

## PHOSPHORUS RECOVERY FROM WASTEWATER BY HYDROTALCITE AND ZEOLITE

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**ABSTRACT:** A system using hydrotalcite and zeolite is developed for the recovery of phosphorus from wastewater having low phosphate concentrations. As HT or Ze is independently used, redundant ion species are produced in a desorbing solution. As HT and Ze are used in combination, however, the opposite redundant ion species can be used to desorb  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$ , respectively. Simple alkaline NaCl solution is used to desorb/regenerate HT and Ze. Moreover, desorbed substances can be recovered as magnesium ammonium phosphate (MAP) by the addition of Mg. In this paper, the desorption of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  from HT and Ze into a single desorbing solution and phosphorus recovery from the desorbing solution as MAP are experimentally investigated. It is verified that the single desorbing solution can simultaneously desorb HT and Ze. Whereas 95% of phosphate was recovered from the desorbing solution in which  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  were accumulated, most of the recovered phosphorus was not MAP but  $\text{Mg}_3(\text{PO}_4)_2$  (MP). However, when the initial concentrations of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  in the desorbing solution increased, MAP was produced rather easily and more than 90% of P was recovered. Further investigation into application for the practical plant is necessary.

**Keywords:** Hydrotalcite, zeolite, phosphorus recovery, adsorption, desorbing solution

### INTRODUCTION

Water bodies in lowlands tend to be eutrofied due to water stagnation, and levels of nutrients such as nitrogen or phosphorus then have to be controlled. Fishery cultivation, for which nutrients are needed, is usually active in coastal areas along lowlands.

Phosphorus (P) is produced only at specific sites in the world. There are several estimations that P will be exhausted in 60 or 100 years from now (Kuroda 2005). Consequently, the United States has stopped exporting P because of its strategic importance, and China has added a 100% export tax, essentially stopping P exports from that country. Unfortunately, Japan has had to import 100% of the phosphate rock it uses for fertilizer and industrial applications.

Phosphorus is conveyed in various ways into the environment until it finally reaches the sea. Sewer systems are thought to be effective P collection systems because 20 to 40% of imported P in Japan is contained in wastewater. Methods such as the phostrip, magnesium ammonium phosphate (MAP), and crystallization-methods have been practically used to recover P in some wastewater treatment plants in Japan. However, these methods can be applied only to water having high P

concentrations such as that resulting from the dewatering of return sludge (Kato 2007).

This paper introduces a newly developed ion exchange method in which hydrotalcite (HT) is used together with zeolite (Ze) as an adsorbent for cation exchange and anion exchange, respectively. Hydrotalcite, like aluminum hydroxide and ion exchange resin, is a phosphorus-selective adsorbent. HT has a greater adsorption capacity than these materials and can be used several times after desorption and regeneration, thus it is considered a suitable material for P recovery (Kawamoto et al. 1999), (Kuzawa et al. 2006), (Oshima et al. 2007).

An alkaline salt, such as NaCl, is used to desorb  $\text{PO}_4^{3-}$  by  $\text{Cl}^-$ , and then unnecessary  $\text{Na}^+$  is produced. In general, proper treatment and disposal are necessary due to the high concentration of this  $\text{Na}^+$  ion and high pH. This unnecessary ion problem is the same in other ion exchange methods such as that using Ze. (Figure 1) Therefore, the authors invented the HT/Ze system, which uses alkaline NaCl for the desorption/regeneration of HT and Ze, and discharges no unnecessary ions. In this method, ammonia and phosphorus are accumulated at high concentrations in a single desorption liquid, and thus both N and P can be easily recovered just by adding Mg to crystallize MAP or struvite.

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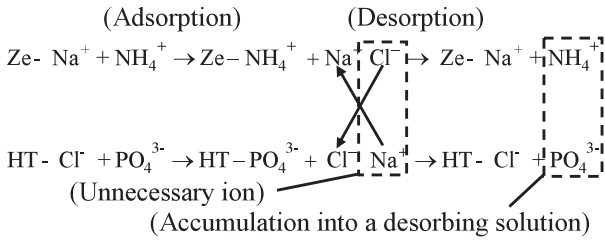


Fig. 1 Principal reaction of adsorption and desorption of HT and Ze respectively

This paper reports some experimental results and discussions on the conjugated desorption by using NaCl and MAP production.

Figure 1 shows an example of HT/Ze method applied to a conventional activated sludge process.

- 1) Withdrawing the water from a secondary settlement tank may be suitable, because the SS is already separated and various forms of P in wastewater are decomposed to  $\text{PO}_4^{3-}$ .
- 2)  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  are adsorbed to saturation levels in HT and Ze, respectively.
- 3) In the desorption process, alkaline NaCl desorbs  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$ . Ze is regenerated by  $\text{Na}^+$  at the same time, but an additional process is necessary for HT regeneration by  $\text{MgCl}_2$ .
- 4) MAP is crystallized by adding Mg into the desorbed liquid in which  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  are accumulated.
- 5) After P and N are recovered, desorbing solution is reused by re-adjustment of pH.

The desorbed liquid after crystallization still contains enough  $\text{Na}^+$  and  $\text{Cl}^-$ , and then is reused after pH adjustment.

MATERIALS AND EXPERIMENT

HT and Ze

HT is the general name for various compounds, as  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}]$ , that have anions in a layered structure.

In this molecular formula,  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are divalent and trivalent metal ions, respectively, and  $\text{A}^{n-}_{x/n}$  is the anion between the layers. The HTs employed in the experiments are Mg as the divalent metal ion, Al as the trivalent metal ion, and  $\text{Cl}^-$  as the exchangeable anion, namely Mg-Al-Cl-type HT. HT granulated by a ceramic binder, whose diameter is 0.8 to 2.0 mm, was used.

The composition of Ze, a Na-A type zeolite, is expressed as  $\text{Na}_2 \cdot 2\text{SiO}_2 \cdot \text{AlO}_3 \cdot 4.5\text{H}_2\text{O}$ . The diameter is 2 to 5 mm and its CEC (cation exchange capacity) is 250 meq/100 g.

This type of Ze can exchange its  $\text{Na}^+$  and  $\text{NH}_4^+$  in water.

Saturated Quantity Adsorption

Saturated quantity adsorption is necessary to preparing HT and Ze which adsorb  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  up to saturated amount. In this section, the saturated adsorption amount was determined from an adsorption isotherm by observing data. The initial concentration in the experiments was set 1 to 10 mg-P/L ( $\text{Na}_2\text{HPO}_4$ ), which was the same range as treated wastewater, whereas it was 1 to 50 mg-N/l ( $\text{NH}_4\text{Cl}$ ) in the case of Ze.

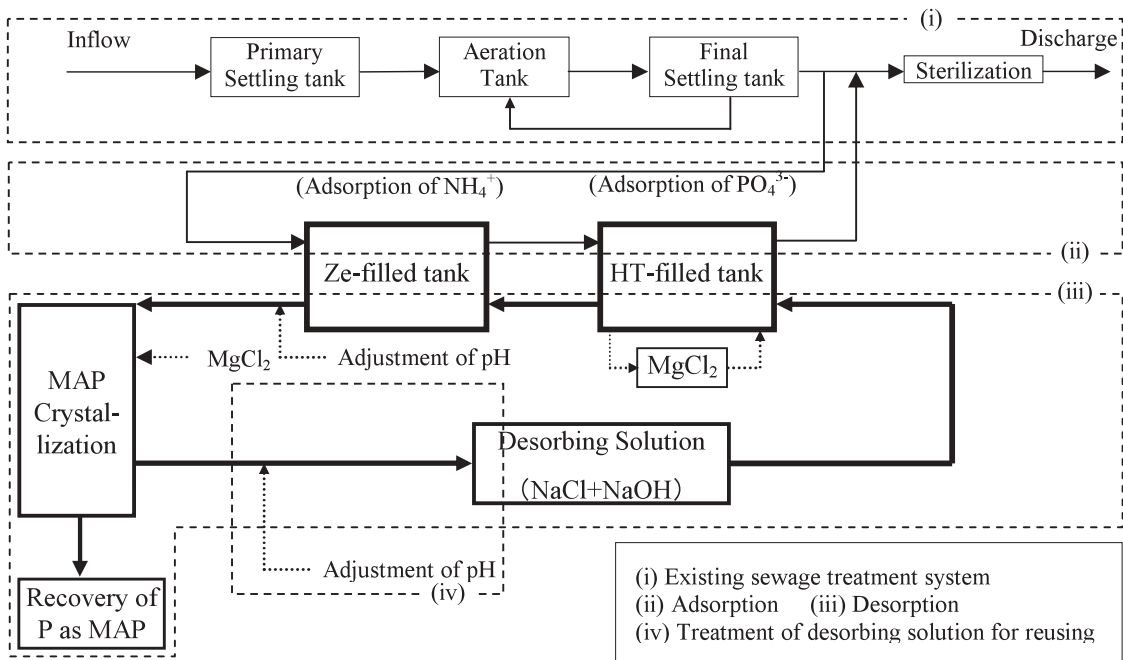


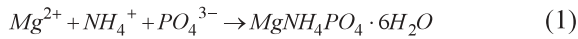
Fig.2 Diagram of P recovery system

Composition of Desorbing Solution

When alkaline NaCl is used as the desorbing solution, Cl<sup>-</sup> and Na<sup>+</sup> affect the desorption efficiency of HT and Ze, respectively. Alkalinity and reaction time also affect HT and Ze, respectively. To obtain suitable compositions of NaCl and NaOH, the desorption efficiencies of HT and Ze were examined by changing the concentration ratios of Cl<sup>-</sup> to PO<sub>4</sub><sup>3-</sup> and that of Na<sup>+</sup> to NH<sub>4</sub><sup>+</sup>, respectively. Using adsorption materials amount is HT of 5.0g and Ze of 1.0g, PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub><sup>+</sup> is adsorbed up to saturated amount in advance. In this experiment, adsorbed P means this saturated amount. The concentrations of NaOH were 0.25 and 0.75 mol-NaOH/L for HT, and the Cl/P ratios were 1, 10, 100, and 1000. The Na/NH<sub>4</sub> ratio was automatically determined according to the ratio of Cl/P, because it is necessary to use the same desorbing solution. Thus Na/NH<sub>4</sub> ratio becomes 151, 160, 250 and 1150 corresponding to the Cl/P ratios of 1, 10, 100 and 1000. It was stirred till reaction of desorption reached the equilibrium.

Phosphorus Recovery

MAP is crystallized with PO<sub>4</sub><sup>3-</sup>: NH<sub>4</sub><sup>+</sup>: Mg = 1:1:1 as shown in Eqn (1).



The Mg/P ratio and initial pH each have a rather strong effect on the crystallization. Therefore, we tried to produce MAP at first in pure water. According to the results of this pre-test, the actual crystallization was conducted in the real desorbing solution of alkaline NaCl. The experimental conditions are summarized in Table 1. As the table shows, 10 sets of experiments were carried out with various Mg and initial pH levels. Dilute hydrochloric acid was used for adjustment of pH.

Table 1 Experimental conditions

No.	Mg/P	pH	Solvent
1		8	
2	1	9	pure water
3		10	
4		8	
5	2	9	pure water
6		10	
7	5	10	desorbing solution
8		12	
9	2	10	desorbing solution
10	5	10	desorbing solution
11	1	12	desorbing solution

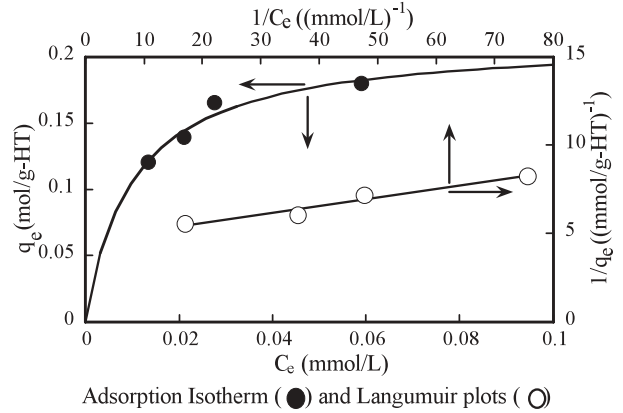


Fig. 3 Adsorption isotherm and Langmuir plots of HT

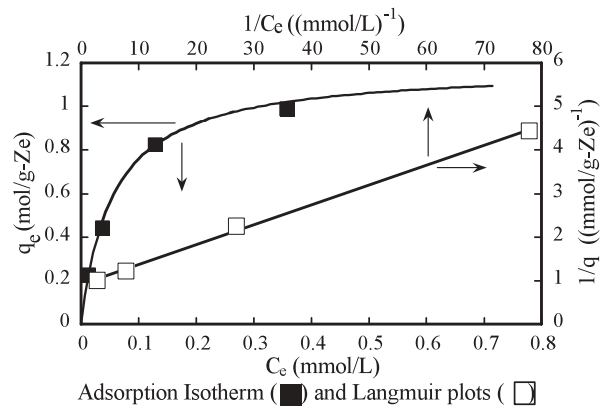


Fig. 4 Adsorption isotherm and Langmuir plots of Ze

The concentrations of PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub><sup>+</sup> were determined in the same manner as after the desorption of each substance, namely 5 mmol-P/L and 6.5 mmol-N/L. Crystallized material was redissolved by dilute hydrochloric acid in order to redissolved PO<sub>4</sub>-P, NH<sub>4</sub>-N, and Mg<sup>2+</sup> into the solution. The concentrations PO<sub>4</sub>-P, NH<sub>4</sub>-N, and Mg<sup>2+</sup> in the resolution were then analyzed to determine the recovery amount and the crystallization rate.

EXPERIMENTAL RESULTS AND DISCUSSION

Adsorption Characteristics of HT and Ze

The obtained adsorption isotherms of HT and Ze are shown in Figs. 3 and 4, respectively. In these figures, Langmuir plots are also shown in order to fix the parameters of the Langmuir relationship.

In both HT and Ze, the adsorption can be represented by the following Langmuir equation (Kondo 1991).

$$1/q_e = 1/q_s + (1/aq_s)(1/C_e) \quad (2)$$

Where  $q_e$  is the adsorption amount (mmol/g),  $q_s$  is the saturated adsorption amount (mmol/g),  $a$  is the equilibrium constant (mmol/L), and  $C_e$  is the equilibrium concentration (mmol/L).

From the analysis above, the saturation adsorption amount was determined as 0.21 mmol-P/g-HT. This is about 10% of Kawamoto's result (2.23 mmol P/g-HT) (Kawamoto 1999), which was obtained by powder-type HT and at a high P concentration of 800 mg/l. As mentioned above, the granular HT with a rather low P concentration was used consistent with that of wastewater. This is the reason for such a large difference in the saturation adsorption amount.

A saturation adsorption amount of 1.15 mmol-N/g-Ze was obtained. This corresponds to 46% of the CEC of the original powder-type Ze. In the experiments, the granular-type Ze after the binding of this powder type was used, and thus the saturation adsorption amount became lower than that of the powder type.

#### Composition of Desorbing Solution

Figure 5 shows the relationship between the desorption rate of  $\text{PO}_4^{3-}$  and the  $\text{Cl}^-/\text{PO}_4^{3-}$  ratio. The desorption efficiency is defined as the proportion of desorbed P amount to adsorbed P. The desorption rate tends to be higher under high alkalinity; that is, 0.97 mmol (97%)  $\text{PO}_4^{3-}$  was desorbed under the conditions of 0.75 mol-NaOH/L and a  $\text{Cl}^-/\text{PO}_4^{3-}$  ratio of 1,000. This obtained desorption rate almost equals that of the powder type (Sato 2007). This finding shows that P recovery by HT is highly feasible through the various HT adsorbent shapes.

Figure 6 demonstrates the relationship between the desorption rate of  $\text{NH}_4^+$  and the  $\text{Na}^+/\text{NH}_4^+$  ratio. This ratio should be determined by considering NaOH as alkaline. Thus, it is difficult to immerse a lot of Ze in the desorbing solution in order to adjust the ratios 1 and 10 due to the limitations on the volume in liquid and Ze. Moreover, because the desorption rate was highest in the case of 0.75 mol-NaOH/L, the experiments were not conducted at Na/N ratios of 1 and 10, and were conducted only under the condition of 0.75 mol-NaOH/L because 150mmol of  $\text{Na}^+$  was added as NaOH and there is little difference between Na/N ratios of 1 and 10.

The desorption rate was higher when the mol ratio of  $\text{Na}^+/\text{NH}_4^+$  was higher, while 96.4% (1.26 mmol) of  $\text{NH}_4^+$  was desorbed. This high rate may include the effect of ammonia stripping, not  $\text{NH}_4^+$  but  $\text{NH}_3$ , due to a high pH (13.2) (Omori 1987). This phenomenon might sometimes be a problem of this system. Under the

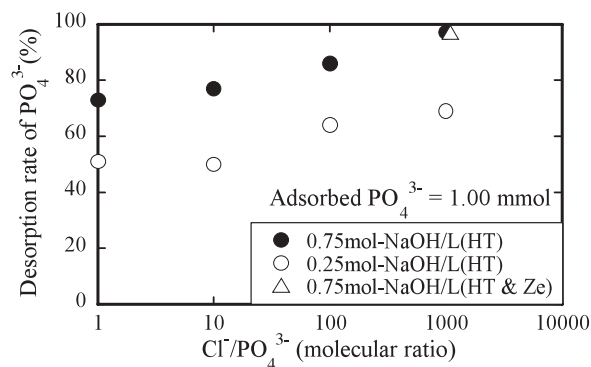


Fig. 5 Relationship between desorption rate and  $\text{Cl}^-/\text{PO}_4^{3-}$

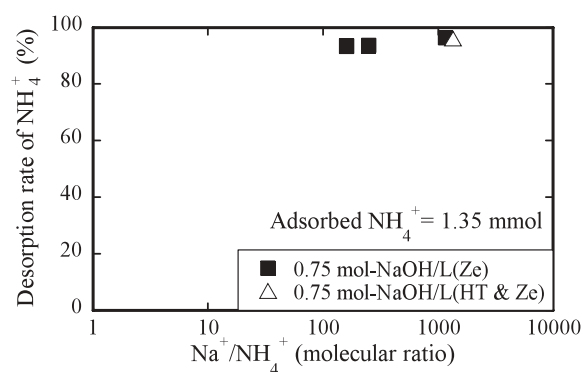


Fig. 6 Relation between desorption rate and  $\text{Na}^+/\text{NH}_4^+$

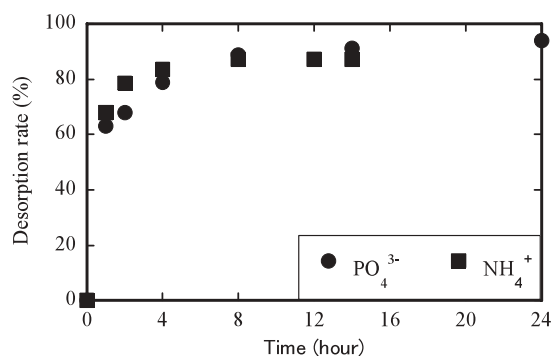


Fig. 7 Time changes in desorption rate of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  (0.75mmol-NaOH/L,  $\text{Cl}^-/\text{P}=1,000$ )

specific conditions in which ammonia exists as  $\text{NH}_3$  (free ammonia), Ze hardly adsorbs it.

Figure 7 shows time changes in the desorption rates of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$ . The desorption rate of  $\text{PO}_4^{3-}$  increased slightly between 8 and 24 hrs. In the case of powder-type HT, a report shows the desorption was completed in 14 hrs. This difference in the rate was a function of the shape of HT.

On the other hand, the desorption rate of Ze peaked

at around 8 hrs. This means that the difference in desorption time between  $\text{PO}_4^{3-}$  (HT) and  $\text{NH}_4^+$  (Ze) is important in the design and operation, specifically for deciding on suitable conditions depending on a kind of wastewater. One of these conditions is that ammonia existing as free  $\text{NH}_3$  is easily stripped into the air. This suggests that the desorption of HT should occur first and that, after P desorption in HT, Ze should be desorbed to prevent the stripping of free ammonia due to high pH.

After the fundamental experiments described above, an experiment was conducted to examine the actual system according to the practical process; that is, at first HT is desorbed and then Ze is desorbed in the same desorbing solution. As shown in Figs. 4 and 5, desorption rates of more than 90% were attained in both HT and Ze.

### Phosphorus Recovery

Table 2 shows the final results of P recovery. As the table shows, the recovery rate and MAP ratio are represented by Eqns (3) and (4).

$$\text{Recovery rate} = P_R / P_{in} \cdot 100 \quad (3)$$

$$\text{MAP Crystallization rate} = N_R / P_R \cdot 100 \quad (4)$$

where P is the  $\text{PO}_4^{3-}$  amount (mmol), N is the  $\text{NH}_4\text{-N}$  (mmol), "in" is the initial amount and "R" is the amount at recovery.

According to the stoichiometry shown in equation (3), P/N is 1. Thus it is possible to calculate the amount of P crystallized through the  $\text{NH}_4^+$  amount.

The P recovery rate was higher when levels of Mg and pH were high. In the experiments in this paper, the P recovery rate was highest under condition- 8, which pH is the highest and Mg is the most. However, the MAP ratio was only 2.1% in the crystallized substance. In the case of high pH, the added Mg rather easily makes  $\text{Mg}(\text{OH})_2$  instead of MAP by combining with  $\text{OH}^-$  first.  $\text{Mg}(\text{OH})_2$  is hardly soluted in water, and its activity is lower than that of  $\text{Mg}^{2+}$ . Thus it cannot contribute to the production of MAP. At the same time, there is a possibility that the production of MP (magnesium phosphate) became dominant over MAP due to a high Mg/P ratio; that is, the solubility of MP is lower than that of MAP (Nojiri and Araki 1990).

Considering the results discussed above, examination under the conditions- 9 and 10 were conducted which seemed to result of condition- 6 in a high P recovery rate and a high MAP ratio. As a result, the P recovery rate was almost the same as under condition- 6. However, the

Table 2 Result of P recovery

No.	Mg/P	pH	Solvent	Recovering rate (%)	MAP crystallization rate (%)
1		8		11.1	0.00
2	1	9	pure water	31.6	84.0
3		10		77.0	60.9
4		8		17.8	0.00
5	2	9	pure water	25.6	3.00
6		10		83.8	62.5
7		10	pure water	91.3	2.00
8	5	12	water	94.3	2.10
9	2	10	desorbing solution	82.0	2.10
10	5	10	desorbing solution	95.0	2.30
11	1	12	desorbing solution	95.2	51.9

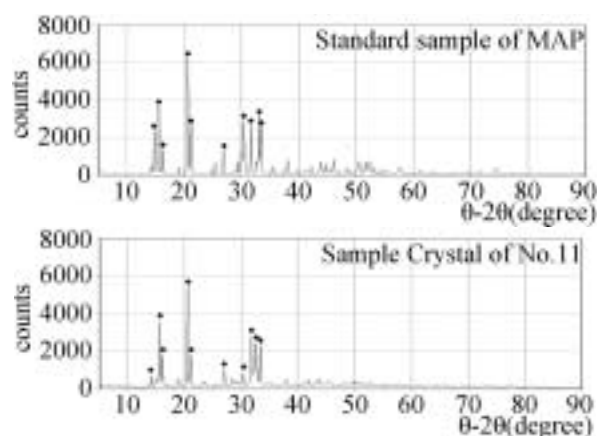


Fig. 8 X-ray diffraction patterns of standard sample of MAP and sample crystal obtained under condition- 11

MAP ratio decreased because the ionic strength was high due to a high concentration of  $\text{NaCl}$ , and then finally the effective concentrations of  $\text{PO}_4^{3-}$ , and  $\text{Mg}^{2+}$ , and  $\text{NH}_4^+$  decreased.

Therefore, MAP crystallization was examined under condition- 11, in which the initial  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  concentrations are each five times that of  $\text{PO}_4^{3-}$ ,  $\text{Mg}^{2+}$ , and  $\text{NH}_4^+$  in conditions- 1 to 10. From the phosphorus recovery experiments, it was expected that the crystallization reaction of P will become inactive when the initial pH is less than 10. In this experiment, 95.2% of P was recovered and 51.9% of P became MAP. Figure 8 shows X-ray diffraction patterns of a standard sample of MAP and a sample crystal obtained under condition 11. It is confirmed by comparing the peak of the standard sample with the peak of the sample crystal of

condition 11 that the sample crystal of condition 11 includes MAP. When MP is produced,  $\text{NH}_4^+$  is not used for MAP and remains in the desorbing solution. This remaining  $\text{NH}_4^+$  is stripped as  $\text{NH}_3$  when the pH of the solution is re-adjusted to be high in alkalinity for the reuse of the solution. Therefore,  $\text{NH}_4^+$  may not accumulate after repeated use.

## CONCLUSIONS

In this paper, a newly invented P recovery system is proposed and a fundamental examination of absorption and desorption is carried out.

(1) High desorption of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  was attained by single desorbing solution (alkaline NaCl). This solution can regenerate of HT and Ze as well.

(2) The optimum composition of the desorbing solution and the optimum reaction time were revealed.

(3) When the initial concentrations of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  in the desorbing solution increased, MAP was produced rather easily and more than 90% of P was recovered. More accumulation of  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  in the desorbing solution is necessary.

(4) From these experimental results, it is indicated that 5M NaCl solution of 200L as the desorbing solution is need to keep the high desorption rate when  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  of 1mol was adsorbed respectively. And adsorbed  $\text{PO}_4^{3-}$  of 92.2% can be recovered.

(5) Although further examination is necessary for MAP production, it was shown that the HT/Ze system is useful for the recovery of P from wastewater.

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