Adsorption Mechanism of Selenite (Se^{4+}) by Redox within Condensed-tannin Gel under Concentrated Hydrochloric Acid Solution

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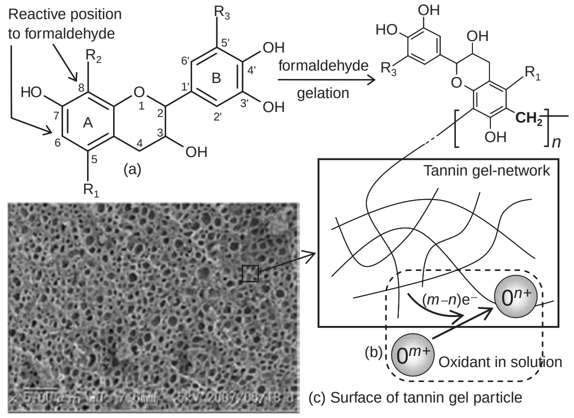
Se^{4+} is adsorbed and retained as a reduced elemental Se^0 on tannin gel network through redox reaction mechanism in very strong hydrochloric acid solution.

Selenium (Se), existing as selenate (Se^{6+}), selenite (Se^{4+}), elemental selenium (Se^0), and selenide (Se^{2-}) in natural environment,[1] is toxic even at very small intake, although it has been recognized as one of essential micronutrients.[2]

Tannin gel adsorbent synthesized from condensed-tannin molecule can be one of solutions for Se removal from the wastewater of hydrometallurgical processes where the concentrated hydrochloric acid is usually used for the leaching process and Se^{4+} is predominant. Condensed-tannin extracted from plants has a strong interaction with heavy metal ions and a redox potential favorable in relation to some oxidants,[3] resulting from the multiple adjacent polyhydroxyphenyl groups[4] such as pyrocatechol and pyrogallol in its chemical structure (Scheme 1a).[5,6] To overcome the solubility of tannin molecule, Nakano et al. have succeeded in developing a novel tannin adsorbent by gelation.[7] The C6, C8 positions of condensed-tannin molecule are highly reactive with formaldehyde, because of the strong nucleophilicity of A-ring, by which the condensed-tannin can be gelated with the methylene bridge linkages ($-CH_2-$).[8]

The tannin adsorbent was prepared by gelation of Wattle tannin powder (28 g), one of condensed-type tannins, in a basic catalyst (50 mL of 0.225 M NaOH solution) with formaldehyde (37 wt %, 6 mL), a cross-linking agent, at 353 K for 24 h. The macroporous tannin gel synthesized in hermetically sealed container without solvent evaporation, was then grounded into small particles and sieved to a size of 125–250 µm in diameter. The micro-sized tannin gel particles were washed with distilled water, 0.05 M HNO_3 and consecutively distilled water. Finally, the tannin gel particles were kept in a refrigerated storage after freeze-drying. The macroporous tannin adsorbent with the three-dimensional gel-network structure (Scheme 1c) has 60–70 wt % of the water content on a wet basis, which allows high adsorption capacity and low intraparticle mass transfer resistance.[7e] Furthermore, the gel-network structure prepared by cross-linking provides enough stability for the adsorbent to resist the strong acidic condition, especially the hydrohalogenic acid system.



Scheme 1. Synthesis of tannin gel adsorbent from condensed-tannin, flavan-3-ol unit of condensed-tannins (a),[6] basic concept of reductive adsorption (b) and SEM image of particle surface (c).

From the viewpoint of adsorption mechanism, selenium ions can be retained in adsorbents by physisorption or chemisorption and in both ways.[9] In some cases of adsorption related with the electronic orbital pattern and valence force, adsorptive and adsorbate may be chemically different species which can be detectable by suitable physical means such as spectroscopy. To make sure whether there are any changes in substances involved in Se^{4+} adsorption, XRD and FT-IR analyses were utilized for the species of selenium (adsorbate) and tannin gel (adsorbent), respectively.

For XRD analysis of the adsorbed selenium, tannin gel particles were sampled after Se^{4+} adsorption at [HCl] 1 M and then freeze-dried. The peaks corresponding to those of crystalline elemental selenium were observed clearly at $2\theta = 23.44$, 29.68, 41.16, 43.6, 45.36, 48.04, 51.72, 55.64, 61.32, 65.24, 68.36, and 71.4 degrees (Figure 1), which confirms that Se^{4+} is reduced to elemental Se^0 and crystallized on the tannin gel network. Considering pK_as ($H_2SeO_3 + H_2O \rightleftarrows HSeO_3^- + H_3O^+$, $pK_a = 2.7$ and $HSeO_3^- + H_2O \rightleftarrows SeO_3^{2-} + H_3O^+$, $pK_a = 8.54$),[1] the chemical species of Se^{4+} at [HCl] 1 M is H_2SeO_3 whose reduction is expressed as the following half-reaction.

$$H_2SeO_3(aq) + 4H^+ + 4e^- \rightleftarrows Se(s) + 3H_2O, E^\circ = 0.74\,(V) \quad (1)$$

which implies the oxidation of tannin gel adsorbent during Se^{4+} adsorption.

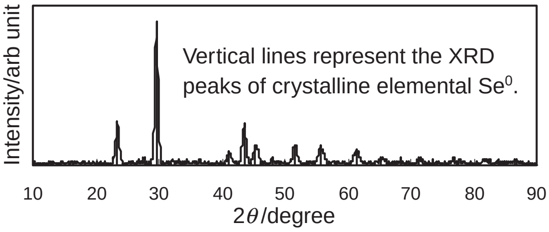


Figure 1. XRD pattern of the selenium adsorbed onto tannin gel particles. Conditions of adsorption experiment are Se^{4+} 1000 ppm, [HCl] 1 M, tannin gel adsorbent 5 g/L and 333 K, where the high Se^{4+} concentration brought an enough adsorption amount for XRD sample preparation.

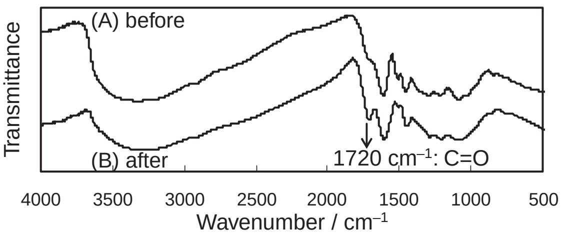


Figure 2. IR spectra of tannin gel particles before (A) and after (B) Se^{4+} adsorption at [HCl] 1 M and 333 K.

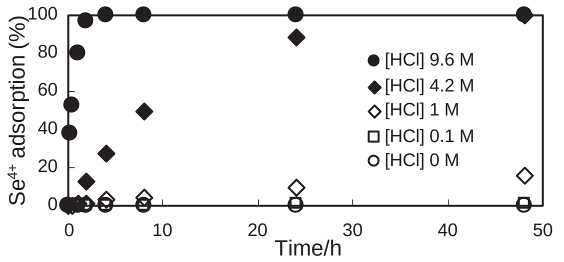


Figure 3. Effect of H^+ concentration on Se^{4+} adsorption rate at Se^{4+} 10 ppm, tannin gel adsorbent 1 g/L and 298 K.

IR spectra of tannin gel particles before and after Se^{4+} adsorption at [HCl] 1 M were taken to observe any change in the chemical structure caused by a reaction with Se^{4+} and are shown in Figure 2. In both spectra, the absorbances at 3200–3500, 1100–1300, 1450, 1500, and 1600 cm^{-1}, assign to stretching vibration of O–H, stretching vibration of C–O–C, bending vibration of C–H, and stretching vibration of aromatic C=C, respectively, resulting from the functional groups of tannin gel (Scheme 1a). Meanwhile, the absorption band at 1720 cm^{-1} assigning to stretching vibration of C=O, appears sharply in only the tannin gel particles that adsorbed selenium. The formation of C=O indicates that the hydroxy groups of tannin gel are oxidized to carbonyl groups by the redox reaction with Se^{4+} species, which can be expressed as the following half-reaction.

$$\text{R–OH} \rightleftarrows \text{R=O} + H^+ + e^- \qquad (2)$$

From the above two half-reactions (eqs 1 and 2), the following redox mechanism between H_2SeO_3 and tannin gel can be proposed for the Se^{4+} adsorption at [HCl] 1 M and over.

$$H_2SeO_3(aq) + 4\text{R–OH} \rightleftarrows 4\text{R=O} \cdot Se(s) + 3H_2O \qquad (3)$$

The redox-induced adsorption might lead the consecutive reduction to Se^{2-} that is extremely toxic. However, the redox potential of tannin gel, assumed to be enough higher than that of Se^0/Se^{2-} couple (-0.115 to -0.641 (V)),[1,7a,7c] is not favored for such a problematic reaction, formation of Se^{2-}.

The effect of [HCl] was investigated over the range of 0 to 9.6 M in a batchwise system. The adsorption amount was calculated by considering the mass balance of Se^{4+} the concentration of which was determined by ICPS and shown in Figure 3. It is obvious that the adsorption rate increases drastically as [HCl] increases. No considerable adsorption was observed in the pH level (1 to 6) where the tannin gel, a weakly acidic cation-exchanger,[7b] can not adsorb Se^{4+} existing as anionic species ($HSeO_3{}^-$ and/or $SeO_3{}^{2-}$) and the Se^{4+} reduction to Se^0 is also difficult because of deficient H^+ (eq 1). However, in this experimental system, Se^{4+} is disposed completely from the solution in 4 h at [HCl] 9.6 M and was detected as almost 0 ppm in solution, which can meet satisfactorily the industrial effluent standards, e.g. 0.1 ppm in Japan. The marked dependence of adsorption rate on $[H^+]$ may be caused by that the Se^{4+} reduction needs H^+ (eq 1) and suggests that some kind of selenite-proton intermediate might be formed on the reductive site of adsorbent before the electron transfer of eq 3. Cl^- can also play a role as reductant and affect the reduction rate of selenium, but not in this study because its potential is only related with the reduction of Se^{6+} to Se^{4+} and not favored in the reduction to Se^0.[10]

In addition to the effect of H^+ on the adsorption rate, it can also affect the adsorption capacity because it is directly related with the redox potentials of Se^{4+} oxo species. The distinct dependence of Se^{4+} reduction on H^+ (eq 1) indicates that the equilibrium potential (E_{eq}) increases with an increase of $[H^+]$, as shown in eq 4 derived from the half-reaction of eq 1 on the basis of Nernst equation at 298 K: this relationship, the higher $[H^+]$ the thermodynamically more favored potential to be reduced, is usually seen among the oxo-anionic species.[11]

$$E_{eqSe} = 0.741 + 0.0591\log[H^+] + 0.0148\log[H_2SeO_3] \qquad (4)$$

$$E_{eqTG} = E^{\circ}{}_{TG} + 0.059\{\log[H^+] - \log([\text{R–OH}]/[\text{R=O}])\} \qquad (5)$$

where the subscripts, Se and TG, represent selenium and tannin gel, respectively. The dissociative protons of tannin gel also induce an increase of E_{eqTG} as $[H^+]$ increases (eqs 2 and 5), which may result in weak dependence of Se^{4+} adsorption capacity on $[H^+]$. However, Se^{4+} can be still reduced at high [HCl] by equilibrium relation between E_{eqSe} and E_{eqTG}.

Further detailed investigations on the redox potential of tannin gel will be very helpful in verifying the above-proposed mechanism and are currently underway. The results of the present investigation on Se^{4+} adsorption onto tannin gel adsorbent, contrary to common metal ions in terms of H^+ effect, can provide a clue as to how to remove Se^{4+} selectively from the mixture with other metal ions, as well as the efficient Se^{4+} removal at high [HCl].

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