ADSORPTION CHARACTERISTICS OF TANNIN FOR HEAVY METAL IONS

Yoshitake SUZUKI, Kentaro SAWADA and Kazuyuki CHIHARA

Department of Industrial Chemistry, Meiji University
1-1-1 Higashimita, Tama-ku, Kawasaki 214-8571, Japan
ysuzuki1@ isc.meiji.ac.jp

Prepared for presentation at

AIChE 2003 Annual Meeting
November 7 - 12, 2004, Austin Convention Center, Austin, TX
Session [265]-Poster Session: Fundamentals of Adsorption and Ion Exchange

“Date November/2004”

UNPUBLISHED

ABSTRACT

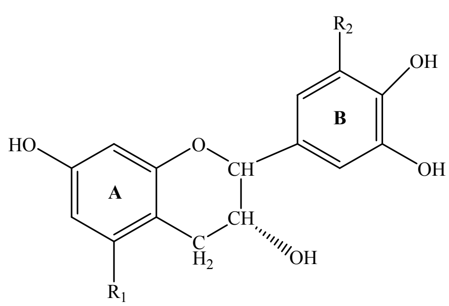
Tannins gel was investigated as an adsorbent for heavy metal ions, such as lead, cadmium, copper, and others. The gel used in the present work was made by Mitsubishi Nuclear Fuel Co. Ltd. (MNF). It was found that the gel showed high adsorption capacity of heavy metal ions and the adsorption isotherms were correlated well by the Langmuir equation. The maximum adsorption capacity was influenced by some factors, as following: initial pH of solutions, kinds of heavy metal ion species and counter ion species. These results suggest that the gel can capture a few heavy metal ion species selectively from their mixture.

INTRODUCTION

Heavy metal ions, such as lead, cadmium and copper have been detected at high concentrations in wastewater of many industries and soil. It has been serious problems because they exist as contaminants and are accumulated in living organisms. It has been strictly prohibited to discharge these ions in many countries.

There are various methods, such as precipitation, ion exchange and membrane filtration, used to remove these ions from wastewater. However, those approaches are not efficient, because their treatment cost is comparatively high in the case of low concentrations and it is difficult to clear legal limits. Therefore, it needs to use low-cost materials for removal of those ions from waste water. There is tannin to leaves and bark in many kinds of plant. Tannin is usually extracted from them, it is used as a tanning agent in leather industry and a raw material in manufacturing of adhesives. Other than application above-mentioned, it investigated to apply tannin as an adsorbent to capture various kinds of chemical species. Randall *et al*. (1974, 1975, 1976, 1977 and 1978) found that a certain bark including tannin adsorbed some heavy metal ions selectively and they were able to improve the adsorption ability by putting some process. The use of some bark including tannin have been reported: *Coniferous wood* (Fuji *et al*.,1988), *peanut inner skin* (Nakajima *et al*., 1990), pinus pinaster (Vazquez *et al*., 2002), pinus radiata (Palma *et la*., 2003) and pinus sylvestris (Taty-Costodes *et al*., 2003). Yamaguchi *et al*. (1992) produced a resin from condensed tannin and found that copper ion (Cu^{2+}) was adsorbed on the resin by physical adsorption. Nakano et al. (2000) reported that a gel made by gelation of natural condensed tannin shown in **Fig. 1** is capable of adsorbing hexavalent chromium ions (Cr^{6+}). Zhan *et al*. (2001, 2003) developed an adsorbent synthesized from condensed tannin including sodium ions (Na^{+}) and found two Na^{+} ions in the gel were exchanged by one lead ion (Pb^{2+}), as shown in **Fig. 2**. Mitsubishi Nuclear Fuel Co., Ltd. (MNF) (1997) produced a certain tannin gel (TANNIX) from cross-linking “wattle tannin” (condensed tannin) and formaldehyde and developed a liquid waste treatment system to remove uranium and the gel. MNF reported the gel had some following characteristics; during incineration, discharged elements were carbon, hydrogen and oxygen, the volume was dramatically reduced and the gases generated were harmless to the environment. The properties and the SEM photographs of the gel are shown in **Table 1** and **Phot. 1,** respectively.

In present study, a tannin gel including Na^{+} ions was used and the adsorption characteristics by the gel for removel of heavy metal ions, such as lead, cadmium, copper and zinc were investigated.



R_1 = H for resorcinol ;
R_1 = OH for phloroglucinol ;
R_2 = H for pyrocatechol ;
R_2 = OH for pyrogallol

Fig. 1 An example of molecular formula of condensed tannin

Table 1 Properties of tannin gel

Functional group	Na
Water content [%]	74
True density [g/cm^3]	1.1
Particle size [mm]	1.2-0.5

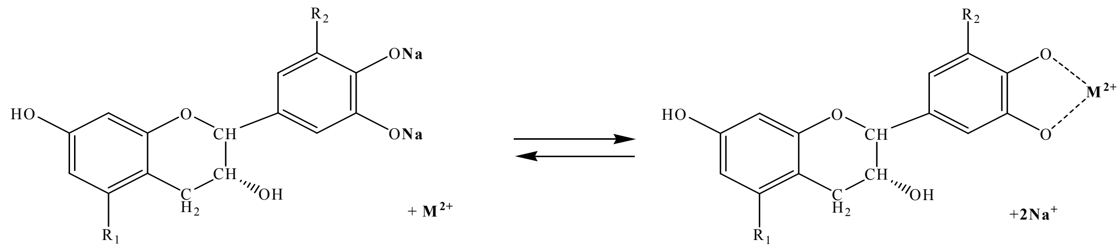
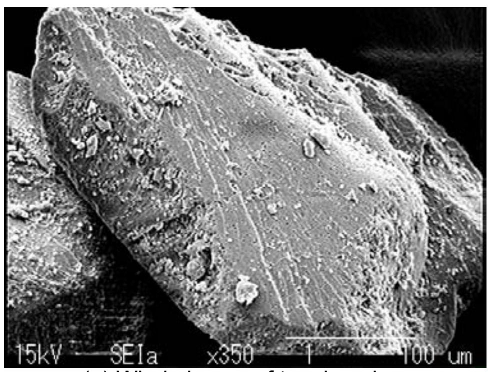
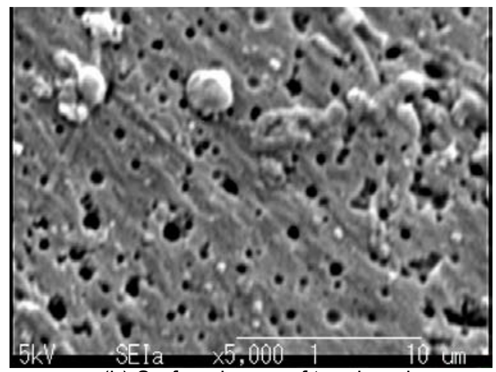


Fig. 2 Ion exchange of 2 Na^+ and M^{2+} (divalent metal ions) on condensed tannin



(a) Whole image of tannin gel



(b) Surface image of tannin gel

Phot. 1 SEM photograph of tannin gel

METHODS AND MATERIALS

Effect of initial pH and ion species on adsorption of heavy metal ions, Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} ions were investigated as follows. The prescribed amount of the gel (with wet base) was weighed, and 50 ml of a heavy metal ion solution was added. These ion aqueous solutions were prepared using nitrates, respectively. The pH of each solution was adjusted to desired values with HNO_3 solution or NH_4OH solution and measured with a pH meter (HM-30V, TOA Electronics Ltd.). The batch wise adsorption test was performed in a thermostat with a shaker for 48 hours, 100 rpm at 298 K. The supernatant was collected and the ion concentration in solutions was analysed with an atomic absorption spectrophotometer (AAnalyst-100, Perkin Elmer Ltd.,). The amount of adsorption on the gel was determined from the difference in concentration before and after the test as the following equation.

$$q^* = V\,(C_0 - C^*)\,/\,m \qquad (1)$$

where q^* is the amount adsorbed at equilibrium [mmol/g-dry gel], C_0 and C^* are initial and equilibrium concentration [mmol/l], V is the volume of aqueous solution [l] and m is the weight of the gel [g-dry gel].

Effect of temperature on adsorption for Pb^{2+} ions was determined as follows. Manner of adsorption test was almost the same above-mentioned except that the pH values were adjusted to 4.0 and experimental temperatures were 298 K, 308 K and 318 K.

To evaluate influence of counter ion species in association with heavy metal ions on the adsoroption, adsorption test of Pb^{2+} ions in the form of $PbCl_2$, $Pb(CH_3COO)_2$ and $Pb(NO_3)_2$ were performed with initial pH = 4.0. Also, before and after thr adsorption of Pb^{2+} ions, the gel was dried and identified atomic species on the surface of the gel by X-ray photoelectron spectroscopy (XPS, JPS-9000SX, JEOL Ltd.).

RESULTS AND DISCUSSION

Relationships between the concentrations and the amount adsorbed by the gel for Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} ions were well correlated with Langmuir equation, as shown in **Fig. 3** and **4** to **6**, respectively.

$$q^* = K q_\infty C^* / (1+ KC^*) \qquad (2)$$

where K and q_∞ are Langmuir parameters and indicate an affinity [l/mmol] and the maximum adsorption capacity [mmol/g-dry gel], respectively. Langmuir equation is usually used for homogeneous surfaces. Those adsorption isotherms showed different results for four heavy metal ion species, respectively. Langmuir parameters for each ion at each initial pH value are shown in **Table 2**. The adsorptivity for these ions was found to be $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$. These results partially show the effect of electronegativity because heavy metal ions which have the bigger one might be more attractive to O^- ions in the gel.

For all ion species, it was found that the maximum adsorption capacity obtained form each isotherm was increased with initial pH values. These results indicate that the adsorption for these ions on the gel was performed by ion exchange reaction. When the initial pH values were low, electric repulsion between H^+ ions in solutions and Na^+ ions in the gel wolud occurred and adsorption would be inhibited.

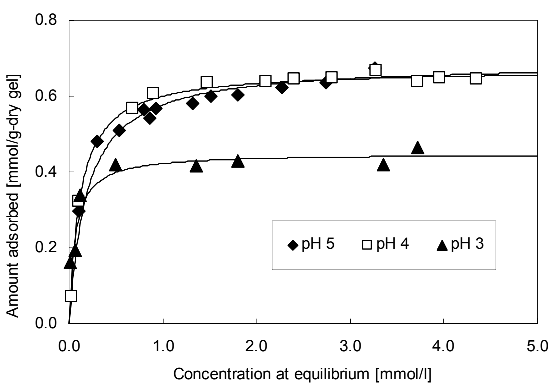


Fig. 3 Adsorption isotherms for Pb^{2+}(at 298 K)

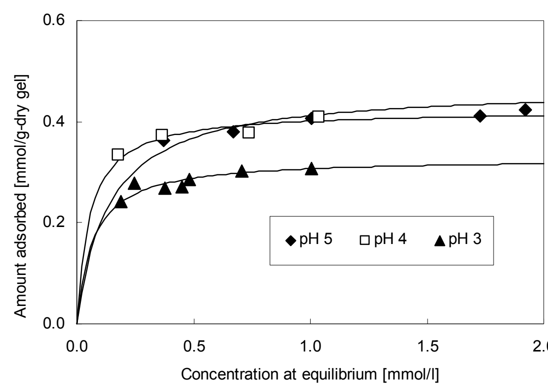


Fig. 4 Adsorption isotherms for Cd^{2+}(at 298 K)

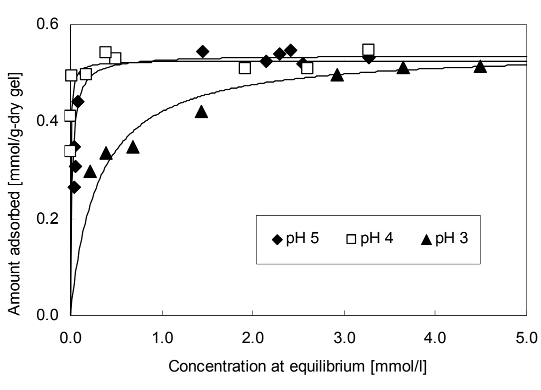


Fig. 5 Adsorption isotherms for Cu^{2+}(at 298 K)

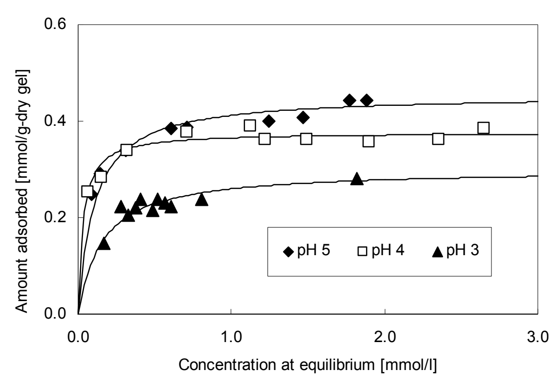


Fig. 6 Adsorption isotherms for Zn^{2+}(at 298 K)

Table 2　Langmuir parameters (at 298 K) and electronegativity

Metal ion species	Initial pH [-]	*K* [l/mmol]	q_∞ [mmol/g]	Pauling electronegativity
Pb(Ⅱ)	5	5.3	0.69	2.33
	4	8.5	0.67	
	3	16	0.45	
Cu(Ⅱ)	5	50	0.54	1.90
	4	214	0.53	
	3	3.3	0.55	
Cd(Ⅱ)	5	7.3	0.47	1.69
	4	18	0.42	
	3	15	0.33	
Zn(Ⅱ)	5	9.7	0.45	1.65
	4	32	0.38	
	3	6.5	0.30	

When initial pH values were over 6.0 for each ion, precipitation of hydrate was observed in their solutions because of their small solubility, so that it was impossible to evaluate amount adsorbed.

Adsorption isotherms and Langmuir parameters for Pb^{2+} ions at 298 K, 308 K and 318 K are shown in **Fig. 7** and **Table 3**. It was found that effect of temperature was a little throughout the range of adsorption at 298 K, 308 K and 318 K. It suggests that the adsorption for heavy metal ions on the gel is performed by ion exchange.

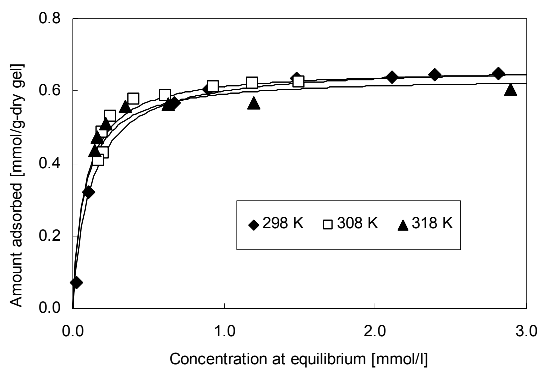


Fig. 7　Adsorption isotherms for Pb^{2+} (at 298 K, 308 K and 318 K)

Table 3　Langmuir parameters for Pb^{2+} ions (at 298 K, 308 K and 318K)

Temperature [K]	*K* [l/mmol]	q_∞ [mmol/g]
298	8.45	0.671
308	12.3	0.661
318	12.7	0.638

Fig. 8 and **9** show effect of counter ion species in association with Pb^{2+} ions on the maximum adsorption capacity. It was found that the adsorptivity for Pb^{2+} ions was $Pb(CH_3COO)_2$ > $Pb(NO_3)_2$ > $PbCl_2$. It was thought that maximum adsorption capacity of Pb^{2+} ions was improved by buffer action of materials and ion species were adsorbed more efficiently.

XPS spectra (wide scan) obtained before and after adsorption for Pb^{2+} ions are shown in **Fig. 10**. **Fig. 11** (narrow scan) shows that doublets characteristics of lead appear at 141.8 eV (assigned to Pb $4f_{7/2}$) and at 146.6 eV (assigned to Pb $4f_{5/2}$) after adsorption for Pb^{2+} ions . On the other hands, **Fig. 12** (narrow scan) shows the sodium peak at 1073.4 eV (assigned to Na 1s) before and after adsorption for Pb^{2+} ions. Peak of sodium was decreased after adsorption for Pb^{2+} ions. These results suggest that Na^+ ions in the gel are taken part in Pb^{2+} ions.

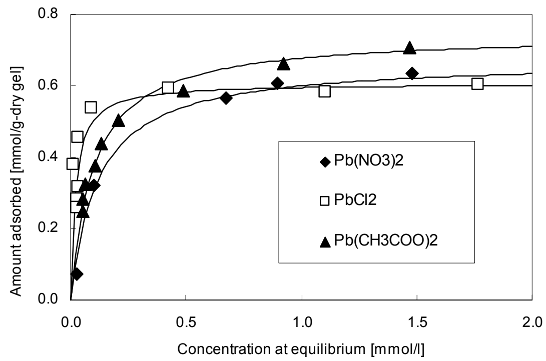


Fig. 8 The adsorption isotherms for each material (at 298 K)

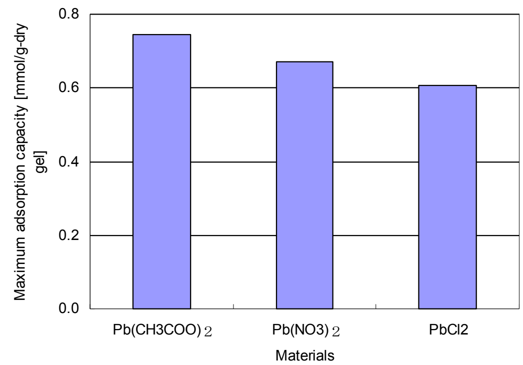


Fig. 9 Maximum Adsorption capacity for each materials (at 298 K,)

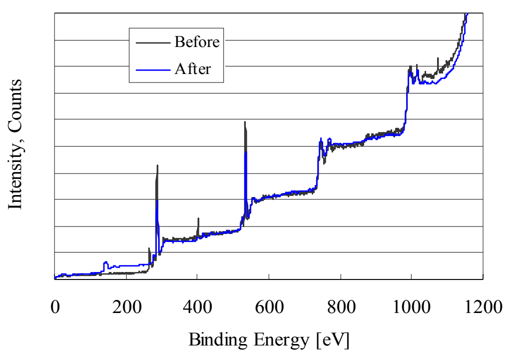


Fig. 10 XPS spectra of tannin gel before and after adsorption for Pb^{2+} ions

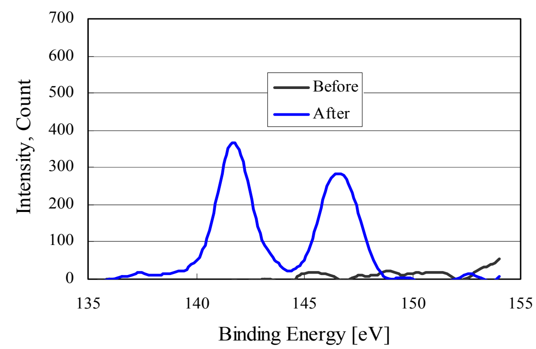


Fig. 11 XPS spectra of tannin gel before and after adsorption for Pb^{2+} ions (135-155 eV)

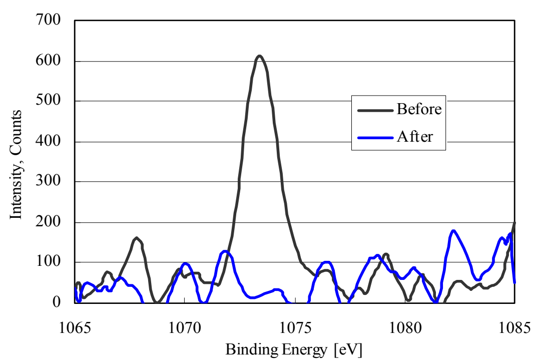


Fig. 12 XPS spectra of tannin gel before and after adsorption for Pb^{2+} ions (1065-1085 eV)

CONCLUSIONS

Adsorption mechanism for heavy metal ions with the tannin gel including Na^{+} ions was ion exchange reaction. Adsorption equilibrium could be correlated with Langmuir equation. Adsorption capacity was higher in the order of Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} ions. Adsorption for these ions was strongly influenced by initial pH in solutions and heavy metal ion species. It is concluded that the use of tannin gel as an adsorbent for heavy metal ions is useful.

ACKNOWLEDGEMENTS

Authors gratefully acknowledge Mitsubishi Nuclear Fuel Co., Ltd., for supplying the tannin gel.

REFERENCES

V. Christian Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix ; Removal of Cd and Pb ions, from aqueous solutions, by adsorption onto sawdust of *pinus sylvestris*," *J. Hazardous. Materials*, **B105**, 121-142 (2003)

Michihiro Fuji, Shin-ichiro Shioya, and Akira Ito : "Chemically Modified Coniferous Wood Barks as Scavengers of Uranium from Sea Water," *Holzforschung*, **42**, No. 5, 295-298 (1988)

S. Gier and W. D. Johns ; "Heavy metal-adsorption on micas and clay minerals studied by X-ray photoelectron spectroscopy," *Applied Clay Science*, **16**, 289-299 (2000)

Akira Nakajima, and Takashi Sakaguchi : "Recovery and Removal of Uranium by Using Plant Wastes," *Biomass*, **21**, 55-63 (1990)

Y. Nakamura, K. Hamaguchi, W. Shirato, Y. Nakano and E. Kawamoto ; Development of a system for removal and recovery of hexavalent chromium eluted from used magnesia/chromium using tannin gel particles," *Mokuzai Gakkaihsi*, **37**, 815-820 (1991)

Y. Nakamura, W. Shirato, H. Yamakawa and Y. Tomonaga ; "Liqid Waste Treatment system with insoluble tannin," *Waste Water (WM'98)*, 374 (1998)

Y. Nakano, M. Tanaka, Y. Nakamura and M. Konno ; "Removal and recovery system of hexavalent chromium from waste water by tannin gel particles," *J. Chem. Eng. Japan*, **33**, No. 5, 747-752 (2000)

Y. Nakano, K. Takeshita and T. Tsutsumi ; "Adsorption mechanism of hexavalent chromium by redox within condensed-tannin gel," *Water Research*. **35**, No. 2, 496-500 (2001)

J. M. Randall, R. L. Bermann, V. Garrett, and A. C. Waiss, Jr. : "Use of Bark to Remove Heavy Metal Ions From Waste Solutions," *FOREST PRODUCTS JOURNAL*, **24**, No. 9, 80-84 (1974)

John. M. Randall, F. William Reuter, and Anthony C. Waiss : "Removal of Cupric Ion from Solution by Contact with Peanut Skins," *J. Appl. Polym. Sci*, **19**, 1563-1571 (1975)

J. M. Randall, E. Hautala, A. C. Waiss, Jr., and J. L. Tschernits : "Modified Barks as Scavengers For Heavy Metal Ions," *FOREST PRODUCTS JOURNAL,* **26**, No. 8, 46-50 (1976)

John. M. Randall : "Variation in Effectiveness of Barks as Scavengers for Heavy Metal Ions," *FOREST PRODUCTS JOURNAL*, **27**, No. 11, 51-856 (1977)

John. M. Randall, Earl Hautala, and Gary Mcdonald : "Binding of Heavy Metal Ions by Formaldehyde-Polymerized Peanut Skins," *J. Appl. Polym. Sci*, **22**, 379-387 (1978)

Y. Suzuki, K. Chihara and K. Sawada ; " Uptake mechanism for heavy metal ions from their aqueous solutions on tannin gel," Annual meeting of AIChE, San Francisco, CA, USA (2003)

The Chem. Soc. of Japan ; "Kagaku-Binran, Kiso-Hen," **5th ed.**, 152, 779, Maruzen, Tokyo (2004).

G. Palma, J. Freer and J. Baeza ; Removal of metal ions by modified *pinus radiata bark* and tannina from water solutions," *Water Research*, **37**, 4974-4980 (2003)

G. Vazquez, J. Gonzalez-Alvarez, S. Freire, M. Lopez-Lorenzo and G. Antorrena ; "Removal of cadomium and mercury ions from aqueous solution by sorption on treated *pinus pinaster* bark: kinetics and isotherms," Bioresouce Technology, **82**, 247-251 (2002)

H. Yamaguchi, M. Higuchi and I. Sakata ; “Methods for preparation of adsorbent microspherical tannin resins,” *J.Appl.Polym.Sci*, **45**, 1455-1462 (1992)

H. Yamaguchi, R. Higashida, M. Higuchi and I. Sakata ; “Adsorption mechanism of heavy-metal Ion by microspherical tannin resin,” *J.Appl.Polym.Sci*, **45**, 1463-1472 (1992)

H. Yao, N. Saito, I. S. N. Mkilaha and I. Naruse ; “ Comparative study of lead and cadmium compounds capture by sorbents,” *J. Chem. Eng. Japan*, **35**, No. 5, 401-408 (2002)

XM. Zhan, A. Miyazaki and Y. Nakano ; “Mechanism of lead removal from aqueous solutions using a novel tannin gel adsorbent synthesized from natural condensed tannin,” *J. Chem. Eng. Japan*, **34**, No.10, 1204-1210 (2001)

XM. Zhan and X. Zhao ; “Mechanism of lead adsorption from aqueous solutions using an adsorbent synthesized from natural condensed tannin,” *Water Res*earch, **37**, 3905-3912 (2003)

Su Zhixing, Guangyao Zhan, Xingyin Luo, and Qiaosheng Pu : “Synthesis and Efficiency of an Epoxy-Tannin Chelating Resin for Preconcentrating and Separating Various Rare Elements,” *Analytica Chimica Acta*, **310**, 493-499 (1995)