Adsorption of Uranium by Chitin Phosphate and Chitosan Phosphate*

Takashi Sakaguchi, Takao Horikoshi and Akira Nakajima

Department of Chemistry, Miyazaki Medical College,
Kiyotake, Miyazaki 889-16, Japan

Received January 8, 1981

The adsorption of uranium by chitin phosphate and chitosan phosphate was investigated to obtain information on uranium recovery from aqueous systems, especially sea water and uranium mine waste water. The adsorption of uranium by chitin phosphate and chitosan phosphate was much greater than copper, cadmium, manganese, zinc, cobalt, nickel, magnesium and calcium. The adsorption of uranium was very rapid during the first 10 min and was affected by pH of the solution, temperature, granule radius and the co-existence of carbonate ion. The amounts of uranium adsorbed on the adsorbents increased linearly as the external uranium concentration increased. Uranium adsorbed on chitin phosphate easily desorbed with diluted sodium carbonate solution. On the other hand, uranyl and cobalt ions were separated from each other by using chitin phosphate.

The recovery of uranium from aqueous systems, especially from sea water and uranium mine waste water, merits attention because a severe shortage of uranium is expected by the end of the century. We have hitherto investigated the accumulation of heavy metal elements for the recovery or removal from aqueous systems using various microorganisms and biological substances.1~14) Previous papers from this laboratory7,8) have shown that phosphorylated derivatives of chitin and chitosan can accumulate large amounts of heavy metals such as copper, cadmium and cobalt from aqueous systems. The development of the excellent adsorbent for uranium using chitin, a most abundant organic resource, and its derivatives is of special significance.

The present investigation was undertaken to obtain fundamental information on the recovery of uranium from aqueous systems using chitin phosphate and chitosan phosphate.

* Studies on the Accumulation of Heavy Metal Elements in Biological Systems. Part XX.

MATERIALS AND METHODS

Phosphorylation of chitin and chitosan. Chitin phosphate was synthesized as follows: Ten grams of powdered chitin, 100 g of urea, and 5 g of 100% orthophosphoric acid were added into 100 ml of dimethylformamide. The mixture was reacted at 150°C for 1 hr. After cooling, the reaction mixture was filtered. The precipitate was washed thoroughly with deionized water and freeze-dried. The yield of chitin phosphate was 6.5 g and its phosphorous content was 2.48%. On the other hand, chitosan phosphate was prepared as follows: Twenty grams of chitosan, 100 g of urea, and 20 g of 100% orthophosphoric acid were added into 200 ml of dimethylformamide. The mixture was reacted in the same conditions as described above. The yield of chitosan phosphate was 18.3 g and its phosphorous content was 5.84%.

Adsorption experiments.

i) Adsorption of uranium. The adsorbents were suspended in 200 ml of the solution containing uranium. Uranium was given as uranyl nitrate. Unless otherwise stated, the adsorption experiments were performed under the following conditions: 20 mg of adsorbent (granule radius, 0.177~0.250 mm), pH value of 5.0, room temperature, and 10⁻⁴ M of uranium concentration. After adsorption, the adsorbents were collected by filtration. Then the residual uranium in the filtrate was determined by spectrophotometry using Arsenazo III.

ii) Selective adsorption of metal ions. Fifty milligrams of adsorbents were suspended in 50 ml of the solution containing equivalent concentrations of Mg²⁺, Ca²⁺,
Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, and UO_{2}^{2+} with constant stirring at room temperature. Each cation was given as its nitrate in the concentration of 10^{-4} M. The pH value of the solution was adjusted to 5.0. After 1 hr, the adsorbents having taken up metal ions were collected by filtration. Then the residual metal ions except uranyl ion in the solution were determined by atomic absorption spectroscopy with Hitachi 170-30.

Desorption of uranium adsorbed on chitin phosphate. After 10^{-5} mol of uranium had been adsorbed on 30 mg of chitin phosphate, the column (6 x 7 mm) was washed thoroughly with deionized water and then desorbed with linear gradient of sodium carbonate solution from 0 to 2 M at a flow rate of 2 ml/min. Fractions of 5 ml were collected and determined uranium by spectrophotometry.

Chromatographic separation between uranyl and cobalt ions by chitin phosphate. The solution containing uranyl and cobalt ions (each ion, 2 x 10^{-5} mol) was adsorbed on a column (10 x 168 mm) of chitin phosphate. The column was washed well with deionized water and then eluted with 0.5 and 6 N hydrochloric acid. The eluents were collected and determined cobalt and uranium.

RESULTS AND DISCUSSION

Selective adsorption of metal ions by chitin phosphate and chitosan phosphate

As pointed out in a previous paper, chitin phosphate and chitosan phosphate captured strongly heavy metal ions, Cu^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, and Ni^{2+}. The present experiment was made to investigate selective adsorption among several ions by chitin phosphate and chitosan phosphate from the solution containing equivalent concentration of Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and UO_{2}^{2+}. As shown in Table I, the relative order of magnitude of metal ions adsorption by the adsorbents appeared to be UO_{2}^{2+} > Cu^{2+} > Cd^{2+} > Mn^{2+} > Zn^{2+} > Mg^{2+} > Co^{2+} > Ni^{2+} > Ca^{2+} for chitin phosphate and UO_{2}^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+} > Ca^{2+} for chitosan phosphate. As described above, the adsorption of uranyl ion by each adsorbent was much greater than those of other metal ions. These results indicate that chitin phosphate and chitosan phosphate have the excellent ability to accumulate uranium from aqueous systems.

Factors affecting uranium adsorption by chitin phosphate and chitosan phosphate

The adsorption of uranium by chitin phosphate and chitosan phosphate was very rapid during the first 10 min following the addition of uranium. An analysis of some factors that influence uranium adsorption such as pH, temperature, co-existing ions is necessary for the purpose of understanding the recovery of uranium from aqueous systems.

It is apparent from Fig. 1 that the amounts of uranium adsorbed by both chitin phosphate and chitosan phosphate during 10 min were maximum at pH 5, whereas above and below pH 5, there was rapid decrease in uranium adsorption. As described above, it was recognized that the amount of uranium adsorbed on both chitin phosphate and chitosan phosphate differs markedly with the pH value of the solution.

In the temperature range from 20 to 80°C,

Table I. Selective Adsorption of Metal Ions by Chitin Phosphate and Chitosan Phosphate

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Mg^{2+}</th>
<th>Ca^{2+}</th>
<th>Mn^{2+}</th>
<th>Co^{2+}</th>
<th>Ni^{2+}</th>
<th>Cu^{2+}</th>
<th>Zn^{2+}</th>
<th>Cd^{2+}</th>
<th>UO_{2}^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption ratio*</td>
<td>Chitin phosphate</td>
<td>11.1</td>
<td>0.0</td>
<td>16.7</td>
<td>10.9</td>
<td>9.7</td>
<td>28.3</td>
<td>14.7</td>
<td>17.2</td>
</tr>
<tr>
<td>Chitosan phosphate</td>
<td>15.3</td>
<td>12.3</td>
<td>28.2</td>
<td>19.7</td>
<td>17.9</td>
<td>43.0</td>
<td>29.8</td>
<td>37.2</td>
<td>76.1</td>
</tr>
</tbody>
</table>

* ((Initial metal concentration - Residual metal concentration in the solution)/Initial metal concentration in the solution) x 100
Adsorption of Uranium by Chitin Phosphate and Chitosan Phosphate

Fig. 1. Effect of Initial pH on the Adsorption of Uranium by Chitin Phosphate and Chitosan Phosphate. Twenty milligrams of chitin phosphate (○) and chitosan phosphate (●) were suspended in 200 ml of the solution containing $10^{-4}$ M of uranium for 10 min. The pH of the solution was adjusted with 1 N HCl or 1 N NaOH solution.

Fig. 2. Relation between log $K_d$ and $1/T$.

Chitin phosphate (20 mg) was suspended in 200 ml of the solution containing $10^{-4}$ M of uranium for 10 min.

Fig. 3. Effect of the External Uranium Concentration on the Adsorption of Uranium by Chitin Phosphate and Chitosan Phosphate. Twenty milligrams of chitin phosphate (○) and chitosan phosphate (●) were suspended in 200 ml of the solution containing a desired amount of uranium for 6 hr.

The amounts of uranium adsorbed by chitin phosphate increased with increasing temperature. It is evident from Fig. 2 that the logarithm of the distribution coefficient, $K_d$ (concentration of uranium adsorbed/residual uranium concentration) decreased linearly with increasing the reciprocal of temperature. The enthalpy of uranium adsorption was estimated from the slope of the curve to be 17.9 kJ/mol. These results suggested that the adsorption of uranium by chitin phosphate was endothermic reaction.

With increasing the granule radius of the adsorbent, the amounts of uranium adsorbed increased and reached a plateau below the granule radius of 0.177~0.250 mm. In general, as the adsorbent with larger granule radius is better for the practical use, it is considered that chitin phosphate with the granule radius of 0.177~0.250 mm is best for the recovery of uranium from aqueous systems.

It can be noted from Fig. 3 that the amounts of uranium adsorbed by both chitin phosphate and chitosan phosphate (mg uranium/g adsorbent) increased linearly as the external uranium concentration increased. The concentration factors (uranium in the adsorbent/uranium in the solution) of the adsorbents were as follows: chitin phosphate 9460, chitosan phosphate 9600. When the external uranium concentration was 100 $\mu$M, 1.23 mol of uranium was combined with 1 mol of phosphoryl group of chitin phosphate, assuming that uranium was only combined with phosphoryl group of the adsorbent. Similarly
in the case of chitosan phosphate, 0.53 mol of uranium was combined with 1 mol of phosphoryl group of the adsorbent. The amounts of uranium adsorbed by chitin phosphate and chitosan phosphate (mg uranium/g adsorbent) decreased as the amount of the adsorbent increased. When the amount of adsorbent was 20 mg, 92.7% of uranium existing in the external solution was accumulated by chitin phosphate and 1.17 mol of uranium was combined with 1 mol of phosphoryl group of the adsorbent. In the case of chitosan phosphate, 95.8% of uranium was accumulated and 0.51 mol of uranium was combined with 1 mol of phosphoryl group.

In order to obtain basic information on the recovery of uranium from sea water by chitin phosphate, the effect of carbonate ion on the adsorption of uranium was examined. It is considered that uranium in sea water exists mainly as the complex ions, $\text{UO}_2\text{(CO}_3\text{)}_2^-$ or $\text{UO}_2\text{(CO}_3\text{)}^2$. It is apparent from Fig. 4 that the amounts of uranium adsorbed by both chitin phosphate and chitosan phosphate were little affected by sodium hydrogencarbonate in the concentration range from 0 to 0.3 mM. However, the high presence of carbonate ions in the uranium solution had the tendency to retard uranium adsorption. From the uranium solution co-existing 2.34 mM of sodium hydrogencarbonate, which is the same carbonate concentration of natural sea water, chitin phosphate could adsorb about 35,000 ppm of uranium, but chitin could not accumulate large amounts of uranium.

**Desorption of uranium adsorbed on chitin phosphate**

As described above, chitin phosphate and chitosan phosphate have the ability to adsorb large amounts of uranium from aqueous systems. To obtain practical information on recovery of uranium using chitin phosphate and chitosan phosphate, the following experiments were carried out. Firstly, the desorption of uranium adsorbed on chitin phosphate was examined. After uranium of $10^{-5}$ mol had been adsorbed on chitin phosphate and then desorbed with linear gradient of sodium carbonate from 0 to 2 M. It is evident from Fig. 5 that uranium adsorbed on chitin phosphate was easily desorbed with dilute sodium carbonate solution. As described in the next chapter, uranium adsorbed on chitin phosphate was desorbed with 6 N HCl, but it was difficult to desorb uranium with dilute hydrochloric acid below 6 N.

**Separation between uranium and cobalt by using chitin phosphate**

Secondary, the separation between uranium and cobalt by using chitin phosphate was examined. A desired amount of NaHCO$_3$ was added into the solution containing $10^{-4}$ M of uranium. Twenty milligrams of chitin (●) and chitin phosphate (○) were suspended for 2 hr in 200 ml of the solution mentioned above. The pH of the solution was adjusted to 8.0.
Adsorption of Uranium by Chitin Phosphate and Chitosan Phosphate

After $2 \times 10^{-5}$ mol of uranium and cobalt had been adsorbed on chitin phosphate column (10 x 168 mm) and then eluted with 0.5 and 6 N HCl. ○ shows Co$^{2+}$ and ●, UO$_2^{2+}$.

and other metal, cobalt using chitin phosphate was examined. After $2 \times 10^{-5}$ mol of uranium and cobalt had been adsorbed on chitin phosphate, these ions were eluted with 0.5 N and 6 N HCl. It is observed from Fig. 6 that uranyl and cobalt ions were separated from each other with hydrochloric acid by using chitin phosphate.

Thus far, it is evident from the results of the present study that chitin phosphate and chitosan phosphate have ability to accumulate relatively large amounts of uranium from aqueous systems. And it has also been shown that the adsorption of uranium varies with some factors such as pH, temperature, external uranium concentration, amount of adsorbent and co-existence of carbonate ion. Uranium adsorbed on chitin phosphate easily desorbed with dilute sodium carbonate solution. Along with the present basic research, further developmental studies are being directed toward the recovery of uranium from aqueous systems, especially sea water and uranium mine waste water by chitin phosphate and chitosan phosphate.

REFERENCES