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Recovery of Gold from Hydrochloric Acid by means of Selective Coagulation with Persimmon Extract

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Abstract: Gold was selectively precipitated with solution of persimmon extract which contains persimmon tannin, a kind of polyphenol. Quantitative recovery of gold was achieved in the concentration range of hydrochloric lower than $0.5\,mol{\cdot}dm^{-3}$. X-ray diffraction analysis and a digital micrograph of the filtered cake indicated the formation of gold particle during recovery process. High selectivity of persimmon extract is ascribed to the reduction of Au(III) to elemental form.

Keywords: Coagulation, gold, persimmon extract, recovery

INTRODUCTION

Persimmon extract, kakishibu solution, is produced by the extraction of immature persimmon and the subsequent fermentation for use as a clarifying agent of Sake and as a coating material for houses. Kakishibu contains persimmon tannin, the chemical structure of which is shown in Scheme 1, at approximately 5–6% (1). By the fermentation, polyphenols in tannin are cross-linked via condensation reaction.

Polyphenols in tannin compounds have strong reduction power for metal ions. Nakano et al reported that by using Mimosa (Wattle) tannin gel Cr(VI), Au(III), and Pd(II) were reduced to Cr(III), Au(0), and Pd(0), respectively (2–4). Nakajima also reported that Cr(VI) and V(V) were reduced to Cr(III) and V(IV), respectively, in the adsorption on adsorbent

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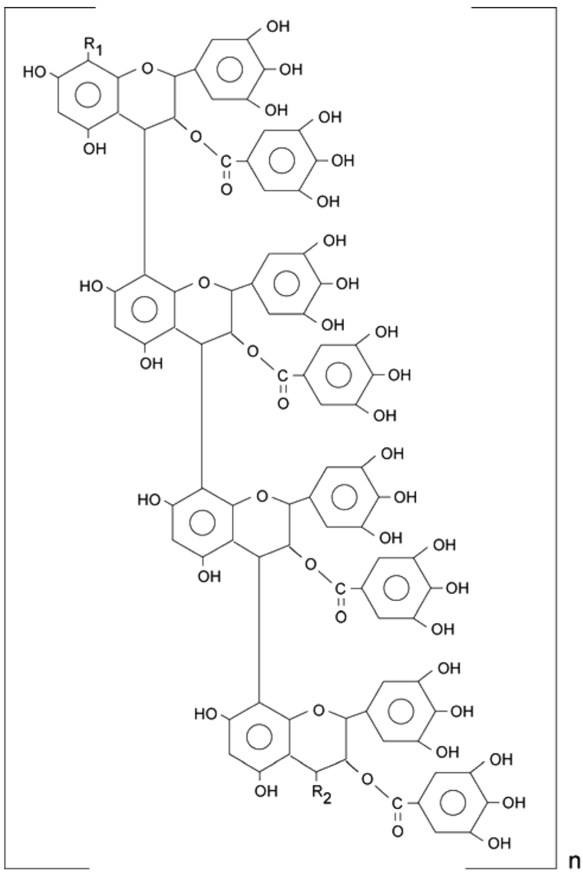


Scheme 1. Persimmon tannin structure.

prepared from persimmon tannin (5,6). In the previous work, we prepared adsorption gel from astringent persimmon peel generated in the production of dried persimmon and found that it adsorbs gold selectively from HCl solution and forms fine gold particles of the size around 10–100 μm (7).

Coagulation is useful to selectively separate metal ions or proteins. Synthetic (8) and natural polymers (9) are popular as polymeric coagulation reagents. Polyphenol is also used as coagulation reagent for zinc and iron (10), and protein (11). In the previous work, we found that kakishibu was effective to remove a large amount of protein from cadmium-containing dilute sulfuric acid leach liquor of scallop waste (12).

At present, precious metals such as gold, palladium, and platinum are used extensively not only in traditional jewelry materials but also as useful components in a variety of well-known advanced applications such as electric and electronic devices, catalysts, and medical instruments. Because these metals are limited resources existing only in small amounts on Earth, these metals must be effectively recovered from various wastes for recycling and reuse purposes. From an economic point of view, the recovery process should be such that the precious metals are highly selectively separated from base metals such as iron, copper, and zinc that often coexist with the precious metals in disproportionate amounts.

Due to the high price of precious metals, they have been recovered from various wastes for many years. According to the classical method of precious metals refining, feed materials including various wastes are leached with aqua regia, where gold, platinum and palladium are dissolved leaving other precious metals like silver and secondary precious metals as well as base metals in leach residue. From the leach liquor, gold is recovered, first as gold sponge reduced with various reducing agent like ferrous sulphate, followed by the recovery of platinum and palladium with ammonium chloride (13). This classical method is tedious and expensive, and the purity of the recovered sponge metals is not high. In addition, due environmental regulations, the use of nitric acid has become difficult. In recent years, the classical method is being replaced by new methods consisting of total dissolution of feed materials with chlorine containing hydrochloric acid except for silver followed by solvent extraction and ion exchange or distillation for selective separation into high purity of each precious metal. In the total dissolution, chlorine is dissociated into hydrochloric acid and hypochlorous acid which functions as oxidation agent and is converted into hydrochloric acid. Consequently, the mutual separation among precious metals by means of solvent extraction and ion exchange is carried out from hydrochloric acid. Solvent extraction reagents as well as diluents and ion exchange resins, synthetic organic materials, are not environmentally benign taking account of their dissolution in water and the treatments after their use. On the view point as such, we attempted to use astringent persimmon extract, "kakishibu," a natural material, for the refining of gold in the present work.

EXPERIMENTAL PROCEDURE

Material

Kakishibu was kindly denoted by Tomiyama Corp., Japan. Analytical grade chloride salts of copper, iron, palladium, and zinc were used to prepare test solutions of respective metals. Analytical grade $HAuCl_4.H_2O$ and $H_2PtCl_6.6H_2O$ were used to prepare gold and platinum solutions, respectively. The filter used in this study was ADVANTEC 5 C, with an average pore diameter of 80 μm. Other chemicals were of analytical grade or higher.

Coagulation of Metal Ions by Kakishibu

Coagulation behavior of metal ions by kakishibu was tested batchwise without agitation. Fifteen cm^3 of individual metal solution of 0.4 $mmol/dm^3$ of varying HCl concentrations was mixed together with 10 (v/v)% of kakishibu water. The solution was incubated for a required time and filtered. The metal concentrations in the filtrate were determined by AAS (Shimadzu, AA-6650) and ICP-AES (Shimadzu, ICPS-8100). Percent recovery was calculated as follows,

$$\begin{aligned}\% \text{ recovery} = 100 \times [&(\text{initial metal concentration}) \\ &- (\text{metal concentration after precipitation})] \\ &/[\text{initial metal concentration}]\end{aligned} \tag{1}$$

The coagulation test was performed for individual metal solutions. The formation of gold particles during the coagulation was confirmed by digital microscopy (Keyence VH-5000). After filtration, gold particle contained in filtered cake was measured by X-ray diffraction (Rigaku RINT-8829).

Determination of Polyphenol Content in Kakishibu

Pure water (3.3 cm^3) and 0.1 (v/v)% kakishibu solution (200 mL) was mixed. Folin-Denis reagent (200 mL) (14) was added to the prepared solution, and then saturated sodium carbonate solution was added and incubated for 30 min. The absorbance of the solution was determined by UV-VIS (Hitachi, U-3310) at 700 nm. Catechin was used as a standard reagent to make a calibration curve. As a result, $4.8 \times 10^3\ mg/dm^3$ of polyphenol was found to be contained in 10 (v/v)% kakishibu solution.

RESULTS AND DISCUSSION

Selective Gold Separation by Means of Coagulation with Kakishibu

Figure 1 shows the time variation of percent recovery of gold from 0.1 M hydrochloric acid at 303 K calculated from the concentration of gold in the filtrate as mentioned earlier. The percent recovery increases with increasing reaction time and tends to approach a constant value of equilibrium after about 50 h.

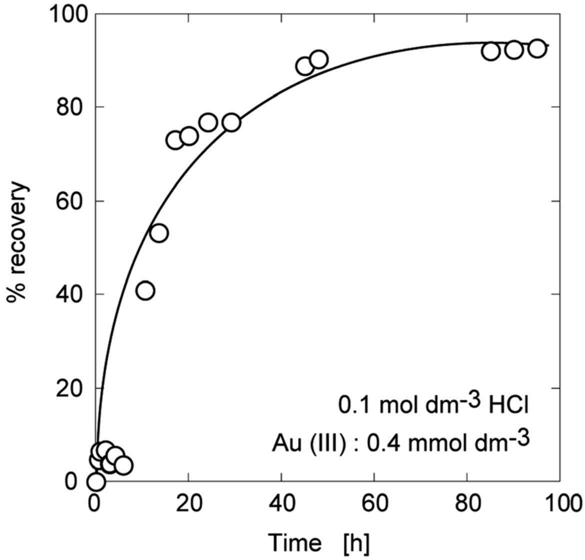


Figure 1. Time course curve of Au(III) recovery. Volume of 10 (v/v)% kakishibu added to 15 cm^3 sample is 0.25 cm^3. Temp.: 303 K.

Figure 2 shows the percent recovery of gold as a function of volume ratio of 10 (v/v)% kakishibu solution added to the test solution containing 0.4 mM gold(III) in 0.1 M hydrochloric acid at 303 K.% recovery increases with increasing volume ratio of kakishibu added and quantitative recovery was achieved at around 3.0 (v/v)% addition.

Figure 3 shows the effect of hydrochloric acid concentration of the test solution individually containing 0.4 mM gold(III), platinum(IV), palladium(II), copper(II), zinc(II) or iron(III) on percent recovery of gold. As seen from this figure, only gold can be selectively recovered over other metal ions by the addition of kakishibu. In addition, quantitative recovery of gold was achieved in the concentration range of hydrochloric acid less than 0.5 M.

Figure 4 shows a digital micrograph and results of X-ray diffraction of the filter cake after the recovery of gold. In the photograph, aggregates of fine gold particles were observed. Four sharp peaks in the X-ray diffraction pattern observed at 38.2, 44.4, 64.6 and 77.5 suggest the existence of metallic gold. As shown in Scheme 1, persimmon tannin contained in kakishibu have large numbers of functional groups of catechol and pyrogallol, which function as strong reducing agents. These phenomena are due to the strong reducing function by these functional groups and the same with those observed in the adsorption on astringent persimmon peel

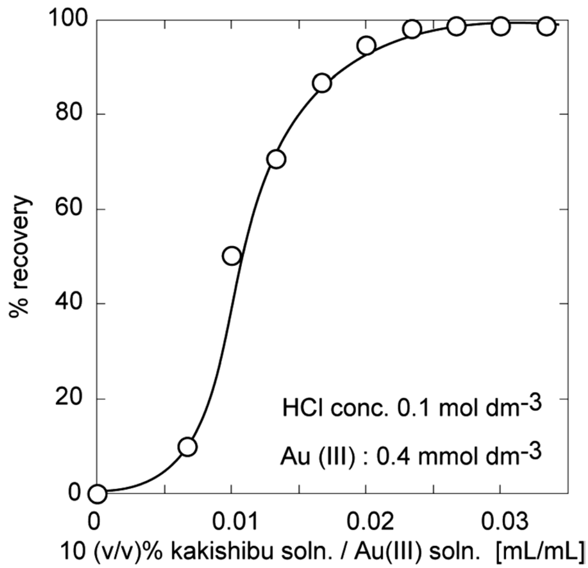


Figure 2. Effect of liquid of kakishibu solution per solid ratio on Au(III) recovery percentage. Reaction time: 72 h. Temp.: 303 K.

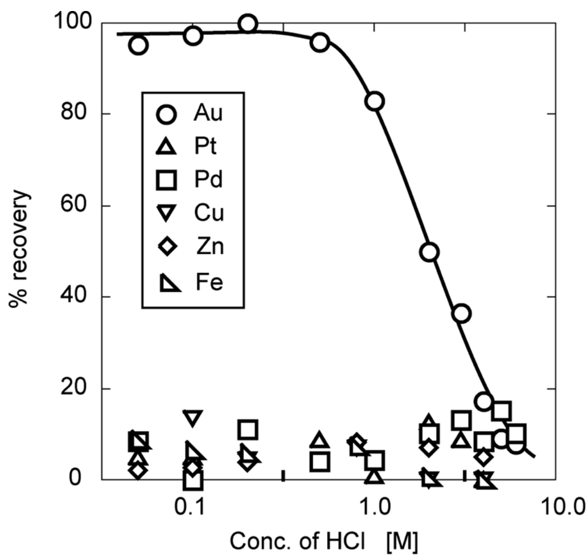
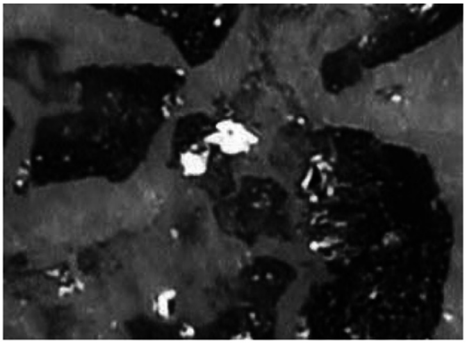
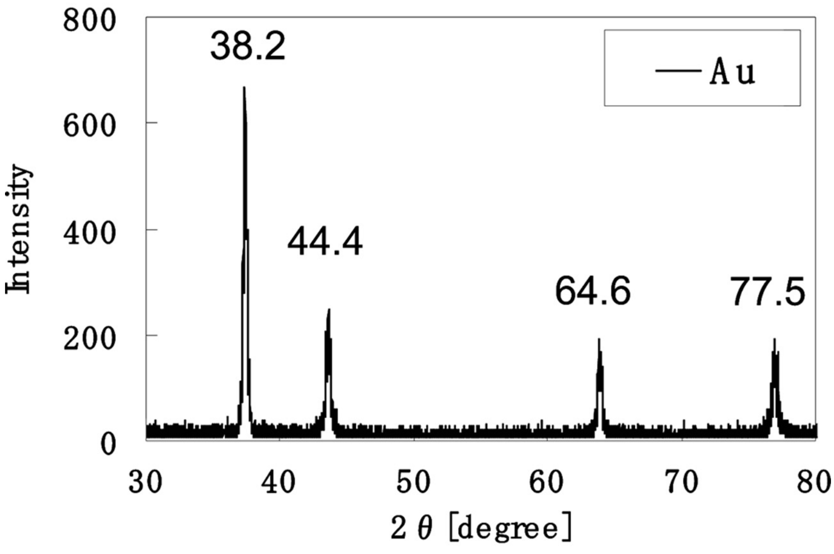


Figure 3. Selective Au(III) recovery compared with some metal ions. 10 (v/v)% kakishibu : 1 cm^3; Conc. of metal : 0.4 $mmol{\cdot}dm^{-3}$; Temp.: 303 K.



(a)



(b)

Figure 4. Confirmation of gold particle formation. (a) Digital microscopy image, and (b) XRD spectrum of a particle.

gel reported in the previous work (7). Kim et al. (2) performed Pd(II) adsorption using condensed-tannin gel in pH region, different from our work. The precious metals containing wastewater are at high concentrated acid solution. The selective recovery of Au(III) by using persimmon extract used in this study at high acid concentration resulted from the reduction phenomena, rather than adsorption.

Temperature Dependence of Gold Coagulation

Figure 5 shows the time variation of the % recovery of gold at different temperatures from 0.1 M hydrochloric acid. As seen from this figure, the rate of gold recovery increases with increasing temperature. On the assumption that the coagulation of gold follows the pseudo-first order rate expression, the kinetic data shown in Fig. 5 were replotted according to Eq. (2) as shown in Fig. 6.

$$\ln[(\mathrm{Au})/(\mathrm{Au})_0] = -\mathrm{kt} \tag{2}$$

where k was rate constant of the pseudo-first-order reaction.

The coagulation of gold observed in the present work is considered to be consisted of following 3 steps:

1. diffusion of gold(III) ion to functional groups of catechol and pyrogallol on polymer matrices of kakishibu,
2. adsorption followed by reduction of gold (III) ion by these functional groups and
3. coagulation of the fine gold particle formed in the preceding step.

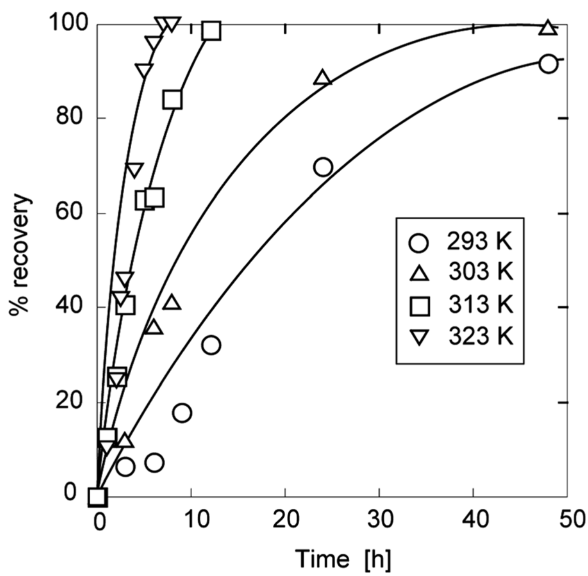


Figure 5. Time course curve of temperature dependence on Au(III) recovery percentage 0.1 mol·dm^{-3} HCl Conc. of Au : 0.4 mmol·dm^{-3}. 10 (v/v)% kakishibu soln. : 0.25 cm^3.

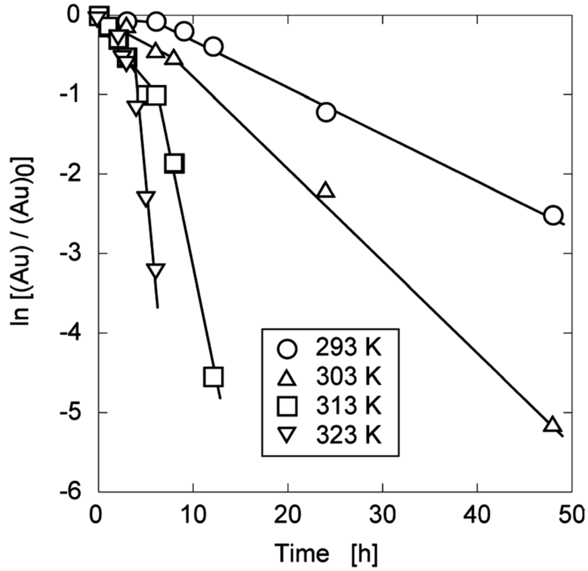


Figure 6. Pseudo-first-order equation fitting to determine kinetic parameter.

In Fig. 6, the plots lie on 2 straight lines for each of 4 different temperatures, suggesting that two different rate-determining processes consecutively occurred during gold coagulation. Similar results were observed in the adsorption of gold on astringent persimmon peel gel in the previous work (7). The rate constants of the pseudo-first order reaction were calculated from the slopes of two different straight lines at each temperature. Figure 7 shows the Arrhenius plots of the evaluated rate constants at two different steps. From this figure, it is seen that the plots lie on two straight lines with different slopes, from which the activation energies were evaluated for two rate-determining steps; i.e. it was evaluated as 61.8 and 77.2 kJ/mol for the first and second steps, respectively. Because the activation energy of physical process is less than 20 kJ/mol, the diffusion step (1) cannot be considered as the rate-determining step. It is reasonably considered that other steps, (2) and (3), the adsorption of gold(III) ion followed by the reduction to metallic gold by the functional groups of polyphenols and subsequent aggregation of thus formed fine gold particles governs the overall process. That is, it is inferred that, at the initial stage, step (2) is rate-determining and in the course of time the rate-determining step is shifted to the step (3).

In the adsorption of gold on astringent persimmon peel gel, the activation energy was evaluated as 81.7 kJ/mol for the first step and as 85.0 kJ/mol for the second step, which are nearly the same value with those evaluated for the coagulation process in the present work.

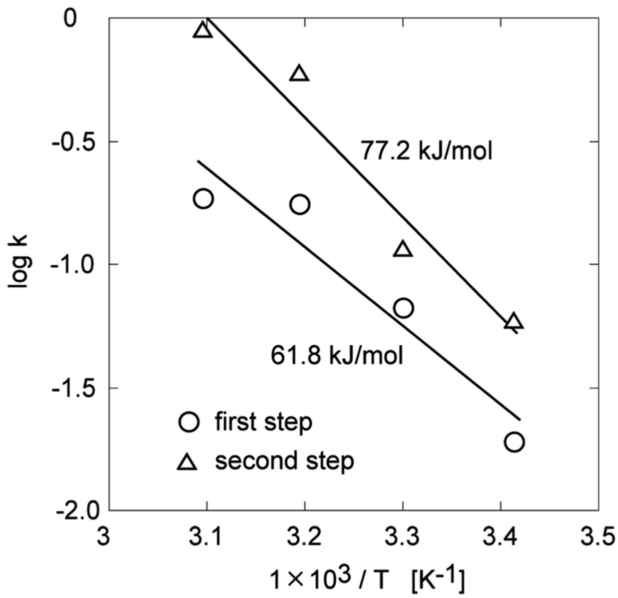


Figure 7. Arrhenius plots of Au(III) recovery kinetics.

CONCLUSIONS

Gold was highly selectively recovered over other metals such as palladium, platinum and base metals from hydrochloric acid by means of precipitation/coagulation method using kakishibu which contains large amount of polyphenols. The observation by digital microscopy and X-ray diffraction indicated the formation of fine gold particles.

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