Iron, Copper, and Nickel Removal with Calcium Hydrogen Phosphate and Calcium Pyrophosphates in Solution

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Abstract Calcium phosphate is an important material used in ion exchangers and adsorbents. In this work, calcium hydrogen phosphate dihydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, was prepared from calcium nitrate solution and phosphoric acid. This phosphate transformed to calcium hydrogen phosphate un-hydrate, CaHPO_4 , by heating at 200°C, and calcium pyrophosphate, $\text{Ca}_2\text{P}_2\text{O}_7$, by heating at 400 and 700°C. These calcium phosphates were used to remove trivalent iron cation, Fe^{3+} in solution. Samples without heating and those heated at 200°C indicated a high iron removal ratio. By the addition of these calcium phosphates and stirring for 5 minutes, a high ratio of iron cation was removed from the solution. This removal depended not only on the substitution of calcium to iron, but also on the precipitation of iron hydroxide. Calcium phosphates were also used to remove copper and nickel cations, Cu^{2+} and Ni^{2+} . The removal ratios of copper and nickel cations were lower than those of iron cation.

Keywords Calcium Phosphate, Transition Metal, Purification of Water, Precipitation

concerned hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and other phosphates were less reported.

There are however other kinds of calcium phosphates, for example, $\text{Ca}_3(\text{PO}_4)_2$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, etc. [11-14]. The formation of these phosphates was affected from a Ca/P mixing ratio of raw materials, heating temperature and time, additives, and so on [15-17]. Further, phosphate materials produce condensed phosphate in a dehydration reaction [18, 19]. These condensed phosphates have the possibility of having different properties than orthophosphate. Therefore, the study about these phosphates is required to obtain novel ion exchangers and adsorbents to remove harmful ions.

In our previous work, calcium hydrogen phosphates di-hydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, were prepared with corbicula shells, and then used to remove iron cation in solution [20]. Iron cation was removed with this phosphate in this limited condition. Therefore, in the present work, we study the removal of transition metal cations with calcium hydrogen phosphates di-hydrate, calcium hydrogen phosphates, and calcium pyrophosphate, $\text{Ca}_2\text{P}_2\text{O}_7$.

1. Introduction

Phosphates have been used in ceramic materials, catalysts, adsorbents, fluorescent materials, dielectric substances, biomaterials, metal surface treatments, fertilizers, detergents, food additives, fuel cells, pigments, and other applications [1-8]. In these phosphate materials, calcium phosphate is an important compound used for many applications, such as in ion exchangers and adsorbents [9, 10]. These materials are useful to obtain clean water without harmful cations. Because calcium phosphates are high affinity for living organisms, they can be used as a filter to remove harmful ions from water. Furthermore, these materials are easy to synthesize without expensive apparatus. Therefore, the use of these materials is expected all over the world. However, these reports mainly

2. Materials and Methods

Calcium nitrate solution (0.1 mol/L) was mixed with phosphoric acid (0.1 mol/L), and then adjusted to pH 5 and 7 with ammonia solution. The precipitates were filtered and dried. A part of the precipitates were heated at 200, 400, and 700°C for one hour. All chemicals were purchased from Wako Chemical Industries Ltd. (Osaka Japan), of commercial purity, and used without further purification.

The chemical composition of the powdered precipitates was determined using X-ray diffraction (XRD) and Infrared (IR) spectra. The XRD patterns were recorded on a Rigaku MiniFlex X-Ray diffractometer using monochromated $\text{CuK}\alpha$ radiation. IR spectra of samples were recorded on a HORIBA FT-IR 720 (Horiba Ltd.) using the KBr disk method.

The substitution properties of the products were estimated using iron nitrate solutions. 5 and 10 mmol/L of

iron (+III) nitrate solution was prepared at pH 3 with sodium hydroxide. 0.1 g of the sample was added to this iron nitrate solution (100 mL), and stirred for five minutes. The resulting precipitates were filtered off. The filtered solution was estimated using ultraviolet–visible (UV–Vis) spectroscopy with a UV2100 spectrometer (Shimadzu Corp., 290 nm). The pH values of the filtered solution were also measured.

Further, the removal of copper and nickel was also estimated. The calcium phosphate (pH5, without heating) was added to 100 mmol/L of copper and nickel nitrate solutions (50 mL), and then stirred for 5, 30, 60, 360, and 1,440 min. The amount of calcium phosphate was determined to be in Cu/Ca=1/1 and Ni/Ca=1/1 conditions. The precipitates were filtered off. The filtered solution was estimated with a UV2100 spectrometer (Cu; 810nm, Ni; 410nm).

3. Results and Discussion

3.1. Preparation of Calcium Phosphates

Figure 1 shows XRD patterns of samples prepared at pH5 and then heated at several temperatures. Sample without heating indicated XRD pattern of calcium hydrogen phosphate di-hydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The peak pattern of calcium hydrogen phosphate un-hydrate, CaHPO_4 was observed in a XRD pattern of samples heated at 200°C. Samples heated at 400 and 700°C indicated the peaks of $\text{Ca}_2\text{P}_2\text{O}_7$. From these results, samples are considered to form in the following reactions.

Samples prepared at pH 7 showed the same patterns with samples prepared at pH 5 and then heated at each temperature.

Figure 2 shows IR spectra of samples prepared at pH 5 and then heated at several temperatures. The multiple peaks observed in the regions $1200\text{--}400\text{ cm}^{-1}$ of IR spectrum of non-heated sample can be due to P-O internal vibration in CaHPO_4 [19]. The strong peaks at 1140 , 1060 , and 980 cm^{-1} are assigned to stretching vibration of the P-O band. The peaks at 580 and 520 cm^{-1} are due to the O-P-O deformations. The sample without heating had an absorption peak at 1650 cm^{-1} due to water. This peak disappeared by heating at 200°C . The sample heated at 400°C had similar spectra with that at 700°C . The absorption peak at 720 cm^{-1} was due to P-O-P bonding in condensed phosphate [19]. These IR results correspond with the above XRD results.

Figure 1. XRD patterns of samples prepared at pH 5 and then heated at several temperatures, (a) R.T., (b) 200°C , (c) 400°C , and (d) 700°C , $\circ$; $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, Δ ; CaHPO_4 , $\diamond$; $\text{Ca}_2\text{P}_2\text{O}_7$.

Figure 2. IR spectra of samples prepared at pH5 and then heated at several temperatures, (a) R.T., (b) 200°C , (c) 400°C , and (d) 700°C .

3.2. Removal of Iron with Calcium Phosphate

Table 1 shows the removal ratio of iron cation with calcium phosphates prepared in various conditions. Samples without heating indicate a higher removal ratio than 90%. Because the main composition of these materials was $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, 0.1 g of samples included 5.81×10^{-4} mol of calcium cation. On the other hand, 5 and 10 mmol/L of iron nitrate solutions (100mL) included 5×10^{-4} and 1×10^{-3} mol of iron cation, respectively. In the conditions of 10mmol/L, the amount of removed iron cation was much higher than that of calcium cation in samples. Therefore, the removal of iron cation took place not only by the substitution from calcium to iron but also by precipitation of iron hydroxide. Table 2 shows the pH value of solutions after the iron removal process. Because samples were prepared at pH 5 and 7, the pH value of solution increased from the original 3 by the addition of prepared calcium phosphates, then iron hydroxide was formed. Samples heated at 200°C also indicated higher removal ratio than 90%. The amount of calcium cation in 0.1g of sample was about 7.35×10^{-4} mol. Calculated from that the main composition was CaHPO_4 . In the conditions of 10mmol/L, iron hydroxide was also formed by samples heated at 200°C. By heating at 400 and 700°C, CaHPO_4 transformed to $\text{Ca}_2\text{P}_2\text{O}_7$ in equation (3). Because 0.1 g of $\text{Ca}_2\text{P}_2\text{O}_7$ includes 7.87×10^{-4} mol, samples prepared at pH 5 indicated lower than 78.7% in the condition of 10mmol/L. The difference between pH 5 and 7 appeared by heating at 400 and 700°C. Because phosphate materials were sintered by heating, the reactivity of materials became lower. Therefore, the pH shift by the addition of samples prepared at pH 5 became smaller and iron hydroxide was limited to form. This effect in a sample prepared at pH 7 also became smaller; however, the removal ratio of iron cation was high. It is difficult to understand why this removal ratio is high in the condition treated with samples prepared at pH 7.

Table 1. Removal ratios of iron cation with calcium phosphates prepared at pH 5 and 7 and then heated at various temperatures %

	pH 5		pH 7	
	5 mmol/L	10 mmol/L	5 mmol/L	10 mmol/L
R.T.	97.8	99.8	91.7	99.7
200°C	97.5	99.8	98.6	99.4
400°C	94.1	41.5	98.6	95.8
700°C	16.7	22.5	92.3	99.7

Table 2. pH value of solution after iron removal process with calcium phosphates prepared at pH 5 and 7 and then heated at various temperatures

	pH 5		pH 7	
	5 mmol/L	10 mmol/L	5 mmol/L	10 mmol/L
R.T.	5.73	6.21	6.00	6.00
200°C	5.79	5.66	5.99	6.00
400°C	3.62	3.65	5.87	5.85
700°C	3.50	3.28	2.87	2.92

Figure 3 shows XRD patterns of samples prepared at pH 5 and then treated in an iron removal process (10 mmol/L). The peaks of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaHPO_4 in samples without heating and heated at 200°C disappeared by iron removal process, on the other hand the peaks of $\text{Ca}_2\text{P}_2\text{O}_7$ in samples heated at 400 and 700°C became weak. By heating at 400 and 700°C, the reactivity of samples became low, and the un-reacted $\text{Ca}_2\text{P}_2\text{O}_7$ was detected in XRD analysis.

Figure 3. XRD patterns of samples prepared at pH 5, heated at several temperatures, and then treated in Fe removal process (10 mmol/L), (a) R.T., (b) 200°C, (c) 400°C, and (d) 700°C, ◇; $\text{Ca}_2\text{P}_2\text{O}_7$.

3.3. Removal of Copper and Nickel with Calcium Phosphates

As another transition metal solution, we attempted to remove a copper solution. All conditions, with samples prepared at pH 5 and 7, and then heated at several temperatures, indicated much smaller copper removal ratios than iron removal ratios. Because iron cation is trivalent, iron phosphate was easy to form the iron removal ratio became higher. On the other hand, copper cation is bivalent, copper phosphate was more difficult to form. Calcium phosphates showed difficulty removing the copper cation by stirring for 5 min. Therefore, we studied stirring time as a means to remove copper cation. In addition, nickel solution was also studied. Table 3 shows the removal ratio of copper and nickel with samples prepared at pH 5 (without heating). The removal ratio of copper at five minutes was 16.2 % and those over 30min indicated 51-56 %. The removal of copper cation needs a large

amount of time. On the other hand, the removal ratio of nickel cation was five percent lower until 360 min. The removal rate was much different between copper and nickel. Because the ionic radius of copper was close to that of nickel, it is difficult to explain this difference from ionic radii.

Table 3. Removal ratio of Cu and Ni with samples prepared at pH 5 %

Time /min.	Cu ²⁺	Ni ²⁺
5	16.2	0.7
30	51.7	0.8
60	55.9	1.2
120	53.5	3.8
360	54.7	3.5
1440	54.1	20.6

4. Conclusions

Calcium hydrogen phosphate di-hydrate, CaHPO₄•2H₂O, was prepared from calcium nitrate solution and phosphoric acid. This phosphate transformed to calcium hydrogen phosphate un-hydrate, CaHPO₄, by heating at 200°C, and calcium pyrophosphate, Ca₂P₂O₇, by heating at 400 and 700°C. These calcium phosphates were used to remove iron, copper, and nickel cations in solution. Samples without heating and heated at 200°C, CaHPO₄•2H₂O and CaHPO₄, indicated a high iron removal ratio. This removal depended not only on the substitution of calcium with iron but also on the precipitation of iron hydroxide. The removal ratios of copper and nickel cation with calcium phosphates were lower than those of iron cation.

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