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Selective Gold Recovery Using Orange Waste

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Abstract: Orange waste was crosslinked with sulfuric acid to immobilize the hesperetin-like molecule. Au(III) was selectively recovered from hydrochloric acid, exhibiting the negligible affinity to other precious metals and base metal ions. The isotherm demonstrated that the maximum loading capacity on the crosslinked orange waste is approximately 10 mol/kg, suggesting that orange waste has a high possibility for commercial application for gold recovery.

Keywords: Acid media, biomass, gold recovery, orange waste, polyphenol

INTRODUCTION

Gold is one of the most versatile of metals possessing many unique properties. Apart from various traditional uses, for example, as jewelry, its application to many technical purposes is now increasing. Meanwhile, a big proportion of gold is being wasted in the form of used electronic and electrical devices, such as cellular phones etc. Taking into account the declining resource of gold with its ever-increasing applications, efforts should be made for its recovery and recycling from used appliances. The precious metals are leached by using aqua regia or chlorine containing hydrochloric acid from the above-mentioned used electric and electronics devices. For the recovery of gold from the leach liquor containing precious metals, a number of solvent extraction reagents, ion exchangers, and adsorbents have been developed. Some of them are commercially

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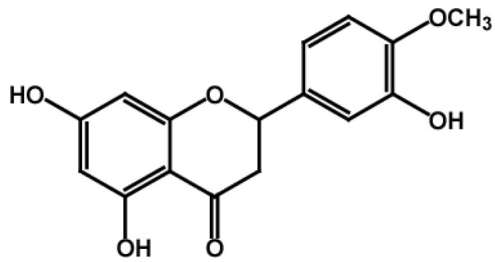

Scheme 1. Key structure of phenol derivative in orange waste.

employed at present. However, the research for an environmentally-benign and a cost-effective method for gold recovery is now still continuing from the viewpoints of selectivity, capacity, and durability.

Tannin is a kind of polyphenol compounds and used as an adsorption gel (http://www.mnf.co.jp/nbrdc/tannix/tannixj.htm). A great majority of the research work on tannin is concerned with tannin extracted from persimmon (1–3). Polyphenol has an interesting characteristic to selectively adsorb gold in an acidic chloride media because hydroxyl groups in polyphenol reduce the uptaken gold ion to elemental gold. In the previous works, we found that persimmon peel (4), grape peel (5), lemon peel (6), and chestnut peel (7) were effective to selectively recover gold in concentrated acidic chloride media.

Orange waste after juicing contains hesperetin, a kind of polyphenol compound, the chemical structure of which is shown in Scheme 1. From the viewpoint of gold recovery, the component having a catechol-like structure in orange waste appears to be effective because the key structure is the same with the polyphenol compounds contained in the fruit-peel wastes investigated in the previous works.

In this study, orange waste after juicing was crosslinked with concentrated sulfuric acid to avoid the leakage of the component having a catechol-like structure from the waste into water during the recovery of gold ion. A gold recovery test was carried out in acidic chloride media to examine whether the same performance as the peels of persimmon, lemon, and chestnut can be observed or not.

EXPERIMENTAL

Materials

Orange waste residue was provided from a juice factory of JA Beverage Saga Co. Ltd., Japan. Analytical grade chloride salts of copper, iron,

palladium, and zinc were used to prepare the test solutions of corresponding metals. Analytical-grade $HAuCl_4 \cdot 4H_2O$ and $H_2PtCl_6 \cdot 6H_2O$ were used to prepare solutions of gold and platinum, respectively. Other chemicals were of analytical grade or higher.

Preparation of Orange Waste Particle

For the preparation of the orange waste particle, 96% sulfuric acid was used as a crosslinking agent by means of condensation reaction between hydroxyl groups of polyphenols and polysaccharides. Raw orange waste was crushed into fine pieces by using a Dalton model P-3S power mill. Fifteen grams of crushed orange waste was mixed with 20 mL of concentrated sulfuric acid and the mixture was stirred for 24 h at 373 K in order to enhance the condensation reaction for crosslinking. The product was filtered, neutralized with sodium hydrogen carbonate solution, washed several times with distilled water, dried in a convection oven for 24 h, and finally crushed to obtain fine particles. The mean diameter of the particle was set at less than 300 μm. The resultant adsorbent was abbreviated as OW hereafter.

Measurement of the Concentration of Polyphenols in OW

An approximate quantity of polyphenols contained in OW was measured by means of the Folin-Denis method (8). The Folin-Denis reagent was prepared by dissolving 10 g of sodium tungstate dihydrate ($NaWO_4 \cdot 2H_2O$), 2.0 g of phosphomolybdic acid, and 5.0 ml of phosphoric acid in 70 ml of distilled water, and heated at 110°C for 2 h. After cooling, the volume of the above solution was set at 100 mL by diluting with distilled water to use as a Folin-Denis reagent. Sodium carbonate was dissolved in 5 mL distilled water, and its supernatant was used as a saturated sodium carbonate solution. About 0.1 g OW was crushed and mixed together with 10 ml of 80% methanol using a homogenizer. The mixture was centrifuged for 10 min at 2000 rpm, and the supernatant liquid was collected. The same process was repeated for 6 times, and the supernatant liquid of each time was collected in the same flask and was referred to as sample 1. A mixture of 10.2 ml sample 1, 3.2 ml distilled water, 0.2 ml Folin-Denis reagent, and 0.4 ml saturated sodium carbonate was incubated for 30 min at ambient temperature to obtain the final test solution. The concentration of polyphenol in the solution was measured by using a UV-Visible spectrometer at 760 nm. For the evaluation of total polyphenols, the calibration curve was drawn using a standard solution of gallic acid.

Adsorption Tests

The adsorption behavior of the OW for metal ions was first tested batchwise. 0.2 mM of metal solutions were prepared in varying concentration of hydrochloric acid. Ten mL of the metal solution was mixed together with 10 mg of OW and shaken for 24 h at 30°C to attain equilibrium. The % adsorption for each metal ion was calculated according to Eq. (1), where C_i is the initial concentration of metal ion and C_e stands for the equilibrium concentration measured after adsorption on the adsorbent.

$$\%\,\text{Adsorption} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

The kinetics of recovery of Au(III) on OW was studied at various hydrochloric acid concentrations by taking 10 mL of 2 mM Au(III) solution together with 10 mg OW. The adsorption isotherm study for Au(III) was performed by varying initial concentration of Au(III) in 0.1 M hydrochloric acid solution. Metal concentration before and after adsorption was measured by using a Shimadzu model AA-6650 atomic absorption spectrophotometer and Shimadzu model ICPS-8100 ICP-AES spectrometer. A morphology of the surface of OW was observed by using a digital micrograph (VHX/VH, KEYENCE model).

RESULTS AND DISCUSSION

Content of Polyphenols in OW

As mentioned earlier, the content of polyphenols in OW was determined by means of the Folin-Denis method. The concentration in the resultant solution was measured as 225 mg/L. This value is the same with that in lemon peel reported by Parajuli et al. (6).

Effect of Hydrochloric Acid Concentration on the Adsorption of Metal Ions

Figure 1 shows the %adsorption of Au(III), Cu(II), Fe(III), Pd(II), Pt(IV), and Zn(II) on OW gel at varying hydrochloric acid concentrations. The highest selectivity was observed for Au(III), whereas the gel was found to exhibit only weak adsorption for other metal ions at less than 5%. The %adsorption of Au(III) was nearly independent of hydrochloric acid concentration. Although some adsorption was observed for Pt(IV), it was much lower in comparison to Au(III). From this result,

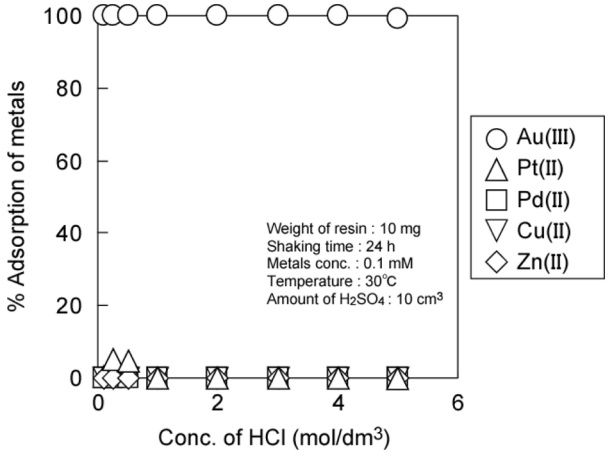

Figure 1. Effect of conc. of HCl on Au(III) adsorption by OW.

it is obvious that the OW gel has very high selectivity for Au(III) and is expected to uptake Au(III) preferentially from a number of co-existing precious or base metals tested so far.

Effect of the Amount of Sulfuric Acid Added in the Preparation of Adsorption Gel

In preparation of the OW gel, the important fact is that a flavonoid-like structure should be contained in the OW gel during the crosslinking treatment with sulfuric acid. To change the structure of OW gel, the concentration of sulfuric acid added in the preparation of adsorption gel was changed. Figure 2 shows the %adsorption of gold on the gel prepared by adding a different volume of sulfuric acid as a function of HCl concentration. Adsorption of gold was lowered by increasing the concentration of sulfuric acid, indicating that the key structure for uptaking gold was created in the gel by crosslinking treatment. Because the gel to recover gold was usually used in acid media, the treatment with sulfuric acid excluded foreign molecules, soluble polysaccharides, from the OW gel.

Adsorption Isotherm of Au(III) on OW

As the OW gel was found to be selective only for Au(III), the adsorption isotherm was investigated for Au(III) ion. Figure 3 shows the adsorption isotherm of Au(III) at HCl concentration of 0.1 M. From this figure, it is

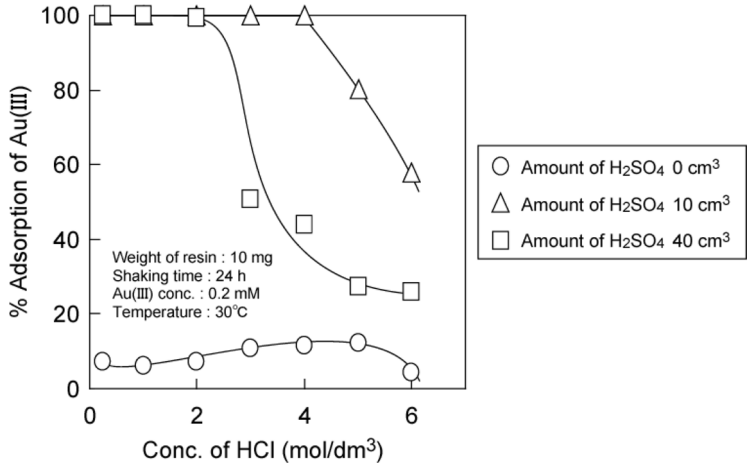

Figure 2. Effect of H_2SO_4 concentration during the preparation of OW on gold adsorption.

clear that the adsorption increases with increasing gold concentration in a low concentration region and tends to approach a constant value of approximately 10 mol/kg dry gel. As the commercially available activated carbon used has the maximum adsorption capacity for gold ion at about 2.5 mol/kg (9), the OW gel is an adsorbent with a much higher potential than conventional adsorbents. Only by a simple crosslinking with sulfuric

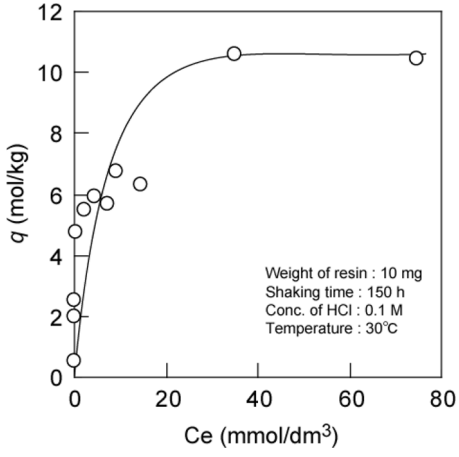

Figure 3. Isotherm curve of gold ion to OW.

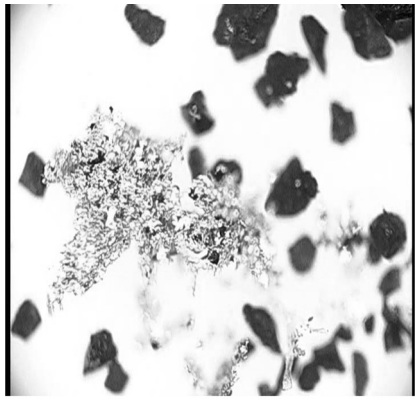

Figure 4. Gold particle formation by OW at high gold concentration (×150).

acid, this kind of useless material, orange waste, can become material for recovering gold with excellent selectively and very high loading capacity.

Figure 4 shows the digital microphotograph of OW after the recovery of gold. In this figure, we can see the aggregate of gold particles separated from gel particles, from which it appears promising to recover gold as elemental gold particles even from a very low concentration level. In contrast to many commercial processes including ion exchange or solvent extraction, the application of this gel avoids the use of any additional reducing agents for the recovery of Au(III) in elemental form.

Recovery Kinetics of Au(III) on OW

The time course of Au(III) ion adsorption at different HCl concentration is shown in Fig. 5. The decrease of HCl concentration accelerated the Au(III) adsorption rate. Because the gold ion formed a chloro-complex in HCl media, the gold ion would be stable when the concentration of Cl^- increased, having difficulty in adsorbing the gold ion to the OW gel. The time to reach equilibrium took longer than 100 h irrespective of the concentration of HCl, indicating the slow rate of adsorption by OW compared with the conventional adsorption. It is clear that the reduction of Au(III) is accompanied by the exchange of ligands between $AuCl_4^-$ and polyphenolic groups of substrates followed by reduction of Au(III) to an elemental form, as mentioned earlier. In the previous work (10), the authors investigated the precipitation of gold using the fermentated persimmon extract, in which the rate determining step of the

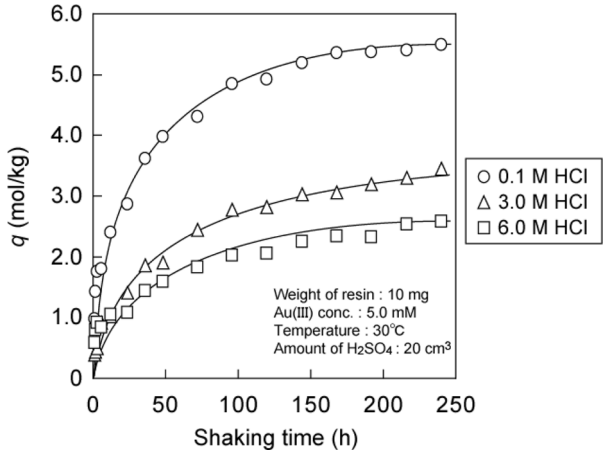

Figure 5. Time course curve of gold adsorption by changing HCl concentration.

precipitation was inferred to be the reduction reaction of Au(III) to Au(0). The recovery mechanism of OW is the same as that of polyphenol in OW, indicating that the rate-determining step of the Au(III) recovery by OW is the reduction reaction of Au(III), resulting in the slow recovery rate of Au(III).

CONCLUSIONS

It was found that orange waste is highly effective for recovering Au(III) from hydrochloric acid by simple crosslinking with sulfuric acid. Its excellent selectivity and very high loading capacity make it a high prospective substrate for Au(III) recovery from a mixture of several metal ions. As the adsorption was found to be followed by reduction to an elemental form, the gold recovered using orange waste gel is expected to be free from foreign elements. Orange waste gel, one of the experimentally available biomasses that exhibits selectivity only for Au(III) and comprises high capacity as well, is a promising material for gold recovery.

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