

## Removal of lead ions in aqueous solution by hydroxyapatite/polyurethane composite foams

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### Abstract

We have prepared hydroxyapatite/polyurethane (HAp/PU) composite foams with two different HAp contents of 20 and 50 wt.% and investigated their removal capability of Pb<sup>2+</sup> ions from aqueous solutions with various initial Pb<sup>2+</sup> ion concentrations and pH values of 2–6. HAp/PU composite foams synthesized exhibited well-developed open pore structures which provide paths for the aqueous solution and adsorption sites for Pb<sup>2+</sup> ions. With increasing the HAp content in the composites, the removal capability of Pb<sup>2+</sup> ions by the composite foams increases owing to the higher adsorption capacity, whereas the removal rate is slower due to the less uniform dispersity of HAp in composite foams. The removal rate of Pb<sup>2+</sup> ions is also slower with increasing the initial Pb<sup>2+</sup> ion concentration in aqueous solutions. The removal mechanism of Pb<sup>2+</sup> ion by the composites is varied, depending on the pH value of aqueous solution: the dissolution of HAp and precipitation of hydroxypyromorphite is dominant at lower pH 2–3, the adsorption of Pb<sup>2+</sup> ions on the HAp/PU composite surface and ion exchange reaction between Ca<sup>2+</sup> of HAp and Pb<sup>2+</sup> in aqueous solution is dominant at higher pH 5–6, and two removal mechanisms compete at pH 4. The equilibrium removal process of Pb<sup>2+</sup> ions by the HAp/PU composite foam at pH 5 was described well with the Langmuir isotherm model, resulting in the maximum adsorption capacity of 150 mg/g for the composite foam with 50 wt.% HAp content.

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**Keywords:** Adsorbent; Composite foam; Heavy metals; Hydroxyapatite; Polyurethane

### 1. Introduction

Heavy metal ions exist in wastewater of many industries such as metal plating facilities, mining operations, agricultural activities, etc. The presence of toxic heavy metal ions in industrial wastewater has generated considerable concern in recent years. Among the toxic heavy metal ions which present potential danger to human health are copper, lead, cadmium, and mercury. These heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Therefore, the removal of hazardous heavy metals in wastewater has received much attention in recent years. Traditional methods of removal are chemical precipitation, ion exchange, filtration,

electrochemical treatment, and reverse osmosis. In the last few years, adsorption has been showed to be an alternative method for removing dissolved metal ions from wastewater. Great efforts have been contributed to develop new adsorbents such as hydroxyapatite, activated carbons, biomass, silica gels, zeolites, clays, carbonaceous, and synthetic polymers [1–6]. The most widely studied adsorbent is activated carbon, while the application of other adsorbent materials for metal ion removal is now receiving considerable attention.

Hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, HAp], a major inorganic constituent of bone, teeth, and natural source of phosphate, has a high removal capacity for divalent heavy metal ions [7,8]. Immobilization of lead (Pb<sup>2+</sup>) ions on synthetic or natural HAp is becoming a promising way for remediation of wastewater and soil. Such ability of HAp has stimulated intensively research to understand the mechanisms involved in removal of Pb<sup>2+</sup> ions in aqueous solution by synthetic apatite and to evaluate the envi-

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ronmental application of this material [9–13]. HAp is usually obtained in powder or calcined pellets form. To improve its applicability for the purification of wastewater, there is a necessity to immobilize HAp powders or pellets into certain forms.

Making composite materials composed of polymers and adsorbents is an emerging method. Alhakawati and Banks have applied the hydrophilic urethane, Hypol 2002 (Dow Chemical Co., Ltd. UK branch), to synthesize composites with the absorbent of *Ascophyllum nodosum*, and claimed their potential use in the removal of copper from aqueous solution [14]. Polyurethane (PU) foams with other adsorbents such as activated carbon, zeolite, and pillared clay have been also synthesized and their adsorption characteristics have been investigated [15]. Despite the wide application of PU foams as an immobilization matrix, there have been no reports on the immobilization of HAp into PU foams and their adsorption behaviors of heavy metals from aqueous solution.

In this study, we prepare HAp/PU composite foams with two different HAp contents and investigate their removal capability of  $Pb^{2+}$  from aqueous solutions with various initial  $Pb^{2+}$  ion concentrations and pH values of 2–6. The effects of initial  $Pb^{2+}$  ion concentration and HAp content on the removal capability of the composite foams are investigated based on the pseudo-second order kinetic model. Removal mechanism of  $Pb^{2+}$  ions by the composite foams in the aqueous solutions with different pH 2–6 is discussed. Finally, equilibrium removal performance of HAp/PU composite foams is analyzed by using Langmuir adsorption isotherm model.

## 2. Experimental

### 2.1. Preparation of HAp/PU composite foams

HAp/PU composite foams were synthesized by using Hypol 3000, HAp, and deionized water. Hypol 3000 (Dow Chemical Co., Ltd.) is a PU prepolymer with urethane groups in the main chain and isocyanate groups at their chain ends. HAp [ $Ca_{10}(PO_4)_6(OH)_2$ ] powder was supplied by SamJo Industry Co., Ltd. (Korea). HAp was immobilized into polyurethane foam using the technique reported in the literature [14]. Typically, Hypol 3000 prepolymer (8 g) and HAp (4 or 8 g) were mixed in a container to make composites with two different HAp contents of 20 and 50 wt.%. Subsequently, the deionized water of 8 g was added. The weight ratio of Hypol to water, a crucial factor influencing the final morphology of PU composite foams, was chosen to be 1. The mixtures were then stirred vigorously for 30 s until homogeneity was achieved. After forming the stable foam structures, HAp/PU composite foams were allowed to cure and dry at 80 °C for 24 h in vacuum oven. The foaming and curing reactions during manufacturing HAp/PU composites are well known in the literature [16]. HAp/PU composite foams were then cut into uniform size of 2–3 mm.

### 2.2. Removal of $Pb^{2+}$ ions by HAp/PU composite foams

Removal performance of  $Pb^{2+}$  ions by HAp/PU composite foams was investigated by monitoring the change of  $Pb^{2+}$  ion

concentration in the aqueous solution. In order to determine absorption isotherms, HAp/PU composite foam of 0.5 g was put into the aqueous solution of 500 ml with various initial  $Pb^{2+}$  ion concentrations and pH values. The initial concentration of  $Pb^{2+}$  ions in the aqueous solution was controlled to be 44–184 mg/l by diluting the  $Pb^{2+}$  1000 mg/l standard solution (Kanto Chemical Co., Ltd.) with deionized water. The pH value was adjusted to be from 2 to 6 by adding 0.1 M NaOH solution. All the experiments were carried out at a room temperature and an agitation speed of 300 rpm for 48 h.

The change of  $Pb^{2+}$  ion concentration in the aqueous solution was measured by using an atomic adsorption spectrophotometer (AAS, SHIMADZU AA-6701F). Before the measurement, a linear calibration curve between the  $Pb^{2+}$  ion concentration and the absorption intensity was obtained for quantitative analysis.

The morphological and compositional analyses of HAp/PU composite foams were carried out from selected samples using a scanning electron microscope (SEM, JEOL JSM-6380) equipped with an energy dispersive X-ray spectrometer (EDS).

## 3. Results and discussion

### 3.1. Morphology of HAp/PU composite foams

The SEM images of HAp/PU composite foams with different HAp content of 20 and 50 wt.% are shown in Fig. 1. Both composite foams synthesized exhibited well-developed open pore structures, independent of HAp content (left-side images of Fig. 1). These open pore structures are expected to provide the enhanced accessibility of  $Pb^{2+}$  ions in aqueous solutions to HAp immobilized in the composites. The right-side SEM images of Fig. 1 also reveal that HAp particles in the composite foam with 20 wt.% HAp content are more uniformly dispersed in smaller sizes, compared with the composite with 50 wt.% HAp.

### 3.2. Effect of HAp content in composite foams

The content of HAp in HAp/PU composite foams is one of important parameters for affecting the removal amount of  $Pb^{2+}$  ions in aqueous solutions. For the composite foams with 20 and 50 wt.% HAp contents, the removal performance of  $Pb^{2+}$  ions from the aqueous solution with the initial  $Pb^{2+}$  concentration of 184 mg/l at pH 5 was investigated. The time-dependent amount ( $q_t$  in mg/g) of  $Pb^{2+}$  ions removed by the composite foam was calculated using following expression:

$$q_t = \frac{(C_0 - C)V}{B} \quad (1)$$

where  $C_0$  is the initial  $Pb^{2+}$  ion concentration (mg/l),  $C$  the residual  $Pb^{2+}$  ion concentration (mg/l),  $V$  the volume of the solution (l), and  $B$  is the weight of the HAp/PU composite foam (g). The ultimate amount of  $Pb^{2+}$  ions removed by the composite foam with 50 wt.% HAp content is much higher than that of the one with 20 wt.% HAp, as can be seen in Fig. 2. It is because the composite with higher HAp content provides the larger adsorption pores for  $Pb^{2+}$  ions from aqueous solutions.

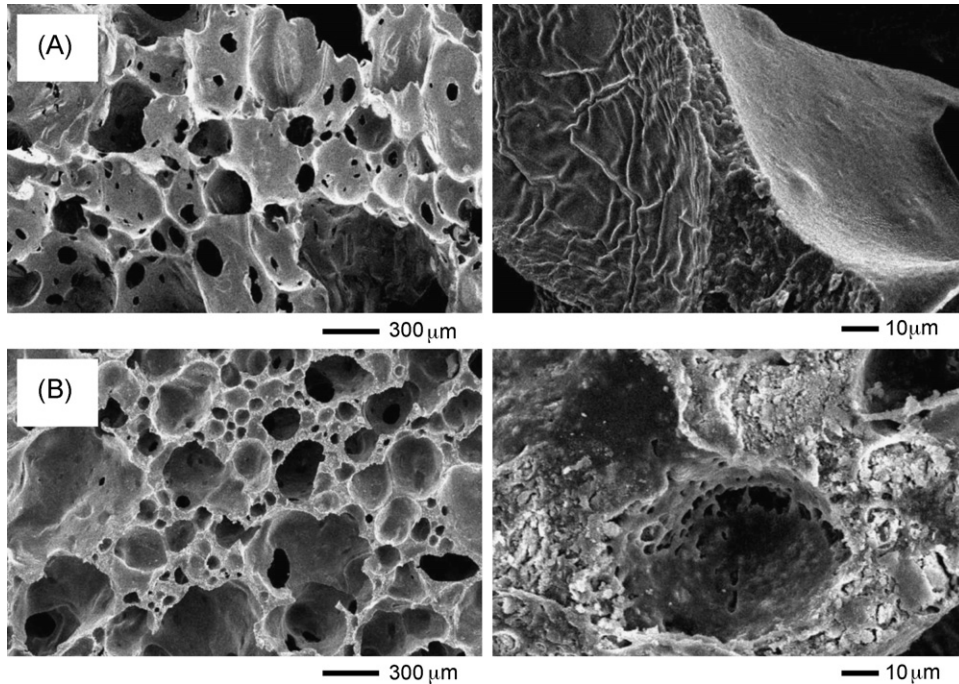


Fig. 1. SEM images of HAp/PU composite foams with different HAp content: (A) 20 wt.%; (B) 50 wt.%.

The removal kinetics of  $Pb^{2+}$  ions by the composite foams was also analyzed based on the pseudo-second order kinetic model, which is expressed as [17–19]:

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

where  $t$  is the contact time (h),  $q_t$  and  $q_e$  the amounts of  $Pb^{2+}$  removed at an arbitrary time  $t$  and at equilibrium (mg/g), respectively, and  $k$  is the rate constant (g/mg h). Plots of  $t/q_t$  versus  $t$  for the removal kinetics of  $Pb^{2+}$  ions by the composite foams

are shown in Fig. 3. As results, the  $q_e$  values for the composites with 20 and 50 wt.% HAp contents are estimated to be 94.6 and 170.2 mg/g, respectively, and the  $k$  values are  $2.97 \times 10^{-3}$  and  $6.4 \times 10^{-4}$  g/mg h. It indicates that the removal rate of the composite containing 20 wt.% HAp is somewhat faster than that of the composite with 50 wt.% HAp. This result is expected to be from the fact that HAp particles in the composite with 20 wt.% HAp are more uniformly dispersed than those in the composite with 50 wt.% HAp and that  $Pb^{2+}$  ions in aqueous solution are easily accessible to the smaller HAp particles in the composite foam with 20 wt.% HAp.

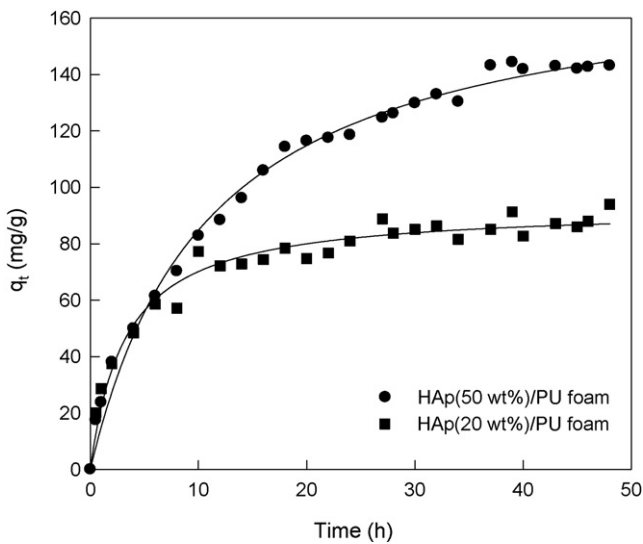


Fig. 2. The time-dependent amount ( $q_t$ ) of  $Pb^{2+}$  ions removed by the HAp/PU composite foams with different HAp content in aqueous solution with initial  $Pb^{2+}$  ion concentration of 184 mg/l at pH 5.

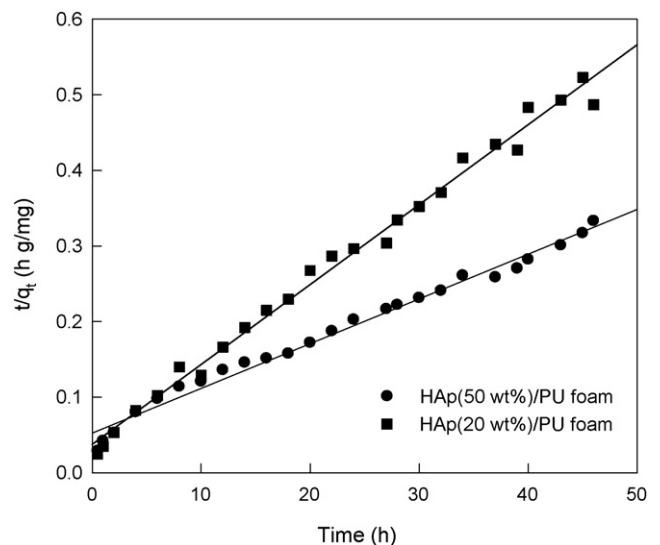


Fig. 3. The removal kinetics analysis of  $Pb^{2+}$  ions by the HAp/PU composite foams with different HAp content.

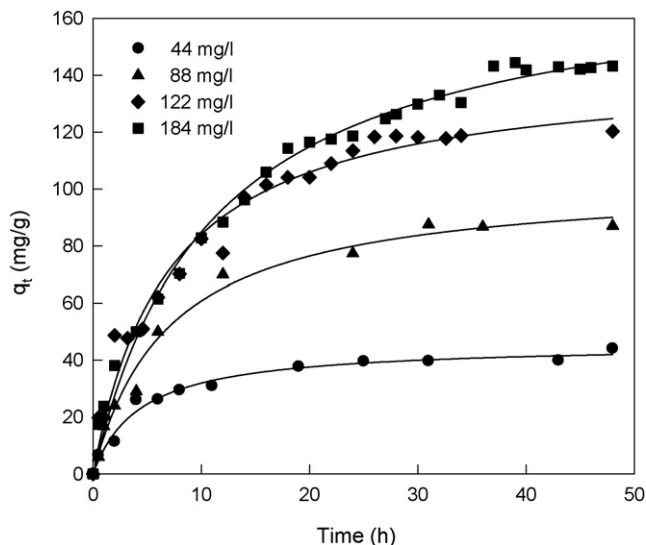


Fig. 4. The time-dependent amount ( $q_t$ ) of  $Pb^{2+}$  ions removed by the HAp (50 wt.%) / PU composite foam in aqueous solutions with various initial  $Pb^{2+}$  ion concentrations of 44–184 mg/l at pH 5.

### 3.3. Effect of initial $Pb^{2+}$ ion concentration

The effect of the initial  $Pb^{2+}$  ion concentration (44, 88, 122, and 184 mg/l) on the removal performance of the composite foam with 50 wt.% HAp content was investigated. The pH value of the aqueous solutions was controlled to be 5. The ultimate amount of  $Pb^{2+}$  ions removed by the composite foam increased with increasing the initial concentration of  $Pb^{2+}$  ions in aqueous solution from 44 to 184 mg/l, as can be seen in Fig. 4.

The removal efficiency of  $Pb^{2+}$  ion by the HAp/PU composite foams in the aqueous solutions with various  $Pb^{2+}$  ion concentrations is calculated based on following equation:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (3)$$

As shown in Fig. 5, the ultimate removal efficiency of the composite foam in aqueous solutions with initial  $Pb^{2+}$  ion concentrations of 44, 88, and 122 mg/l was close to 100%, while that at the initial  $Pb^{2+}$  ion concentration of 184 mg/l was approximately 77.8%. Therefore, it is expected from the above results that the maximum removal amount of  $Pb^{2+}$  ions by the composite foam with 50 wt.% HAp content is between 122 and 184 mg/l. This is consistent with the above result that the estimated equilibrium removal amount ( $q_e$ ) of the composite with 50 wt.% HAp content is 170.2 mg/g.

According to the pseudo-second order kinetic model of Eq. (2), the  $k$  values for the initial  $Pb^{2+}$  concentrations of 44, 88, 122, and 184 mg/l were calculated to be  $4.88 \times 10^{-3}$ ,  $1.68 \times 10^{-3}$ ,  $1.47 \times 10^{-3}$ , and  $0.64 \times 10^{-3}$  g/mg h, respectively. It demonstrates that the removal rate of the composite containing 50 wt.% HAp is slower with increasing the initial  $Pb^{2+}$  ion concentration in the aqueous solution. This result reveals that the kinetic constant decreases with increasing the initial concentration of the systems, which is consistent with the result reported in the literature [5].

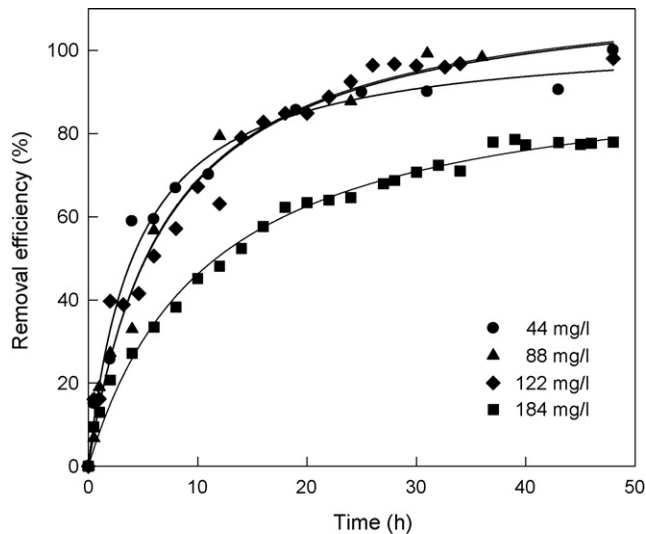


Fig. 5. The time-dependent removal efficiency of  $Pb^{2+}$  ion by the HAp (50 wt.%) / PU composite foam in aqueous solutions with various initial  $Pb^{2+}$  ion concentrations of 44–184 mg/l at pH 5.

### 3.4. Effect of pH in aqueous solution

The pH value in the aqueous solution on the removal capacity of  $Pb^{2+}$  ion by HAp/PU composite foams is an important parameter to be considered. Removal experiments at various pH values of 2–6 were conducted for the HAp/PU composite foam with 50 wt.% HAp content in aqueous solution with the initial  $Pb^{2+}$  ion concentration of 200 mg/l. The amount ( $q_{t=48h}$ ) of  $Pb^{2+}$  ions removed by the composite foam after 48 h contact time was measured and compared, as can be seen in Fig. 6. The amount of  $Pb^{2+}$  ions removed by the composite foam with 50 wt.% HAp was quite similar ( $\sim 140 \pm 10$  mg/g), independent of pH value of aqueous solution, except for pH 4.

Two dominant mechanisms for the ability of HAp to take up divalent cations have been proposed [9–11,13]. The first mech-

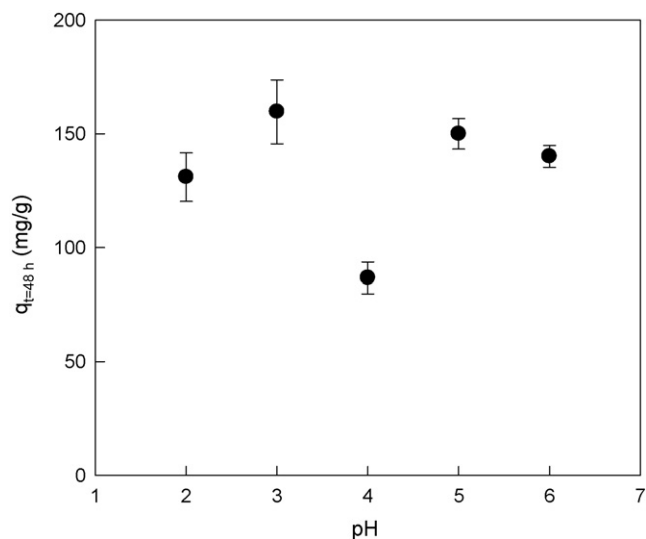


Fig. 6. The effect of pH on the amount ( $q_{t=48h}$ ) of  $Pb^{2+}$  ions removed by the HAp (50 wt.%) / PU composite foam in aqueous solution with the initial  $Pb^{2+}$  ion concentration of 200 mg/l after 48 h contact time.



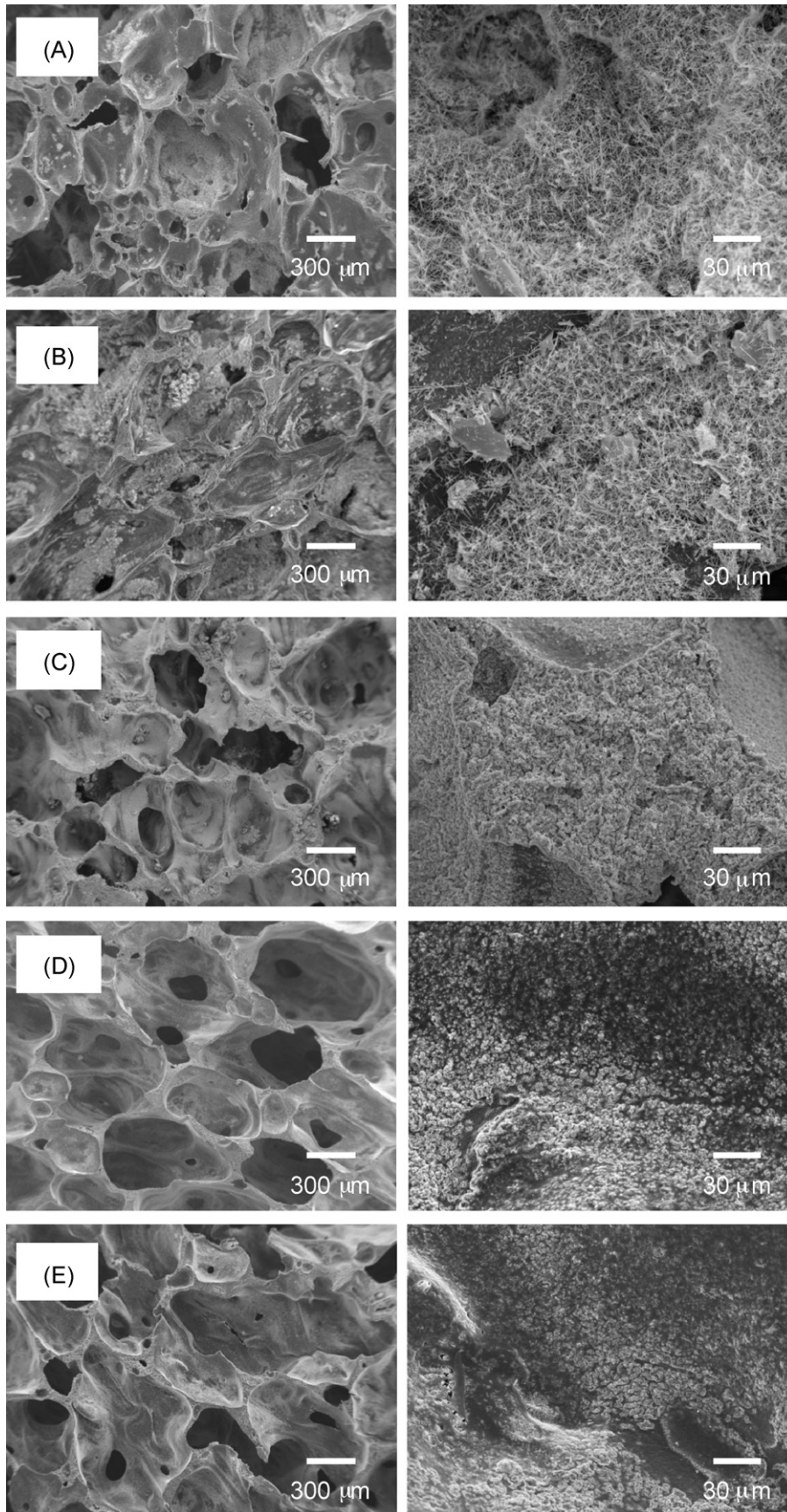
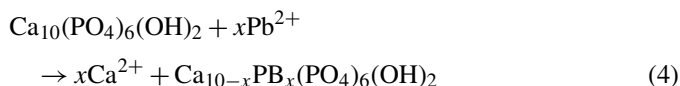
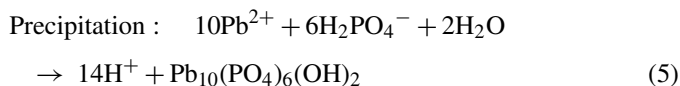
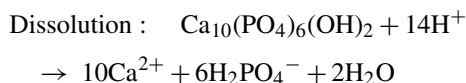


Fig. 7. SEM images of HAp (50 wt.%) / PU composite foams experimented at various pH values: (A) pH 2; (B) pH 3; (C) pH 4; (D) pH 5; (E) pH 6.

anism is the adsorption of  $\text{Pb}^{2+}$  ions on the HAp surfaces and following ion exchange reaction between  $\text{Pb}^{2+}$  ions adsorbed and  $\text{Ca}^{2+}$  ions of HAp [9]. This ion exchange reaction mechanism is expressed as:



The second mechanism is the dissolution of HAp in aqueous solution containing  $\text{Pb}^{2+}$  ions followed by precipitation of hydroxypyromorphite [ $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HPy], i.e., the dissolution–precipitation mechanism [10,11], which is written as:



In order to investigate the removal mechanism of  $\text{Pb}^{2+}$  ions by HAp/PU composite foams in aqueous solutions at various pH values, SEM images of the composite foam surfaces after the  $\text{Pb}^{2+}$  ion removal experiments were obtained, as shown in Fig. 7. The overall morphology of the composite foams was found to be remained unchanged even after the experiments (left-side images of Fig. 7), while the local surface morphology of composites is quite different, depending on pH value of aqueous solutions (right-side images of Fig. 7). At pH 2–3, the needle-shaped precipitants were observed on the composite surfaces, whereas the surface morphologies (domain structures dispersed in PU matrix) of the composites experimented at pH 5–6 is almost identical with that of the original composite foam. It indicates that the removal mechanism of  $\text{Pb}^{2+}$  ions by the HAp/PU composite foams is quite different between pH 2–3

and pH 5–6. The magnified SEM image (Fig. 8A) and associated EDS spectrum (Fig. 8C) of the composite foams experimented at pH 2–3 support the fact that HAp is firstly dissolved out from the composite foams and, simultaneously, the needle-shaped HPy crystallites are formed and precipitated on the composite surfaces. On the other hand, the SEM image (Fig. 8B) and related EDS spectrum (Fig. 8C) of the composite foams experimented at pH 5–6 confirm that the domains dispersed in the PU composite matrix are mostly composed of HPy. It reveals that the removal of  $\text{Pb}^{2+}$  ions by the composite foams at pH 5–6 stems from the mechanism of adsorption of  $\text{Pb}^{2+}$  ions on the HAp/PU composite surfaces and following ion exchange reaction between  $\text{Pb}^{2+}$  ions in aqueous solution and  $\text{Ca}^{2+}$  ions of HAp in the composites. On the other hand, it is conjectured that the lowest removal amount of  $\text{Pb}^{2+}$  ions at pH 4 (Fig. 6) is caused by the competition of above two removal mechanisms, i.e., HAp is hardly dissolved out owing to relatively low concentration of  $\text{H}^+$  ions and the ion exchange reaction from HAp to HPy is also limited by the competing concentrations of  $\text{H}^+$  and  $\text{Pb}^{2+}$  ions. This is confirmed that the magnified SEM image (right-side of Fig. 7C) of the composite foam experimented at pH 4 is rather different from the images of the composite foams experimented at pH 2–3 and 5–6. Overall, it is valid to conclude that the removal mechanism of  $\text{Pb}^{2+}$  ions by the HAp/PU composite foams is varied, depending on the pH value in aqueous solution: the mechanism of dissolution of HAp and precipitation of HPy is dominant at lower pH 2–3, the mechanism of adsorption of HAp and ion exchange between  $\text{Ca}^{2+}$  of HAp and  $\text{Pb}^{2+}$  in aqueous solution prevails at higher pH 5–6, and two mechanisms compete at pH 4.

### 3.5. Adsorption isotherm

The equilibrium adsorption performance of the HAp/PU composite foam with 50 wt.% HAp content for  $\text{Pb}^{2+}$  ions was

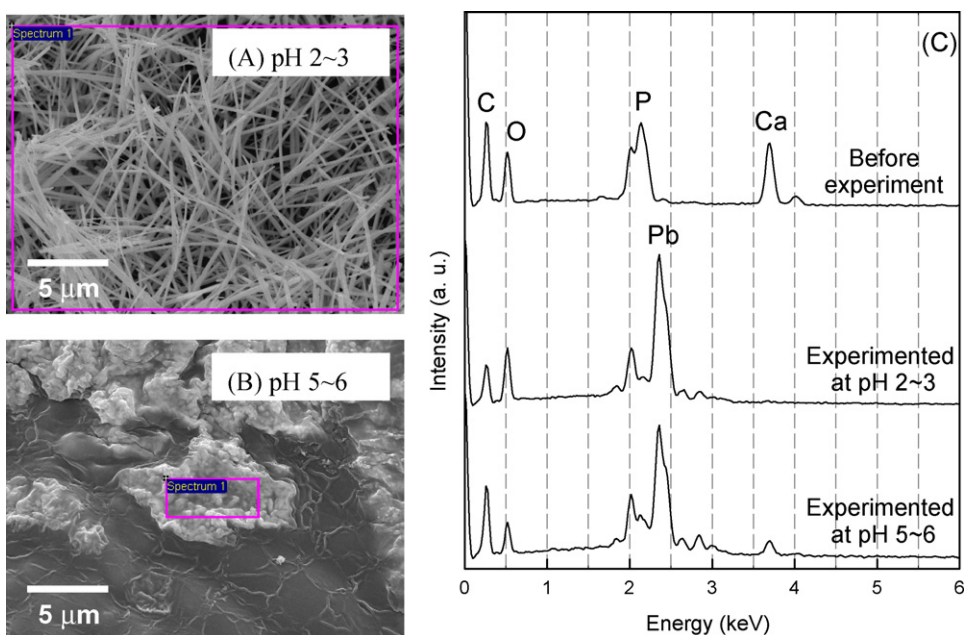


Fig. 8. Magnified SEM images (A and B) and associated EDS spectra (C) of HAp (50 wt.)/PU composite foams experimented at various pH values of 2–3 and 5–6.

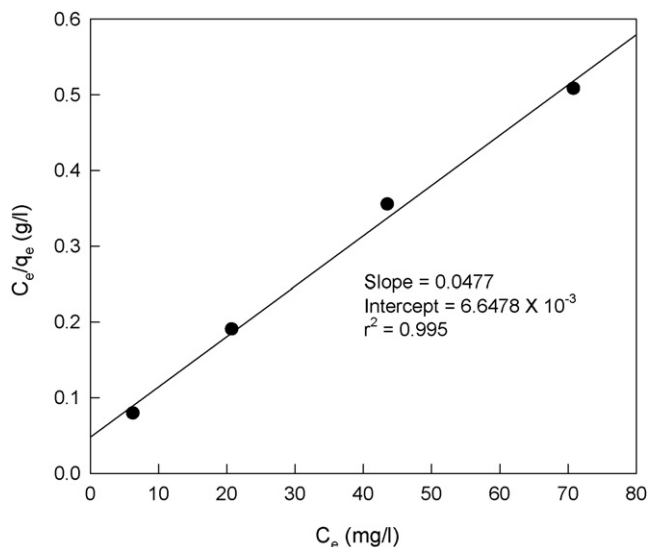


Fig. 9. Langmuir isotherm plot for the adsorption of Pb ions by HAp (50 wt.%) / PU composite foam in aqueous solution at pH 5.

examined at pH 5 where the ion exchange mechanism is dominant for the removal of  $Pb^{2+}$  ions from aqueous solution. Several mathematical adsorption isotherm models have been developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration. The most widely used model is the Langmuir adsorption isotherm model, which is expressed as [20]:

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

where  $C_e$  (mg/l) is the equilibrium concentration,  $q_e$  (mg/g) the amount adsorbed per amount of adsorbent (mg/l),  $K_e$  the Langmuir equilibrium constant (l/mg), and  $q_{max}$  is the amount of adsorbate adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage. The linear plot of  $C_e/q_e$  against  $C_e$  based on the Langmuir equation gives a fairly good linear fit to the adsorption isotherms for the composite foam, as shown in Fig. 9, yielding  $q_{max}$  (150 mg/g) and  $K_e$  (0.139 l/mg) from the slope and intercept, respectively. The  $q_{max}$  of 150 mg/g for the composite with 50 wt.% HAp estimated by the Langmuir isotherm model matches well with the value (170 mg/g) obtained by the pseudo-second order kinetic model, within the experimen-

tal error. When the  $q_{max}$  value of the HAp/PU composite foam with 50 wt.% HAp was compared with those of other adsorbents (Table 1), the adsorption capability of the composite foam with 50 wt.% HAp content for  $Pb^{2+}$  ions was found to be comparable or even superior to others adsorbents. This result reveals that HAp/PU composite foams are effective adsorbents for  $Pb^{2+}$  ions from wastewater.

#### 4. Conclusions

The aim of this work was to synthesize HAp/PU composite foams and to investigate their removal ability of  $Pb^{2+}$  ion from aqueous solutions with a variety of initial  $Pb^{2+}$  ion concentrations and pH values of 2–6. We have prepared two composite foams with 20 and 50 wt.% HAp contents, which displayed well-developed open pore structures. The composite foam with 50 wt.% HAp exhibited the higher removal efficiency of  $Pb^{2+}$  ions due to higher adsorption capacity, compared to the composite with 20 wt.% HAp, and showed the slower removal kinetics owing to the less uniform dispersity of HAp particles. The removal rate of  $Pb^{2+}$  ions by the composite foam with 50 wt.% HAp content was slower with increasing the initial  $Pb^{2+}$  ion concentration in aqueous solutions. The removal mechanism of  $Pb^{2+}$  ion was very sensitive to the pH value in aqueous solution, although the removed amount of  $Pb^{2+}$  ions at different pH value was nearly same within the experimental error. The mechanism of dissolution of HAp in the composite foam and precipitation of HPy was dominant at lower pH 2–3, the mechanism of adsorption of  $Pb^{2+}$  ions on the composite surface and ion exchange reaction between  $Ca^{2+}$  of HAp and  $Pb^{2+}$  ions in aqueous solution was dominant at higher pH 5–6, and neither removal mechanisms was dominant at pH 4. The equilibrium removal process of  $Pb^{2+}$  ions by the composite foam at pH 5 was described well with the Langmuir isotherm model. The maximum adsorption capacity of the composite foam with 50 wt.% HAp was found to be 150 mg/g, indicating that the HAp/PU composite foam is a promising adsorbent for  $Pb^{2+}$  ions from aqueous solution at higher pH values of 5–6 and could be used as a purifier for wastewater.

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Table 1  
Adsorption capacities of  $Pb^{2+}$  ions by various adsorbents

Adsorbents	$q_{max}$ (mg/g)	Reference
Activated carbon	31.2	[3]
Polyacrylamide/bentonite composite	33.12	[21]
Polyacrylamide/zeolite composite	58	[21]
PHEMA/chitosan membranes	68.81	[22]
Wheat bran	87	[5]
Palm shell activated carbon	95.2	[6]
Natural phosphate	115.3	[2]
HAp (50 wt.%) / PU composite foam	150	This work
Activated phosphate	155	[2]

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