount \\ - outflow\ OP\ amount)/inflow\ OP\ amount\} \times 100 \quad (2)$$

As a result, the TP removal ratio was 97%, and the OP removal ratio exceeded 99.5%. This system can remove phosphorus at very high removal ratio.

Desorption process

Desorption ratio

After breakthrough, the adsorbent in the first column was treated with an alkaline aqueous solution (8 wt% NaOH) to desorp the adsorbed phosphorus. The solution was passed through the column for 4 h at SV 3 h^{-1}. The desorption ratio was calculated as follows. Both after breakthrough and after desorption, the adsorbent in the first column was sampled, and the phosphorus (P) content was measured with XRF.
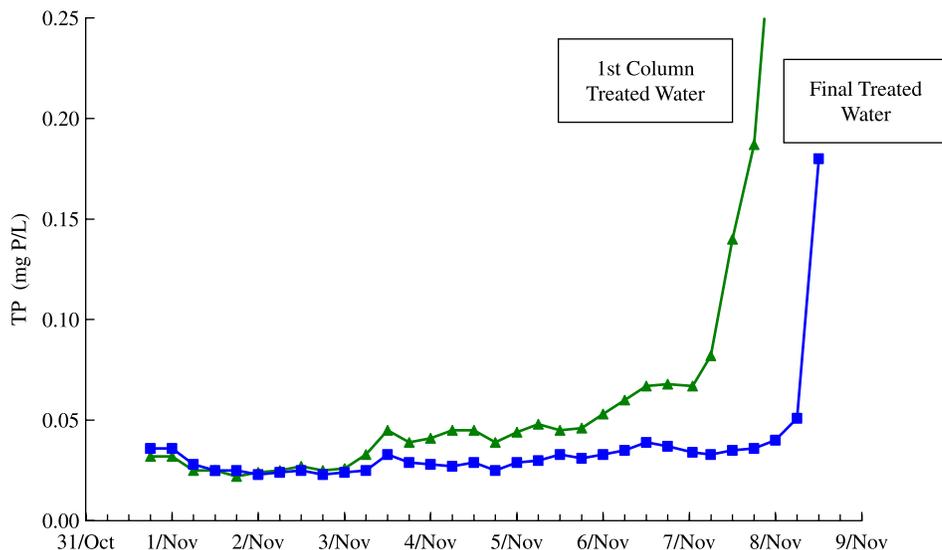

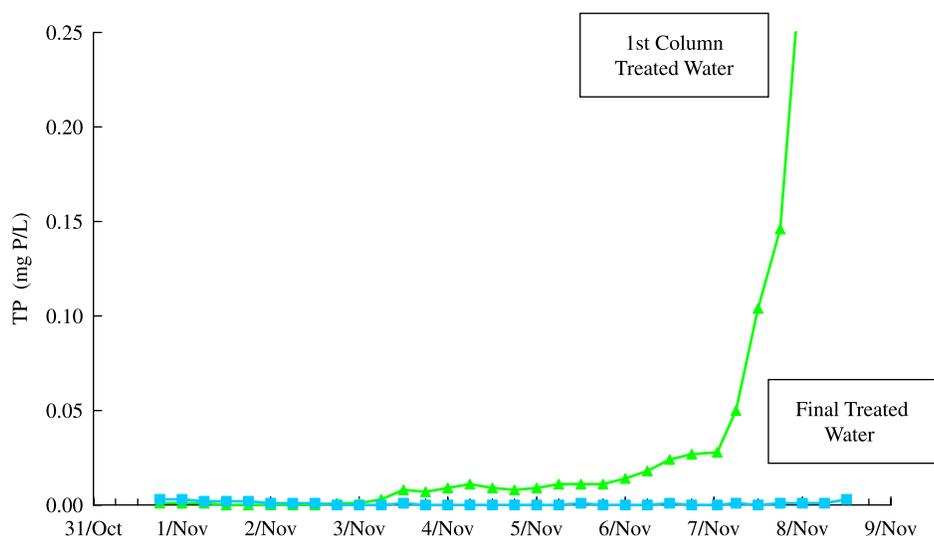**Figure 4** │ TP in the adsorption process. Condition: SV 15 h^{-1}.

Figure 5 │ OP in the adsorption process. Condition: SV 15 h^{-1}.

The sampling of the adsorbent was performed after sufficiently mixing the adsorbent in the column by backwashing. The "n-th adsorption amount" was calculated using Equation (3), and the "n-th desorption amount" was calculated using Equation (4).

$$\text{N-th adsorption amount} = \text{P content after the n-th adsorption}$$
$$- \text{P content after the} \qquad (3)$$
$$(n-1)\text{-th desorption}$$

$$\text{N-th desorption amount} = \text{P content after the n-th adsorption}$$
$$- \text{P content after the} \qquad (4)$$
$$\text{n-th desorption}$$

Then, using Equation (5), the "n-th desorption ratio" was calculated.

$$\text{N-th desorption ratio (\%)} = (\text{n-th desorption amount}/$$
$$\qquad (5)$$
$$\text{the n-th adsorption amount}) \times 100$$

Figure 6 shows the phosphorus content of the adsorbent after repeated cycles of adsorption and desorption with the desorption ratio. While the desorption ratio at the initial desorption process was somewhat low, as 72%, that in the second desorption process or later was high as 97% on average. This means that this phosphorus adsorption and recovery system can provide the removed phosphorus to recovery process with high efficiency.

Recovery process

Composition of the recovered phosphorus

Calcium hydroxide was added to the alkaline aqueous solution containing the desorbed phosphorus at Ca/P mole ratio of 2.0, and the phosphorus was precipitated as calcium phosphate. Then, the precipitate was neutralized with hydrochloric acid aqueous solution and washed with water, followed by solid–liquid separation to recover the precipitate. Figure 7 shows the X-ray diffraction pattern of the precipitate (recovered phosphorus). The main component of the recovered phosphorus was apatite-type
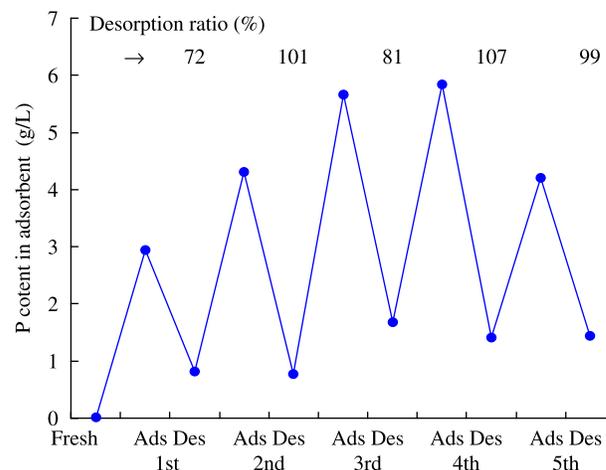
Figure 6 │ Phosphorus contents in the adsorbent and the desorption ratio.
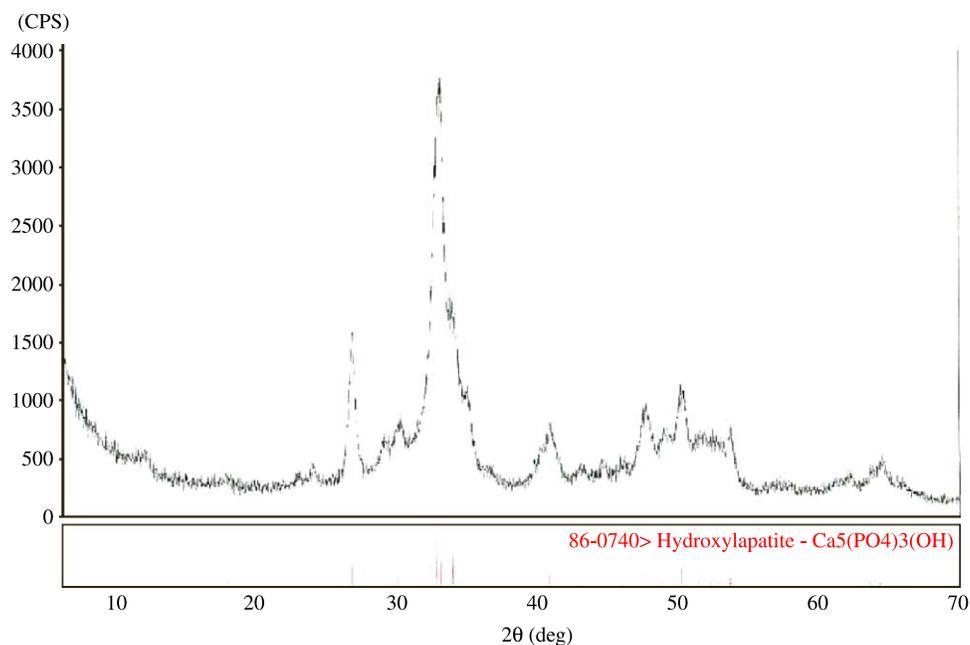
Figure 7 | X-ray diffraction pattern of the precipitate (recovered phosphorus).

calcium phosphate. This is a compound form that can be easily used as a phosphorus resource. Also, no residual calcium hydroxide was detected in the precipitate. The hydrochloric acid aqueous solution neutralizing the precipitate contained calcium of 9,900 mg/L and phosphorus of 0.46 mg/L. These results indicate that the neutralizing by hydrochloric acid aqueous solution is an effective means of increasing the phosphorus content of the recovered phosphorus.

Table 1 shows the contents of calcium, phosphorus, and sodium in the recovered phosphorus. The phosphorus content was 16%, which corresponds to BPL value (bone phosphate of lime) of 80%. BPL is the criterion to evaluate the quality of phosphorus ore. BPL value of 77% or more means to be high-grade. Though the recovered phosphorus was taken from the sodium hydroxide aqueous solution by solid–liquid separation, the sodium content was very low as 0.50%.

Table 2 shows the contents of hazardous elements in the recovered phosphorus, along with the recommendation levels by ICRCL (Interdepartmental Committee on the Redevelopment of Contaminated Land) for land used as a playground, which are most stringent among the recommendation levels by ICRCL. As for the contents of hazardous elements, a high content of arsenic compared with other elements was noticed. This is attributed the fact that the absorbent used for the phosphorus removal adsorbs arsenic. However, all of the elements shown in Table 2 were determined at contents that were significantly lower than

Table 1 | Elemental contents of the recovered phosphorus

Element	Content (%)
Ca	41
P	16
Na	0.50

Table 2 | Hazardous element contents in the recovered phosphorus

Element	Recovered phosphorus (mg/kg)	ICRCL Recommendation level for playgrounds (mg/kg)
As	7.2	20–25
Cd	<0.2	2–10
Cr	1.1	50–200
Cu	2.9	50
Hg	<0.1	0.5–1.0
Ni	2.0	40–70
Pb	0.35	200
Zn	24	300

the recommendation levels. This results from high phosphorus selectivity of the adsorbent.

These results indicate that the phosphorus recovered in this system can be used as an alternative for phosphorus ore, or as a phosphate fertilizer.

CONCLUSIONS

The field tests of the phosphorus adsorption and recovery were performed using municipal wastewater secondary effluent.

- This system can remove phosphorus from the secondary effluent effectively. Even at a high SV $15\,h^{-1}$, the TP removal ratio was 97% and the OP removal ratio exceeded 99.5%. Therefore the TP of the final treated water remained in the range of $0.02-0.04\,mg\,P/L$ and the OP was $0.003\,mg\,P/L$ or less.
- The desorption ratio in this system was high as 97% on average; this system can provide the removed phosphorus to recovery process with high efficiency.
- This system could recover phosphorus as high purity calcium phosphate with BPL value of 80%. This BPL value meets the criterion for high-grade phosphorus ore. Therefore the recovered phosphorus can be applied to an alternative for phosphorus ore, or to a phosphate fertilizer.

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