Recovery of uranium from uranium refining waste water by using immobilized persimmon tannin

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Some attempts were made to examine the practical conditions for uranium recovery from uranium refining waste water. The adsorbent recovered uranium highly effectively, and the uranium adsorption was affected by pH, temperature, and uranium concentration of uranium refining waste water. The adsorbent also recoverd uranium effectively in column system. The adsorbent aquires better mechanical properties and can be used repeatedly in the uranium adsorption-desorption cycles.

Introduction

The recovery and removal of nuclear elements, such as uranium and thorium, from aqueous systems has recently become the center of a wide interest in exploiting undeveloped energy sources and environmental control. Previously, we found that the immobilized persimmon tannin has an extremely high affinity for uranium and can adsorb 1.71 g of uranium per g adsorbent from aqueous systems, and also showed that the adsorbent would be applicable to recover and removal of uranium from contaminated resources.[1]

In this paper, some attempts were made to recover and remove uranium from uranium refining waste water sampled at the uranium mine in Ningyo-toge by using the immobilized persimmon tannin and some practical conditions for uranium recovery from the waste water were also examined.

Experimental

Materials

The immobilized persimmon tannin was prepared as described previously.[1]

Uranium removal tests

The waste water was sampled at the uranium mine of the Ningyo-toge.

Removal tests in batch system were conducted as follows: Five milligrams of the

adsorbent were suspended in 100 ml of the waste water supplied 5 ppm of uranium, and the suspension was stirred for 0.5 h at 30 °C.

Removal tests in column system were conducted as follows: (1) Desired amounts of the waste water were passed through a column (diameter 8mm, bed volume 2 - 8 ml) of the adsorbent at the flow rate of 80 - 320 ml/h. (2) Twenty or fifty liters of the waste water were passed through a column (diameter 25mm, bed volume 80 ml) of the adsorbent at the flow rate of 1 - 8 liter/h.

Determination of metals

Uranium in aqueous system (ppm order) was determined by spectrophtometry using Arsenazo(III).[2] Low concentration of uranium (ppb order) was determined by fluorometry using $NaCO_3$-NaF flux.[3] Other metal ions in the waste water were determined by the inductively coupled plasma quantometer (Shimadzu ICPQ-1000II).

The contents of metals in the adsorbent were determined by the neutron activation analysis. The air-dried adsorbents were irradiated at the Japan Atomic Energy Research Institute, in a JRR-4 reactor for 10 min at a thermal neutron flux of 5×10^{13} $n/cm^2 \cdot sec$. After few min (Ca), 1 hr (Mn) and 2-3 days (U) cooled, the irradiated samples were counted with a Ge(Li) detector and a 4,000 channel analyzer. The 228 and 277 KeV gamma rays from ^{239}Np were utilized for the uranium analysis, 846.9 KeV from ^{55}Mn for manganese and 3083 KeV from ^{48}Ca for calcium.

Determination of anions

Anions, such as Cl^-, SO_4^{2-} and NO_3^-, in the waste water were determined by the

ion-chromatography (Shimadzu HIC-6A). The measurement conditions were as follows: column, Shim-pak IC-A1; carrier, 2.5 mM phthalic acid and 2.4 mM tris(hydroxymethyl)-aminomethane (pH 3.96); oven temperature, 40 $^{\circ}$C; pressure, 120 kgf/cm^2; flow rate, 1.5 ml/min; sample amount, 20 μl.

Results and discussion

Basic features of uranium recovery from waste water by immobilized persimmon tannin

Previously it was recognized that the immobilized persimmon tannin can adsorb great amounts of uranium from aqueous systems.[1] However, the adsorption of uranium by the immobilized persimmon tannin was affected by some factors, such as pH of the solution, retention time, and uranium concentration. Therefore, in this section, several conditions for uranium recovery tests, such as pH, temperature, uranium concentration of the waste water, and desorbents, were examined.

The recovery of uranium by the immobilized persimmon tannin was affected by the pH of waste water, and was most effective at around pH 6 (Fig. 1). As shown in Fig. 1, the adsorbent can abundantly recover uranium from the waste water in wide pH region from 5 to 8, which is slightly different from the previous results on the adsorption of uranium from the solution containing uranium only (dashed line).[1] Regardless the pH value of the waste water was varied between 6.5 and 7.5, the high efficiency can be kept in the uranium recovery by the adsorbent in this variation range

of pH.

The recovery of uranium by the immobilized persimmon tannin was strongly affected by the temperature of the waste water, and far less effective at lower temperature below 10 °C (Fig. 2). However, above 30 °C, the uranium was completely recovered. It is evident from Fig. 3 that the logarithm of the distribution coefficient, Kd (concentration of uranium adsorbed/residual uranium concentration), decreased linearly with increasing reciprocal of temperature. The enthalpy of uranium adsorption was estimated from the slope of the curve to be 89.6 kJ/mol. This suggested that the adsorption of uranium by the immobilized persimmon tannin was the endothermic reaction. As shown in previously, the adsorption of gold by the immobilized persimmon tannin also endothermic, which enthalpy was 77.6 kJ/mol.[4] These results indicated that the adsorptin of uranium by the immobilized persimmon tannin is neither by physical adsorption nor an ion-exchange reaction.

Previously, we found that the immobilized persimmon tannin has extremely high ability to adsorb uranium from aqueous systems.[1] As shown in Table 1, the immobilized persimmon tannin could completely recover uranium from the waste water. These results confirmed our previous results and also indicated that the adsorbent can adsorb high amounts of uranium from the waste water.

Recovery of Uranium from Waste Water in Column System

Along with the fundamental results described in above sections, uranium recovery

tests from the uranium refining waste water in column system by using the immobilized persimmon tannin were conducted. For the practical use of uranium recovery and removal by using immobilized persimmon tannin in column systems, some factors were examined.

First, the recovery of uranium from the uranium refining waste water by the immobilized persimmon tannin in bench-scale column system (diameter 8 mm, bed volume 2 ml) at the flow rate of 80 ml/h (Table 2). As a result, uranium in the waste water was completely recovered after 4 liter of the waste water were treated. These results indicates that more than 2,000 times of the bed volume of the column can be treated for the recovery of uranium.

Next, the recovery tests were conducted in larger column system (diameter 26 mm, bed volume 80 ml) at various flow rates as a step of scale-up for practical use. As shown in Table 3, at low flow rate, such as 1 liter/h, uranium in the waste water can be completely recovered by the immobilized persimmon tannin. However, at higher space velocity, such as 4 and 8 liter/h, the recovery efficiencies were decreased. When the waste water passed through a column, temperature of the waste water was increased, and some bubbles broke out, which reduced the effectiveness of uranium adsorption. To avoid the bubble effect, an extra column should be adopted (pre-colum system), and then uranium was completely adsorbed even if at the higher flow rates.

Adsorption of Other Ions in Waste Water

In the waste water, there exists some metal ions and anions except uranium. To

know whether is there any change in these ions after treated with the immobilized persimmon tannin, cations in the adsorbent and anions in the treated waste water were determined. Contents of metal ions and anions in the untreated waste water were listed in Table 4 and 6. From Table 5, it is recognized that metal ions in the waste water, such as Ca^{2+} and Mn^{2+}, were hardly adsorbed by the immobilized persimmon tannin. Table 6 indicated that the concentration of anions also hardly changed after passing through the column.

Repetition Test of Uranium Adsorption-Desorption

Previous results showed that the uranium adsorbed on the immobilized persimmon tannin easily desorbed with very dilute acid solutions.[1] Therefore, 0.1 N HCl was used as desorbent in the repetition test of the uranium adsorption-desorption cycle. The ability of the immobilized persimmon tannin to recover uranium did not decrease after 17 repetitions of the adsorption-desorption cycle in column system (Fig. 3). Thus, the immobilized persimon tannin acquires better mechanical properties and can be used repeatedly in the uranium adsorption-desorption cycles.

Conclusion

Some attempts were made to examine the practical conditions for uranium recovery from uranium refining waste water. The adsorbent recovered uranium highly

effectively, and its uranium adsorption was affected by pH, temperature, and uranium concentration of uranium refining waste water. The adsorbent also recoverd uranium effectively in column system. The adsorbent aquires better mechanical properties and can be used repeatedly in the uranium adsorption-desorption cycles.

References

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Table 1. Recovery of uranium from waste water supplemented uranium

U concentration (ppm)	U recovered (%)
1	100
5	100
10	100
20	100
50	100

Five hundred milliliters of the waste water supplemented with each concentration of uranium were passed through a column (diameter 10 mm, bed volume 8 ml) of the immobilized persimmon tannin at the flow rate of 320 ml/h.

Table 2. Recovery of uranium from waste water by the immobilized persimmon tannin in bench-scale column system

Volume of waste water (ml)	U recovered (%)
4063	100
3769	100

Desired volume of the waste water (pH 7.93, uranium content 11.2 ppb) were passed through a column (diameter 8 mm, bed volume 2ml) of the adsorbent at flow rate of 80 ml/h.

Table 3. Recovery of uranium from waste water by the immobilized persimmon tannin in larger scale column system

Flow rate (liter/h)	U recovery (%)	
1	100	
4	96.8	
	100	(a)
8	82.2	
	100	(a)

Twenty liters of the waste water (uranium content: 15.5 ppb) were passed through a column (diameter 26 mm, bed volume 80 ml) of the adsorbent at each flow rate.

(a) Results in pre-column system.

Table 4. Concentrations of metals in the waste water

Metals	Concentration (ppm)
Ca	67.0
Mg	4.7
Mn	1.5
Sr	0.24

Table 5. Adsorption of cations in the wastewater by the immobilized persimmon tannin

Cation	Metal adsorbed	
	(mg)	(%)
Ca	26.2	1.3
Mn	1.9	4.2

Thirty liters of the waste water were passed through a column (diameter 26 mm, bed volume 80 ml) of the adsorbent at flow rate of 1 liter/h. Metal contents in the adsorbent were determined by the neutron activation analysis.

Table 6. Variation of anions in the waste water before and after the treatment of the immobilized persimmon tannin

Anion	Concentration (ppm)	
	Untreated	Treated
Cl^-	17.1	17.0
SO_4^{2-}	147.8	147.1
NO_3^-	0.44	0.33

Anions in the waste water were determined by the ion-chromatography (Shimadzu HIC-6A). Measurement conditions were as follows: column, Shim-pak IC-A1; carrier, 2.5 mM phthalic acid and 2.4 mM tris(hydroxy-methyl)-aminomethane (pH 3.96); oven temperature, 40°C; pressure, 120 kgf/cm^2; flow rate, 1.5 ml/min; sample amount, 20 μl.

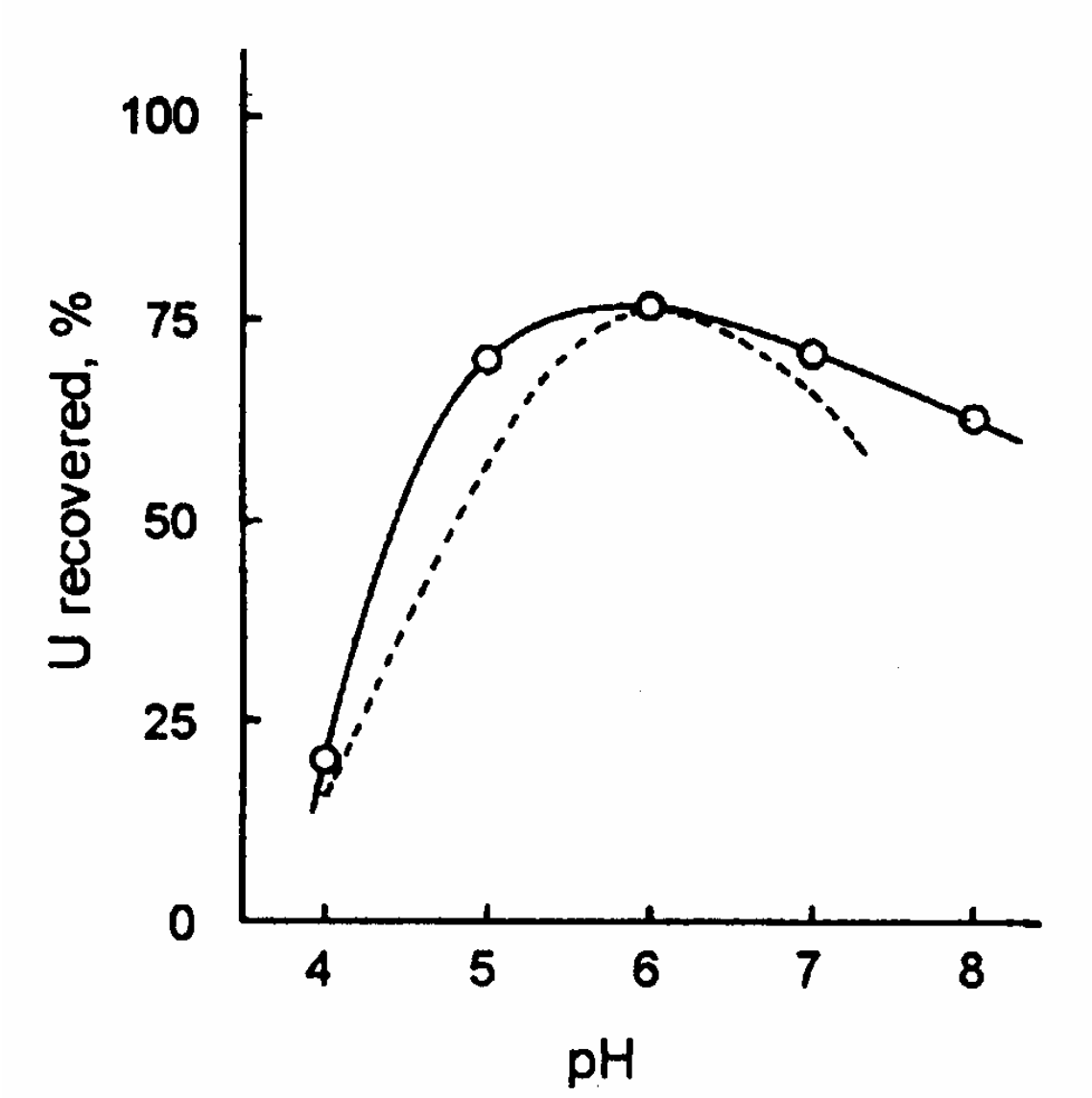

Fig. 1. Effect of pH on the recovery of uranium from the waste water by the immobilized persimmon tannin. Five milligrams of the adsorbents were suspended in 150 ml of the waste water supplemented with 5 ppm of uranium for 0.5 h. Dashed line indicates the previous results on the uranium adsorption from the solution containing uranium only.

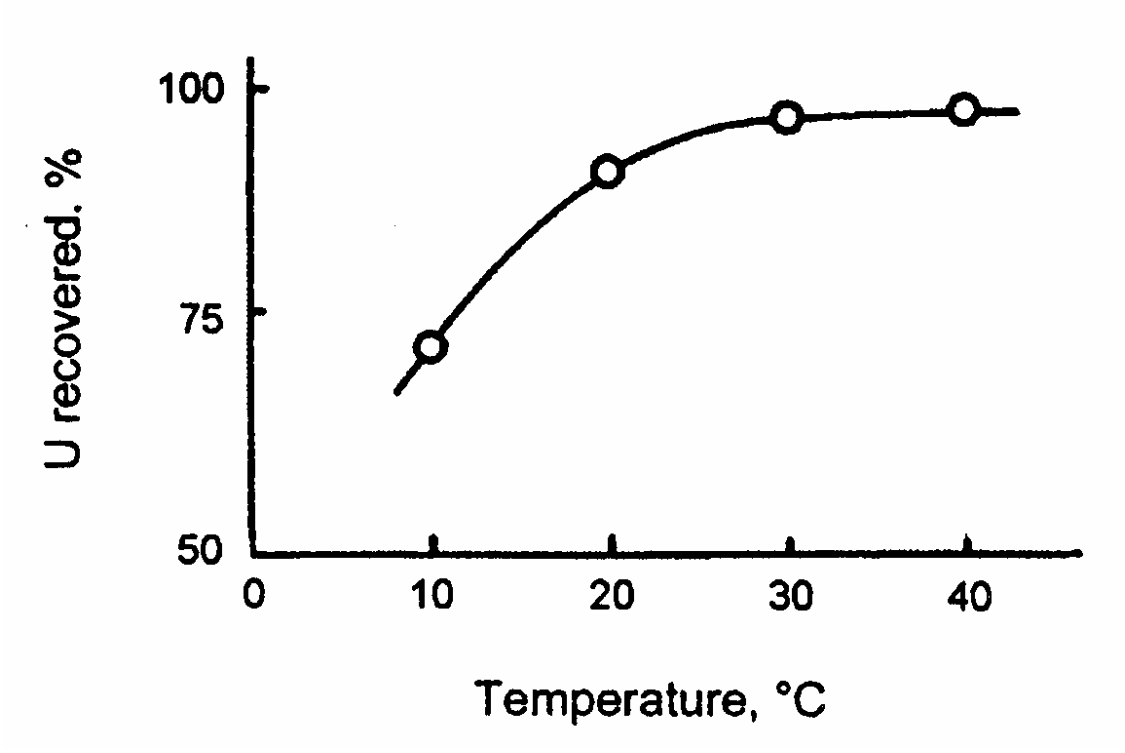

Fig. 2. Effect of temperature on the recovery of uranium from waste water by the immobilized persimmon tannin. Five milligrams of the adsorbents were suspended in 150 ml of the waste water supplemented with 5 ppm of uranium for 0.5 h.

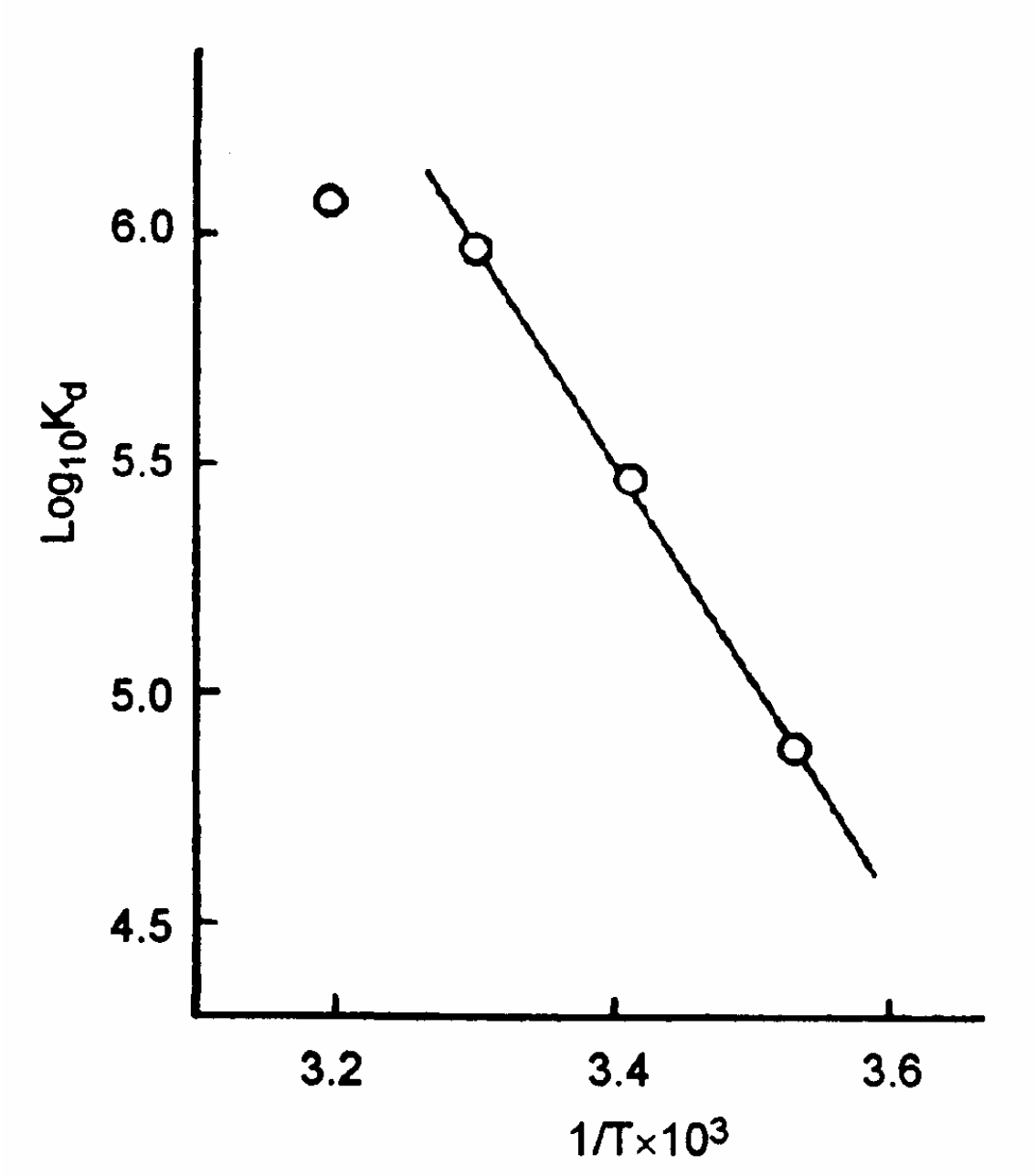

Fig. 3. Relation between log Kd and 1/T.

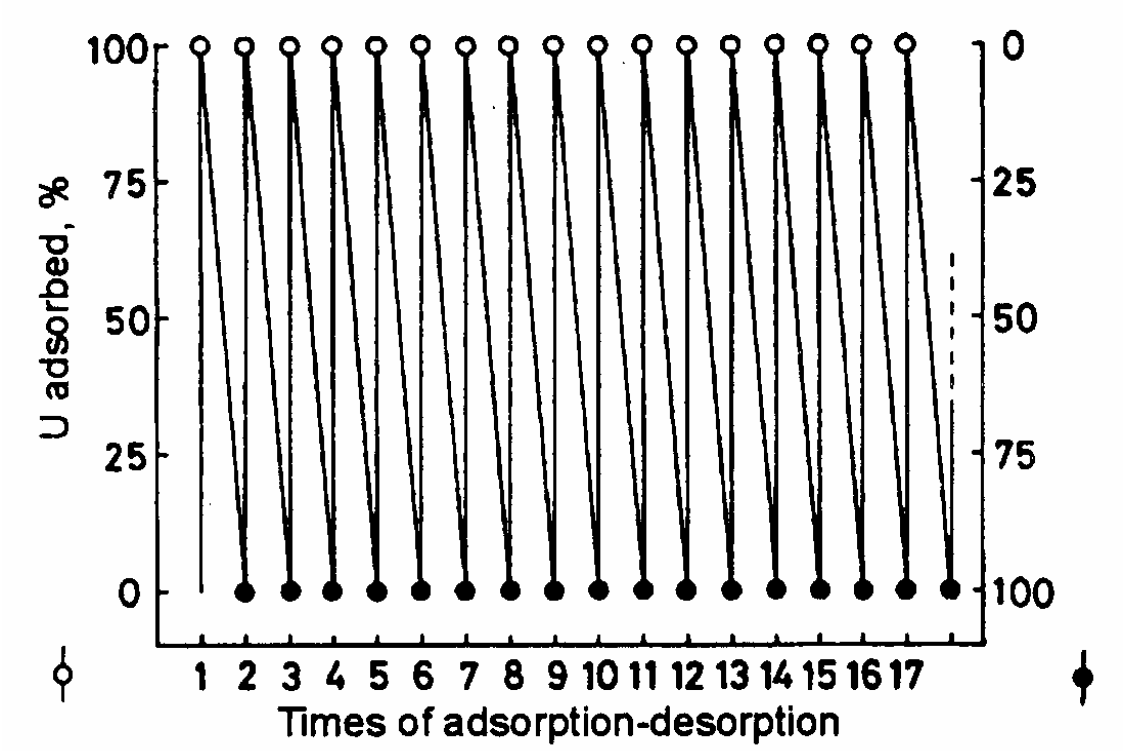

Fig. 4. Repetition test of uranium adsorption(○)-desorption(●) cycle by the immobilized persimmon tannin. Fifty milliliters of the waste water supplemented with 5 ppm of uranium were passed through a column (diameter 8 mm, bed volume 5 ml) of the adsorbent at the flow rate of 200ml/h. Uranium adsorbed was desorbed with 20 ml of 0.1 N HCl at the flow rate of 100ml/h.