



## Preparation and lead ion removal property of hydroxyapatite/polyacrylamide composite hydrogels

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### ARTICLE INFO

#### Article history:

Received 12 August 2007

Received in revised form 11 January 2008

Accepted 11 February 2008

Available online 16 February 2008

#### Keywords:

Adsorbent

Heavy metal

Hydrogel

Hydroxyapatite

Polyacrylamide

### ABSTRACT

We report the synthesis of hydroxyapatite/polyacrylamide (HAp/PAAm) composite hydrogels with various HAp contents by free radical polymerization and their removal capability of Pb<sup>2+</sup> ions in aqueous solutions with controlled initial Pb<sup>2+</sup> ion concentrations and pH values of 2–5. The swelling ratio of the composite gels in aqueous solutions decreases with increasing the HAp content in the gels. The composite gel with higher HAp content exhibits the higher removal capacity of Pb<sup>2+</sup> ions owing to the higher adsorption sites for Pb<sup>2+</sup> ions, but shows the slower removal rate of Pb<sup>2+</sup> ions due to the lower degree of swelling. The removal mechanism of Pb<sup>2+</sup> ion is very sensitive to the pH value in aqueous solution, although the removed amount of Pb<sup>2+</sup> ion is nearly same, regardless of pH values of 2–5. The removal mechanism, the dissolution of HAp in the composite gel and subsequent precipitation of hydroxypyromorphite (HPy), is dominant at lower pH 2–3, whereas the mechanism, the adsorption of Pb<sup>2+</sup> ions on the composite gel and following cation exchange reaction between Pb<sup>2+</sup> ions adsorbed and Ca<sup>2+</sup> of HAp, is dominant at higher pH 4–5. The equilibrium removal process of Pb<sup>2+</sup> ions by the composite gels at pH 5 is described well with the Langmuir isotherm model. The equilibrium removal capacities of the composite gels with 30, 50, and 70 wt.% HAp contents are evaluated to be 123, 178, and 209 mg/g, respectively.

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### 1. Introduction

The environmental pollution caused by industrial effluents including toxic heavy metals is of great concern, because heavy metals such as copper, lead, cadmium, and mercury are not biodegradable and accumulate in humans and other living organisms, eventually causing various diseases and disorders. Therefore, removal methods of heavy metals from industrial effluents have been investigated considerably for last few years. Chemical precipitation, adsorption, ion exchange, filtration, electrochemical treatment, and reverse osmosis are associated with typical methods for removing heavy metals from wastewater. Among them, adsorption has been recognized as a cost-effective alternative for removing metal ions existing in wastewater. Intense efforts have been aimed at the development of new adsorbents such as activated carbons, agricultural wastes, biomass, clays, hydroxyapatite, silica gels, zeolites, natural and synthetic polymers [1–6].

Hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, HAp], a major inorganic constituent of the hard tissue (bone and teeth) in the human body, has recently attracted considerable interest because of its high removal capacity for divalent heavy metal ions from aqueous solu-

tions [7–15]. Great researches on HAp have been carried out to understand the immobilization mechanism of heavy metals from aqueous solutions and to evaluate its usage for environmental remediation [7–12]. Overall, immobilization of heavy metal ions on synthetic or natural HAp is becoming a promising way for remediation of wastewater and soil. However, HAp is usually provided in powder or calcined pellets form, which might be a disadvantage to recover this material after removing heavy metal ions from wastewater.

Several studies showed that polymer composites incorporating adsorbents provide an emerging method for removing heavy metals from aqueous solutions [16–18]. For instance, preparation and heavy metal removal property of polyurethane composites including adsorbents such as *Ascophyllum nodosum*, activated carbon, clay, and zeolite have been recently reported [16,18]. Polyacrylamide composites with bentonite and zeolite as adsorbents were also prepared and their removal property of lead (Pb<sup>2+</sup>) ions was examined [17]. However, polymer composite systems including HAp as an adsorbent for removing heavy metals from aqueous solutions have not been reported. We have recently prepared hydrophilic polyurethane composite foams with various HAp contents and investigated their removal capacity of Pb<sup>2+</sup> ions from aqueous solutions [19]. As our continuing efforts to develop polymer composites incorporating HAp for the wastewater remediation, we have considered that a crosslinked polyacrylamide (PAAm) hydrogel has

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high potential as a polymer matrix due to its high hydrophilic, swelling, and non-toxic properties [20].

In this present study, we synthesize a series of HAp/PAAm composite hydrogels with various HAp contents by free radical polymerization, characterize their morphology and swelling behavior by using scanning electron microscopy, and investigate their removal capability of  $\text{Pb}^{2+}$  ions in aqueous solutions with controlled initial  $\text{Pb}^{2+}$  ion concentrations and pH values by using atomic absorption spectrometry. The removal rates of the composite gels with different HAp content are investigated based on the pseudo-second order kinetic model. The removal mechanism at various pH values of 2–5 is also discussed. Finally, the equilibrium removal performance of the composite gels is analyzed according to the Langmuir adsorption isotherm model.

## 2. Experimental

### 2.1. Materials

HAp powder was supplied by SamJo Industry Co., Ltd. (Korea). Acrylamide (AAm) monomer and *N,N'*-methylenebisacrylamide (NMBA) crosslinking agent for synthesizing the crosslinked PAAm hydrogels were purchased from TCI and Aldrich, respectively. Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) and potassium hydrogen sulfate ( $\text{KHSO}_3$ ) as radical initiators were purchased from Sigma–Aldrich and Fluka, respectively. Lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ ] and HCl solution of extra pure grade were used for adjusting the initial  $\text{Pb}^{2+}$  ion concentration and pH value in aqueous solutions, respectively. All chemicals obtained were used as received without further purification.

### 2.2. Preparation of HAp/PAAm composite hydrogels

A series of HAp/PAAm composite hydrogels with various HAp contents of 30, 50, and 70 wt.% were prepared by free radical polymerization of AAm and NMBA in deionized water including HAp powders as follows. The deionized water (450 ml) was bubbled with nitrogen gas for 30 min to remove the dissolved oxygen and HAp (21.4, 50, and 116.6 g), AAm (50 g), and NMBA (0.5 g) were then added. After heating each reaction mixture to 70 °C,  $\text{K}_2\text{S}_2\text{O}_8$  (0.15 g) and  $\text{KHSO}_3$  (0.15 g) as radical initiators were added with stirring. The reaction was carried out for 30 min. The composite gels synthesized were washed and purified in aqueous solution to remove the unreacted monomers or partially reacted oligomers. The final HAp/PAAm composite gels were cut into uniform sizes of ~5 mm and dried in a high vacuum oven.

### 2.3. Swelling of HAp/PAAm composite hydrogels

After swelling HAp/PAAm composite hydrogels in deionized water for 48 h, the degree of swelling was determined gravimetrically by using the following equation:

$$\text{Swelling ratio (\%)} = \frac{W_s - W}{W} \times 100 \quad (1)$$

where  $W_s$  is the weight of swollen gel (g) and  $W$  is the weight of dried gel (g).

### 2.4. Removal experiment of $\text{Pb}^{2+}$ ion in aqueous solution

Removal experiments of  $\text{Pb}^{2+}$  ions by the composite gels (0.5 g) were carried out in aqueous solutions (500 ml) with controlled initial  $\text{Pb}^{2+}$  concentrations and pH values. The initial  $\text{Pb}^{2+}$  ion concentrations of aqueous solutions were controlled to be 50–300 mg/l by dissolving lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ ] in deionized water. The pH

**Table 1**

The degree of swelling for HAp/PAAm composite hydrogels

HAp content (wt.%)	Swelling ratio (%)	
	For overall composite gels	For only PAAm component
30	1147	1653
50	501	1002
70	222	740

values of aqueous solutions with a controlled initial  $\text{Pb}^{2+}$  ion concentration were adjusted to be 2–5 by adding 0.1 M HCl standard solution in deionized water of pH 6.5.

The time-dependent  $\text{Pb}^{2+}$  ion concentration in aqueous solutions during removal experiments was measured for 120 h by using an atomic absorption spectrophotometer (AAS, Shimadzu Co.). For the quantitative measurement, a calibration curve between the absorption intensity and the  $\text{Pb}^{2+}$  ion concentration was obtained before experiments.

The morphology and composition of composite gels before and after removal experiments were analyzed by using a scanning electron microscope (SEM, JSM-6380, JEOL Ltd.) equipped with an energy dispersive X-ray spectrometer (EDS). To characterize the morphology of composite gels swollen in aqueous solutions, all the samples for SEM analysis were prepared by freeze-drying.

X-ray diffraction patterns of HAp powder and HAp/PAAm composite gels before and after removal experiments were obtained with an aide of a Rigaku X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ , 40 V, 200 mA) at a scanning rate of 5 °/min.

## 3. Results and discussion

### 3.1. Characterization of HAp/PAAm composite hydrogels

The network structure of PAAm gels is known to be highly dependent on the ratio of AAm to NMBA during polymerization [20]. In general, the crosslink density and rigidity of gels increase with the increment of the amount of NMBA crosslinking agent, thus reducing the degree of swelling in aqueous solutions. In this study, the ratio of AAm to NMBA was kept to be 0.01 for all the composite gels. When the equilibrium swelling ratio of the overall composite gels with different HAp content of 30, 50, and 70 wt.% was measured, it decreased with increasing the HAp content in the composite gels, as listed in Table 1. The swelling ratio of only PAAm component in the composite gels also decreased with increasing the HAp content in the composite gels (Table 1). These results implicate that the reduced degree of swelling for the composite gel with higher HAp content originates from the lower relative content and swelling capability of PAAm component in the composite gels. Consequently, the pore size of composite gels showed a tendency to decrease with increasing the HAp content in the composite gels, as can be seen in SEM images of the composite gels of Fig. 1. It should be mentioned that the samples for SEM images were obtained by freeze-drying the composite gels in swollen state.

### 3.2. Removal experiment of $\text{Pb}^{2+}$ ions from aqueous solution

#### 3.2.1. Effect of HAp content in HAp/PAAm composite hydrogels

The HAp content in HAp/PAAm composite hydrogels is an important factor to affect the removal capacity of the composite gels because  $\text{Pb}^{2+}$  ions are removed by the HAp component. The amount ( $q_t$ , mg/g) of  $\text{Pb}^{2+}$  ions removed per unit mass of HAp/PAAm gels as a function of contact time was calculated using following expression:

$$q_t = \frac{(C_0 - C)V}{B} \quad (2)$$

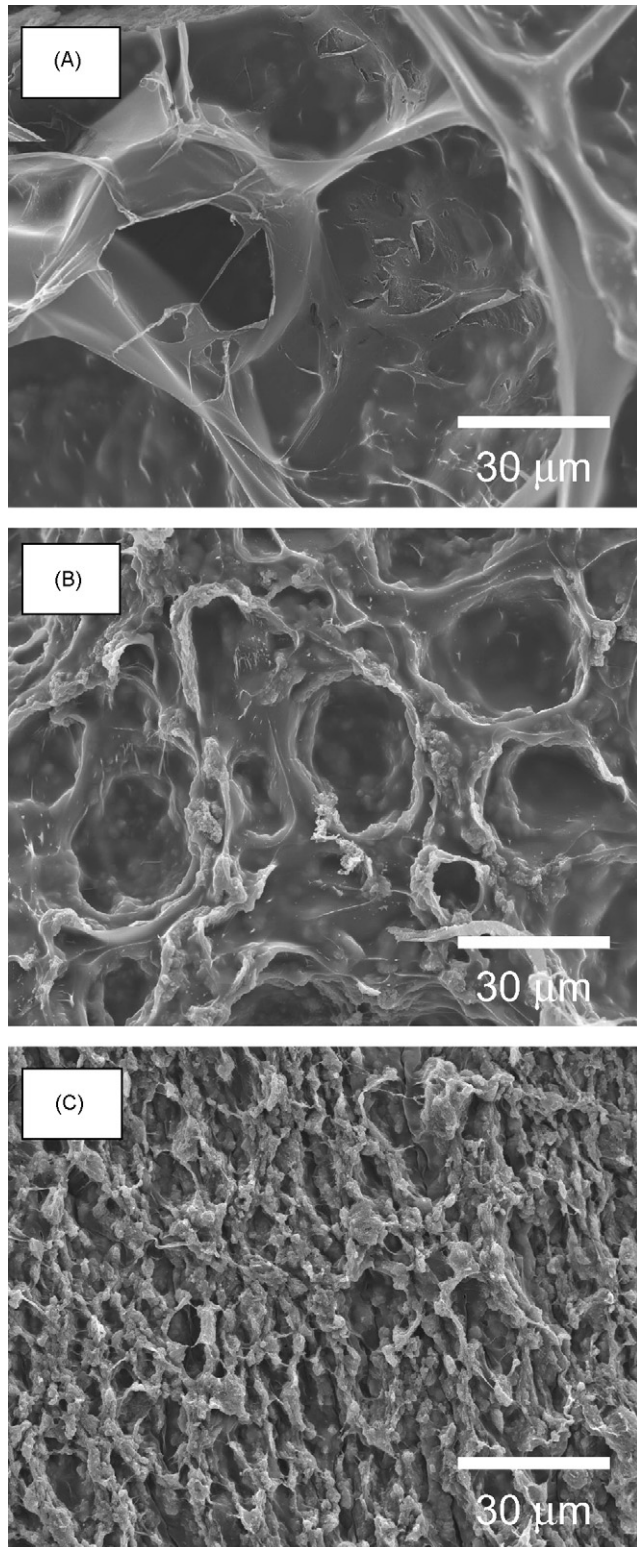


Fig. 1. SEM images of HAp/PAAm composite hydrogels with various HAp contents: (A) 30 wt.%; (B) 50 wt.%; (C) 70 wt.%.

where  $C_0$  is the initial  $Pb^{2+}$  ion concentration (mg/l),  $C$  the residual  $Pb^{2+}$  ion concentration (mg/l) at an arbitrary time  $t$ ,  $V$  the volume of the solution (l), and  $B$  the weight of the HAp/PAAm gel (g). The time-dependent amounts of  $Pb^{2+}$  ions removed by HAp/PAAm composite gels with various HAp contents in aqueous solution (initial  $Pb^{2+}$  ion concentration of 275 mg/l and pH 5.0) were presented in

Fig. 2. The data show that the ultimate amount of  $Pb^{2+}$  ions removed by HAp/PAAm composite gels increases with increasing the HAp content in composite gels, due to the increased adsorption sites of HAp for  $Pb^{2+}$  ions.

For 100 wt.% HAp powder of 0.5 g, removal experiments were also conducted in the same aqueous solution condition and the results were represented in Fig. 2. It was found that almost all  $Pb^{2+}$  ions in the aqueous solution were removed by the HAp powder in less than 1 h. The rapid removal rate of  $Pb^{2+}$  ions of HAp powder used in this study is quite consistent with that of the previous report [8]. It is believed that the rapid removal rate of HAp powder alone is due to its higher surface area and higher quantity of absorption sites to  $Pb^{2+}$  ions, compared with HAp/PAAm composite gels. On the other hand, it should be mentioned that, although the ultimate contact time of 120 h in Fig. 2 is a typical time to observe the equilibrium adsorption process of HAp/PAAm composite gels, such a long process time may be a limitation from an application point of view.

The removal kinetics of  $Pb^{2+}$  ions by HAp powder alone and HAp/PAAm composite gels was analyzed on the basis of the pseudo-second order kinetic model, which is expressed as [21]:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (3)$$

where  $t$  is the contact time (h),  $q_t$  and  $q_e$  are the amounts of  $Pb^{2+}$  ions removed at an arbitrary time  $t$  and at equilibrium (mg/g), respectively, and  $k$  is the rate constant (g/mg h). From the experimental data of Fig. 2, plots of  $t/q_t$  versus  $t$  for the removal rates of  $Pb^{2+}$  ions by the composite gels are obtained, as shown in Fig. 3. As results, the  $q_e$  values for the composite gels with 30, 50, and 70 wt.% HAp contents were calculated to be 128, 173, and 234 mg/g, respectively, indicating that the equilibrium removal amount of  $Pb^{2+}$  ions increased with increasing the amount of HAp in composite gels. On the other hand, the  $k$  values were  $7.52 \times 10^{-4}$ ,  $4.02 \times 10^{-4}$ , and  $1.06 \times 10^{-4}$  g/mg h for composite gels with 30, 50, and 70 wt.% HAp, respectively. It reveals that the removal rate of  $Pb^{2+}$  ions is faster for the composite gel with lower HAp content. As noted above, the swelling ratio (or water content) of the composite gels increased with decreasing the HAp content. As a result,  $Pb^{2+}$  ions in absorbed water are more easily accessible to HAp particles of the composite gel with lower HAp content, thus yielding the faster removal rate. For comparison, the  $q_e$  and  $k$  values for the 100 wt.% HAp

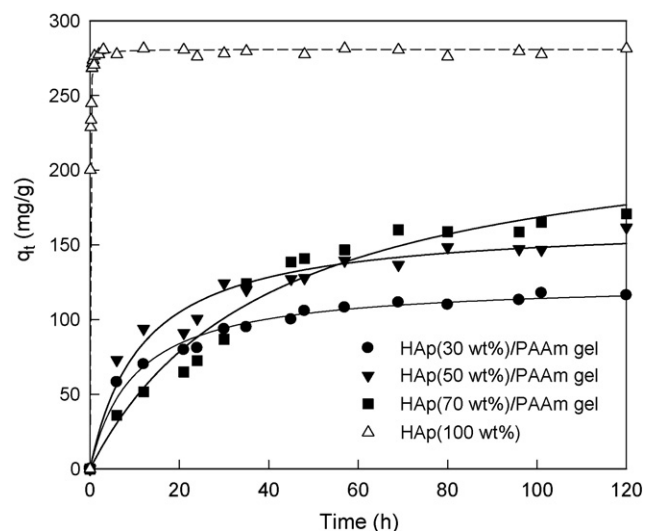
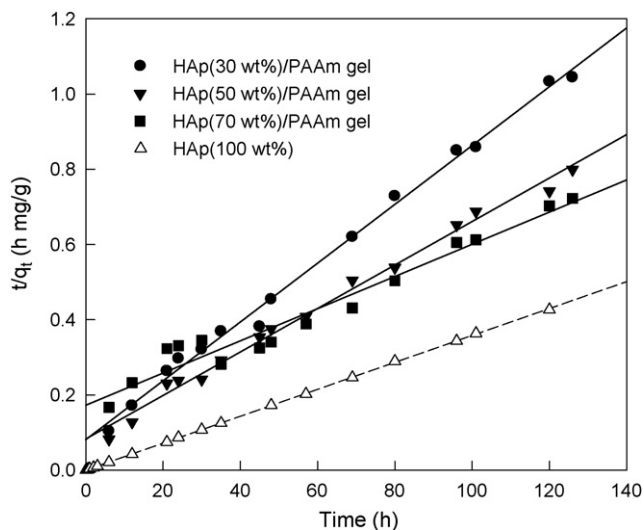


Fig. 2. The time-dependent amount ( $q_t$ ) of  $Pb^{2+}$  ions removed by HAp powder alone and HAp/PAAm composite gels with various HAp contents in aqueous solution (initial  $Pb^{2+}$  ion concentration of 275 mg/l and pH 5).



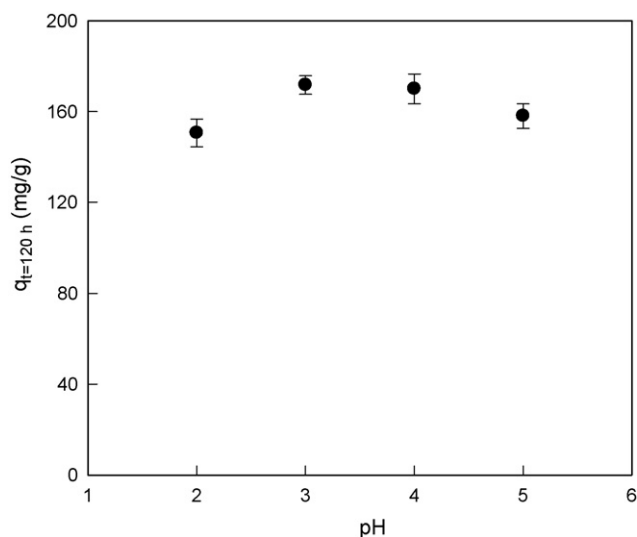
**Fig. 3.** The removal kinetics analysis of Pb<sup>2+</sup> ions by HAp powder alone and HAp/PAAm composite gels with various HAp contents on the basis of the pseudo-second order kinetic model.

powder were evaluated to be 279 mg/g and  $8.82 \times 10^{-2}$  g/mg h, respectively.

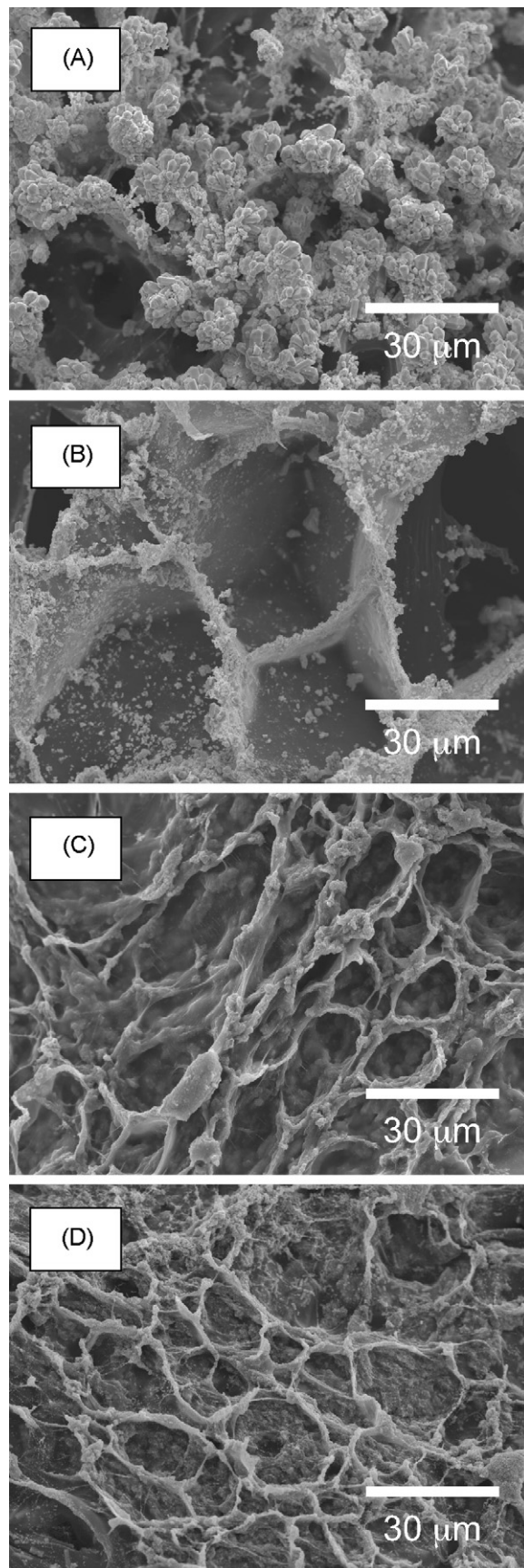
### 3.2.2. Effect of pH value in aqueous solution

The pH value in aqueous solution is a very critical parameter affecting on both the removal capacity and the removal mechanism of Pb<sup>2+</sup> ions by HAp [7–9,11,12]. Removal experiments were performed for the composite gel with 50 wt.% HAp content in aqueous solutions with the initial Pb<sup>2+</sup> ion concentration of 180 mg/l and various pH values of 2–5. When the ultimate amounts (mg/g) of Pb<sup>2+</sup> ions removed by the composite gel after 120 h contact time were measured, they were found to be almost identical within the experimental error, regardless of the pH value in aqueous solution, as presented in Fig. 4.

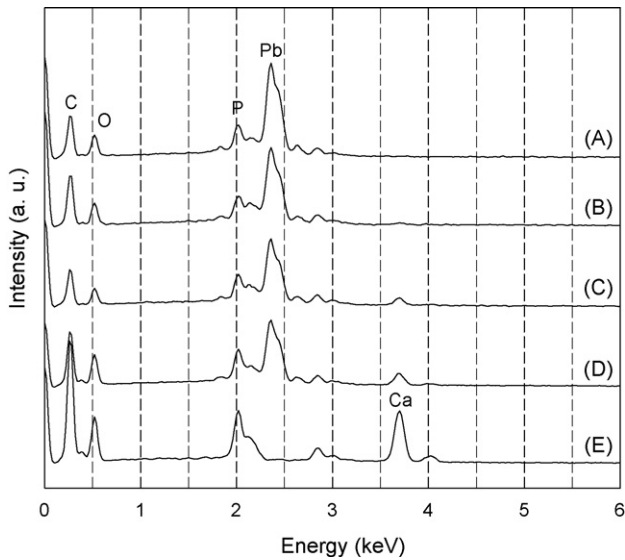
Fig. 5 shows the SEM images of the freeze-dried composite gels with 50 wt.% HAp after removal experiments at various pH values of 2–5. The morphology of the composite gels experimented at pH 4 and 5 is nearly same with that (Fig. 1B) of the original gel, but it is quite different from those of the gels experimented at pH 2 and 3. It means that the removal mechanism of Pb<sup>2+</sup> ions by the com-



**Fig. 4.** The ultimate amount ( $q_{t=120h}$ ) of Pb<sup>2+</sup> ions removed by HAp(50 wt.)/PAAm composite gels in aqueous solution at various pH values of 2–5.



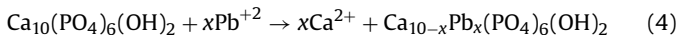
**Fig. 5.** SEM images of HAp(50 wt.)/PAAm composite gels after removal experiments at various pH values: (A) pH 2; (B) pH 3; (C) pH 4; (D) pH 5.



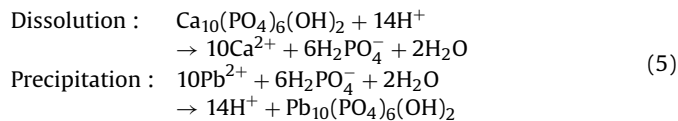
**Fig. 6.** EDS spectra of HAp(50 wt.)/PAAm composite gels before and after removal experiments at various pH values: (A) pH 2; (B) pH 3; (C) pH 4; (D) pH 5; (E) before removal experiment.

posite gel is quite different, depending on the pH value in aqueous solution, although the ultimate removal amounts of  $\text{Pb}^{2+}$  ions are independent of the pH value (Fig. 4).

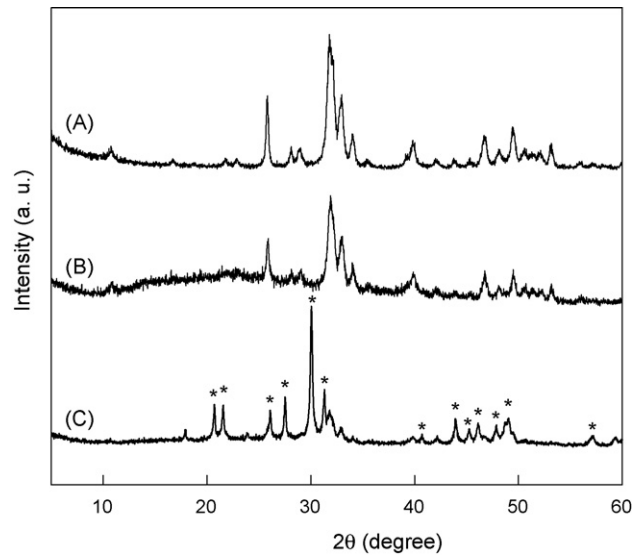
Two general mechanisms for removing of divalent cations by HAp have been proposed [7–9,12]. The first mechanism is the adsorption of  $\text{Pb}^{2+}$  ions on the HAp surfaces followed by the ion exchange reaction between  $\text{Pb}^{2+}$  ions adsorbed and  $\text{Ca}^{2+}$  ions of HAp [7]. This ion exchange reaction mechanism is expressed as:



The second mechanism is the dissolution of HAp in aqueous solution containing  $\text{Pb}^{2+}$  ions and subsequent precipitation of hydroxypyromorphite [ $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HPy] [8,9]. The dissolution–precipitation mechanism can be written as:

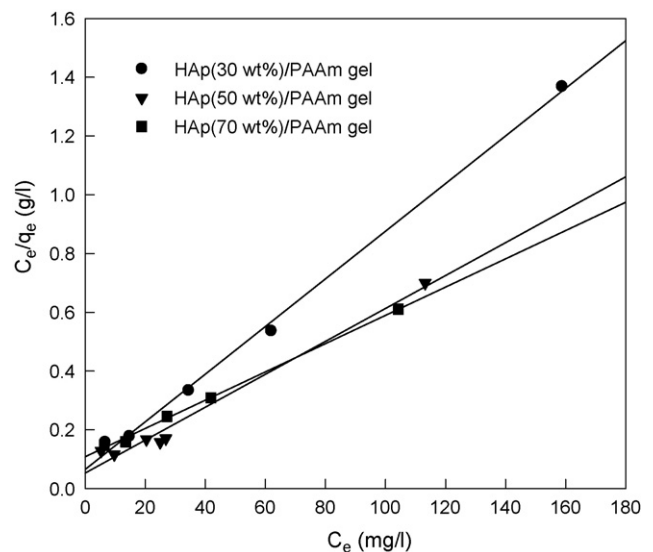


For the composite gels experimented at pH 2 and 3, granular precipitants were observed, as shown in Fig. 5A and B. To identify the constituent of the composite gels experimented at various pH values, EDS spectra were obtained, as can be seen in Fig. 6. EDS spectra of the composite gels experimented at pH 2 and 3 demonstrate that those granular precipitants are composed of HPy particles, as shown in Fig. 6A and B, where no absorption peaks of Ca atom were observed. On the other hand, for the composite gels experimented at pH 4 and 5, strong absorption peaks of Pb atom as well as weak peaks of Ca atom were detected (Fig. 6C and D), although their overall morphologies are same with that the original sample before experiments, as noted above. Therefore, it seems reasonable to conclude that the removal mechanism of  $\text{Pb}^{2+}$  ions by the composite gels is varied, depending on the pH values in aqueous solutions: the dissolution of HAp and following precipitation of HPy is the dominant removal mechanism at lower pH 2 and 3, whereas the adsorption of  $\text{Pb}^{2+}$  ions on the composite gels followed by the cation exchange reaction between  $\text{Ca}^{2+}$  of HAp and  $\text{Pb}^{2+}$  ions is the dominant one at higher pH 4 and 5. The existence of weak absorption peaks of Ca atom in Fig. 6C and D implicates that  $\text{Ca}^{2+}$  ions of HAp in the composite gel were not totally replaced by  $\text{Pb}^{2+}$  ions via the cation exchange reaction mechanism.



**Fig. 7.** X-ray diffraction patterns of (A) HAp powder and HAp(50 wt.)/PAAm composite gel (B) before and (C) after removal experiment at pH 5. The asterisk indicates the reflection peaks from HPy component.

Fig. 7 shows the X-ray diffraction patterns of original HAp powder and composite gel with 50 wt.% HAp content before and after removal experiment at pH 5. The diffraction patterns support the facts that HAp powder was successfully incorporated into PAAm gels without their structural changes (Fig. 7A and B) and that HAp in the composite gel is transformed into HPy via the adsorption of  $\text{Pb}^{2+}$  ions followed by the cation exchange reaction (Fig. 7B and C).



**Fig. 8.** Langmuir isotherm plots for the adsorption of  $\text{Pb}^{2+}$  ions on HAp/PAAm composite gels with various HAp contents in aqueous solutions at pH 5.

**Table 2**

Langmuir coefficients ( $q_{\text{max}}$  and  $K_e$ ) for the adsorption of  $\text{Pb}^{2+}$  ions on HAp/PAAm composite gels in aqueous solutions at pH 5, together with the regression coefficient ( $R^2$ )

Adsorbent	Langmuir model		
	$q_{\text{max}}$ (mg/g)	$K_e$ (l/mg)	$R^2$
HAp(30 wt.)/PAAm gel	123	0.124	0.997
HAp(50 wt.)/PAAm gel	178	0.105	0.982
HAp(70 wt.)/PAAm gel	209	0.044	0.997

**Table 3**  
Removal capacities ( $q_{\max}$ ) of  $Pb^{2+}$  ion by various adsorbents

Adsorbent	$q_{\max}$ (mg/g)	Reference
Activated carbon	31.2	Machida et al. [2]
Crop milling waste	49.97	Saeed et al. [23]
PHEMA/chitosan membranes	68.81	Genc et al. [24]
Wheat bran	87	Bulut et al. [4]
Palm shell activated carbon	95.2	Issabayeva et al. [5]
Natural phosphate	115.3	Mouflih et al. [25]
Activated phosphate	155	Mouflih et al. [25]
HAp(50 wt.%) / PAAm gel	178	This work

### 3.2.3. Adsorption isotherm of $Pb^{2+}$ ions at pH 5

The equilibrium removal performance of the HAp/PAAm composite hydrogels with 30, 50, and 70 wt.% HAp contents for  $Pb^{2+}$  ions was examined at pH 5 where the cation exchange reaction following the adsorption of  $Pb^{2+}$  ions occurs dominantly. The Langmuir adsorption isotherm has been widely used as a mathematical model expressing the quantitative relationship between the extent of sorption and the residual solute concentration. The Langmuir adsorption isotherm equation is represented as [22]:

$$\frac{C_e}{q_e} = \frac{1}{K_e q_{\max}} + \frac{C_e}{q_{\max}} \quad (6)$$

where  $C_e$  is the equilibrium concentration (mg/l),  $q_e$  the amount adsorbed per amount of adsorbent (mg/g),  $K_e$  the Langmuir equilibrium constant (l/mg), and  $q_{\max}$  the amount of adsorbate required to cover a monolayer (mg/g). The Langmuir equation was found to give a fairly good fit to the adsorption isotherms of  $Pb^{2+}$  ions on the composite gels, as shown in Fig. 8. The values of  $q_{\max}$  and  $K_e$  from the slope and intercept of linear plots of  $C_e/q_e$  versus  $C_e$  were calculated, together with the regression coefficients, as summarized in Table 2. The  $q_{\max}$  values increased with increasing the HAp content of the composite gels, as discussed above. In addition, the  $q_{\max}$  values of the composite gels obtained by the Langmuir equation were quite consistent with those obtained on the basis of the pseudo-second order kinetic model.

When the equilibrium removal amount of  $Pb^{2+}$  ions by the composite gel with 50 wt.% HAp content was compared with the data of other adsorbents (Table 3), it was found to be comparable or even superior to other available adsorbents. It reveals that the HAp/PAAm composite gel is a very promising adsorbent for  $Pb^{2+}$  ions and could be served as a purifier for wastewater.

## 4. Conclusions

We synthesized a series of HAp/PAAm composite hydrogels with different HAp content (30, 50, and 70 wt.%) and investigated their removal capability of  $Pb^{2+}$  ions from aqueous solutions with various pH values of 2–5. The swelling ratio of composite gels decreased with increasing the HAp content because of the decreased amount of PAAm component that absorbs water. The removal capacity of the HAp/PAAm composite gels increased with increasing the HAp content due to the increased removal sites for  $Pb^{2+}$  ions. In contrast, the removal rates decreased with increasing the HAp content owing to the lower swelling ratio for the composite gel with higher HAp content. The ultimate amounts of  $Pb^{2+}$  ions removed by the composite gel with 50 wt.% HAp content measured at 120 h contact time were almost identical, irrespective of the pH value in aqueous solution. However, the removal mechanism of  $Pb^{2+}$  ions was quite dependent on the pH value. The mechanism of HAp dissolution and following HPy precipitation was dominant at lower pH 2 and 3, whereas the mechanism of adsorption of HAp and cation exchange reaction between  $Ca^{2+}$  of HAp and  $Pb^{2+}$  ions was dominant at higher pH 4 and 5. Based on the Langmuir adsorption isotherm, the equi-

librium removal amount of  $Pb^{2+}$  ions by the composite gels with 30, 50, and 70 wt.% HAp contents in aqueous solutions at pH 5 was evaluated to be 123, 178, and 209 mg/g. These results showed that the HAp/PAAm composite hydrogel can be used as an effective adsorbent for removing  $Pb^{2+}$  ions from aqueous solution, specifically at pH values above 4.

## Acknowledgements

This work was supported by grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry, and Energy (MOCIE).

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