Removal of Phosphorus with Corbicula Shells from Resemble Wastewater and Adsorptive Properties of By-Products

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Abstract- Corbicula shells, their main composition is calcium carbonate, were tried to remove phosphorus from wastewater. The concentration of phosphorus became lower by the adsorption with corbicula shells. Calcium phosphate was formed as a by-product. The obtained by-products were tried to use as an adsorbent for trimethylamine gas, fluoride anion, iodine, methylene blue in water. The concentrations of fluoride anion and iodine became lower with the by-products. The products from waste water and sea shells waste worked to improve water environment.

Keywords: Removal of Phosphorus; Corbicula Shells; Waste Water; Calcium Phosphates; By-Products

I. 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 is common food in Japan. Its shell is about 3 cm in size and black color.

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 CaHPO₄·2H₂O. 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.

In this work, we tried to remove phosphorus from wastewater with corbicula shell. Calcium phosphate was expected to form as a by-product. The chemical composition and powder properties of precipitates were investigated. The obtained by-product was also used as an adsorbent for basic stinking gas, fluoride anion, iodine, and organic compounds in water [9]. The adsorptions of basic stinking gas, fluoride anion, iodine, and organic compounds in water are important to improve air and water environments.

II. EXPERIMENTAL

Corbicula shells were washed and milled to powder condition. The shell powder (0.2 g) was set in a column, then the phosphorus – rich water (0.07 mol/l of phosphoric acid) went through this column. Commercial calcium carbonate was used for comparison with corbicula shells in the same process. Resemble phosphorus waste water, 0.7 mol/l of phosphoric acid and 4.4 wt% of sodium acetate, was treated in the same way with phosphorus – rich water. The concentration of phosphorus and calcium in the by-products was estimated by ICP (Inductively coupled plasma) apparatus, using SPS1500VR, Seiko Instruments Inc.

To obtain the sufficient by-products, 2 g of corbicula shells were treated with 10 times as volume as wastewater. The chemical composition and powder condition of by-products were estimated by ICP measurements, XRD (X-ray diffraction) analysis, and SEM (Scanning electron microscopy) images. A part of solid sample was dissolved in hydrochloric acid solution, and then measured with ICP apparatus. The ratios of phosphorus and calcium in the by-products were calculated from ICP results of these solutions. XRD patterns were recorded on a Rigaku MiniFlex X-Ray diffractometer using monochromated CuKα radiation. SEM images of by-products were observed using JGM-5510LV, JEOL Ltd.

The adsorptive properties of by-products were estimated with trimethylamine gas, fluoride anion, iodine, and methylene blue in water. The adsorption of trimethylamine gas on phosphates was estimated at room temperature. 0.01 g of a sample was placed in a gas bag (3000 cm³) of polyethylene, which was then filled with trimethylamine gas (14.4 ppm). The concentration of trimethylamine gas after standing for 10 minutes was determined with a Kitagawa gas detector. 0.1 g of sample was added to fluoride and iodine solution (20 ppm, 100 ml), and then stirred for 1, 3, 6 hours. The fluoride solution was prepared with sodium fluoride. The concentration of fluoride ion was determined by ion meter (METTLER TOLEDO SEVEN MULTI S40) with fluoride ion selective electrode (ORION 9609BNWP) [10]. The iodine solution (20 ppm) included 300 ppm of potassium iodide. The concentrations of triiodide ion were measured with light absorption at 350 nm using Shimadzu UV-2100. As a similar process, 0.1 g of sample was added to 1 mmol/l of methylene...
blue solution (50 ml), and then stirred for 1, 3, 6 hours. The solution was estimated from the light adsorption at 660 nm using Shimadzu UV-2100.

II RESULTS AND DISCUSSION

A Removal of Phosphorus from Wastewater

Figure 1 shows the concentration of phosphorus and calcium in filtered solutions. The concentration of phosphorus was 2,168 ppm in the phosphorus - rich water before the treatment. In the case of commercial calcium carbonate, the concentration of phosphorus was low at 0-30 ml of the corbicula shell filtered solution. The concentration of phosphorus increased by pouring over 30 ml of phosphorus – rich water. The theoretical volume of phosphorus – rich water was 28.6 ml from the following reaction.

\[ \text{CaCO}_3 + \text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2 \]  

(1)

At over 30 ml of phosphoric acid, the phosphorus concentration increased, because the surface of calcium carbonate reacted to CaHPO$_4 \cdot$2H$_2$O. By the pouring over 40 ml, the filtered solution had higher phosphorus concentration than original one. A part of calcium phosphate was eluted to the filtered solution. The concentration of calcium cation was corresponding with that of phosphorus. The commercial calcium carbonate was effective to remove phosphorus from phosphoric acid solution. In the case with corbicula shells and phosphoric acid solution, the concentration of phosphorus kept lower concentration than original one (Fig. 1(B)). Corbicula shells adsorbed the certain degree of phosphorus in this region of phosphoric solution (~60 ml). Calcium cation was also eluted to the filtered solution. Only first step indicated low concentration of phosphorus and calcium cation in the case of corbicula shells and resemble wastewater (Fig 1(C)). The concentration of phosphorus in the filtered solution indicated near original one after 2 steps (10-60 ml). The concentration of calcium cation also increased form corbicula shells. Sodium acetate had influence on the reactivity between calcium carbonate and phosphoric acid. Corbicula shells removed phosphorus from the small volume of the resemble wastewater.

Figure 1. Concentrations of phosphorus and calcium in filtered solutions, (A) commercial calcium carbonate, phosphoric acid, (B) corbicula shells, phosphoric acid, (C) corbicula shells, resemble wastewater, (a) phosphorus, (b) calcium.

B Powder Properties of By-Products

Figure 2 shows XRD patterns of samples prepared in various conditions. The peaks of calcium carbonate were observed in samples prepared with commercial calcium carbonate and 100 ml of phosphoric acid (Fig. 2(A)(a)). The peaks of calcium carbonate became weak with the increase of the poured phosphoric acid solution (Fig. 2(A)). After the pouring of phosphoric acid solution, the peaks of di-calcium hydrogen phosphate di-hydrate, CaHPO$_4 \cdot$2H$_2$O, were appeared. The typical peak of CaHPO$_4 \cdot$2H$_2$O was at about 12 degree. This peak became strong with the volume of phosphoric acid solution. In the case with corbicula shells and phosphoric acid solution (Fig. 2(B)), the overall peak intensity became weak, because of the impure composition of corbicula shells. CaHPO$_4 \cdot$2H$_2$O was also formed in samples with corbicula shells and resemble wastewater (Fig. 2(C)). From the concentration in the filtered solution (Fig. 1(C)), corbicula shells seemed less to react with phosphoric acid. However, from XRD analysis (Fig. 2(C)), corbicula shells reacted with phosphoric acid in resemble wastewater.
Table 1 shows P/Ca ratios in samples from ICP measurements. The P/Ca ratios of calcium carbonate and di-calcium hydrogen phosphate dihydrate were 0 and 1, respectively. This P/Ca ratio increased from 0 to 1 with the reaction between calcium carbonate and phosphoric acid. Over 0.5 in P/Ca ratio was observed at samples with commercial calcium carbonate and 300-600 ml of phosphoric acid. Commercial calcium carbonate was easy to react with phosphoric acid solution. Samples obtained from corbicula shells had over 0.1 in P/Ca ratio. A part of corbicula shells reacted with phosphoric acid solution and resemble wastewater. Because corbicula shells contained the impure composition, they indicated the different ratio with those of commercial calcium carbonate.

Table 1 P/Ca ratio of by-products obtained in various conditions

<table>
<thead>
<tr>
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<th>CaCO₃</th>
<th>Corbicula shells</th>
<th>Corbicula shells resemble wastewater</th>
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<tbody>
<tr>
<td>- 100 ml</td>
<td>0.16</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>- 200 ml</td>
<td>0.29</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>- 300 ml</td>
<td>0.75</td>
<td>0.07</td>
<td>0.16</td>
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<tr>
<td>- 400 ml</td>
<td>0.52</td>
<td>0.18</td>
<td>0.14</td>
</tr>
<tr>
<td>- 500 ml</td>
<td>0.62</td>
<td>0.25</td>
<td>0.23</td>
</tr>
<tr>
<td>- 600 ml</td>
<td>0.60</td>
<td>0.15</td>
<td>0.18</td>
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Figure 3 shows SEM images of samples prepared in various conditions (Phosphorus solution; 600 ml). All samples had various shape and size of particles. Generally, di-calcium hydrogen phosphate dihydrate (DCPD) forms plate-like particles \(^{(1)}\). Some planes were observed on particles in samples prepared with commercial calcium carbonate. By-products obtained in this work had less arranged particles, because calcium carbonate reacted incompletely with phosphoric acid.

Figure 2. XRD patterns of by-products synthesized in various conditions, (A) commercial calcium carbonate, phosphoric acid, (B) corbicula shells, phosphoric acid, (C) corbicula shells, resemble wastewater, (a) - 100 ml, (b) - 200 ml, (c) - 300 ml, (d) - 400 ml, (e) - 500 ml, and (f) - 600 ml; \(\Delta\) CaCO₃, \(\circ\) CaHPO₄ • 2H₂O.
Because phosphate materials are known as solid state adsorbents, by-products used as an adsorbent for trimethylamine gas and methylene blue in solution. Residual ratio, on the other hand, samples prepared with calcium carbonate and phosphoric acid indicated low tendency with that of fluoride anion. The reason that the residual ratio of iodine had the different indicated low residual ratio of iodine. It is difficult to clear that the residual ratio of iodine had the different tendency with that of fluoride anion.

Figure 4 shows the residual ratio of fluoride anion with various by-products. Samples prepared with commercial calcium carbonate and phosphoric acid indicated low residual ratio, on the other hand, samples prepared with corbicula shells had high residual ratio of fluoride anion. Figure 5 shows the residual ratio of iodine with various by-products. Samples prepared with corbicula shells indicated low residual ratio of iodine. It is difficult to clear the reason that the residual ratio of iodine had the different tendency with that of fluoride anion.

**IV Conclusion**

Phosphorus was removed from wastewater with corbicula shells. From XRD analysis, di-calcium hydrogen phosphate di-hydrate, CaHPO$_4$$\cdot$2H$_2$O, was formed as a by-product. The obtained by-products from corbicula shells and phosphoric acid adsorbed iodine in solution. The products from waste water and seashells waste worked to improve water environment.

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**REFERENCES**


