

Phosphorus mineralization for resource recovery from wastewater using hydrothermal treatment

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We investigated the resource recovery of phosphorus from aqueous media containing various inorganic phosphorus compounds by hydrothermal mineralization treatment. The hydrothermal treatment was carried out for the model wastewaters containing 2000 mg/dm³ of phosphorus in forms of P^VO₄³⁻, P^{III}O₃³⁻, P^IO₂³⁻ or a mixed aqueous solution of P^{III}O₃³⁻ and P^IO₂³⁻ with mineralizer Ca(OH)₂. The phosphorus concentration in the treated water, which contained P^VO₄³⁻, was less than 0.1 mg/dm³. On the other hand, the hydrothermal mineralization treatments with solid-liquid separation under hydrothermal conditions were required for the treatment of P^{III}O₃³⁻ and P^IO₂³⁻, in order to accomplish the national effluent standard of Japan (16 mg/dm³). In this case, the phosphorus concentration in the solution treated under the optimal conditions was 0.20 mg/dm³. Thus, the hydrothermal mineralization with Ca(OH)₂ is recommended as one of the detoxification and recovery techniques of phosphorus in aqueous solution.

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1. Introduction

Phosphorus is an essential element for everyday life, and it is also one of the important but finite industrial resources for fertilizers and medical uses on Earth. All the phosphate rocks have been imported from abroad in Japan, which is poor in mineral resources production. Recently, the U.S.A. stopped exporting them in 1995. On the other hand, it is well known that phosphorus discharged into surface water would cause nutrient enrichment of rivers and lakes. Thus, the national effluent standard of Japan (NESJ) has been set at 16 mg/dm³. Removal and recovery treatment of phosphorus from wastewater containing phosphorus compounds discharged by the sewage facilities, fertilizers and plating industries is necessary to meet the required regulations.

Some recovery techniques of phosphorus resources from aqueous media have been reported only by treating P^VO₄³⁻ dissolved in aqueous media. Mg and NH₄ are crystallized to form struvite (magnesium ammonium phosphate: (MAP)) when the pH of wastewater rises to 8–9.¹⁾⁻³⁾ Ca also crystallizes with P^VO₄³⁻ and forms hydroxyapatite (HAP: Ca₁₀(PO₄)₆(OH)₂). And the other treatment methods such as biological and adsorption methods are actively investigated.⁴⁾⁻⁸⁾ However, phosphorus compounds with different oxidation states such as P^VF₆⁻, P^{III}O₃³⁻ and P^IO₂³⁻ exist in aqueous media in actual cases, especially used as ionic liquids or discharged in wastewater from the electroless Ni-P plating industry.⁹⁾ It is well known that these ions do not precipitate by the above reported technique and there are no effective removal treatments from aqueous media. Therefore, the establishment of the phosphorus recovery system, which can be applied regardless of its oxidation state, 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 aqueous solution with oxo-anions such as B(OH)₄⁻, As^VO₄³⁻ and As^{III}O₃³⁻.^{10),11)} This technique is

the precipitation technique of very stable anions by imitating a natural mechanism for forming minerals from such anions in aqueous media under hydrothermal conditions. Precipitation mechanism is explained by the effect of decreasing solubility of formed minerals into aqueous solution with an increase in temperature.

In this study, the resource recovery from wastewater containing phosphorus anions, mainly P^{III}O₃³⁻ and P^IO₂³⁻, by hydrothermal mineralization treatment was investigated.

2. Experimental

2.1 Batch-type hydrothermal mineralization treatment

Model wastewaters with various phosphorus species (2000 mg/dm³) were prepared by dissolving H₃P^VO₄, H₃P^{III}O₃ and H₃P^IO₂ in distilled and deionized water, respectively. These model wastewaters (30 cm³) were sealed in a pressure vessel lined with fluorocarbon resin with mineralizer Ca(OH)₂, and in some cases, with H₂O₂ as oxidizer. Hydrothermal treatment was carried out by leaving the vessel in a dry oven for 2–24 h at a given temperature in the range of 100–200°C. After the hydrothermal treatment, the vessel was naturally cooled down for 1 h. Precipitates were filtered and collected.

2.2 In situ sampling-type hydrothermal mineralization treatment

In-situ sampling type treatment apparatus shown in Fig. 1 was used in order to analyze the phosphorus concentration under hydrothermal conditions. In this apparatus, the liquid-solid separation under the hydrothermal conditions was carried out by using a sintered metallic mesh filter with 0.5 μm porosity. Model wastewaters of 60 cm³ which contained phosphonic acid (P^{III}O₃³⁻, P: 1000 mg/dm³) and phosphinic acid (P^IO₂³⁻, P: 1000 mg/dm³) were sealed in the pressure vessel as shown Fig. 1 with 1.0 g of Ca(OH)₂ mineralizer. Thermal adjustment was carried

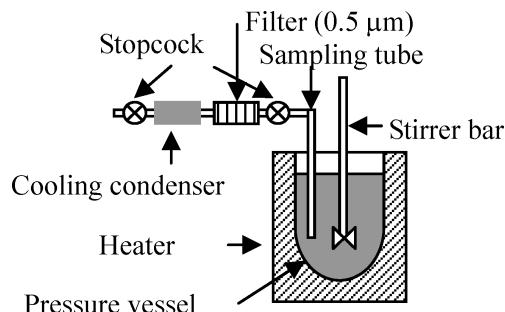


Fig. 1. Schematic diagram of in-situ sampling-type hydrothermal treatment autoclave.

out by using a temperature controller (CHINO Corporation, DZ1000).

2.3 Analysis

The precipitates were identified by X-ray diffraction (XRD; RIGAKU Co., Rint-2500) using Cu K α radiation. The microstructure observation and qualitative element analysis of precipitates were performed by scanning electron microscopy (SEM; JEOL Ltd., 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; 12 mM NaHCO₃, 0.6 mM Na₂CO₃ aqueous solution, Column; Shim-pack IC-SA2) with conductivity detector (Shimadzu Co., CDD-10A).

3. Results and discussion

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

At first, we confirmed the treatment effect for removing and recovering penta-valent phosphoric ions from aqueous media by using ordinary batch-type treatment apparatus with equivalent amount of Ca(OH)₂ mineralizer for forming HAP at 150°C. As a result, P concentration in the treated water was less than 0.1 mg/dm³, which showed very high removal and recovery yield. On the next stage, we investigated the treatment for aqueous media which contained tri-valent phosphonic acid (P^{III}O₃³⁻). **Figure 2** shows the treatment time dependence of the phosphorus concentration in treated-water, with 0.50 g Ca(OH)₂ mineralizer at 150°C. The phosphorus concentration before the hydrothermal treatment (*i.e.*, only by addition of Ca(OH)₂, it is shown as 0 h treatment in Fig. 2) was ca. 100 mg/dm³. The decrease in phosphorus concentration was derived from the formation of calcium phosphate compound as will be described later. The phosphorus concentration after the hydrothermal treatment was ca. 5.0 mg/dm³, which is sufficiently lower than the NESJ. **Figure 3** shows the XRD patterns of the precipitates obtained before and after the treatment at 150°C. Diffraction peaks of Ca(HPO₃)₂(H₂O) was observed in both patterns. This result indicates that the solubility of formed precipitate Ca(HPO₃)₂(H₂O) under hydrothermal conditions is lower than that under the normal temperature and pressure conditions. Thus, low P concentration after the treatment was achieved by solid liquid separation before reaching equilibrium state under normal conditions. Phosphorus concentration in hydrothermally treated model wastewater will become the same value as that in the non-treatment wastewater (ca. 100 mg/dm³), if the liquid-solid separation is not accomplished instantly in the cooling process. These results indicate that the

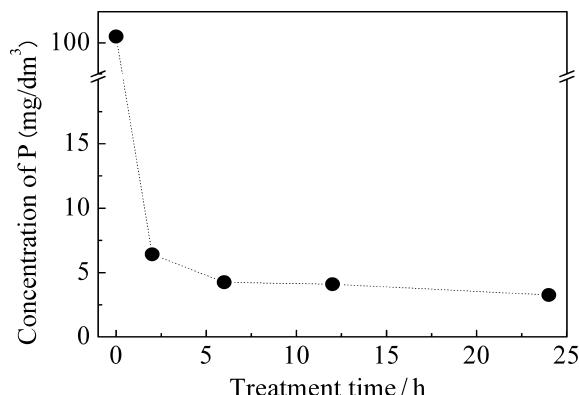


Fig. 2. Dependence of concentration of P in the treated-water on treatment time. Initial P^{III}O₃³⁻ concentration: 2000 mg/dm³, Ca(OH)₂: 0.50 g, 150°C.

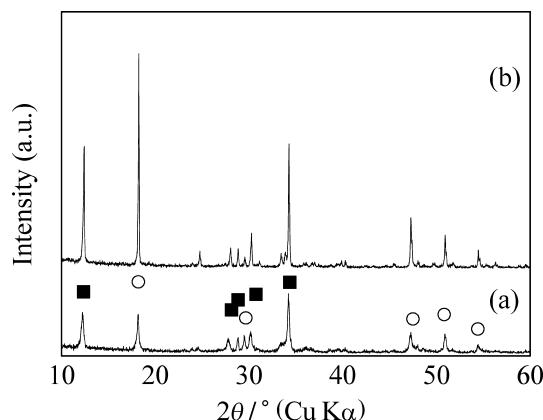


Fig. 3. XRD patterns of the precipitates (a) before and (b) after the treatment for 24 h at 150°C. (○)Ca(OH)₂, (■) Ca(HPO₃)₂(H₂O).

present hydrothermal mineralization treatment would be more effective by separating solids and liquids as soon as possible before reaching the dissolution equilibrium state after the hydrothermal treatment. Thus, we investigated the hydrothermal mineralization treatment by using the in-situ sampling-type treatment apparatus.

3.2 Treatment for model wastewater containing phosphinic acid with Ca(OH)₂

The result of hydrothermal mineralization treatment against model wastewater which contains 2000 mg/dm³ phosphinic acid P^IO₂³⁻ at 100–200°C with 0.50 g Ca(OH)₂, is shown in **Fig. 4**. Phosphorus concentration decreased less by the addition of Ca(OH)₂ (0 h treatment) or after the hydrothermal treatments at 100°C and 150°C. However, it decreased considerably down to 13.3 mg/dm³ in the treated water at 200°C for 24 h. Therefore, the hydrothermal mineralization treatment is definitely effective for reducing the amount of P^IO₂³⁻ in aqueous media. **Figure 5** shows the XRD patterns of precipitates obtained by the treatment at various temperatures. The precipitates formed were Ca(HPO₃)₂(H₂O), which was the same crystal structure as the precipitate after the hydrothermal mineralization treatment for phosphonic acid. This result suggests that P^IO₂³⁻ was oxidized from mono-valence to tri-valence by H₂O molecules under the hydrothermal condition. In our previous study,¹¹⁾ it was found that H₂O could play the role of oxidizer under hydrothermal con-

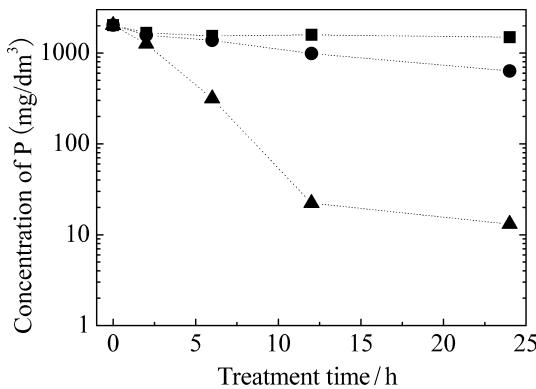


Fig. 4. Dependence of concentration of P in the treated-water on the treatment time. Initial $\text{P}^{I}\text{O}_2^{3-}$ concentration: 2000 mg/dm³, Ca(OH)_2 : 0.50 g, (■) 100°C, (●) 150°C, (▲) 200°C.

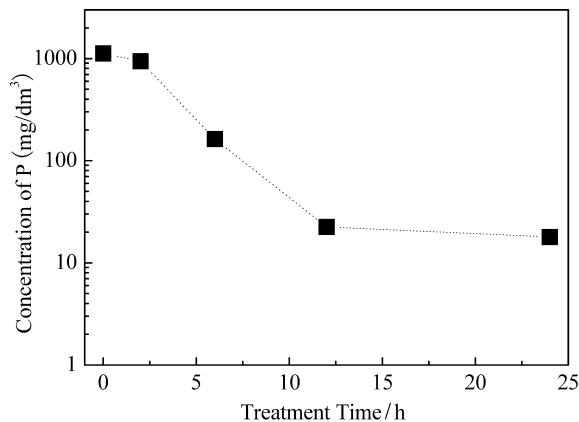


Fig. 6. Dependence of P concentration in the treated water after hydrothermal treatment at 200°C on the treatment time. (Initial P concentration: 2000 mg/dm³, Ca(OH)_2 : 0.50 g).

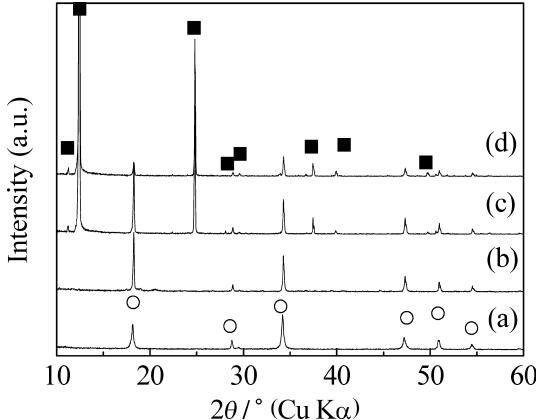


Fig. 5. XRD patterns of the precipitates (a) before and after the treatment for 24 h, (b) at 100°C, (c) at 150°C, (d) at 200°C; (○) Ca(OH)_2 , (■) $\text{Ca(HP}^{\text{III}}\text{O}_3\text{)}(\text{H}_2\text{O})$.

ditions. At the optimal treatment condition, therefore, the present method can decrease the concentration of $\text{P}^{\text{I}}\text{O}_2^{3-}$ less than NESJ, and at the same time, the phosphinic acid in the wastewater can be finally recovered as a natural resource, $\text{Ca(HP}^{\text{III}}\text{O}_3\text{)}(\text{H}_2\text{O})$.

Figure 6 shows the treatment time dependence on P concentration for the mixed aqueous solution of 1000 mg/dm³ $\text{P}^{\text{III}}\text{O}_3^{3-}$ and 1000 mg/dm³ $\text{P}^{\text{I}}\text{O}_2^{3-}$ using ordinary batch-type treatment apparatus at 200°C. P concentration in the model wastewater after the addition of Ca(OH)_2 was 1100 mg/dm³. It indicates that the formation of $\text{Ca(HP}^{\text{III}}\text{O}_3\text{)}(\text{H}_2\text{O})$ occur only for the $\text{P}^{\text{III}}\text{O}_3^{3-}$. P concentration in the treated-water shows the same tendency as the result of $\text{P}^{\text{I}}\text{O}_2^{3-}$ treatment. Thus, it is expected that the mono-valent $\text{P}^{\text{I}}\text{O}_2^{3-}$ would be oxidized to tri-valent $\text{P}^{\text{III}}\text{O}_3^{3-}$. However, P concentration in the treated-water at the optimal treatment condition was 17.9 mg/dm³, which is higher than that of NESJ. Analyses of treated-water by using ion-chromatography, shown in **Fig. 7**, were carried out in order to demonstrate the change of concentration of each ion. Both the final concentrations of $\text{P}^{\text{III}}\text{O}_3^{3-}$ and $\text{P}^{\text{I}}\text{O}_2^{3-}$ were lower than the NESJ. However, $\text{P}^{\text{III}}\text{O}_3^{3-}$ concentration was constant with an increase in treatment time despite the $\text{P}^{\text{I}}\text{O}_2^{3-}$ concentration decreased. This result indicates the oxidation reaction of $\text{P}^{\text{I}}\text{O}_2^{3-}$ to form $\text{P}^{\text{III}}\text{O}_3^{3-}$ is attributed to the increase in $\text{P}^{\text{III}}\text{O}_3^{3-}$ concentration. Therefore, the enhancement of $\text{P}^{\text{I}}\text{O}_2^{3-}$ oxidation would be effective for detoxification treatment of mixed aqueous solution. The hydrothermal miner-

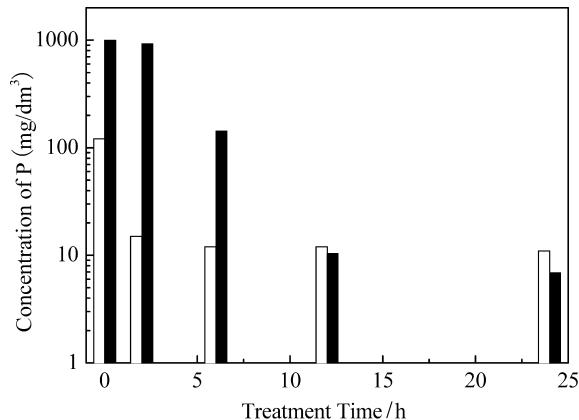


Fig. 7. Treatment time dependence of concentrations of phosphonic and phosphinic acids in the treated water after hydrothermal treatment at 200°C. (Initial P concentration: 2000 mg/dm³, Ca(OH)_2 : 0.50 g, black bar: phosphonic ion, white bar: phosphinic ion).

alization treatments with 0.50 g of Ca(OH)_2 as a mineralizer in the presence of 1 vol% H_2O_2 as an oxidizer were carried out in order to enhance the oxidation reaction of $\text{P}^{\text{I}}\text{O}_2^{3-}$ at 200°C against the model wastewater containing both $\text{P}^{\text{III}}\text{O}_3^{3-}$ and $\text{P}^{\text{I}}\text{O}_2^{3-}$ (figure not shown). The decreasing rate of phosphorus concentration was faster than that without H_2O_2 , but the recovery and removal yields at the optimal treatment conditions were not improved. This result suggests that the promotion of the oxidation reaction of $\text{P}^{\text{I}}\text{O}_2^{3-}$ to $\text{P}^{\text{III}}\text{O}_3^{3-}$ by H_2O_2 stimulates the production of precipitate, $\text{Ca(HP}^{\text{III}}\text{O}_3\text{)}(\text{H}_2\text{O})$. When the hydrothermal mineralization treatment with 3 vol% of H_2O_2 was performed, the phosphorus concentration in the treated wastewater was less than 0.10 mg/dm³ at 200°C for 24 h. It is concluded that the hydrothermal mineralization treatment with Ca(OH)_2 and H_2O_2 enables effective recovery of phosphorus regardless of the model wastewaters containing phosphonic and phosphinic acids. Therefore, the hydrothermal mineralization treatment shows the possibility of an internal phosphorus resource circulation.

3.3 Hydrothermal mineralization treatment by using the in-situ sampling-type autoclave

Hydrothermal mineralization treatment by using the autoclave as shown in Fig. 1 was carried out in order to separate the pre-

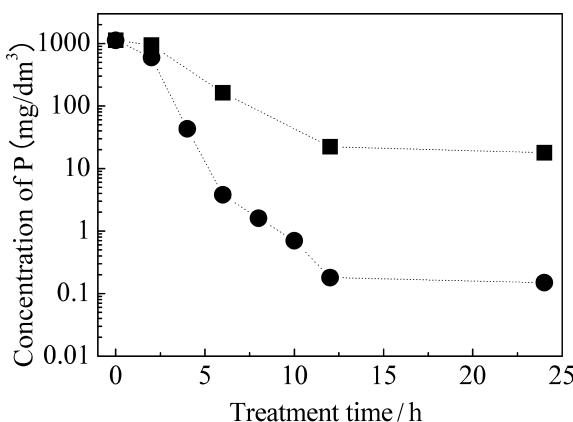


Fig. 8. Dependence of concentration of P in the treated water on the treatment time at 200°C. Initial $\text{P}^{\text{III}}\text{O}_3^{3-}$ concentration: 1000 mg/dm³, initial $\text{P}^{\text{I}}\text{O}_3^{3-}$ concentration: 1000 mg/dm³, $\text{Ca}(\text{OH})_2$: 1.0 g, (■) batch, (●) in-situ.

cipitate from solution under hydrothermal conditions. Results obtained by this treatment would give us the information on the solubility of formed minerals under hydrothermal conditions and the possibility to use actual flow-type treatment equipment.

Figure 8 shows the results of hydrothermal mineralization treatment against the mixed aqueous solution of 1000 mg/dm³ $\text{P}^{\text{III}}\text{O}_3^{3-}$ and 1000 mg/dm³ $\text{P}^{\text{I}}\text{O}_3^{3-}$ using an ordinary batch type autoclave and the in-situ sampling type treatment autoclave. Phosphorus concentration decreased to 1100 mg/dm³ by the addition of $\text{Ca}(\text{OH})_2$ mineralizer. After that, it was 0.20 mg/dm³ after the treatment for 12 h, which was much lower than the result of the treatment by using ordinary batch type treatment apparatus. This result is evidence that the solubility of formed mineral $\text{Ca}(\text{HP}^{\text{III}}\text{O}_3)(\text{H}_2\text{O})$ decreases with an increase in temperature of the solution. The separations of precipitates from aqueous solution under hydrothermal conditions can contribute to both the reduction of treatment time and the recovery yield of phosphorus, 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 phosphorus in wastewater as natural resources.

4. Conclusions

Precipitation recovery of phosphorus and detoxification of

model wastewater containing phosphoric ($\text{P}^{\text{V}}\text{O}_4^{3-}$), phosphinic ($\text{P}^{\text{III}}\text{O}_3^{3-}$), phosphonic ($\text{P}^{\text{I}}\text{O}_3^{3-}$) acids and the mixture of phosphonic and phosphinic ions were investigated. Mineralization of penta-valent phosphorus species by hydrothermal treatment with $\text{Ca}(\text{OH})_2$ was effective to precipitate phosphorus as $\text{Ca}_5(\text{P}^{\text{V}}\text{O}_4)_3(\text{OH})$ mineral with high yield. Phosphinic and phosphonic ions were also recovered as $\text{Ca}(\text{HP}^{\text{III}}\text{O}_3)(\text{H}_2\text{O})$ by hydrothermal mineralization.

The hydrothermal mineralization treatment is more effective to precipitate phosphorus species from aqueous media by the sampling-type hydrothermal treatment autoclave. The treatment apparatus completely prevents the re-dissolution of formed minerals by solid liquid separation under hydrothermal conditions. The phosphorus concentration after the treatment for 12 h decreased down to 0.20 mg/dm³ regardless of their ionic states. Therefore, the hydrothermal mineralization with $\text{Ca}(\text{OH})_2$ is recommended as one of the detoxification and recovery techniques of phosphorus in aqueous solution.

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