

THE REMOVAL OF HEAVY METALS USING HYDROXYAPATITE

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Abstract : The study was conducted to investigate the removal of heavy metals by using Hydroxyapatite (HAp) made from waste oyster shells and wastewater with high concentration of phosphorus. The maximum calcium concentration for the production of HAp in this study was released up to 361mg/L at pH of 3 by elution experiments. When the pH was at adjusted 6, the maximum calcium released concentration was 41mg/L. During the elution experiment, most of the calcium was released within 60 minutes. This reaction occurred at both pH levels of 3 and 6. The result of the XRD analysis for the HAp product used in this study shows the main constituent was HAp, as well as OCP. The pH was 8.6. As the temperature increased, the main constituent did not vary, however its structure was crystallized. When the pH was maintained at 3, the removal efficiency decreased as the heavy metal concentration increased. The order of removal efficiency was as follows: Fe^{2+} (92%), Pb^{2+} (92%) > Cu^{2+} (20%) > Cd^{2+} (0%). Most of these products were dissolved and did not produce sludge in the course of heavy metals removal. As the heavy metal concentration increased at pH of 6, the removal efficiency increased. The removal efficiencies in all heavy metals were over 80%. From the analysis of the sludge after reaction with heavy metals, the HAp was detected and the OCP peak was not observed. Moreover, lead ion was observed at the peaks of lead-Apatite and lead oxidant. In the case of cadmium, copper and iron ions, hydroxide forms of each ion were also detected.

Key Words : Oyster shells, HAp(Hydroxyapatite), XRD, OCP(Octa-Calcium Phosphate), heavy metals removal

INTRODUCTION

With the rapid growth of industrialization in Korea, concentration of toxic heavy metals in wastewater increases and results in serious water pollution. To solve the problem, the removal of heavy metals is greatly emphasized in the treatment of wastewater.

In order to remove the heavy metals from wastewater, processes such as adsorption, solidification, stabilization, and ion exchange have been

suggested and widely employed.¹⁻⁴⁾ Lately, developments and application of processes using ion exchangers or materials with the characteristics of ion exchange has been actively sought after.⁵⁾ Among these materials, Hydroxyapatite(HAp), composed of calcium and phosphorus combined hydroxide has been greatly studied.^{6,7)} Many researchers have reported that high removal efficiency of the heavy metals can be achieved by using HAp.^{8,9)} Recent studies focused commonly on synthesis of HAp and then its use in the removal of heavy metals. HAp is also produced as a by-product in the removal of phosphorus by the advanced treatment. The

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sludge containing HAp, used to be disposed off by dumping on the ocean, or by incineration and landfill. But as the ocean dumping was banned in 2000 and the regulation sewage treatment of sludge was regulated in Korea. The disposal of sludge on the land was directly prohibited in 2003, and now we expect that the future studies will focus on the improvement of sludge reuse and re-treatment.

In this study, HAp was made from waste oyster shells and wastewater with high concentration of phosphorus, as confirmed by batch test. The characteristics of this product were studied through quantitative and qualitative analysis. This study investigated the application of the product to remove heavy metals from wastewater. Therefore, fundamental data obtained from this study is expected to provide insight into the process of sludge reuse using by the treatment of phosphorus removal.

MATERIALS AND METHODS

Material Characteristics

The oyster shells discarded on the coast were used as a source of calcium. In order to hinder calcium carbonate production, oyster shells were incinerated at 900°C for one hour. The incinerated oyster shells were passed through 140-mesh (0.1mm) sieve to obtain a fine powder. Standard phosphorus solution was used as a source of phosphorus to produce HAp.

Method

(1) Hydroxyapatite(HAp)

The batch experiment was performed without the addition of supplementary alkali and without the artificial control of pH. The mole ratio of calcium to phosphorus was 1:1.67 and their concentrations were 571mg/L and 810mg/L, respectively.

The rotary mixer was operated at two different speeds; rapid and slow. The rapid mixing speed was operated at the rate of 150 rotations per minute for 20 minutes and the slow mixing speed had 50 rotations per minute with reaction

time of 12 hours. Constant temperature of 20°C was maintained for both mixing speeds.

(2) Experiments of elution and heavy metals removal

The experiments for elution and heavy metals removal were performed with the same conditions. They were carried out at two different pH levels of 3 and 6 in an agitator using the produced HAp of 1g per 1000ml solution. The mixing speed and temperature were 150 oscillation per minute and 20°C, respectively. At that time, the pH levels were controlled by solutions of HCl and NaOH of 0.1 mole. Samples were taken at 30 minutes interval up to 240 minutes in the elution experiment. Additionally, the experiment for heavy metals removal was applied to ions of Pb^{2+} , Cd^{2+} , Cu^{2+} and Fe^{2+} , which were used after dilution of a standard solution with 1000mg/L. They were reacted with the produced HAp for 60 minutes and then sampled. Each concentration of the heavy metals increased from 50 mg/L to 250 mg/L at intervals of 50mg/L.

Analysis

When the production HAp was complete, precipitate and filtrate were separated using a funnel form filter. The precipitate was made uniformly consistent by drying for 24 hours, crushing with a grinder, and sieving with 140 mesh sieve. The filtrate separated from precipitate was centrifuged for 10 minutes and then diluted. The filtrate from the synthesis, both effluents produced from the experiments for elution and heavy metals removal were analyzed after filtration using Glass Fiber/C. The sludge produced after heavy metals removal was pre-treated in the same way as the production HAp. The precipitate and sludge were qualitatively analyzed using XRD(X-ray diffractometer, Rigaku D/max-2200). The concentrations of the filtrate and effluent were analyzed using ICP-MASS (Inductively Coupled Plasma Mass Spectrometer, Ultra Mass-700). The pH was measured using a pH meter(Orion 920A). The pretreatment of samples followed the procedures described in

standard methods(1995) for the examination of water and wastewater.¹⁰⁾

RESULTS AND DISCUSSION

The Characteristics of Hydroxyapatite(HAp)

After the production of HAp finished, the remaining concentration of calcium and phosphorus from the filtrate were measured as 0.6mg/L and 32mg/L, respectively. In other words, the conversion rates of calcium and phosphorus for production were 99.9% and 96%, respectively. The pH of the HAp was 8.6 and that of HAp prepared by the synthesis method was over 11 and exhibited crystalline structure. This study didn't control the pH and did not supply the reaction with the addition of extra alkali. The elution experiment for this product

was also performed at pH levels of 3 and 6 for 240 minutes. Figure 1 shows the calcium and phosphorus concentrations released from the elution experiment. The maximum calcium released concentrations at the pH levels of 3 and 6 were 41mg/L and 362mg/L, respectively and the maximum phosphorus released concentrations were 62 mg/L and 504 mg/L, respectively. As the result of elution experiment, it was observed that the HAp was dissolved easily in the solution at pH level 3. It was also estimated that most of calcium and phosphorus ions from the produced HAp were released within 60 minutes.

In order to estimate the thermal characteristics of the produced HAp, this study was conducted at different temperatures in the incineration process. Crystallization of HAp was showed positive correlation with the temperature increase. Moreover, HAp changed into β -TCP($(Ca_3(PO_4)_2)$; Tri-Calcium Phosphate) due to the dehydration of hydroxyl group when the temperature was increased from 700°C to 800°C.^{11,12)} Figure 2 shows the results of XRD for qualitative ana-

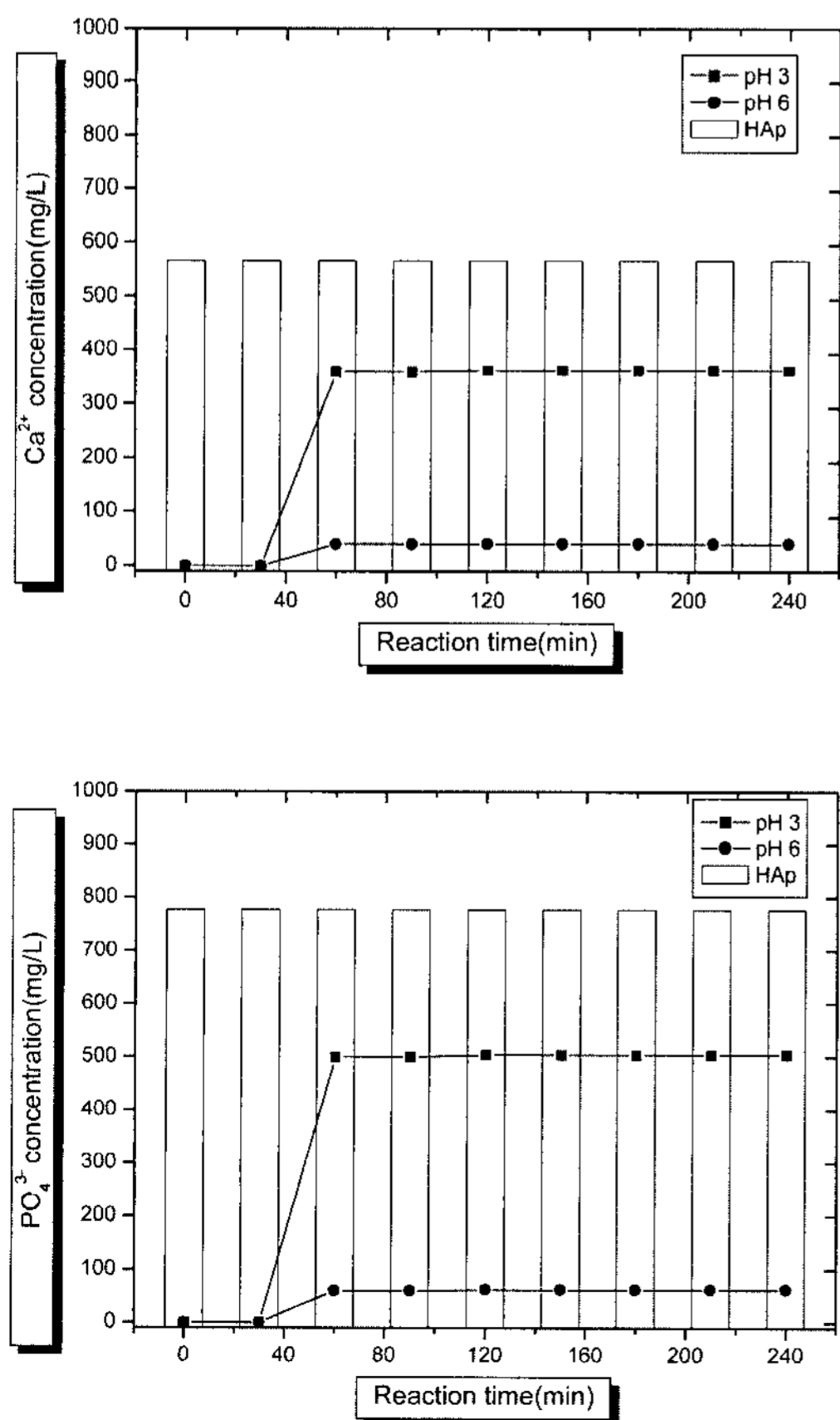


Figure 1. Results of elution experiment for the Production HAp at pH levels of 3 and 6.

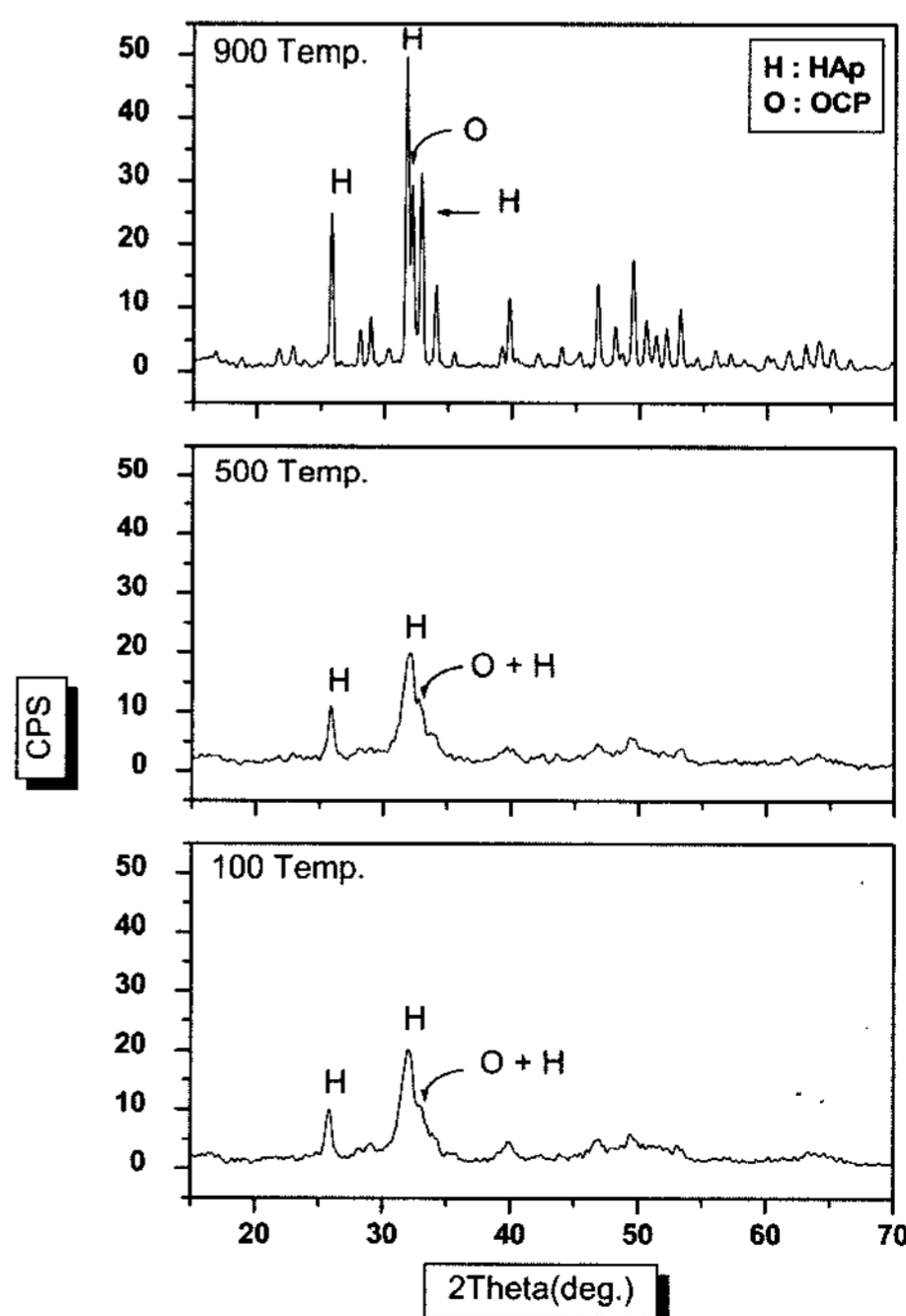


Figure 2. XRD of the production HAp by the Incineration temperature varied.

lysis of the produced HAp incinerated at the temperatures of 100°C, 500°C and 900°C. When the incineration temperatures were 100°C and 500°C, the main constituents of HAp, as well as OCP were identical. When the incineration temperature was 900°C, the main constituents were HAp($\text{Ca}_5(\text{PO})_4\text{OH}$; Hydroxyapatite) and OCP($\text{Ca}_4\text{H}(\text{PO}_4)_3$; Octa Calcium Phosphate). The peak obtained at the incineration temperature of 900°C showed optimum peaks separation of HAp and OCP. In this HAp, the peak of β -TCP was not observed after incineration over 900°C. This indicates that constituent of the peak was not changed with the variation in incineration temperature. And this result also proves that the crystalline structure increased with the increase in the temperature.

The Heavy Metals Removal

The heavy metal removal experiment was carried out at pH levels of 3 and 6, with lead, iron, cadmium and copper ions. This experiment also was investigated the variation of calcium ions. The heavy metals in the solution were removed by the exchange of ions with the calcium in the produced HAp. Calcium ions were released and increased the calcium concentration in the solution during the heavy metals removal.³⁾

Figure 3 shows the removal efficiency with various concentrations of heavy metal at pH levels 3 and 6. When the concentrations of ions of iron and lead at pH3 were from 50mg/L to 250mg/L, removal efficiencies were in the ranged of 80% to 92% and 63 to 92%, respectively. In case of copper, when the concentration was 50mg/L, the removal efficiency was 20% but it was never removed at the heavy metal concentration of 250mg/L. The cadmium ions did not achieve removal at all as the concentrations varied. The order of removal efficiency was Fe^{2+} (80-92%), Pb^{2+} (63-92%) > Cu^{2+} (20-0%). This result also demonstrated the removal of heavy metals in aqueous solution using HAp.¹⁴⁻¹⁶⁾ When the pH level was at 3, the removal efficiency decreased as the con-

centrations of heavy metals increased except cadmium ions. When the pH level was 6, the removal efficiencies for ions of copper and cadmium were 99.5% and 99.8%, respectively. In a case of iron and lead, the removal efficiencies were 95-98.8% and 88-98%, respectively. As the concentration of heavy metals increased, ion removal efficiency of iron and lead increased, but ions of copper and cadmium showed consistent removal efficiencies.

Table 1 shows the mole ratio of heavy metal to released calcium, after the removal of heavy metals. Calcium in the HAp can be lost in the exchange with some heavy metal in the solution, which became as the mole-to-mole reaction.¹⁷⁾ In this study, Calcium concentration at pH levels of 3 and 6 during the elution experiment was subtracted in order to consider the specific concentration of released calcium with heavy metals. After the reaction with ions of lead and cadmium, at pH level of 3, the calcium concentrations were found to be 360mg/L. It was the same concentration as the elution experiment. And then it became zero value. In the case of iron and copper, calcium concentrations were in a range of 335-350mg/L and were lower by about 10-20mg/L than the ones of elution experiment. And then it showed a negative value. This means that the calcium ions adsorbed the hydroxide of iron or copper due to the range of pH. The removal efficiency for lead ions was over 63%, while the removal efficiency of cadmium ions wasn't achieved at all. The removal efficiencies for ions of iron and copper were over 80% and 20%, respectively. It was found that the measuring of released calcium was not related to heavy metal removal. At the pH of 6, the removal efficiency for lead, copper and cadmium increased as the heavy metal concentration increased. Iron ions showed regular concentration of 189mg/L and it was not related to the increase of concentration. Mole ratio of lead, cadmium, copper and iron to calcium were 1:4.35-10.8, 1:2.74-12.9, 1:1.46-4.94 and 1:07-5.90, respectively. As the concentration increased, the mole ratio of heavy metals

Table 1. Mole ratio of heavy metals to calcium during the experiment

Item	Initial Conc.	pH 3					pH 6				
		50	100	150	200	250	50	100	150	200	250
Removed of Pb ²⁺ (%)		92	82	75	70	63	99.8	99.8	99.8	99.8	99.8
Released of Ca ²⁺ (mg/L)		0	0	0	0	0	104	124	152	189	209
Mole ratio of Pb ²⁺ : Ca ²⁺		0	0	0	0	0	1:10.8	1:6.40	1:5.20	1:4.89	1:4.35
Removed of Cd ²⁺ (%)		0	0	0	0	0	80	88	90	96	98
Released of Ca ²⁺ (mg/L)		0	0	0	0	0	184	204	214	225	239
Mole ratio of Cd ²⁺ : Ca ²⁺		0	0	0	0	0	1:12.9	1:6.51	1:4.45	1:3.29	1:2.74
Removed of Cu ²⁺ (%)		20.0	20.0	18.0	15.0	0.0	99.0	99.5	99.5	99.5	99.5
Released of Ca ²⁺ (mg/L)		-25	-15	-10	-5	0	154	157	189	219	229
Mole ratio of Cu ²⁺ : Ca ²⁺		-	-	-	-	0	1:4.94	1:2.50	1:2.01	1:1.74	1:1.46
Removed of Fe ²⁺ (%)		92.0	90.0	88.0	85.0	100.0	90.0	95.0	95.0	96.0	98.8
Released of Ca ²⁺ (mg/L)		-10	-5	-3	-1	0	189	189	189	189	189
Mole ratio of Fe ²⁺ : Ca ²⁺		-	-	-	-	0	1:5.90	1:2.77	1:1.85	1:1.37	1:1.07

to calcium decreased because removed heavy metal concentration was lower than released calcium concentration. These results mean that the amount of released calcium was in an excessive quantity.

From the results of heavy metal removal, HAp is concluded to be responsible for the strong selectivity of lead ions.^{18,19)} In this study, the produced HAP at pH level of 3 was desirable for the lead ion removal, as we didn't observe ion exchange reactions such as Pb-Apatite. It was found that ions of iron and copper were removed in the form of hydroxide compounds such as iron hydroxide(Fe(OH)₃)²⁰⁾ and copper hydroxide(Cu(OH)₂) Therefore, it was estimated that heavy metals removal was affected by pH. Sludge produced after reacting heavy metals at pH of 3 was presented in the form of colloid that didn't precipitate at a lower pH level.

Figure 4(a)-(d) shows the XRD of the pro-

duced HAp and sludge produced after reacting to different heavy metals and produced HAp at pH of 6. <4(a)> shows the XRD of the HAp, the main constituents were HAp and OCP described in the preceding results. <4(b)> shows the main constituents after the reaction with lead were HAp, Pb-apatite, and Dilead trioxide(Pb₂O₃). As shown in <4(c)>, in addition to HAp, the main constituents of iron were iron(ferrous) hydroxide(Fe(OH)₃) In case of cadmium and copper as shown in <4(d)>, the main constituent was HAp. Other constituents weren't detected due to low intensity for peak, but it could verify cadmium hydroxide and copper hydroxide. From the result of XRD after reacting to the heavy metals, the main constituents of all sludge were HAp and on the contrary, the OCP peak was not observed. The OCP was dissolved and then caused the increase of mole ratio as well as increase of calcium in the solution during the heavy metals removal. In general, HAp has an

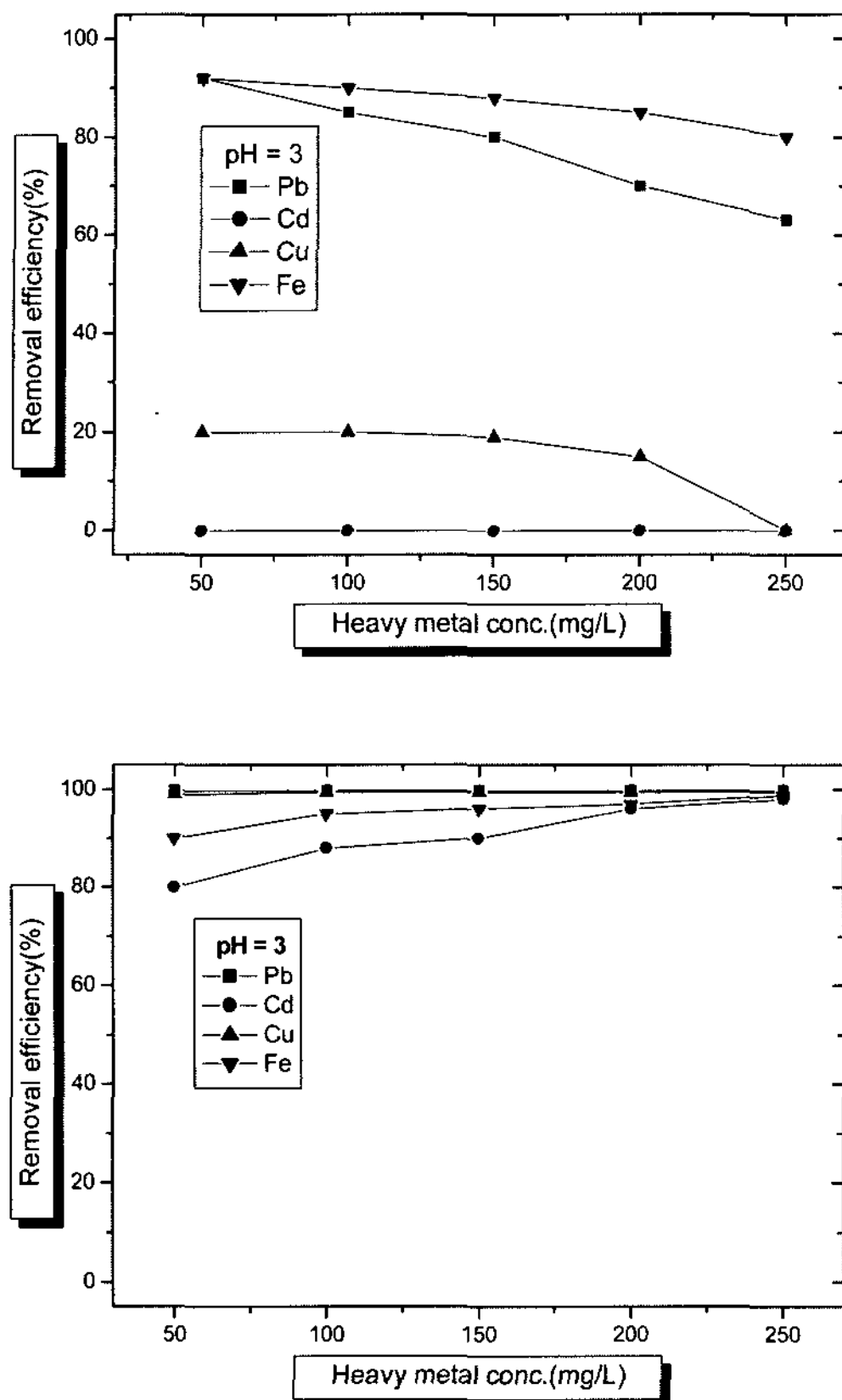


Figure 3. Removal efficiency with various Concentrations of heavy metals at pH levels of 3 and 6.

insoluble crystalline structure, while the OCP is much more soluble with non-crystalline structure.²¹⁾ Also, it was found that lead ion was removed in the form of ion exchange and metallic oxide. Iron ion was removed in the form of precipitation such as iron(ferrous) hydroxide. In case of ions of cadmium and copper, heavy metals were also removed in the form of precipitation such as iron ion. These results confirmed that ions of iron, cadmium, and copper were not governed by ion exchange but by precipitation. Additionally, it seemed that some heavy metals were removed by co-precipitation on the surface of the produced HAp due to a pH of 6 with a weak acid.

HAp made by using the incinerated oyster shells had a non-crystalline structure, and characteristics of weak alkali materials. In spite of these different characteristics compared to con-

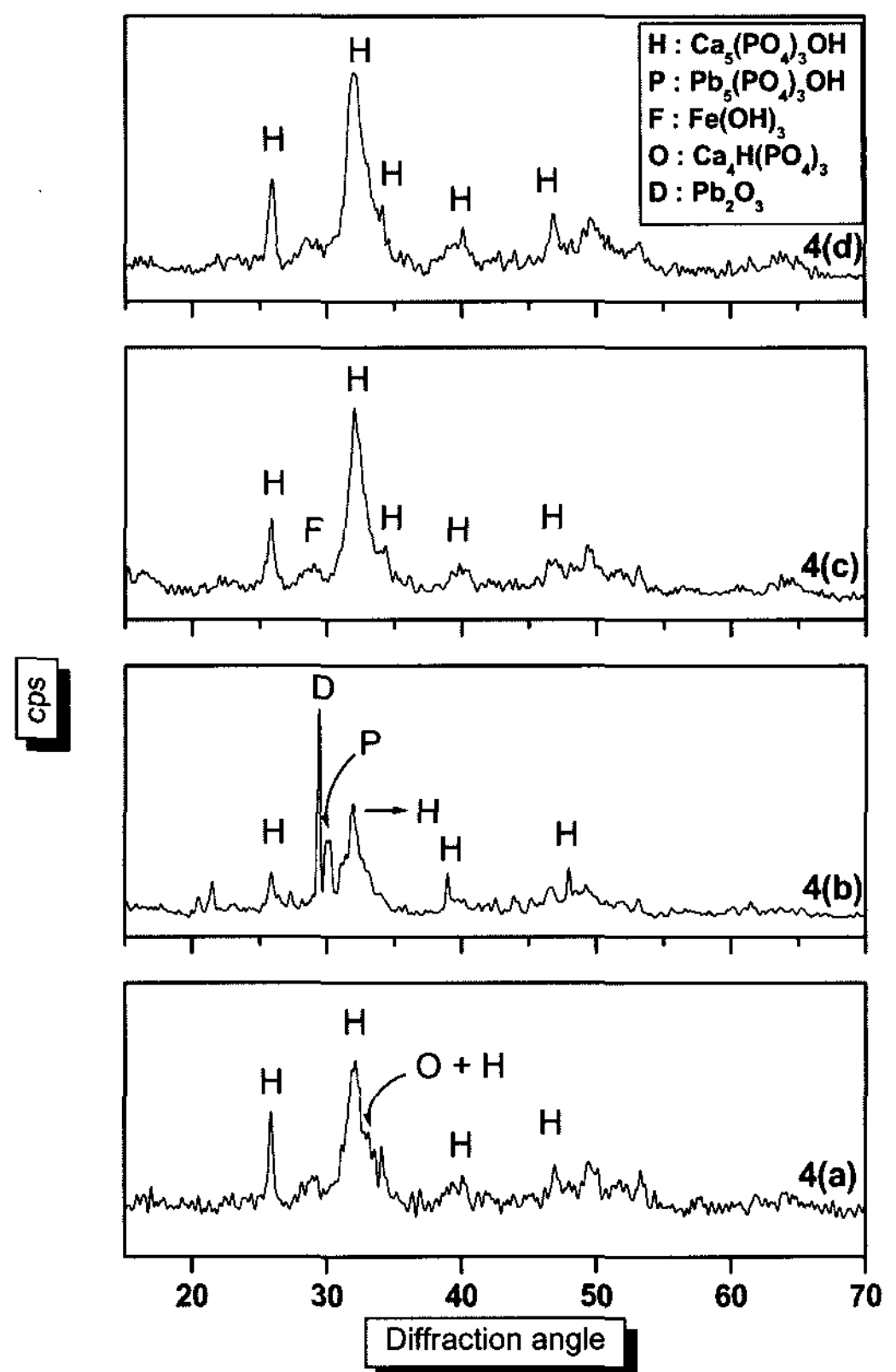


Figure 4. XRD of the production HAp and sludge produced after the removal of heavy metals.

ventional HAp made by various syntheses, it was expected that the produced HAp for this study could help in a recycling of waste solids, make convenience in synthesis without adding alkali, and achieve high removal efficiency for heavy metals with ion exchange reaction in a weak acid solution.

However, after reacting the heavy metals, phosphorus concentration was released as a mole reaction with the calcium concentration. Lee²²⁾ reported that HAp synthesized by precipitation reaction method occurred the same problem. Therefore, the release of phosphorus concentration must be researched.

CONCLUSIONS

The study investigated the removal efficiency and the characteristics of heavy metals using

HAp, which was made from waste oyster shells.

It was observed that most of calcium and phosphorus ions from the produced HAp were released for 60 minutes. This reaction occurred at both levels of pH. The produced HAp was a weak alkaline material, whose main constituents were HAp and OCP. As the incineration temperature increased, the intensity of peak was also increased. Meanwhile, the constituent of peak didn't change with the variation of incineration temperature.

When the heavy metals were removed at pH level 3 using the HAp, the order of efficiency was as follows: Fe^{2+} , $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$. As the concentration of heavy metals increased, the removal efficiency decreased. It was found that most of the produced HAp was dissolved in the solution at pH of 3. It was estimated that heavy metals removal was affected by pH. When the pH level was 6, removal efficiency for all heavy metals showed over 80% and the efficiency increased slightly as the heavy metal concentration increased. The peak of HAp in all sludge was detected and that of OCP was not observed. Lead ion was observed the peak such as Pb-Apatite and Dilead trioxide (Pb_2O_3). In the case of iron ions, it precipitated as iron(ferrous) hydroxide. Ions of cadmium and copper were removed by precipitation as shown in a form of hydroxide precipitate such as cadmium hydroxide and copper hydroxide. In conclusion, when the pH level was 6, the produced HAp made from the oyster shells was expected to achieve the highest removal efficiency with ion exchange reaction and precipitation.

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