Phosphorous Mineralization for Resource Recovery from Wastewater Using Hydrothermal Treatment

Haruki Imaizumi¹, Takeshi Itakura², Ryo Sasai¹,² and Hideaki Itoh²

1. Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya, Japan
2. Division of Environmental Research, EcoTopia Science Institute, Nagoya University, Nagoya, Japan

Abstract: We investigated the resource recovery of phosphorous from wastewater containing diverse phosphorous compounds by hydrothermal mineralization treatment. The hydrothermal treatment was carried out for the model wastewaters containing 2000 mg/dm³ of phosphorous as P⁴⁺, P⁶⁺, P⁴⁺ or a mixed aqueous solution of P⁶⁺ and P⁴⁺ with mineralizer Ca(OH)₂. It was found that phosphorous concentration in the model wastewater containing P⁴⁺ was less than 0.10 mg/dm³ after the hydrothermal treatment, and the precipitate was Ca₃(PO₄)₂(OH). The treatment can reduce phosphorous concentration in aqueous media with P⁴⁺ and P⁴⁺, when the formed mineral was Ca₅(HP₂O₄)₃(H₂O). Hydrothermal mineralization treatment by using the sampling-type autoclave was required for separation of the precipitate from solution under hydrothermal conditions in order to make phosphorous concentration lower than the quantitative effluent standard. The phosphorous concentration in the solution treated under the optimal condition was 0.20 mg/dm³. Thus, the hydrothermal mineralization with Ca(OH)₂ is recommended as one of the detoxification and recovery techniques of phosphorous in aqueous solution.

Keywords: Phosphorous, Wastewater, Resource Recovery, Hydrothermal Mineralization

1. INTRODUCTION
Phosphorous is an essential element for life on Earth, and it is also one of the important but finite industrial resources for fertilizers and medicals. All the phosphate rock has been imported from abroad in Japan, which is poor in mineral resources. Recently, U.S.A. stopped exporting it in 1995. On the other hand, it is well known that phosphorous discharged into surface water would cause eutrophication of rivers and lakes. Thus, the national effluent standard of Japan has been set 16 mg/dm³. Removal and recovery treatment of phosphorous from wastewater containing phosphorous compounds discharged by the sewage facilities, fertilizers and plating industries is necessary to meet the required regulations.

Some recovery techniques for wastewater have been reported only by treating P⁴⁺ dissolved in aqueous media. P⁴⁺, Mg and NH₄ are crystallized to form struvite (magnesium ammonium phosphate: MAP) when the pH of wastewater rises to 8-9 [1, 2]. Ca also crystallizes with P⁴⁺ and forms hydroxyapatite (HAP). However, phosphorous compounds with different oxidation states such as P⁶⁺ and P⁴⁺ exist in aqueous media, especially in the wastewater discharged from electroless Ni-P plating industry [3, 4]. There are no effective treatments of wastewater containing these species. Therefore, the establishment of the phosphorous recovery system is strongly required especially in Japan.

In our previous study, we found that the hydrothermal mineralization using Ca(OH)₂ as a mineralizer could successfully recover resources from the wastewater with some o xoacids such as B⁶⁺(OH)₄, As⁵⁺ and As³⁺[5, 6]. This technique imitates a natural mechanism for forming minerals from various ions in aqueous media under hydrothermal conditions.

In this study, the resource recovery from wastewater containing phosphorous oxoanions such as P⁴⁺, P⁶⁺ and P⁴⁺ by hydrothermal mineralization treatment was investigated.

2. EXPERIMENTAL
2.1 Batch-type hydrothermal mineralization treatment
Model wastewaters with P (2000 mg/dm³ of phosphoric acid, phosphonic acid and phosphinic acid) were prepared by dissolving H₃PO₄, H₃PO₃ and H₃PO₂ in distilled and demineralized water, respectively. These model wastewaters were sealed in a pressure vessel lined with fluorocarbon resin with mineralizer Ca(OH)₂. The vessel was naturally cooled down for 1 h. The phosphorous concentration in the solution treated under 100–200 °C after the hydrothermal treatment was 0.20 mg/dm³. Thus, the hydrothermal mineralization with Ca(OH)₂ is recommended as one of the detoxification and recovery techniques of phosphorous in aqueous solution.

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Corresponding author: H. Imaizumi, h061102m@mbox.nagoya-u.ac.jp
For the analysis of phosphorus concentration under hydrothermal condition, the apparatus shown in Figure 1 was used. In this apparatus, the liquid-solid separation under the hydrothermal conditions was carried out by using a sintered metallic mesh filter. Model wastewaters of 60 cm$^3$ which contained phosphonic acid ($\text{P}^{\text{III}}\text{O}_3^-$, P: 1000 mg/dm$^3$) and phosphinic acid ($\text{P}^{\text{IV}}\text{O}_4^-$, P: 1000 mg/dm$^3$) were sealed in the pressure vessel as shown Fig. 1 with 1.0 g of Ca(OH)$_2$ mineralizer. Thermal adjustment was carried out by using temperature controller (CHINO Corporation, DZ1000).

2.3 Analysis
The precipitates were identified by X-ray diffraction (XRD: RIGAKU, Rint-2500) using CuK$\alpha$ radiation. The microstructure observation and qualitative element analysis of precipitates were performed by scanning electron microscopy (SEM: JEOl, JSM-T20) equipped with energy dispersive X-ray spectrometry (EDS: JED-2140). Concentration of phosphorus ions in the solvent obtained after the hydrothermal treatment was measured by ion chromatograph (IC: Shimadzu, CTO-20AC. Mobile phase; 12mM NaHCO$_3$, 0.6 mM Na$_2$CO$_3$ aqueous solution, Column: Shim-pack IC-SA2) with conductivity detector (Shimadzu, CDD-10A).

3. RESULTS AND DISCUSSION
3.1. Hydrothermal mineralization treatment for phosphoric acid with Ca(OH)$_2$ mineralizer
The phosphorus concentration reduced down to 1.0 mg/dm$^3$ only by addition of Ca(OH)$_2$ to the model wastewater, i.e., before the hydrothermal mineralization treatment. Fig. 2 shows the XRD patterns of the precipitates obtained before and after the treatment at 150 ºC. The precipitate before the hydrothermal treatment was identified as CaH$_3$P$_2$O$_7$(H$_2$O)$_2$ (Fig. 2 (a)). On the other hand, the diffraction peaks of HAP were observed after the treatment (Fig. 2 (b)). The phosphorus concentration was reduced by the hydrothermal mineralization treatment and Ca$_9$(PO$_4$)$_3$(OH) with very low solubility con-

![Fig. 2. XRD patterns of the precipitates (a) before and (b) after the treatment for 24 h at 150 ºC. (○) Ca(OH)$_2$, (□) CaHPO$_4$·H$_2$O, (●) Ca$_9$(PO$_4$)$_3$(OH).](image)

![Fig. 3. Dependence of concentration of P in the treated-water on treatment time. P$^{\text{III}}$O$_3^-$: 2000 mg/dm$^3$, Ca(OH)$_2$: 0.50 g, 150 ºC.](image)

![Fig. 4. XRD patterns of the precipitates (a) before and (b) after the treatment for 24 h at 150 ºC.](image)
the treatment. This predicts that the solubility of formed precipitate Ca(H₃PO₃)(H₂O) under hydrothermal conditions is lower than that under the ordinary temperature and pressure conditions, and the mean re-dissolution rate of precipitates after the treatment is slower during the cooling process of vessel, because the precipitates after the treatment have smaller surface area than the precipitate before the treatment. Therefore, the phosphorous concentration in hydrothermally treated wastewater will become the same value as that in the non-treatment wastewater, when the liquid-solid separation is not performed for a long time, i.e., the present system reaches the dissolution equilibrium state. It is found from these results that the present hydrothermal mineralization treatment is effective to remove phosphorous as natural mineral from wastewater containing phosphonic anions.

3.3. Treatment for model wastewater containing phosphonic acid with Ca(OH)₂

The result of hydrothermal mineralization treatment against model wastewater is shown in Fig. 5, where a mixed aqueous solution of P⁰O₃³⁻ (P: 2000 mg/dm³) is treated at 100, 150 and 200 °C with 0.50 g Ca(OH)₂. The concentration of phosphorous did not decrease before the hydrothermal treatment i.e., only with the addition of Ca(OH)₂. However, phosphorous concentration in the wastewater treated at 200 °C decreased down to 13.3 mg/dm³, which is lower than the standard of discharged water in Japan. Therefore, the hydrothermal mineralization treatment is definitely effective for reducing P⁰O₃³⁻ in aqueous media. Fig. 6 shows the XRD patterns of precipitates obtained by the treatment with 0.50 g Ca(OH)₂ at various temperatures. The precipitates formed by the treatment was Ca(H₃PO₃)(H₂O), which was the same crystal structure as the precipitate after the hydrothermal treatment for phosphonic acid with Ca(OH)₂. This result suggested that P⁰O₃⁻ was oxidized from mono-valence to tri-valence by H₂O molecules under the hydrothermal condition. In our previous study [6], it was already found that H₂O could play the role of oxidizer under hydro-

thermal conditions. At the optimal treatment condition, therefore, the present method can reduce the concentration of P⁰O₃⁻ less than the effluent standard of phosphorous, and at the same time, the phosphoric acid in the wastewater can be finally recovered as a natural resource, Ca(H₃PO₃)(H₂O).

3.4. Treatment for model wastewater containing phosphonic acid and phosphoric acid with Ca(OH)₂ in the absence/presence of H₂O₂ oxidizer

The hydrothermal mineralization was carried out for the model wastewater containing both P⁰O₃⁻ and P⁰O₃³⁻ (1000 mg/dm³ of phosphorous). Fig. 7 shows the treatment time dependence of the phosphorous concentration against the treatment time, when the mineralizer was 0.50 g Ca(OH)₂ and the treatment temperature was 200 °C. The phosphorous concentration before the hydrothermal treatment was ca. 1100 mg/dm³, while that after the hydrothermal treatment for 24 h was ca. 18 mg/dm³. This value was above the quantitative standard value of discharge for phosphorous. The precipitates before and
The crystalline size was found smaller than the precipitates as shown in 3.3 by SEM observation. This result indicates that the re-dissolution rate of precipitates was faster in this case. Therefore, the addition of other oxidizer would be required for complete phosphorous removal from the model mixed wastewater.

The result of hydrothermal mineralization treatment with 0.50 g of Ca(OH)$_2$ as a mineralizer in the presence of 1 vol% H$_2$O$_2$ as a oxidizer at 200 °C is shown in Fig. 9 against the model wastewater containing 1000 mg-P/dm$^3$ of both P$^{III}$O$_4^3-$ and P$^{II}$O$_4^3-$. The decrease rate of phosphorous concentration was faster than that without H$_2$O$_2$. This result suggests that the promotion of the P$^{III}$O$_4^3-$ oxidation by H$_2$O$_2$ stimulates the production of precipitate, Ca(HP$^{III}$O$_3$)(H$_2$O). When the hydrothermal mineralization treatment with 3 vol% of H$_2$O$_2$ was performed, the phosphorous concentration in the treated wastewater was less than 0.10 mg/dm$^3$ at 200 °C for 24 h. Thus, it was concluded that the hydrothermal mineralization treatment with Ca(OH)$_2$ and H$_2$O$_2$ enabled effective recovery of phosphorous regardless of the model wastewater containing phosphonic and phosphinic acids.

Fig. 10 shows XRD patterns of the precipitates after the treatment with 1 % H$_2$O$_2$ (Fig.10. (a)) and 3 % H$_2$O$_2$ (Fig.10. (b)). Diffraction peaks of Ca$_5$(P$^V$O$_4$)$_3$(OH) were observed after the hydrothermal treatment with 3% H$_2$O$_2$. As described in 3.1., the formation of apatite enables an
3.5. Hydrothermal mineralization treatment by using the in-situ sampling-type autoclave

Hydrothermal mineralization treatment by using the in-situ sampling-type autoclave as shown in Fig. 1 was carried out in order to separate the precipitate from solution under hydrothermal conditions.

Fig.11 shows the results of hydrothermal mineralization treatment using an ordinary batch type autoclave and the in-situ sampling-type treatment autoclave. As a result, phosphorous concentration after the treatment for 12 h was 0.20 mg/dm$^3$. This indicates that the separations of precipitates from the treated wastewater under hydrothermal conditions can improve both the shortening of the treatment time and the recovery yield of phosphorous, because this treatment completely prevents the re-dissolution of formed minerals. Therefore, the hydrothermal treatment using in-situ sampling-type autoclave is effective to detoxify the wastewater and recover phosphorous in wastewater as natural resources.

4. CONCLUSIONS

Precipitation recovery of phosphorous and detoxification of model wastewater containing phosphoric, phosphonic, phosphinic acids and the mixture of phosphonic and phosphinic acids were investigated. In order to recover $P^{V}$O$_4^{3-}$, mineralization of phosphonic acid by hydrothermal treatment with Ca(OH)$_2$ was effective to precipitate phosphorous as Ca$_3$(P$^{V}$O$_4$)$_3$(OH) mineral with high yield. Phosphonic acid (P$^{III}$O$_4^{3-}$) was easily recovered as Ca(HP$^{III}$O$_4$)$_3$(H$_2$O) by hydrothermal mineralization for 2 h at 150 °C. The phosphorous concentration in the treated water was ca. 5 mg/dm$^3$. Phosphonic acid (P$^{III}$O$_4^{5-}$) was also recovered by the hydrothermal mineralization at 200°C for 12 h, when the oxidation of P$^{III}$O$_4^{5-}$ occurred and phosphorous was collected as Ca(HP$^{III}$O$_4$)$_3$(H$_2$O).

In order to precipitate phosphorous from mixed solution of phosphonic and phosphinic acids, we succeeded to accomplish simultaneously both mineralization and oxidation by adding H$_2$O$_2$ oxidizer. As a result, phosphorous in wastewater was collected as Ca$_3$(P$^{III}$O$_4$)$_3$(OH) in the co-presence of the H$_2$O$_2$ more than 3 vol%, when the phosphorous concentration in treated water could be reduced less than 0.10 mg/dm$^3$. Therefore, the hydrothermal mineralization using Ca(OH)$_2$ was essential to recover phosphorous from aqueous media containing phosphoric, phosphonic and phosphinic acids. The separation of aqueous solution from precipitate under hydrothermal conditions completely prevents re-dissolution of formed minerals. The phosphorous concentration after the treatment for 12 h decreased down to 0.20 mg/dm$^3$. Therefore, the hydrothermal mineralization treatment is more effective to precipitate phosphorous species from aqueous media by the sampling-type hydrothermal treatment autoclave.

REFERENCES