

Removal of Chromium(VI) from Aqueous Solution Using Persimmon Tannin Gel and Subsequent Recovery as Chromium(III)

Tomonobu Hatano, Takehiko Tsuruta*

Department of Life and Environmental Science, Hachinohe Institute of Technology, Hachinohe, Japan

Email: *tsuruta@hi-tech.ac.jp

How to cite this paper: Hatano, T. and Tsuruta, T. (2018) Removal of Chromium(VI) from Aqueous Solution Using Persimmon Tannin Gel and Subsequent Recovery as Chromium(III). *International Journal of Geosciences*, 9, 593-605.

<https://doi.org/10.4236/ijg.2018.910035>

Received: August 24, 2018

Accepted: October 8, 2018

Published: October 11, 2018

Copyright © 2018 by authors and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

This study herein was investigated the removal of chromium(VI) from an aqueous solution using persimmon tannin gel and its subsequent recovery as chromium(III). At pH 2, Cr(VI) was effectively adsorbed (~80% adsorption) and <20% of this Cr(VI) was reduced to Cr(III) in the solution. More specifically, all adsorbed Cr(VI) from a 50 ppm solution was reduced to Cr(III) on the persimmon gel within 10 min. Although desorption of the Cr(III) species was challenging at 30°C, it was increased upon increasing the temperature and was quantitatively desorbed in the presence of 1 M hydrochloric acid under reflux. In addition, although the quantity of retained Cr(VI) on the tannin gel increased upon increasing the chromium concentration of the original aqueous solution, all the desorbed chromium was successfully reduced to Cr(III). Finally, Cr(VI) removal and recovery as Cr(III) was repeated effectively 8 times using the same persimmon tannin gel sample, thus demonstrating the recyclability of this system.

Keywords

Cr(VI) Removal, Cr(III) Recovery, Persimmon Tannin Gel, Reduction, Adsorption, Desorption

1. Introduction

Chromium is commonly employed in the textile, leather tanning, electroplating, metal finishing, wood treatment, corrosion control, oxidation, and anodizing industries [1]. This can be an issue, as the absorption of high levels of chromium by the body can generate serious health issues, with a concentration of 100 µg/g body wt. being potentially lethal [2]. Currently, the main processes for the eli-

mination of chromium are adsorption, reverse osmosis, and chemical reactions that involve reduction and precipitation [1]. Among these processes, adsorption is a feasible method for removing traces of chromium from wastewater [1] and many adsorbents have been examined for this purpose [2] [3].

In this context, adsorption is the most effective and widely used technique for the removal of toxic heavy metals from wastewater [4]. Although activated carbon has been commonly used for this purpose, it is limited by its high cost and limited availability [1]. To address these issues, various low-cost substances, such as fly ash [5], wood charcoal [6], bituminous coal [7], bagasse and coconut juice [8], rice husk carbon [9], peat [10], red mud [11], used black tea leaves [12], activated carbon from industrial sugar waste [13], and sugarcane bagasse [14] have been examined.

It was previously demonstrated that microorganisms can remove many toxic and useful metals, such as lithium [15], uranium [16], thorium [17], rare earth metals [18], and gold [19] from aqueous solutions. Additionally, immobilized persimmon tannin gel removes gold(III) from a hydrogen tetrachloroaurate(III) solution [20]. Although microorganisms can remove small amounts of chromium from a chromium(VI) solution, the quantities of chromium removed using persimmon tannin gel are significantly greater than those removed using microbial cells [21]. The effects of pH, Cr(VI) concentration, quantities of cell, and process time on the removal of Cr(VI) have also been reported [22]. However, to date, the recovery of chromium from adsorbed Cr in persimmon gel has not been examined. Thus, It was herein reported the removal of Cr(VI) from an aqueous solution following reduction to Cr(III) and effect of temperature on desorption of chromium from adsorbed Cr(VI) using persimmon tannin gel; its subsequent recovery as Cr(III); and recycling removal-desorption of Cr.

2. Material and Methods

2.1. Immobilization of Persimmon Gel

Commercially available kakishibu (an extract naturally fermented from the juice of un ripe persimmon fruit, tannin content, 4.0%) was immobilized as follows. One part of formalin (35% aqueous formaldehyde solution) was mixed with four parts of the above kakishibu solution. After 2 h, a dark red homogeneous gel was obtained. This gel was then crushed into small particles (diameter 150 - 300 μm) and washed thoroughly using deionized water prior to use in the Cr(VI) removal experiments.

2.2. Adsorption and Desorption of Chromium from a Chromium(VI) Solution Using Persimmon Gel

An aqueous solution of Cr(VI) in the form of $\text{K}_2\text{Cr}_2\text{O}_7$ (10 mL, 50 ppm) at pH 2.0 (adjusted using 0.1 M HCl) was passed through a column of persimmon gel (diameter 8 mm; bed volume, 19.3 mL). Desorption was then attempted under both acidic and basic conditions. Under acidic conditions, desorption was car-

ried out by passing a 0.1 M HCl solution (600 mL) followed by a 1 M HCl solution (400 mL) through the column. In contrast under basic conditions, the solutions of 0.1 M Na₂CO₃ (300 mL), 1 M Na₂CO₃ (700 mL), and 0.1 M NaOH (300 mL) were passed through the column. As the persimmon gel was soluble in 1 M NaOH, this solution was not employed during the desorption experiments.

The quantity of Cr(VI) removed by the persimmon gel was then determined using the previously reported diphenyl carbazide method [23] and measuring the absorbance of the solution at 540 nm using a UV-Vis spectrophotometer (U-1800, Hitachi). Finally, the quantities of removed total chromium were determined by atomic absorption spectrometry (AA-6300, Shimadzu, Kyoto, Japan).

2.3. Effect of Temperature on the Desorption of Chromium from Persimmon Gel

A sample of persimmon gel (31.5 mg, dry wt. basis) was added to a solution of potassium dichromate(VI) (100 mL) containing 50.0 ppm Cr(VI) and stirred for 1 h at 30°C. The gels were then collected by filtration through a membrane filter (pore size 0.2 µm). For each experiment, the amount of adsorbed Cr(VI) was 86.9% ± 0.2% and the amount of reduced Cr(III) in the solution was 11.8% ± 0.4% based on the original Cr(VI) solution. The recovered gels were then added to a 1 M HCl solution (100 mL) and stirred for 1 h at the desired temperature (*i.e.*, between 30°C and reflux). Finally, the quantities of removed Cr(VI) and total chromium in the filtrate were quantified using the above-mentioned method.

2.4. Variations in Chromium(VI) Removal and Chromium Oxidation State with Time

A sample of the adsorbent (15 mg, dry wt. basis) was suspended in a solution of potassium dichromate(VI) (10 mL) containing 50 ppm (1.0 mM) Cr(VI) at 30°C for the desired time between 5 min and 24 h. After the appropriate time, the quantities of removed Cr(VI) and total chromium in the filtrate were quantified using the above-mentioned method.

The oxidation state of the chromium species adsorbed on the persimmon gel was then investigated using X-ray absorption fine structure (XAFS) spectroscopy. The X-ray absorption fine spectra were collected at the BL14B2 beamline at the Spring-8 facility in Hyogo, Japan. All measurements were conducted at the Cr K-edge and data were collected in transmission and fluorescence modes for the standard and chromium-adsorbed samples, respectively, between 5660 and 7000 eV. The standard solutions, employed herein were aqueous solutions of Cr(VI) in the form of K₂Cr₂O₇ (2500 ppm) and Cr(III) in the form of Cr(NO₃)₃ (5000 ppm). The chromium-adsorbed gel samples were collected by filtration through a membrane filter (pore size 0.2 µm) as described above for determination of chromium removal from the potassium dichromate(VI) solution by persimmon gel.

2.5. Effect of Chromium(VI) Concentration on the Removal and Oxidation State of Chromium in Persimmon Gel

A sample of the adsorbent (15 mg, dry wt. basis) was suspended in a solution (pH 2.00) containing the desired Cr(VI) concentration (*i.e.*, 50 - 1000 ppm, 10 mL) for 1 h at 30°C. The quantities of removed Cr(VI) and total chromium in the filtrate were determined as described previously.

The oxidation state of the chromium adsorbed on the persimmon gel was then determined by X-ray absorption fine structure XAFS. These X-ray absorption fine spectra were collected at the BL9A beam line at the High Energy Accelerator Research Organization (KEK) in Tsukuba, Ibaraki, Japan, and measurements were carried out as described above but with an energy range of 5500 - 7100 eV.

2.6. Recycling of the Gel Adsorbent and Recovery of Chromium as Chromium(III)

An aqueous solution (1 L) containing 10 ppm Cr(VI) (190 μM) at pH 2.00 was passed through a column (bed volume, 3.8 mL) of persimmon gel (202 mg, dry wt. basis) at a space velocity of 15.8 h^{-1} . The chromium-adsorbed gels sample was then heated in 1 M HCl (100 mL) at reflux for 1 h using a batch system. Following the successful desorption of chromium from the gel, this adsorption-desorption cycles was repeated 8 times (9 cycles in total) to confirm the possibility of recycling of this system. The quantities of Cr(VI) and total chromium in the solution were then determined quantified using the above-mentioned method.

3. Results and Discussion

3.1. Chromium Adsorption/Desorption from a Chromium(VI) Solution Using Persimmon Gel

We initially investigated the extent of chromium adsorption/desorption from a Cr(VI) solution using persimmon gel. As previously reported, the amount of chromium removed from solution using persimmon gel was strongly affected by the pH of the solution [21]. More specifically, we found that a pH of 1 - 2 was optimal for our studies, as this pH resulted in the quantitative removal of Cr(VI) from solution, and any further increase in pH resulted in decreased adsorption [21]. In addition, the quantity of total chromium removed was maximised at pH 2 [21]. We therefore examined the adsorption of chromium at pH 2, while the desorption of chromium from the persimmon gel column was examined using both acidic and basic conditions. As indicated in **Figure 1** and **Figure 2**, the majority of Cr(VI) present in the solution was successfully adsorbed on the persimmon gel column (86.8% for a 49.1 ppm Cr(VI) solution and 86.5% for 54.3 ppm Cr(VI) solution), and a percentage of this Cr(VI) was reduced to Cr(III) in solution (*i.e.*, 13.2% and 13.5% respectively). Furthermore, Cr(III) was not adsorbed under these conditions [21]. We also found that relatively small quantities of chromium were desorbed under acidic conditions (16.0%) using 0.1 M

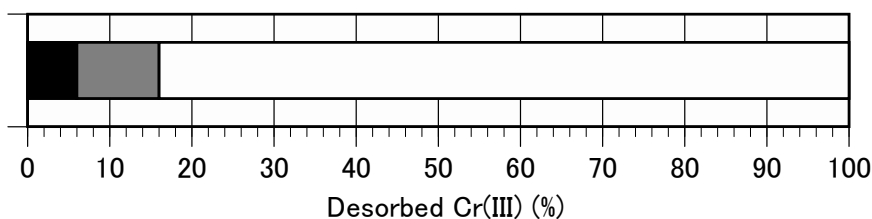


Figure 1. Desorption of chromium from persimmon gel using dilute hydrochloric acid. Black; Desorbed Cr(III) by 0.1M HCl, Gray; Desorbed Cr(III) by 0.1 M HCl, White; Undesorbed Cr.

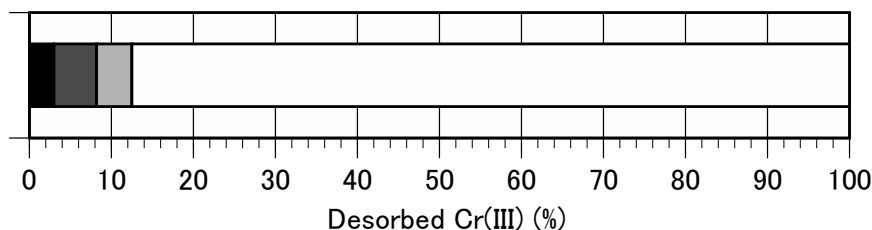


Figure 2. Desorption of chromium from persimmon gel using dilute sodium carbonate and sodium hydroxide solution. Black; Desorbed Cr(III) by 0.1M Na₂CO₃, Dark gray; Desorbed Cr(III) by 1 M Na₂CO₃, Light gray; Desorbed Cr(III) by 0.1 M NaOH, White; Undesorbed Cr.

and 1 M HCl solutions (Figure 1), and under basic conditions (12.5%) using 0.1 M, 1 M Na₂CO₃ solutions or 0.1 M NaOH solution (Figure 2) at 30°C. Moreover, we found that 100% of the desorbed chromium had been reduced to Cr(III).

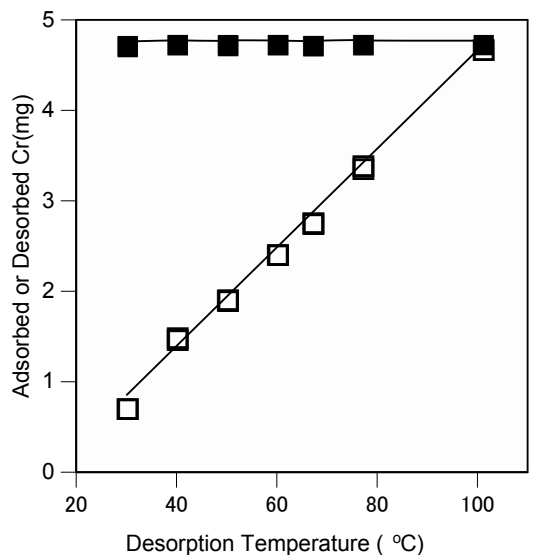
3.2. Effect of Temperature on the Desorption of Chromium from Persimmon Gel

As described above, the quantity of desorbed chromium was rather low at 30°C and slightly greater quantities of chromium were desorbed under acidic conditions compared to under basic conditions. Thus, we moved on to examine the effect of temperature on chromium desorption under acidic conditions. As shown in Figure 3(a), the degree of chromium removal increased significantly with increasing temperature, and the majority of adsorbed chromium (*i.e.*, 99.1%) was successfully desorbed under reflux conditions. Furthermore, all adsorbed Cr(VI) was reduced to Cr(III).

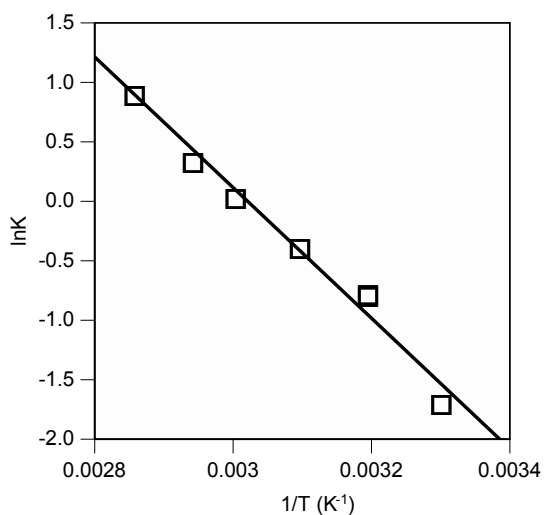
The relationship between the reciprocal of temperature and the natural logarithm of the equilibrium constant is shown in Figure 3(b). As indicated from this plot, the desorption of adsorbed chromium from persimmon gel using hydrochloric acid obeys the Van't Hoff equation,

$$\ln K = -\Delta H^0 / RT + \Delta S^0 / R \quad (1)$$

where K is the equilibrium constant (the ratio of desorbed/residual chromium), ΔH^0 is the enthalpy change (J·mol⁻¹), R is the gas constant (8.314 J·K⁻¹·mol⁻¹), T is the temperature (K), and ΔS^0 is the entropy change (kJ·K⁻¹·mol⁻¹) [24]. The enthalpy change was therefore estimated from the slope of the line to be



(a)



(b)

Figure 3. Effect of temperature on the desorption of chromium from persimmon gel containing adsorbed Cr(VI). Closed; Cr (adsorbed (mg)), Opened; Cr (desorbed (mg)).

$45.6 \text{ kJ}\cdot\text{mol}^{-1}$, which indicates that the desorption of chromium using dilute hydrochloric acid was an endothermic reaction. Furthermore, the entropy change was estimated to be $0.137 \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Moreover, as all desorbed chromium was in the form of Cr(III), it was clear that reduction had taken place on the persimmon gel prior to desorption.

3.3. Effect of Time on Chromium(VI) Removal from Solution Using Persimmon Gel and on the Chromium Oxidation State

The effect of time on both the chromium oxidation state and on Cr(VI) removal from solution using persimmon gel were then examined. As shown in **Figure 4(a)**, the removal of Cr(VI) was rapid with equilibrium being reached within 10 min when a sample of the adsorbent was suspended in the potassium dich-

romate (VI) solution at 30°C. Indeed, ~90% of Cr(VI) was absorbed by the persimmon gel, with 10% of that being reduced to Cr(III) in solution.

As Cr(III) is not adsorbed by persimmon gel below pH 2 [21], it was clear that all chromium adsorption observed herein was in the form of Cr(VI). Therefore, to confirm the variation in chromium oxidation state with time, the adsorbed chromium was analyzed by XAFS. The Cr K X-ray absorption edges were measured for Cr(VI) in a $K_2Cr_2O_7$ standard and for Cr(III) in a $Cr(NO_3)_3$ standard, where the presence of a sharp pre-edge peak at 5992 eV corresponds to Cr(VI) and a broad signal at ~6008 eV corresponds to Cr(III). However, as shown in **Figure 4(b)**, no signal at 5992 eV was observed in the XAFS spectrum after 10 min,

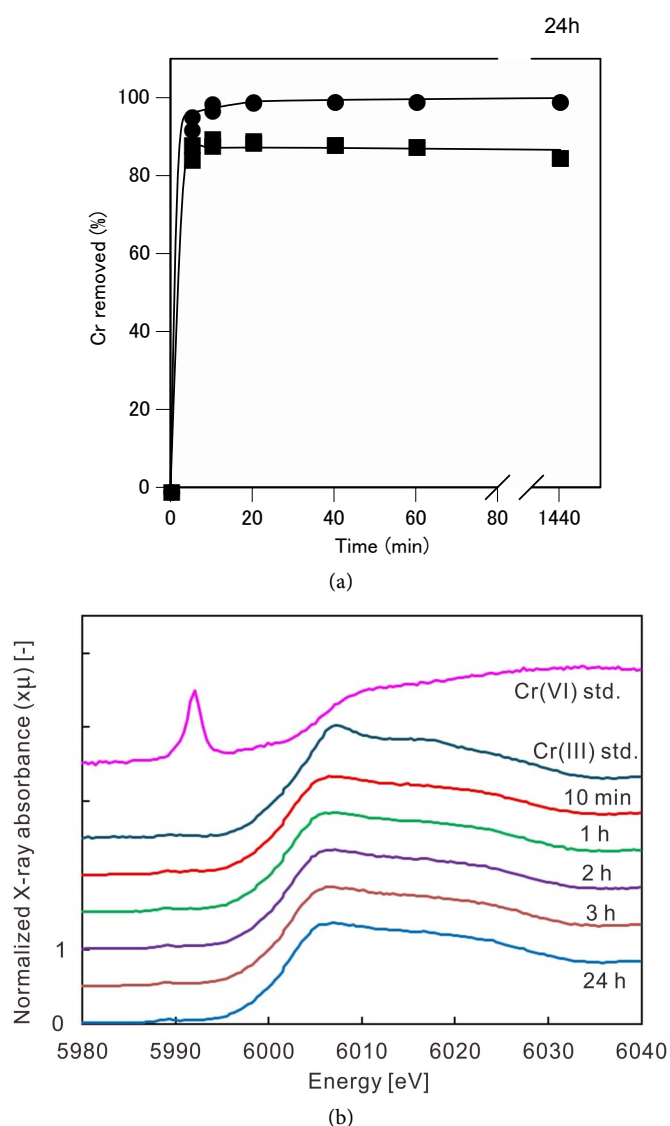


Figure 4. Effect of time on the removal of chromium from the potassium dichromate (VI) solution using the persimmon gel absorbent. (a) Removal of Cr(VI) with time. (b) Variation in the XAFS spectra with time. A sample of the adsorbent (15 mg, dry wt. basis) was suspended in the potassium dichromate (VI) solution (10 mL) at 30°C. Circles; removed Cr(VI), squares; removed chromium (total).

with the presence of a broad signal at ~6008 eV indicating that all adsorbed Cr(VI) had been reduced to Cr(III) within this time.

3.4. Effect of Chromium(VI) Concentration on the Removal and Oxidation State of Chromium in Persimmon Gel

The effect of the Cr(VI) concentration on both the removal of chromium and on the oxidation state of chromium in persimmon gel was then examined. As shown in **Figure 5(a)**, the percentage of Cr(VI) removal from the aqueous solution was quantitative at initial Cr(VI) concentrations <400 ppm (7.7 mM). However, above 400 ppm, the degree of Cr(VI) and total chromium removal decreased at higher initial chromium concentrations. Furthermore, the quantity of Cr(VI) and total chromium removed (μmol chromium/g dry wt. adsorbents) increased linearly upon increasing the concentration of chromium in the aqueous solution up to ~400 ppm (*i.e.* quantitative adsorption up to a maximum concentration of 400 ppm), after which only very small increases were observed. For example, when the original chromium concentration was 1000 ppm, ~7000 μmol of Cr(VI) and 6000 μmol of total chromium/g dry wt. adsorbents was removed (1,000 μmol of Cr(VI)/g dry wt. adsorbents was reduced to Cr(III) in solution), which correspond to approximately 55% and 45% of the Cr(VI) and total chromium present in the original solution, respectively.

The oxidation states of the adsorbed chromium in this experiment were also analysed by XAFS. As shown in **Figure 5(b)**, no signal was observed at 5992 eV after 1 h when an initial Cr(VI) concentration of 50 ppm was employed, thereby indicating that the adsorbed Cr(VI) had been reduced quantitatively. However, upon increasing the original Cr(VI) concentration above 200 ppm, the intensity of this signal increased. As such, the ratio of Cr(VI) to Cr(III) could be calculated using their respective peak areas, as shown in **Table 1**. More specifically, ~60% of Cr(VI) was reduced where an initial Cr(VI) concentration of 800 - 1000 ppm had been employed.

Furthermore, desorption of the adsorbed chromium from the persimmon gel was examined at initial Cr(VI) concentration between 200 and 1000 ppm. As shown in **Figure 5(c)**, the majority of adsorbed chromium was successfully desorbed independent of the initial Cr(VI) concentration. In addition, all desorbed chromium was in the form of Cr(III), thus indicating that any remaining unreduced Cr(VI) adsorbed on the persimmon gel was reduced to Cr(III) during the desorption procedure.

3.5. Recycling of Chromium(VI) Removal and Recovery as Chromium(III)

To obtain an indication of the recyclability of this system, Cr(VI) adsorption and its subsequent desorption as Cr(III) was repeated over 9 cycles. As shown in **Figure 6**, using a 1 M HCl solution at reflux, quantitative Cr(VI) adsorption, reduction to Cr(III), and subsequent, Cr(III) desorption were observed. More specifically, after 8 cycles, Cr(VI) adsorption was quantitative, while reduction to

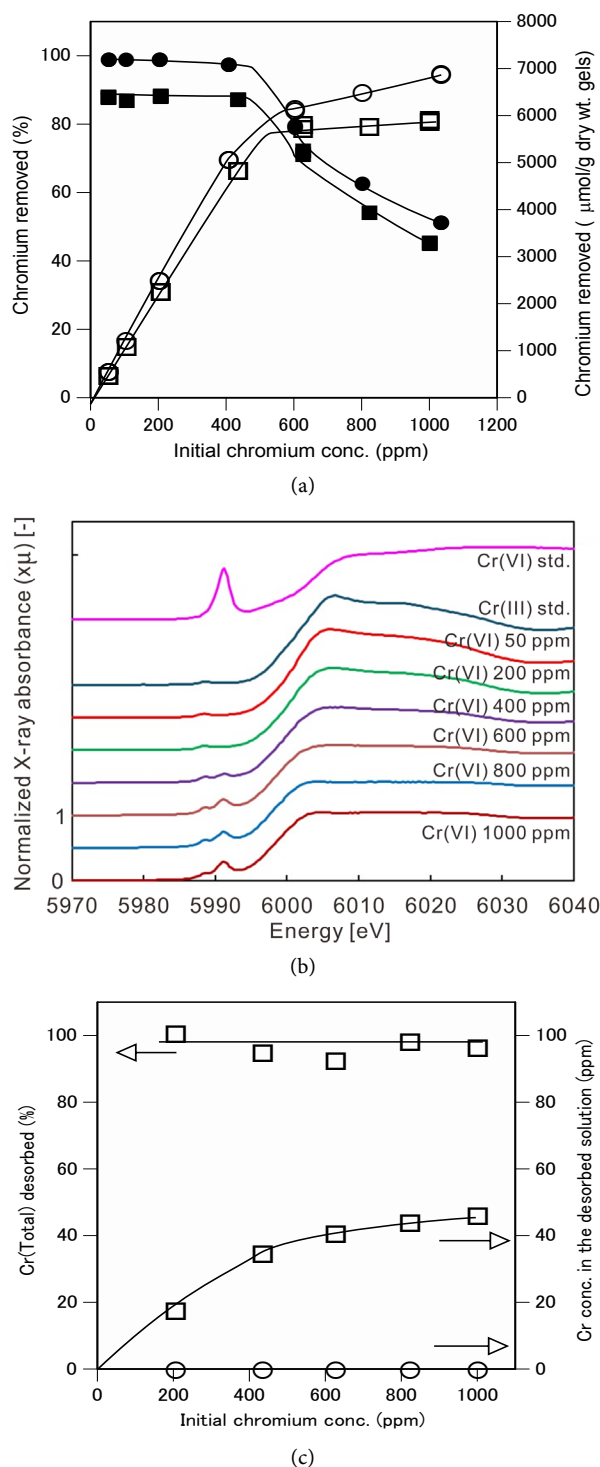
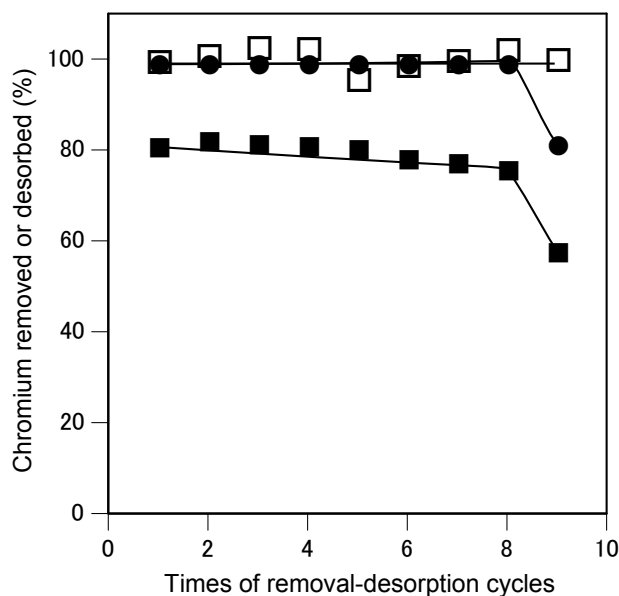


Figure 5. Effect of initial chromium concentration on Cr(VI) removal and on reduction to Cr(III) using the immobilized persimmon gel adsorbent. (a) Variation in chromium removal upon increasing the Cr(VI) concentration of the initial solution. Closed circles; removed Cr(VI)(%), closed squares; removed Cr(total) (%), opened circles; removed Cr(VI) (mol/g dry wt cells), opened squares removed Cr(total) (mol/g dry wt cells). (b) Variation in the XAFS spectra with initial Cr(VI) concentration. (c) Desorption of chromium as Cr(III) from a range of initial Cr(VI) concentrations. Circles; Cr(VI), squares; Cr(III).

Table 1. Oxidation states of chromium adsorbed in the persimmon gel.

Initial Cr(VI) conc. (ppm)	Adsorbed unreduced Cr(VI) (%) in the gel	Adsorbed reduced Cr(III) (%) in the gel
50	0	100
200	6	94
400	14	86
600	35	65
800	43	57
1000	42	58

**Figure 6.** Recyclability of the system by examination of the degree of chromium removal and desorption using persimmon gel over a number of cycles. Circles; removed Cr(VI), closed squares; removed chromium (total), open squares; desorbed chromium (total).

Cr(III) remained at a relatively constant value of ~80%. However, during the 9th cycle, the Cr(VI) adsorption decreased to 82%, and reduction to Cr(III) decreased to <60%, although Cr(III) desorption was remained quantitative. We expect that this decrease in Cr(VI) adsorption was likely due to oxidation of the polyhydroxyphenyl group in the persimmon gel to give a polyquinone moiety. We could therefore conclude that under the conditions examined herein, persimmon gel could be successfully recycled 8 times for the adsorption/reduction/desorption of chromium species from aqueous solutions. It need to oxidized persimmon gel to reduce initial form for more recycle times.

4. Conclusion

It was herein investigated the removal of Cr(VI) from aqueous solutions using persimmon tannin gel and its subsequent recovery as Cr(III). This system proved particularly successful in this process, with the majority of Cr(VI) (*i.e.* >80%) being effectively adsorbed on the persimmon tannin gel at pH 2 and

<20% of this Cr(VI) being successfully reduced to Cr(III). For example, with an initial chromium (VI) concentration of 50 ppm, quantitative reduction to Cr(III) was observed within 10 min. In the context of Cr(III) desorption following reduction, quantitative desorption was achieved using a 1 M hydrochloric acid solution at reflux. Furthermore, although the quantity of retained Cr(VI) on the persimmon gel increased upon increasing the original concentration of chromium in solution, all desorbed chromium was reduced to Cr(III). Moreover, we successfully demonstrated the recyclability of the persimmon gel sample through the successful removal of Cr(VI) and the subsequent recovery of Cr(III) over 8 cycles. It was therefore expected that our reported system for the removal of Cr(VI) using persimmon tannin gel and the subsequent recovery of Cr(III) by desorption using dilute hydrochloric acid at reflux will be applicable for the treatment of Cr(VI) containing wastewater samples.

Acknowledgements

We are grateful thanks to Dr. Hironori Ofuchi of the Industrial Application Division at the Japan Synchrotron Radiation Research Institute (JASRI) and to Assistant professor Dr. Hiroaki Nitani of the Institute of Materials Structure Science Synchrotron Radiation Science Division II (KEK) for XAFS measurements.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Mohamed, Al-M., Hesham, G.I. and Mohamed, M.A. (2008) Equilibrium and Kinetics of Chromium, Adsorption on Cement Kiln Dust. *Proceedings of the World Congress on Engineering and Computer Science*, 54-62.
http://www.iaeng.org/publication/WCECS2008/WCECS2008_pp54-62.pdf
- [2] Schneider, R.M., Cavalin, C.F., Barros, M.A.S.D. and Tavares, C.R.G. (2007) Adsorption of Chromium Ions in Activated Carbon. *Chemical Engineering Journal*, **132**, 355-362. <http://www.sciencedirect.com/science/article/pii/S1385894707000654>
<https://doi.org/10.1016/j.cej.2007.01.031>
- [3] Youssef, A.M., El-Nabarawy, T. and Samra, S.E. (2004) Sorption Properties of Chemically Activated Carbons. 1. Sorption of Cadmium(II) Ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **235**, 153-163.
<http://www.sciencedirect.com/science/article/pii/S0927775703007015>
- [4] Selvi, K., Pattabhi, S. and Kadirvelu, K. (2001) Removal of Cr(VI) from Aqueous Solution by Adsorption onto Activated Carbon. *Bioresource Technology*, **80**, 87-89.
<http://www.sciencedirect.com/science/article/pii/S0960852401000682>
[https://doi.org/10.1016/S0960-8524\(01\)00068-2](https://doi.org/10.1016/S0960-8524(01)00068-2)
- [5] Grover, M. and Narayanswamy, M.S. (1982) Removal of Hexavalent Chromium by Adsorption on Fly Ash. Institution of Engineers. *International Journal of Environmental Engineering*, **63**, 36-39.

- [6] Deepak, D. and Gupta, A.K. (1991) Hexavalent Chromium Removal from Wastewater. *Indian Journal of Environmental Health*, **33**, 297–305.
- [7] Kannan, N. and Vanangamudi, A. (1991) A Study on Removal of Cr(VI) by Adsorption Lignite Coal. *International Journal of Environment and Pollution*, **11**, 241-245.
- [8] Chand, S., Agarwal, V.K. and Pavankumar, C. (1994) Removal of Hexavalent Chromium from Wastewater by Adsorption. *Indian Journal of Environmental Health*, **36**, 151-158.
- [9] Srinivasan, K., Balasubramaniam, N. and Ramakrishna, T.V. (1988) Studies on Chromium Removal by Rice Husk Carbon. *Indian Journal of Environmental Health*, **30**, 376-387.
https://www.researchgate.net/publication/279896854_Studies_on_Chromium_Removal_by_Rice_Husk_Carbon
- [10] Brown, P.A. and Allen, S.J. (2000) Metal Removal from Wastewater Using Peat. *Water Research*, **34**, 3907-3916.
<http://www.sciencedirect.com/science/article/pii/S0043135400001524>
[https://doi.org/10.1016/S0043-1354\(00\)00152-4](https://doi.org/10.1016/S0043-1354(00)00152-4)
- [11] Gupta, V.K., Gupta, M. and Sharma, S. (2001) Process Development for the Removal of Lead and Chromium from Aqueous Solutions Using Red Mud—An Aluminum Industry Waste. *Water Research*, **35**, 1125-1134.
<http://www.sciencedirect.com/science/article/pii/S0043135400003894>
[https://doi.org/10.1016/S0043-1354\(00\)00389-4](https://doi.org/10.1016/S0043-1354(00)00389-4)
- [12] Hossain, M.A., Kumita, M., Michigami, Y. and Mori, S. (2005) Kinetics of Cr(VI) Adsorption on Used Black Tea Leaves. *Journal of Chemical Engineering of Japan*, **38**, 402-406. <https://doi.org/10.1252/jcej.38.402>
- [13] Fahim, N.F., Barsoum, B.N., Eid, A.E. and Khalil, M.S. (2006) Removal of Chromium(III) from Tannery Wastewater Using Activated Carbon from Sugar Industrial Waste. *Journal of Hazardous Materials*, **136**, 303-309.
https://www.researchgate.net/profile/Narges_Fahim/publication/7330451_Removal_of_chromiumIII_from_tannery_wastewater_using_activated_carbon_from_sugar_industrial_waste/links/0fcfd505a2d04ece6c000000.pdf
<https://doi.org/10.1016/j.jhazmat.2005.12.014>
- [14] Khan, N.A. and Mohamad, H. (2007) Investigation on the Removal of Chromium(VI) from Wastewater by Sugarcane Bagasse. *Water and Wastewater Asia*, 37-41.
- [15] Tsuruta, T. (2005) Removal and Recovery of Lithium Using Various Microorganisms. *Journal of Bioscience and Bioengineering*, **100**, 562-566.
<http://www.sciencedirect.com/science/article/pii/S1389172305705107>
<https://doi.org/10.1263/jbb.100.562>
- [16] Tsuruta, T. (2002) Removal and Recovery of Uranyl Ion Using Various Microorganisms. *Journal of Bioscience and Bioengineering*, **94**, 23-28.
<http://www.sciencedirect.com/science/article/pii/S1389172302801116>
[https://doi.org/10.1016/S1389-1723\(02\)80111-6](https://doi.org/10.1016/S1389-1723(02)80111-6)
- [17] Tsuruta, T. (2003) Accumulation of Thorium Ion Using Various Microorganisms. *The Journal of General and Applied Microbiology*, **49**, 215-218.
<https://doi.org/10.2323/jgam.49.215>
- [18] Tsuruta, T. (2006) Selective Accumulation of Light or Heavy Rare Earth Elements Using Gram-Positive Bacteria. *Colloids and Surfaces B. Biointerfaces*, **52**, 117-122.
<http://www.sciencedirect.com/science/article/pii/S0927776506001482>

<https://doi.org/10.1016/j.colsurfb.2006.04.014>

- [19] Tsuruta, T. (2004) Biosorption and Recycling of Gold Using Various Microorganisms. *The Journal of General and Applied Microbiology*, **50**, 221-228.
<https://doi.org/10.2323/jgam.50.221>
- [20] Sakaguchi, T., Nakajima, A. and Tsuruta, T. (1995) Uptake and Recovery of Gold by Immobilized Persimmon Tannin. *Proceedings of the XIXth International Mineral Processing Congress*, **4**, 49-52.
- [21] Tsuruta, T. and Hatano, T. (2015) Removal of Chromium from Chromium(VI) Solutions by Adsorption and Reduction Using Immobilized Persimmon Gel. *Journal of Environmental Science and Engineering*, **4**, 522-531.
<http://www.davidpublisher.org/Public/uploads/Contribute/566f70b765cd0.pdf>
- [22] Nakajima, A. and Baba, Y. (2004) Mechanism of Hexavalent Chromium Adsorption by Persimmon Tannin Gel. *Water Research*, **38**, 2859-2864.
<http://www.sciencedirect.com/science/article/pii/S0043135404001800>
<https://doi.org/10.1016/j.watres.2004.04.005>
- [23] Aoyama, M., Sugiyama, T., Seki, K., Tuda, M. and Cho, N.S. (1999) Removal of Hexavalent Chromium by Japanese Red Pine Leaves. *Journal of the Hokkaido Forest Products Research Institute (Written in Japanese)*, **13**, 15-19.
- [24] Ives, D.J.G. (1971) *Chemical Thermodynamics*. University Chemistry, Macdonald Technical and Scientific, London.