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Original Research

Reaction of sea shells with resemble phosphorus wastewater and application of products

Hiroaki Onoda¹, Ryo Fukatsu¹, Masamoto Tafu²

¹Department of Informatics and Environmental Sciences, Faculty of Life and Environmental Sciences, Kyoto Prefectural University, Kyoto, Japan

²Toyama National College of Technology, Hongo, Toyama, Japan

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Corresponding Author:

Hiroaki Onoda,
Dept. of Informatics and Environmental Sciences, Faculty of Life and Environmental Sciences, Kyoto Prefectural University, 1-5, Shimogamo Nakaragi, Kyoto 606-8522, Japan.
onoda@kpu.ac.jp

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Abstract

Background / Aim: The removal and reuse of phosphorus is necessary to resolve environmental problems. The recovery of rare earth elements is also required for the sustainable developments. The aim of this work is to solve above two problems.

Method: In this work, we tried to remove phosphorus from wastewater with corbicula shell and Japanese littleneck shells. The obtained by-product was also used to recover rare earth cations. The chemical composition of by-products was investigated by ICP, XRD analyses, and SEM images.

Results: The main composition of the precipitates was calcium hydrogen phosphate di-hydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. These calcium phosphates recovered the rare earth cations.

Conclusion: Samples synthesized from seashells had small difference on the recovery of rare earth elements with samples synthesized from commercial calcium carbonate.

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INTRODUCTION

Recently, the interest about the recycling of waste is increasing. From this viewpoint, seashells are tried to use as a raw material for various applications [1,2]. Generally, edible parts of shellfish are small, therefore large amount of waste was produced from the shellfish. Because seashells are easy to gather, they are suitable to use as raw material. At the present time, seashells that have light and little pigment, for example scallop, have been used as calcium resource [3,4]. However, it is difficult to use seashells that have dark and much pigment. Corbicula and Japanese littleneck are common foods in Japan. Corbicula shell is about 3 cm in size and black color, and Japanese littleneck shell is about 5 cm in size.

Moreover, an important environmental problem is eutrophication of rivers, lakes, and other water bodies because of phosphorus derived from human activity. Increased plankton in eutrophic water decreases the concentration of dissolved oxygen, changing affected areas to dead water. The removal and reuse of phosphorus is necessary to resolve environmental problems. Phosphorus can be removed from artificial wastewater using a solution prepared from a highly purified reagent. A low cost process without purified reagents must be developed.

Calcium phosphates are important materials for many applications, ion exchangers, adsorbents, and so on [5,6]. Therefore, calcium phosphates were prepared from sea urchin shells and artificial phosphorus waste

fluid in previous papers [7,8]. The obtained precipitates' main component was $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The precipitates contained organic coloring materials in the process with the sea-urchin shell heated at lower temperature as a pretreatment. Sea urchin shells had too strong coloring materials. In contrast, corbicula shells produced the calcium phosphate with less coloring materials [9].

In general, the addition of rare earth elements gives higher functional properties to the material. Rare earth elements are important resource in the industrial world. Consequently, the recovery of rare earth elements is required for the sustainable developments. It is well known that rare earth phosphates are insoluble for acidic and basic solution in the groups of phosphate materials. The formation of rare earth phosphate is considered to use for recovery of rare earth elements.

In this work, we tried to remove phosphorus from wastewater with corbicula shell and Japanese littleneck shells. Calcium phosphate was expected to form as a product. The chemical composition and powder properties of products were investigated. Further, the obtained product was tried to recover rare earth elements.

MATERIALS AND METHODS

Corbicula and Japanese littleneck shells were washed and milled to powder condition. These shell powders were mixed with phosphoric acid solution (0.1 mol/l) or resemble phosphorus wastewater (0.1 mol/l of phosphoric acid and 0.076 mol/l of sodium acetate) in the ratio of Ca/P=1/1. The composition of resemble phosphorus water was decided from previous works [7,8]. Commercial calcium carbonate was used for comparison with corbicula and Japanese littleneck shells in the same process. The mixed solutions were adjusted to pH 7 with ammonia solution, and then stirred for 0 and 6 hours. The precipitates were filtered off and dried.

The obtained phosphates were tried to recover lanthanum cation in solution. 0.1 g of sample was added to lanthanum nitrate solution (La 200 ppm, 100 ml), and then stirred for 1, 3, 6 hours. The concentrations of lanthanum, calcium, and phosphorus were measured with ICP method.

The chemical composition and powder condition of precipitates were estimated by XRD (X-ray diffraction) analysis, and SEM (Scanning electron microscopy) images. XRD patterns were recorded on a Rigaku MiniFlex X-Ray diffractometer using monochromated $\text{CuK}\alpha$ radiation. SEM images of products were observed using JGM-5510LV, JEOL Ltd. A part of solid sample was dissolved in hydrochloric acid

solution, and then measured with ICP (Inductively coupled plasma) apparatus, using SPS1500VR, Seiko Instruments Inc. The ratios of phosphorus and calcium in the samples were calculated from ICP results of these solutions.

RESULTS

Reaction of seashells and phosphorus wastewater

Figure 1 shows XRD patterns of samples stirred for 0 hour. All samples had unknown peaks. The reaction between calcium carbonate and phosphoric acid needed some stirring time. Figure 2 shows XRD patterns of samples stirred for 6 hours. All samples indicated the peak pattern of calcium hydrogen phosphate di-hydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The difference between commercial calcium carbonate and seashells was small in XRD patterns of precipitates. The corbicula and Japanese littleneck shells were possible to use as calcium resources. Table 1 shows phosphorus / calcium ratio of precipitates from ICP analyses. The precipitate at 6 hours had higher P/Ca ratio than that at 0 hour.

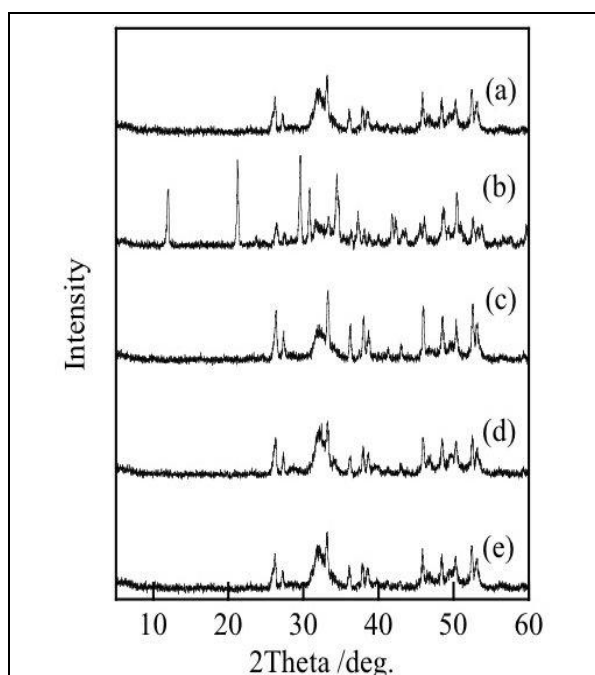


Figure 1. XRD patterns of samples prepared in various conditions (reaction time; 0 h), (a) $\text{CaCO}_3 + \text{H}_3\text{PO}_4$, (b) corbicula shell + H_3PO_4 , (c) corbicula shell + resemble phosphorus wastewater, (d) Japanese littleneck shell + H_3PO_4 , (e) Japanese littleneck shell + resemble phosphorus wastewater.

Figure 3 shows SEM images of samples prepared in various conditions (reaction time; 6 hours). Generally, calcium hydrogen phosphate di-hydrate has the plate

particles in SEM images [8]. All samples stirred for 6 hours in this work had some plate particles. On the other hand, samples stirred for 0 hour had no plate particle (not shown). These SEM results were corresponding with XRD and ICP results.

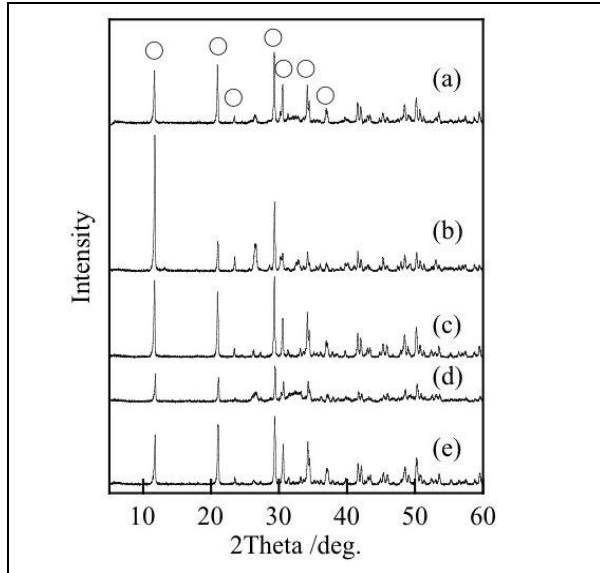


Figure 2. XRD patterns of samples prepared in various conditions (reaction time; 6 h), (a) $\text{CaCO}_3 + \text{H}_3\text{PO}_4$, (b) corbicula shell + H_3PO_4 , (c) corbicula shell + resemble phosphorus wastewater, (d) Japanese littleneck shell + H_3PO_4 , (e) Japanese littleneck shell + resemble phosphorus wastewater, ○; $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

Recovery of lanthanum cation

Figure 4 shows lanthanum concentration treated with various calcium phosphates (stirring time; 0 h). The concentration of lanthanum cation changed to 0 ppm at 6 hours in reaction time. With the precipitates prepared by 6 hours stirring, this concentration became 0 ppm at 1 hour in reaction time.

On the contrary with lanthanum cation, the concentration of calcium cation increased in this process. Figure 5 shows calcium concentration treated with various calcium phosphates (stirring time; 6 h). All samples indicated over 100 ppm of calcium cation. The phosphate products synthesized with 0 hour stirring indicated about 100 ppm of calcium cation at 6 hour of reaction time. These products had similar phenomena with products with 6 hours of stirring (not shown). Figure 6 shows phosphorus concentration treated with various calcium phosphates (stirring time; 6 h). Sample synthesized from commercial calcium carbonate indicated about 58 ppm of phosphorus concentration. Samples synthesized from corbicula shells had higher phosphorus concentration than those from Japanese littleneck shells. This tendency of phosphorus concentration was corresponding with that of calcium concentration. In the cases of all products with 0 hour of stirring, the concentration of phosphorus was 0 ppm.

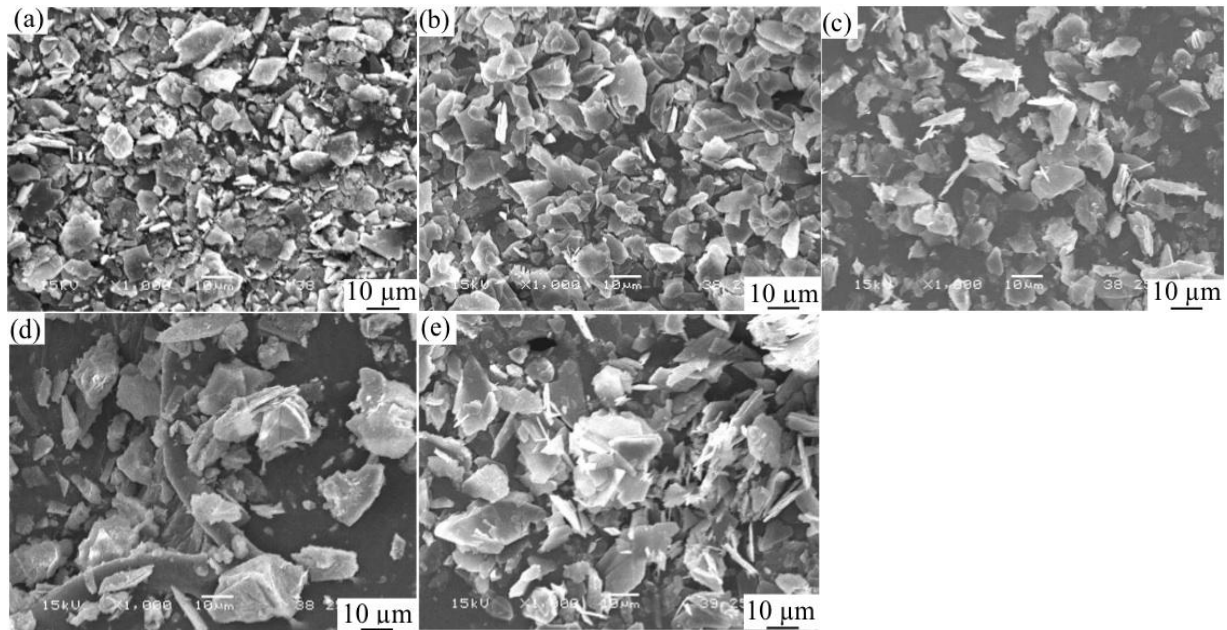


Figure 3. SEM images of samples prepared in various conditions (reaction time; 6 h), (a) $\text{CaCO}_3 + \text{H}_3\text{PO}_4$, (b) corbicula shell + H_3PO_4 , (c) corbicula shell + resemble phosphorus wastewater, (d) Japanese littleneck shell + H_3PO_4 , (e) Japanese littleneck shell + resemble phosphorus wastewater.

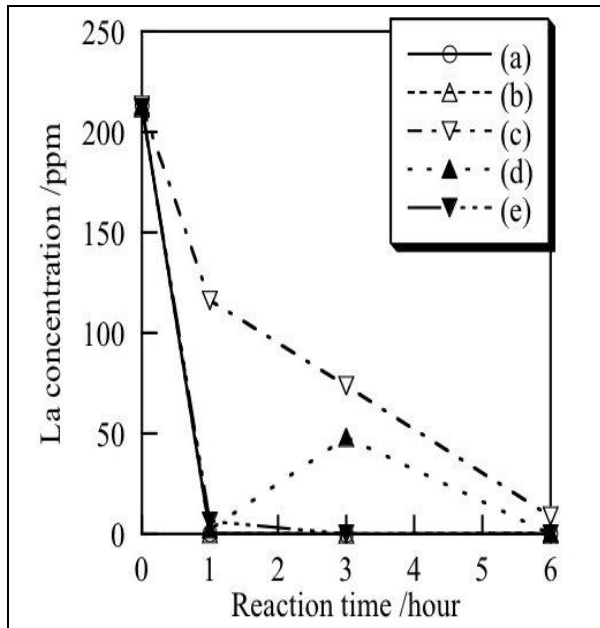


Figure 4. Lanthanum concentration with various precipitates (0 h), (a) CaCO₃ + H₃PO₄, (b) corbicula shell + H₃PO₄, (c) corbicula shell + resemble phosphorus wastewater, (d) Japanese littleneck shell + H₃PO₄, (e) Japanese littleneck shell + resemble phosphorus wastewater.

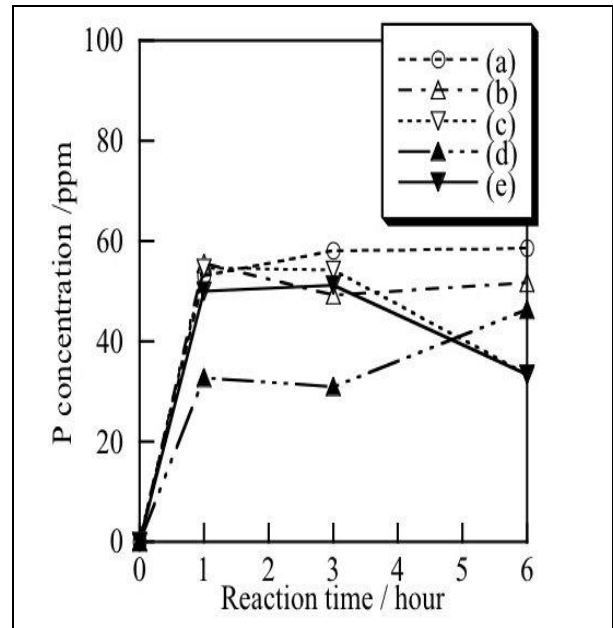


Figure 6. Phosphorus concentration with various precipitates (6 h), (a) CaCO₃ + H₃PO₄, (b) corbicula shell + H₃PO₄, (c) corbicula shell + resemble phosphorus wastewater, (d) Japanese littleneck shell + H₃PO₄, (e) Japanese littleneck shell + resemble phosphorus wastewater.

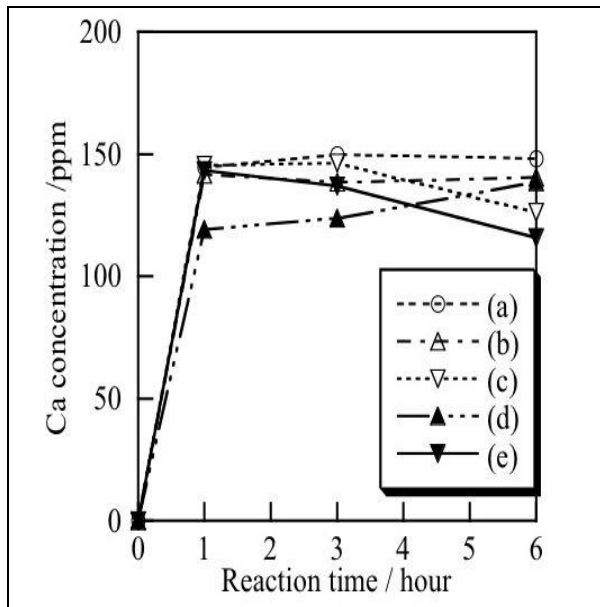
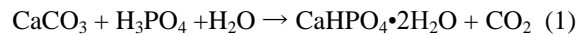


Figure 5. Calcium concentration with various precipitates (6 h), (a) CaCO₃ + H₃PO₄, (b) corbicula shell + H₃PO₄, (c) corbicula shell + resemble phosphorus wastewater, (d) Japanese littleneck shell + H₃PO₄, (e) Japanese littleneck shell + resemble phosphorus wastewater.

DISCUSSION

Reaction of seashells and phosphorus wastewater

The main composition of seashells is calcium carbonate. Therefore, in this work, calcium phosphate was expected to form in the following equation.



When calcium carbonate reacted with phosphoric acid perfectly, the P/Ca ratio was 1. Because the P/Ca ratio of all samples was lower than 1 in Table 1, samples were the mixture of calcium carbonate and calcium phosphate. Samples stirred for 6 hours had higher P/Ca ratio than those for 0 hour. Calcium phosphate was formed with long time stirring. The difference was not clear from seashells, corbicula and Japanese littleneck shells. Samples prepared from commercial calcium carbonate had higher P/Ca ratio than others. Seashells used in this work were a little lower reactivity with phosphoric acid than commercial calcium carbonate. Because samples prepared from resemble phosphorus wastewater had little tendency in this P/Ca ratio, the presence of sodium acetate had little influence on this ratio of precipitates.

Table 1. P/Ca ratio of precipitates prepared in various conditions

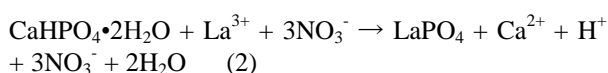
Ca resource	P resource	Reaction time /hours	
		0	6
CaCO ₃ *	H ₃ PO ₄	0.49	0.77
Corbicula shells	H ₃ PO ₄	0.28	0.56
Corbicula shells	Resemble*	0.15	0.54
Littleneck**	H ₃ PO ₄	0.25	0.50
Littleneck**	Resemble*	0.28	0.60

Resemble*; resemble phosphorus waste water

Littleneck**; Japanese littleneck shells

Recovery of lanthanum cation

In this work, lanthanum cation was expected to precipitate in a following reaction.



When all part of products were CaHPO₄•2H₂O and the above reaction took place perfectly, the concentrations of lanthanum and calcium cations in solution changed from 200 to 0 ppm and from 0 to 57.1 ppm, respectively. Because the concentration of lanthanum cation became 0 ppm in all samples, calcium hydrogen phosphate di-hydrate recovered rare earth cations.

The concentration of calcium cation increased in all processes. Because these concentrations were much higher than theoretical concentration (57.1 ppm), phosphate products were not only substituted from calcium cation to lanthanum cation, but a certain degree of products eluted to the solution. Because a certain degree of products eluted to the solution, the concentration of phosphorus increased in the cases of products synthesized with 0 h stirring. Because the increase of calcium concentration was caused from the substitution of calcium cation to lanthanum cation and the elution of products, the increase of phosphorus concentration was much lower than that of calcium concentration. Samples synthesized from seashells had small difference on the substitution from calcium cation to lanthanum cation with samples synthesized from commercial calcium carbonate.

CONCLUSION

Corbicula shells and Japanese littleneck shells reacted with phosphoric acid and resemble phosphorus wastewater. This reaction needed long time stirring. The main composition of the precipitates was calcium hydrogen phosphate di-hydrate, CaHPO₄•2H₂O. The

obtained phosphates recovered rare earth cations. Samples synthesized from seashells had small difference on the recovery of rare earth elements with samples synthesized from commercial calcium carbonate.

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