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Removal, Recovery and Recycle of Gold (III) from Aqueous Solution Using Persimmon Tannin Gel

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Abstract

In order to recover much amount of gold, gold removal-recovery cycle was examined using immobilized persimmon gel, which could remove much amount of gold (III) from the tetrachloroaurate solution at 30˚C. Removal of gold has proceeded different 2 mechanisms stages. At first, gold (III) was adsorbed rapidly on the surface of the persimmon gels until 2 hours and reached adsorption equilibrium. After that, the amount of gold removed was re-increased slowly and also reached equilibrium until 48 hours. The amount of gold removed was affected by the pH of the solution. The amount of Au removed was the highest at pH 5, which was decreased with decreasing or increasing the pH of the solution. The amount of gold removed (mol/g-dry wt. gels) was increased with increasing the gold concentration in the solution, whereas gold removed ratio was decreased. Gold removed ratio was increased with increasing the amount of persimmon gel used, whereas the amount of removed Au (mol/g-dry wt. gels) was decreased. Gold removal-recovery cycles were also examined in detail.

Keywords

Gold (III) Removal, Gold (III) Recovery, Persimmon Tannin Gel, Reduction, Adsorption, Desorption, Recycles

1. Introduction

The demand for gold has increased markedly because of its increasing use in the electrical industry and the development of gold-containing drugs [1]. Therefore, recovering this valuable resource from recycled gold is a subject of wide interest. However, there is little information on the use of adsorbents for the recovery of gold from aqueous system. It is therefore, industrially relevant to address the development of new adsorbents for gold using biological substances.

Recently, several researchers have investigated gold recovery using microbial species, such as bacteria [2], fungi [3] [4] [5], yeasts [6], and algae [7] [8]. However, there is little information on the species of microorganisms that have a high gold absorbing ability.

Previously, we reported that several microorganisms absorb gold. We screened resting forms of 75 microbial strains (19 actinomycetes, 25 bacteria, 17 fungi, and 14 yeasts) and their ability to absorb gold from a hydrogen tetrachloroaurate (III)-containing solution [9]. Hydrogen tetrachloroaurate (III) is used for medical and ceramic materials. Some of the gram-negative bacteria showed great ability to absorb gold from the solution, absorbing over 330 μmol of gold per gram microbial cells (dry weight basis) from the hydrogen tetrachloroaurate (III) solution within 1 h. This rapid gold removal was taken place by biosorption. However, the amount of gold removal was increased for long time contact (−72 h) about 2600 μmol of gold per gram microbial cells by biomineralization [10].

Some researchers were reported gold removal using waste plants, such as modified Bagasse biosorbent [11], porous carbon prepared from barley straw and rice husk [12]. However, the amount of gold removal was relatively small.

Some other types of biological substances, such as immobilized Chinese gallotannin, tea leaves immobilized with formaldehyde, and immobilized persimmon gel, were examined for the removal of gold [13]. In the examined adsorbent, persimmon gel was removed the highest amount of gold from the aqueous hydrogen tetrachloroaurate solution. Metal removal was investigated mainly sorption study. Gold removal using persimmon gel was also investigated by some researchers [14] [15] [16].

Some metal ions removal, such as uranium [17] and hexavalent chromium removal [18] [19] [20] [21], was also reported using persimmon tannin gel.

In this paper, we investigated gold removal mainly by bioreduction process using persimmon tannin gel from gold (III) solution containing relatively high concentration (gold 200 mg/L as hydrogen tetrachloroaurate) for the valuable gold resource recovery. After that, oxidative recovery of gold (III) from the reduced gold (0) using thiourea solution was examined. Additionally, gold reductive removal and oxidative recovery cycles were recycled 5 times.

2. Material and Methods

2.1. Immobilization of Persimmon Gel

Commercially available kakishibu (an extract naturally fermented from the juice of unripe 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 gold (III) removal experiments.

2.2. Gold Removal, Recovery, or Recycles Experiments

Unless otherwise stated, the removal experiments were conducted as follows. Persimmon tannin gel [15 mg dry weight basis] was suspended in 100 mL solution containing containing hydrogen tetrachloroaurate (III). The suspension was shaken for 72 h at 30˚C. Persimmon gel were then removed centrifuged 15,000 rpm and supernatant solution was filtered through membrane filter (0.2 μm pore size). The gold removed by the gel was determined by measuring the gold content in the filtrate with an atomic absorption analysis quantometer (AA-6300, Shimadzu Corporation, Kyoto, Japan).

2.2.1. Effect of pH on the Gold Removal Using Persimmon Gel

An aqueous solution of gold (III) (200 mg/L) in the form of $HAuCl_4$ (100 mL) at pH 1.0 - 6.0 (adjusted using 0.1 M HCl or NaOH) was mixed with persimmon gel (17.0 mg, dry wt. basis) for 21 h at 30˚C.

2.2.2. Effect of Gold (III) Concentration on the Gold Removal by Persimmon Gel

A sample of the adsorbent (15.8 mg, dry wt. basis) was suspended in a solution (pH 5.00) containing the desired gold (III) concentration (*i.e.*, 58.6 - 476 mg/L, 100 mL) for 21 h at 30˚C.

2.2.3. Effect of Gel Amount on Gold (III) Removal Using Perimmon Gel

Desired amounts of the persimmon gels were suspended in a 100 mL solution (pH 5.0) containing hydrogen tetrachloroaurate (III) (Au 198 mg/L) for 21 h at 30˚C.

2.2.4. Variations in Gold (III) Removal with Time

A sample of the adsorbent (14.9 mg, dry wt. basis) was suspended in a solution of hydrogen tetrachloroaurate (100 mL) containing 198 mg/L (1.00 mM) at 30˚C for the desired time between 1 h and 72 h.

2.2.5. Effect of pH on the Oxidation of Reduced Gold by Persimmon Gel

An aqueous solution of gold (III) (50 mg/L) in the form of hydrogen tetrachloroaurate (100 mL) at pH 5.0 (adjusted using 0.1 M NaOH) was mixed with persimmon gel (15.0 mg, dry wt. basis) for 21 h at 30˚C. Reaction mixture was centrifuged 15,000 rpm. After the removal of supernatant solution, remained sediment was mixed with 100 mL of 1.0 M thiourea solution (pH 1.0 - 5.0) for 1h at 30˚C. After the gold oxidation, reaction mixture was centrifuged 15,000 rpm and supernatant solution was filtered through membrane filter.

2.2.6. Effect of Time on the Second Time of Gold (III) Removal in the Gold Removal-Recovery Cycle

An aqueous solution of gold (III) (50 mg/L) in the form of hydrogen tetrachloroaurate (100 mL) at pH 5.0 (adjusted using 0.1 M NaOH) was mixed with persimmon gel (14.6 mg, dry wt. basis) for 21 h at 30˚C. Reaction mixture was centrifuged 15,000 rpm. After the removal of supernatant solution, remained sediment was mixed with 100 mL of 1.0 M thiourea solution (pH 1.0) for 1h at 30˚C. After the gold oxidation, reaction mixture was centrifuged 15,000 rpm. and supernatant solution was filtered through membrane filter. The gold content in the filtrate was measured using the above-mentioned method. After the centrifugation, the residual persimmon gel was mixed with gold (III) (50 mg/L) solution in the form of hydrogen tetrachloroaurate (100 mL) at pH 5.0 for 1 - 8 h at 30˚C.

2.2.7. Recycling of Gold Removal and Recovery by Persimmon Gel

An aqueous solution (100 mL) containing 50 mg/L gold (III) (0.25 μM) at pH 5.00 was mixed with persimmon gel (15.0 mg, dry wt. basis) for 21 h at the first time (for 6 h after the second time) at 30˚C. After gold removal reaction mixture was centrifuged at 15,000 rpm for 20 min. After removal of supernatant solution residual substance was mixed with 1 M thiourea solution (100 mL) for 1 h at 30˚C. These gold removal-recovery cycles were recycled 5 times.

3. Results and Discussion

3.1. Effect of pH on Gold (III) Removal Using Persimmon Gel

We initially investigated the effect of pH on gold (III) removal from a gold (III) solution using persimmon gel. As previously reported, the amount of gold (III) removed from 10 mg/L Au (III) solution using persimmon gel by biosorption was highest at pH 2 to 3 [9]. Recently we found the amount of gold (III) removed from 50 mg/L Au (III) solution using *Candida krusei* cell by biosorption was highest at pH 3 within 1 h, weather that by biomineralization at highest at pH 4 within 72 h [10].

Effect of gold (III) removal was examined an aqueous solution of gold (III) (200 mg/L, 100 mL) and persimmon gel (17.0 mg, dry wt. basis) were mixed at pH 1 - 6 for 21 h at 30˚C. As shown in **Figure 1**, the amount of gold (III) removed

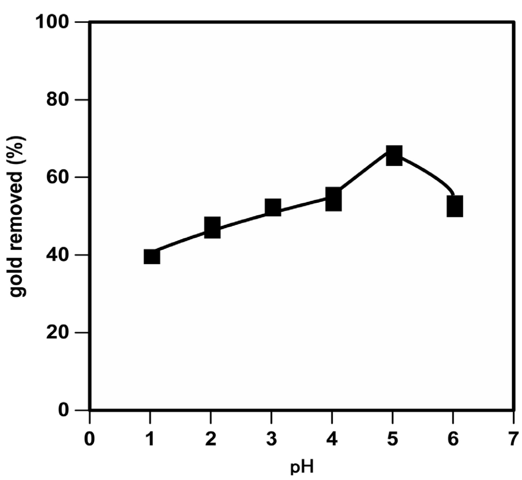
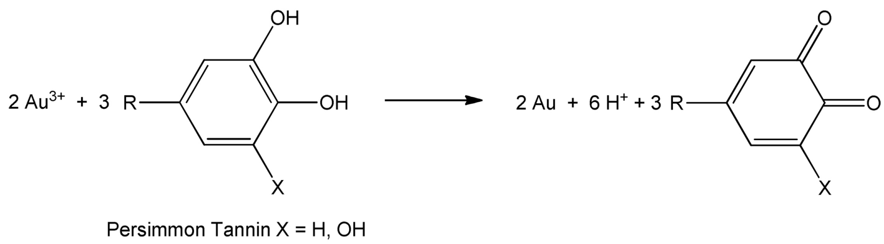


Figure 1. Effect of pH on the gold (III) removal from aqueous $HAuCl_4$ solution using persimmon gel.

was the highest at 5 in this experimental condition.

This result suggests that longer incubation time may change the reaction mechanism responsible for gold removal. The solution containing 10 mg Au/mL nearly colorless for 1 h [13]. However, the color changed to dark red during the 21 h incubation period. Owing to the tetrachloroaurate ion having a negative charge, gold (III) can be effectively removed at pH 3 via adsorption [13]. It can be reduced to atomic gold (0) by the activity of persimmon tannin. Reduction occurred as shown in the following equation.

This equilibrium in an acidic solution is driven to the left; thus, suitable pH changed from 3.0 to 5.0.



3.2. Effect of Gold (III) Concentration on the Gold Removal Using Persimmon Gel

To determine the maximal ability of gold (III) removal at pH 5.0, we examined the mechanism by which the gold (III) concentration affected the gold removal by persimmon gels. The amount of gold removed (μmol/g dry weight gels) by persimmon gels increased with increased gold concentration, whereas the ratio of total amount of gold to the gold concentration decreased (Figure 2). When the gold (III) concentration was 476 mg/L (2420 μM), 5950 μmol gold/gram dry wt. gels were observed at pH 5.0.

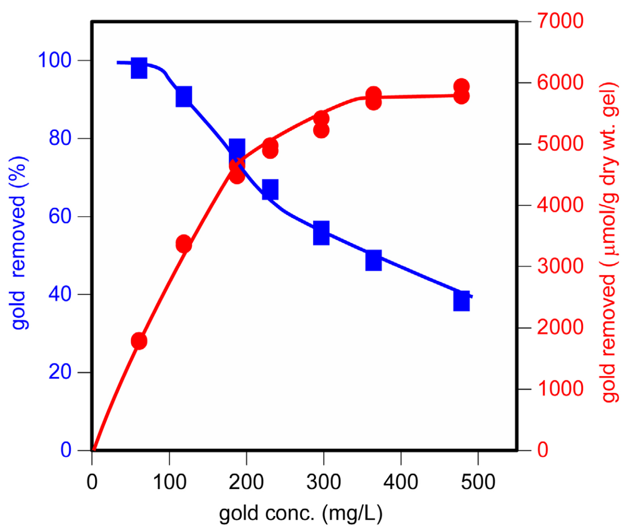


Figure 2. Effect of Initial Gold (III) Concentration on the removal of gold (III) by persimmon Gel. Squares: gold removed (%), Circles: gold removed (μmol/g dry wt. gels).

3.3. Effect of Gel Amount on the Gold Removal Using Persimmon Gel

The amount of gold (III) removed (μmol/g dry wt. cells) by persimmon gel decreased slightly with the increased gel amounts (**Figure 3**). However, increasing the gel amount increased the total gold (III) removal. About 1300 μmol gold/g dry wt. gels were removed using 5.4 mg of the dry wt. basis of persimmon gels in 72-h incubation. Although the solution color did not change after the 1-h incubation period, the color changed to violet after 72 h.

3.4. Effect of Time on Gold (III) Removal Using Persimmon Gel

The effect of time on gold (III) removal from solution using persimmon gel was then examined. As shown in **Figure 4**, the removal of gold (III) was rapid with about half amount removed within 4 h by a sorption precess, when a sample of the gels were suspended in the $HAuCl_4$ solution at 30˚C. After that gold (III) removal proceeded slower rate, and most of the gold (III) was removed until 48 h by reduction process.

3.5. Effect of pH on the Oxidation of Reduced Gold by Persimmon Gel

An aqueous solution of gold (III) (50 mg/L) in the form of $HAuCl_4$ (100 mL) at pH 5.0 (adjusted using 0.1 M NaOH) was mixed with persimmon gel (15.0 mg, dry wt. basis) for 21 h at 30˚C. Gold (III) was reduced to atomic gold (0) quantitatively. After the reduction, reduced substances were mixed with 100 mL of 1.0 M thiourea solution (pH 1.0 - 5.0) for 1 h at 30˚C. As shown in **Figure 5**, Au oxidized (%) was increased by decreasing the pH of the solution pH. About 90% of the gold (0) was oxidized at pH 1 in the solution.

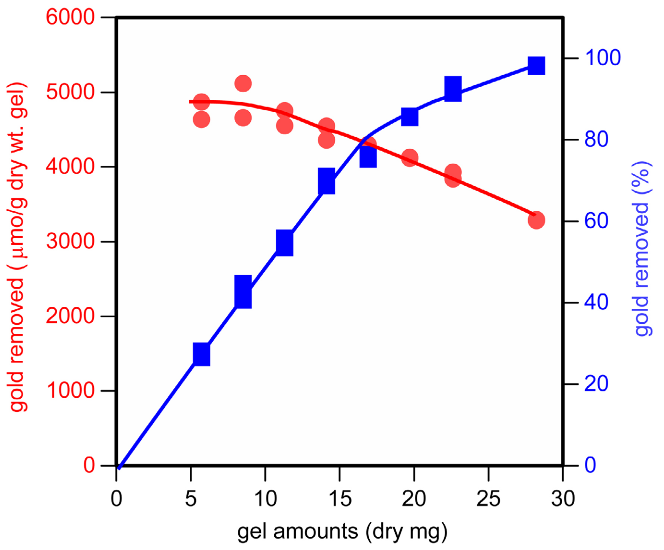


Figure 3. Effect of gel amounts on the removal of gold (III) by persimmon gel. Squares: gold removed (%), Circles: gold removed (μmol/g dry wt. gel).

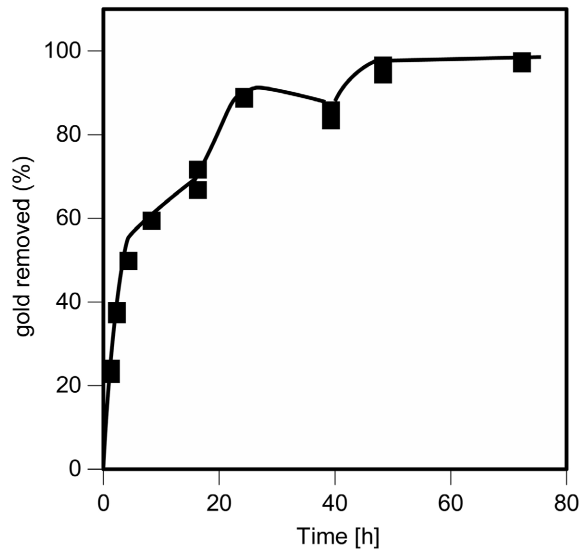


Figure 4. Effect of time on the removal of gold (III) using the persimmon gel absorbent.

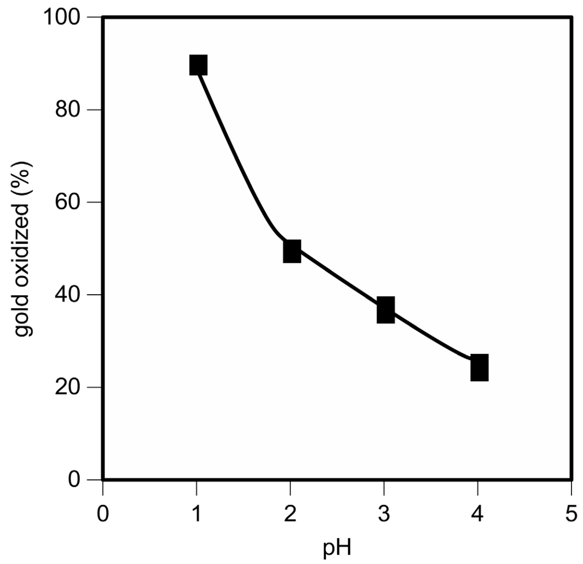


Figure 5. Effect of pH on gold oxidation of reduced gold (0) by thiourea solution.

3.6. Effect of Time on the Second Time of Gold (III) Removal in the Gold Removal-Recovery Cycle

Recently, in the gold removal-recovery cycles using microorganism, such as *Pseudomonas saccharophila* cells, the gold removal rate after second time was markedly faster than that of the first time [22]. Therefore, effect of time on the second time of gold (III) removal in the gold removal-recovery cycle.

Gold removal-recovery at the first time was undertaken almost quantitatively. As shown in **Figure 6**, gold (III) removal at the second time was almost reached equilibrium within 2 h. The gold removal at the second time became faster than that of the first time.

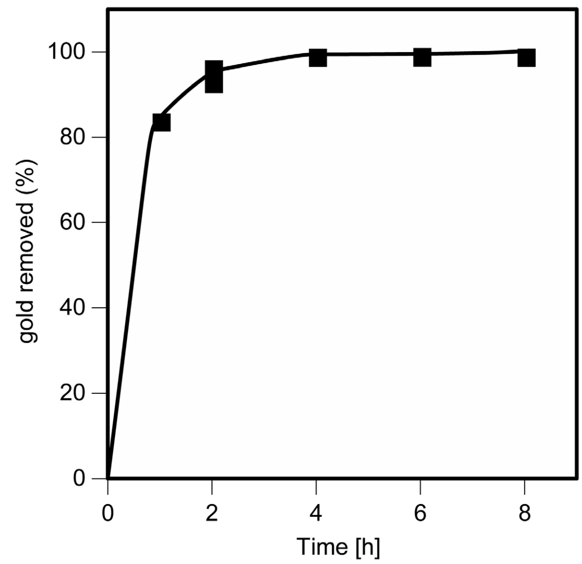


Figure 6. Effect of time on the removal of gold (III) using the persimmon gel absorbent at the second cycle after one time of gold removal-recovery cycle.

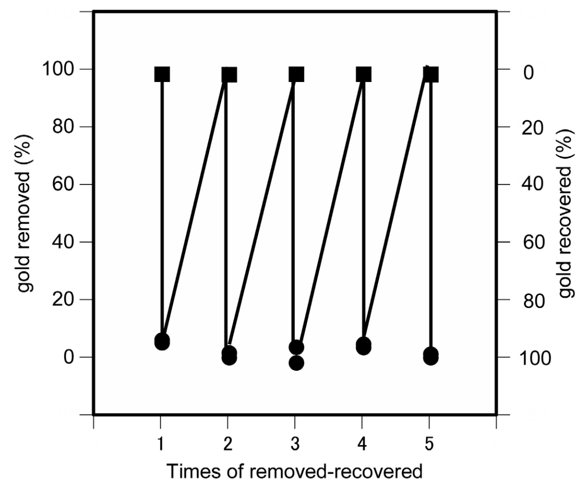


Figure 7. Recycles of gold removal and recovery using the persimmon gel. Squares: gold removed [%], Circles: gold recovered [%].

3.7. Recycling of Gold Removal and Recovery by Persimmon Gel

Gold removal with persimmon gel was performed for 21 h at the first time and that for 6 h after the second time. Gold removal-recovery cycles were recycled 5 times. As shown in Figure 7, these cycles were recycled effectively.

4. Conclusions

It was herein investigated the removal, recovery and recycle of gold (III) from aqueous solutions using persimmon tannin gel.

We observed that about half the amount of gold (III) was removed from the solution by biosorption after a short incubation time (4 h) and the remaining half was reduced from gold (III) to gold (0) by biomineralization after 48-hour incubation. In order to recover much amount of gold, gold removal-recovery cycle was examined using immobilized persimmon gel, which could remove much amount of gold (III) from the tetrachloroaurate solution at 30˚C. Removal of gold was proceeded different 2 mechanisms stages. At first, gold (III) was adsorbed rapidly on the surface of the persimmon gels until 2 hours and reached adsorption equilibrium. After that, the amount of gold removed was re-increased slowly and also reached equilibrium until 48 hours. The amount of gold removed was affected by the pH of the solution. The amount of Au removed was the highest at pH 5, which was decreased with decreasing or increasing the pH of the solution. The amount of gold removed (mol/g-dry wt. gels) was increased with increasing the gold concentration in the solution, whereas gold removed ratio was decreased. Gold removed ratio was increased with increasing the amount of persimmon gel used, whereas the amount of removed Au (mol/g-dry wt. gels) was decreased. The amount of gold (III) removed was reached 6000 μmol/g dry wt. of persimmon gel. Accordingly, gold (III) can be removed using persimmon gel by biomineralization very effectively.

Recycles of gold removal-recovery cycles were next examined. In these cycles, the removal of gold after second time, the removal of gold was much faster than that of the first time. These findings were also observed that the gold removal-recycle cycles using microorganism, such as *P. saccharophila* [22]. Accordingly, the gold removal (72 h for the first time)-recovery (1 h)-removal (2 h for after the second time) cycles can be carried out in this system.

Conflicts of Interest

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

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