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Removal of Chromium from Chromium(VI) Solutions by Adsorption and Reduction Using Immobilized Persimmon Gel

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Abstract: The removal of chromium(VI) from an aqueous solution using persimmon gel was examined. The amount of chromium(VI) removed was strongly affected by the pH of the solution, with all chromium(VI) being removed at pH 2 or lower. However, in a solution containing, 15 mg dry weight of immobilized persimmon gel, the amount of removed chromium(VI) decreased as the pH increased. A part of chromium(VI) was reduced another oxidation stage, mainly chromium(III), by immobilized persimmon gel. The amount of reduced chromium(III) in the solution was increased with decreasing the pH of the solution. As a result, the amount of total chromium removed was maximal at pH 2. The amount of chromium removed were affected by the chromium concentration and the amount of gel. The maximal amount of chromium removed by the column system was also discussed.

Key words: Chromium removal, immobilized persimmon gel, adsorption, Langmuir isotherm, chromium reduction.

1. Introduction

Chromium is used in textile, leather tanning, electroplating, metal finishing industries [1], wood treatment, corrosion control, oxidation and anodizing industries. If high levels of chromium are absorbed by the body, it can generate serious problems and concentration of 100 g/g body wt. can ultimately become lethal [2]. Recently, the main processes for elimination of chromium have been adsorption, reverse osmosis, and chemical reactions that involve reduction and precipitation [1]. Among these processes, adsorption has been shown to be a feasible method for removing traces of chromium from wastewater and many different adsorbents have been tried to remove this toxic metal from wastewater [1-3].

Adsorption is the most effective and widely used technique for the removal of toxic heavy metals from wastewater [4]. Owing to the high cost and difficult procurement of activated carbon, efforts are being directed toward other finding efficient and low cost adsorbent substances [1]. A variety of low cost substances like fly ash, wood charcoal, bituminous coal, bagasse and coconut juice, rice husk carbon, peat, red mud, used black tea leaves, and activated carbon from sugar industrial waste have been examined [5-13].

Previously, microorganisms could be removed many kinds of toxic and useful metals, such as lithium, uranium, thorium, rare earths, and gold from aqueous solution [14-18]. However, microorganisms could remove only small amounts of chromium from the chromium(VI) solution. In other studies, immobilized persimmon gel could be removed gold(III) from hydrogen tetra chloroaurate(III) solution [19]. Further investigations showed that persimmon tannin gel removed chromium(VI) effectively from the chromium(VI) solution [20]. However, the amount of

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adsorbed chromium(VI) and the amount of residual chromium(III) remaining in the solution were not examined in detail [20]. Herein, the removal of chromium from aqueous chromium(VI) solution using immobilized persimmon gel is extended and reported.

2. Material and Methods

2.1 Immobilization of Persimmon Tannin

Commercially available kakishibu (the extracted juice of unripe persimmon fruit, tannin content: 4.0%) was immobilized as follows: one part of glutaraldehyde was mixed with four parts of persimmon tannin. After 2 h, a red-wine-colored homogeneous gel was obtained. The gel was crushed into small particles (less than 60 mesh), washed thoroughly with deionized water, and then used for removal experiments.

2.2 Chromium Removal Experiments

Unless otherwise stated, chromium removal experiments using immobilized persimmon gel were conducted as follows: batch system**:** the gel was suspended with 100 mL of aqueous chromium solution and stirred at room temperature using magnetic stirrer (120 rpm). Chromium was supplied as $K_2Cr_2O_7$ or $Cr(NO_3)_3$. The pH of the solution was adjusted to the desired values with 0.1 mol HNO_3 or NaOH over the range of pH 1-5. The gels were then collected by filtration through a membrane filter (pore size 0.2 μm). Column system: unless otherwise stated, 1,510 mL of gold solution (53.1 mg/L chromium (as $K_2Cr_2O_7$, pH 2) was passed through a column (diameter 8 mm, bedvolume 3.9 mL) of immobilized persimmon gel at a Space Velocity (SV) of 15.7 h^{-1}.

The amounts of removed chromium(VI) were quantified by the diphenyl carbazide method [21] by measuring the absorbance of the solution at 540 nm using spectrophotometer (U-1800, Hitachi). The amounts of removed total chromium were determined by atomic absorption spectrometer (AA-6300, Shimadzu, Kyoto).

3. Results and Discussion

3.1 Effect of pH on Chromium Removal from Aqueous Chromium(VI) Solution Using Immobilized Persimmon Gel

The effect of pH (over the range of pH 1-5) on the removal of chromium(VI) was examined by immobilized persimmon gel from an aqueous solution of chromium(VI) as $K_2Cr_2O_7$ (Fig. 1). The chromium(VI) removal from the potassium bichromate(VI) solution was quantitative at pH 1-2. Above pH 2, rapid decreases in the amount of chromium(VI) removed was observed. In the same solution, the total chromium removal was maximal at pH 2. Above and below pH 2, rapid and gradual decreases of total chromium removal were observed (Fig. 1).

The chromium(VI) (%) remaining in solution increased with increasing the pH of the solution. On the other hand, the amount of reduced chromium(III) in the solution increased as the acidity of the solution decreased. By subtracting the amount of total chromium(%) removed from the amount of removed chromium(VI) (%), the amount of chromium(VI) was reduced to chromium(III) in the solution. Reduced chromium(III) was the chemical species of chromium present in solution at pH 1-2 after removal of chromium(VI). The removal of chromium(VI) using persimmon gel was also investigated [20], however, this is the first finding to clarify the amount of reduced chromium(III) from chromium(VI) in the solution in this system.

Using a solution of chromium(III) nitrate, the role of pH on chromium(III) removal by immobilized persimmon gel was also examined (Fig. 2). The amount of chromium(III) removed increased as the pH of the solution increased. At pH values less than pH 3, this adsorbent could not remove any chromium(III) from solution.

The chemical species of chromium(VI) in the bichromate(VI) solution is mostly hydrogen chromate anion, $HCrO_4^-$ at pH 1-5 [23].

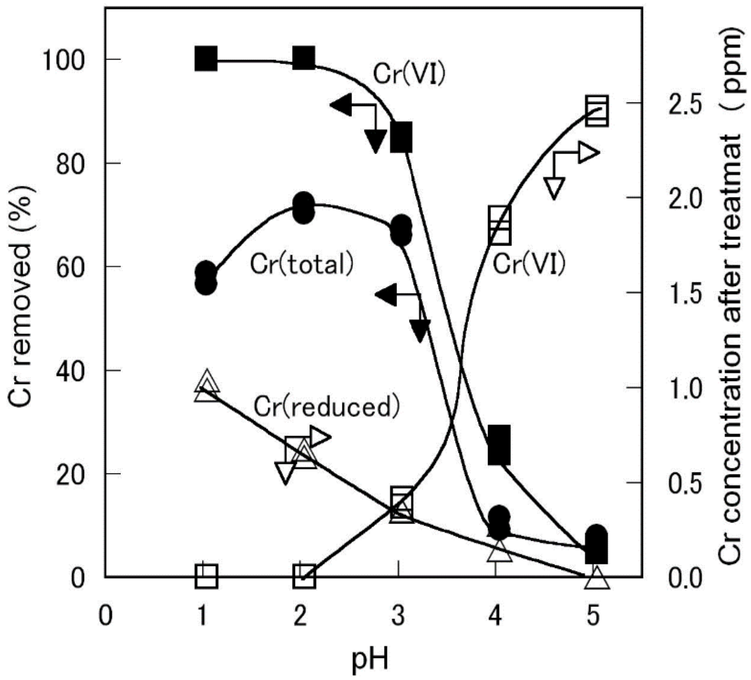

Fig. 1 Effect of pH on the removal and reduction of chromium(VI) from the potassium bichromate(VI) solution using persimmon tannin absorbent.

Adsorbent (15 mg, dry wt. basis) was suspended in 100 mL of the potassium bichromate(VI) solution containing 2.5 ppm of chromium(VI) for 1 h at room temperature, the pH of the solutions was not controlled in all of the experiments.

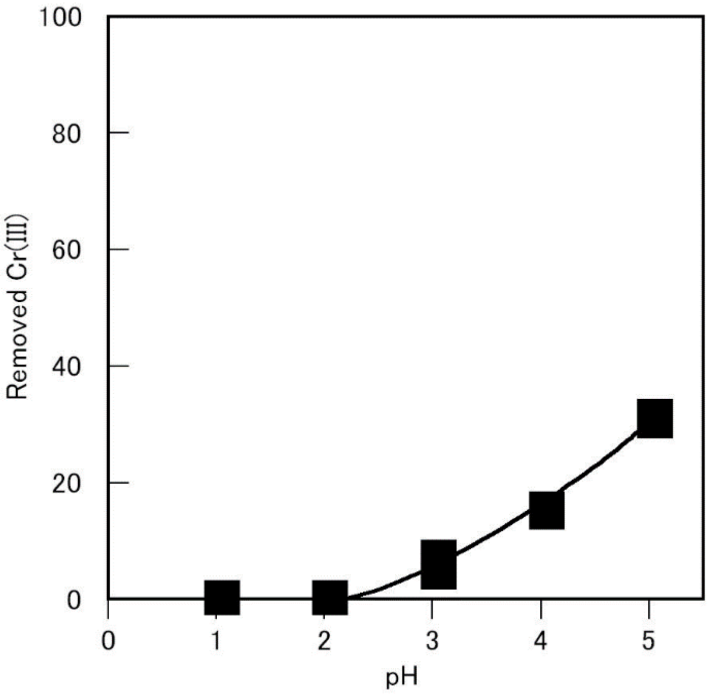

Fig. 2 Effect of pH on the removal of chromium from the chromium(III) nitrate solution by persimmon tannin absorbent.

Adsorbent (15 mg, dry wt. basis) was suspended in 100 mL of the chromium(III) nitrate solution containing 2.5 ppm of chromium(III) for 1 h at room temperature.

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \quad (1)$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \quad (2)$$

It seems reasonable that dichromate anion $Cr_2O_7^{2-}$ was generated from potassium bichromate, followed by hydrolysis generated $HCrO_4^-$. The equilibrium constant of Eq. (1) and acid dissociation constant of Eq. (2) were $10^{-1.68}$ and $10^{-6.45}$, respectively [22]. $HCrO_4^-$ is dominantion between pH 1-5. Chromate anion CrO_4^{2-} is increased and $HCrO_4^-$ is decreased as the pH values of the solution increase up to pH 5. Therefore, the removed chromium(VI) species in this research was mainly in the form of $HCrO_4^-$.

The chemical structure of persimmon tannin was proposed from dimer to pentamer of epigallocatechingallate-epigallocatechingallate-epicatechingallate-epigallocatechin-epigallocatechin-epicatechin [23]. This compound contains two 1,2-dihydroxyphenyl (catechol) and seven 1,2,3-trihydroxyphenyl (pyrogallol) groups, acting as hard bases, in each chemical formula unit [23]. They should combine with $HCrO_4^-$, in similar with CrO_2^{2+} as a hard acid [20], and easily produce chromate ester [24]. Therefore, the removal of chromium(VI) appeared to proceed mainly through esterification of $HCrO_4^-$ and catechol or pyrogallol group in persimmon gel.

On the other hand, this adsorbent has a high tendency toward being a reductant. Additionally, chromium(VI) has high tendency toward accepting electrons, thus, serving as an oxidizing agent. Accordingly, the Fig. 3 is easily generated in acidic solution. In fact, the concentration of reduced chromium(III) increased with the decreasing pH of the solution. About 70% of chromium(VI) was removed by adsorption and 30% of that by reduction at pH 2 from the 2.5 ppm chromium(VI) solution.

3.2 Effect of Chromium Concentration on Chromium Removal from Aqueous Chromium(VI) Solution Using Immobilized Persimmon Gel

When 15 mg (dry wt. basis) of immobilized persimmon gel was used, the removal of chromium(VI) from the aqueous chromium(VI) solution was quantitative at chromium concentrations below 5 ppm (100 μmol) (Fig. 4a). At levels greater than 5 ppm, the ratio of chromium(VI) and total chromium removed with respect to initial chromium (%) decreased as the chromium concentration in the aqueous solution increased. On the other hand, the amount of chromium(VI) and total chromium removal (μmol chromium/g dry wt. adsorbents) increased with increasing concentrations of chromium in the aqueous solution. When the chromium concentration was 1,700 μmol, extremely high chromium of about 4,860 μmol of chromium(VI) and 4,660 μmol of total chromium/g dry wt. persimmon gels was removed, 200 μmol of chromium(VI)/g dry wt. persimmon gels was reduced to chromium(III). The amount of reduced chromium(III) was maximum when the solution

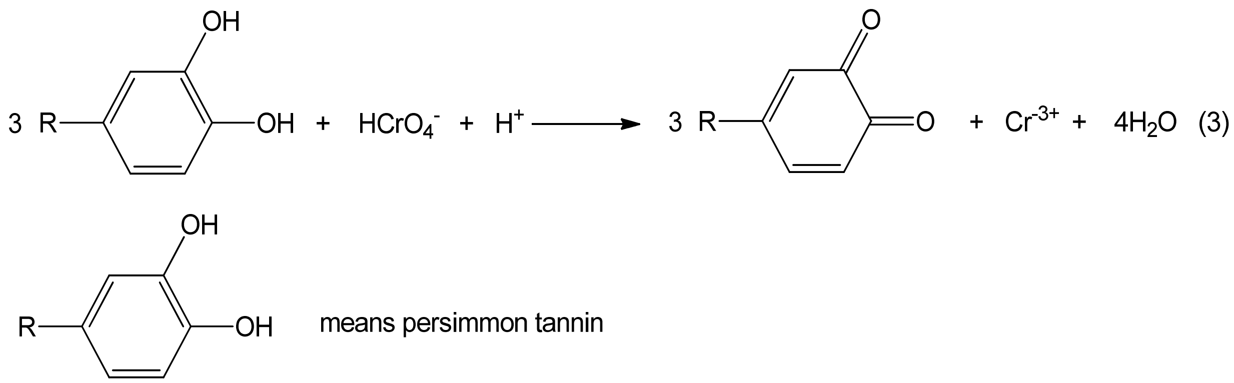

Fig. 3 Oxidation and reduction of persimmon tannin and chromium(VI) in the solution in this system.

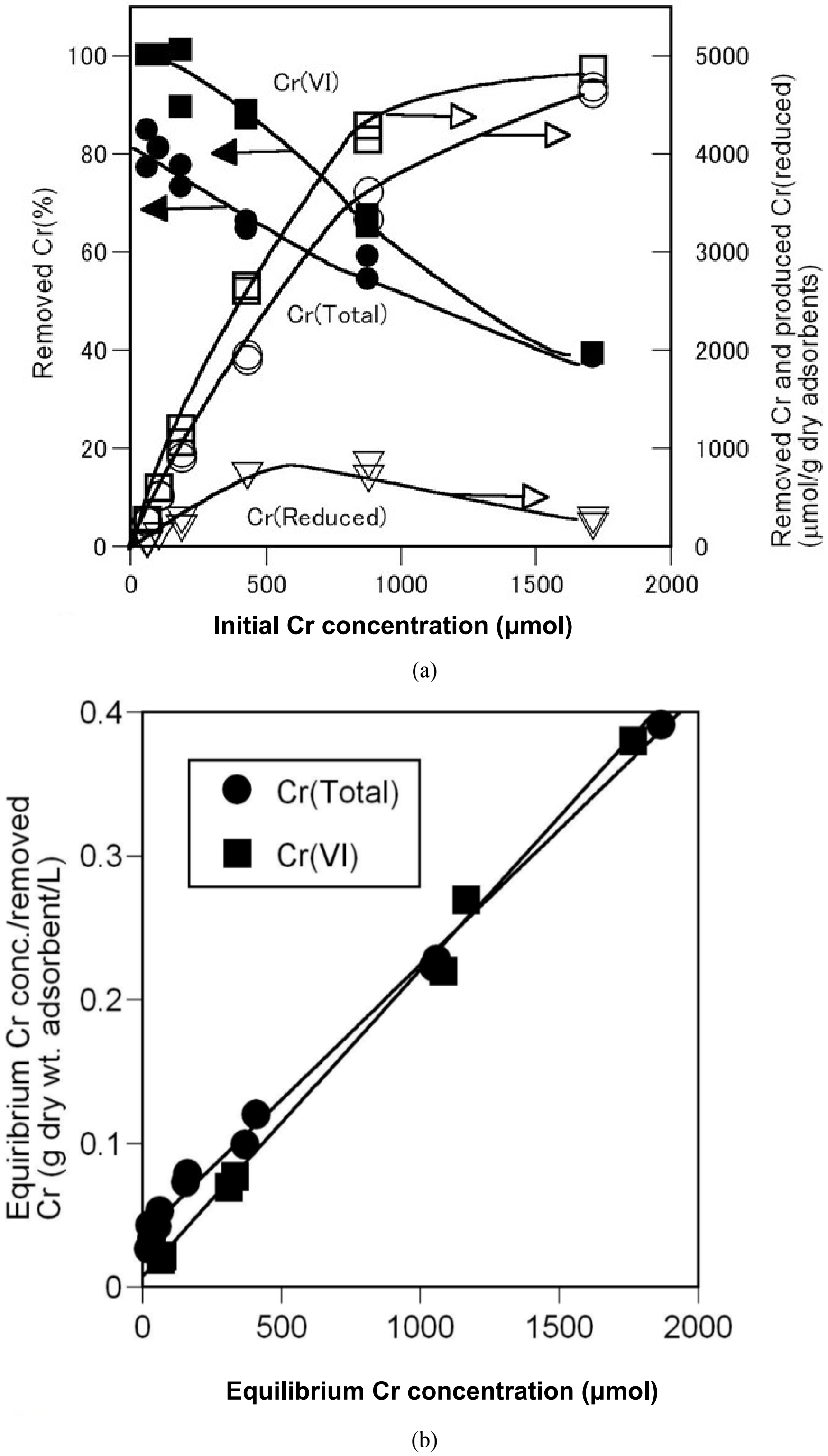

Fig. 4 (a) Effect of chromium concentration on chromium(VI) removal and reduction using immobilized persimmon tannin adsorbent and (b) equilibrium Langmuir isotherm of chromium removal using immobilized persimmon tannin adsorbent.

Adsorbent (15 mg dry wt. basis) was suspended in 100 mL of the solution (pH 2) containing indicated amounts of chromium(VI) for 1 h at room temperature. Symbols: squares, removed chromium(VI), circles, removed chromium (total) and triangles, produced chromium(III).

Table 1 Estimated constants and Q_{max} from the Langmuir isotherm.

	M	*N*	Q_{max} (μmol/g dry wt. adsorbents)
Chromium(VI)	$(2.13 \pm 0.01) \times 10^{-4}$	$(7.97 \pm 4.74) \times 10^{-3}$	4,700 ± 140
Chromium (total)	$(1.88 \pm 0.02) \times 10^{-4}$	$(3.64 \pm 0.45) \times 10^{-2}$	5,320 ± 40

* Experimental condition was same as Fig. 4.

contained 400-800 μmol chromium. Under these conditions, a gradual decrease in removal from the solutions containing above 800 μmol and below 400 μmol of chromium was observed.

3.3 The Effect of the Adsorbent Amount on Chromium Removal Using Immobilized Persimmon Gel

The quantity of immobilized persimmon gel adsorbent was varied over the range of 5-50 mg dry weight and measured chromium removal from a solution that initially contained 5 ppm of chromium (Fig. 5). As the amount of adsorbent increased, the amount of chromium removed (expressed as μmol chromium/g dry wt. adsorbents) decreased, while the ratio of chromium removed/initial chromium concentration (%) increased. The amounts of total reduced chromium increased as the amount of adsorbent increased, however, the amounts of reduced chromium (expressed as μmol/g dry wt. adsorbents) were maximal in the presence of 10-15 mg of absorbents (dry wt. basis).

3.4 Time Course of Chromium Removal with Immobilized Persimmon Gel

Adsorption of chromium(VI) was very rapidly and reached equilibrium within two hours (the residual

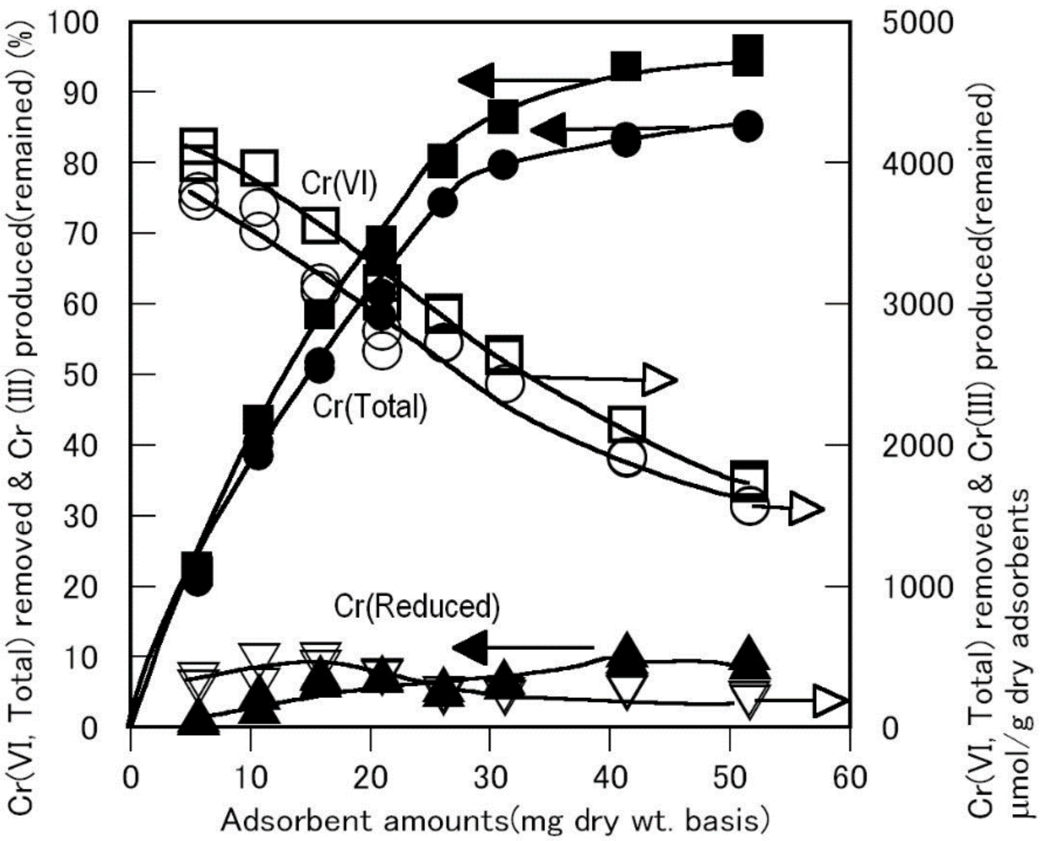

Fig. 5 Effect of adsorbent amounts on chromium removal and reduction using immobilized persimmon tannin gel.
The adsorbent was suspended in 100 mL of the solution (pH 2) containing 5 ppm of chromium(VI) for 1 h at room temperature. Symbols were same as Fig. 4.

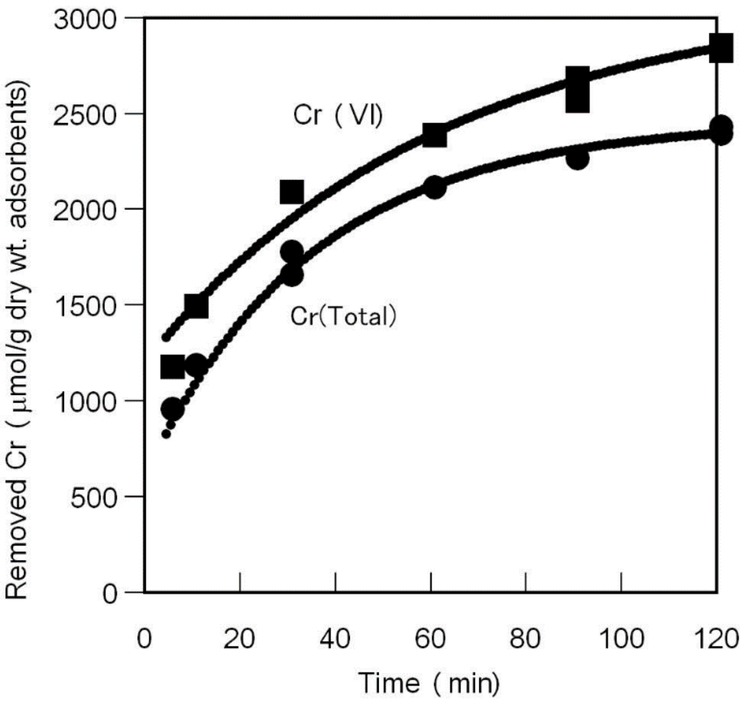

Fig. 6 Time course of chromium removal and reduction using immobilized persimmon tannin gel.

Adsorbent (15 mg, dry wt. basis) was suspended in 100 mL of the potassium bichromate(VI) solution containing 25 ppm of chromium(VI) at room temperature, the Q_e value used was determined by experimental data.

concentration of chromium(VI) at 17 hours was almost same as that at 2 hours) (Fig. 6). Reduction of chromium(VI) was a little lower than the adsorption. These results were fitted by an adsorption model using time-dependent Langmuir equation (Eq. (4)) [25]:

$$Q = Q_e\left(1 - e^{-jt}\right) \quad (4)$$

Where, Q is the amount of the chromium removed, Q_e is the removal amount of equilibrium, $j = k_a + k_d$, k_a is the adsorption rate constant, and k_d is the desorption rate constant [25]. The values of Q_e and j were estimated to be 2,450 μmol/g dry wt. adsorbents and 2.83×10^{-2} min^{-1} for chromium (total) removal (adsorption and reduction), and 3,110 μmol/g adsorbents and 1.61×10^{-2} min^{-1} for chromium(VI) removal (adsorption).

3.5 Selective Removal of Chromium(VI) by Immobilized Persimmon Gel

To determine which heavy metal ions can be most readily removed by immobilized persimmon gel at pH 2, selective removal of heavy metal ions from a solution containing 4×10^{-5} mol Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and $HCrO_4^-$ was examined. As shown in Fig. 7, the relative degree of heavy metal ion adsorption by immobilized persimmon gel was observed to be $HCrO_4^-$ >> others, indicating that immobilized persimmon gel can remove chromium(VI) more readily than other heavy metal ions.

3.6 Chromium Removal Capacity with Immobilized Persimmon Gel

To obtain basic information about the recovery of chromium(VI) using persimmon gel, chromium(VI) removal was examined using column system. As shown in Table 2, immobilized persimmon gel adsorbed 313 mg (6.01 mmol) and reduced 64 mg (1.23 mmol) chromium(VI)/g dry wt. of immobilized persimmon gel.

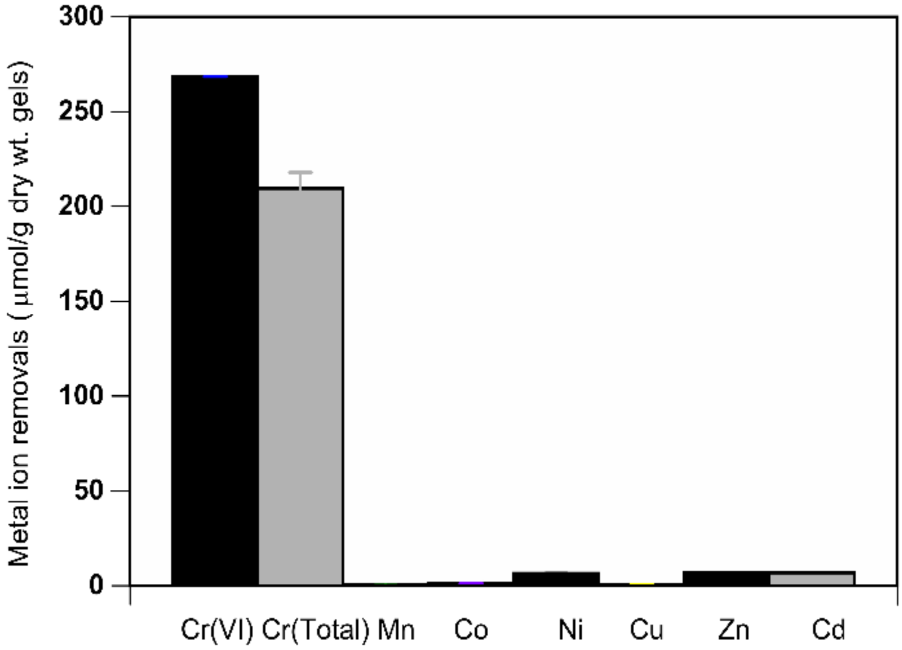

Fig. 7 Selective removal of heavy metals by immobilized persimmon gel.

Adsorbent (15 mg, dry wt. basis) was suspended in 100 mL of a solution (pH 2) containing 4×10^{-5} mol Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and $HCrO^{4-}$ for 1 h at room temperature.

Table 2 Removal of chromium from aqueous chromium(VI) solution using immobilized persimmon gel by column system.

	Removed (%)	Removed (μmol/g dry wt. gels)
Chromium(VI)	89.7	7,280
Chromium (total)	69.2	5,620

* Chromium(VI) solution (53.1 ppm, 1.51 L, pH 2) was eluted on the persimmon gel column (bed volume 3.9 mL, 0.19 g dry wt. basis) at a space velocity of 15.7 h^{-1}.

4. Conclusions

The removal of chromium using persimmon tannin adsorbent was strongly affected by the pH of the solution and at pH 2, chromium(VI) removal was quantitative. At higher pH values, chromium(VI) removal decreased dramatically. The amount of total chromium removed was maximal at pH 2, however, those were decreased with increasing or decreasing the pH of the solution. The positively charged protonated hydroxy groupes of the persimmon tannin and negatively charged hydrogen chromate ions were bonded at low pH. Additionally, the amount of reduced chromium increased in low pH solutions.

The removal of chromium using immobilized persimmon tannin adsorbent was strongly affected by the initial chromium concentration of the solution. Immobilized persimmon tannin adsorbent can remove chromium quantitatively from the solution containing lower 5 ppm chromium(VI), however, the ratio of the amount of chromium(VI) removed with respect to the initial chromium(VI) concentration was decreased with increasing the initial chromium(VI) concentration. The amount of chromium (μmol/g dry wt. adsorbents) was increased with increasing the initial chromium(VI) concentration of the solution. When the initial chromium(VI) concentration was 1,700 μmol, persimmon gel removed 4,860 μmol of chromium(VI). The amount of chromium removed was fitted with Langmuir's isotherm. The amount of reduced chromium was maximal from the solution containing 400-800 μmol chromium(VI).

The removal of chromium using immobilized persimmon tannin absorbents was strongly affected by the adsorbent amounts. The ratio of the amount of removed chromium(VI) per that of initial chromium(VI) was increased with increasing the amount of adsorbent, however, the proportion of chromium removed (μmol/g dry wt. adsorbent) was decreased with increasing the amount of adsorbent. The amount of total reduced chromium was increased with increasing the amount of adsorbent, however, the amounts of reduced chromium (μmol/g dry wt. adsorbent) was maximal using 10-15 mg of adsorbent (dry wt. basis).

Adsorption of chromium(VI) was very rapidly and reached equilibrium within two hours. Reduction of chromium(VI) was a little slower than adsorption. The time course of chromium removal was fitted by an adsorption model using time-dependent Langmuir equation.

The maximum amount of chromium(VI) removed was examined by a column system. Immobilized persimmon gel adsorbed 313 mg (6.01 mmol) and reduced 64 mg (1.23 mmol) chromium(VI)/g dry wt. of immobilized persimmon gel.

On the basis of this research, the removal of chromium(VI) from the aqueous systems should be feasible in the near future.

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