Chapter

Gold Recovery Process from Primary and Secondary Resources Using Bioadsorbents

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Abstract

Bioadsorbents were prepared in a simple manner only by treating in boiling concentrated sulfuric acid from various biomass materials such as various polysaccharides, persimmon tannin, cotton, paper and biomass wastes such as orange juice residue and microalgae residue after extracting biofuel. These bioadsorbents exhibited high selectivity only to gold over other metals and extraordinary high loading capacity for gold(III), which were elucidated to be attributable to the selective reduction of gold(III) ion to elemental gold due to its highest oxidation-reduction potential of gold(III) of metal ions, catalyzed by the surface of bioadsorbents prepared in boiling sulfuric acid. By using these biosorbents, recovery of gold from actual samples of printed circuit boards of spent mobile phones and Mongolian gold ore was investigated. Recovery of trace concentration of gold(I) from simulated spent alkaline cyanide solution was also investigated using the bioadsorbent. Application of bioadsorbents to some recovery processes of gold from cyanide solutions was proposed.

Keywords: gold recovery, biomass materials

1. Introduction

In recent years, accompanied by huge consumption of various metals, metal contents or grade of metal ores have become poor and complex. Under such situation, not only poor and complex natural resources but also secondary resources, i.e., various wastes containing valuable metals in low contents, have to be employed as feed materials to recover valuable metals. The typical wastes containing valuable metals are those of spent electric and electronic appliances, i.e., e-wastes.

For the recovery of valuable metals from such poor and complex feed materials, hydrometallurgical processes are more suitable than pyrometallurgical processes. Hydrometallurgical processes consist of leaching of metals from solid feed materials into aqueous solutions, separation and concentration of the targeted metals from other metals, and final recovery as solid metals of high purity such as ingot metals. For the separation and concentration of the targeted metals, various processes such as precipitation, solvent extraction, ion-exchange including chelating ion-exchange
and adsorption have been employed. Of these processes, precipitation and solvent extraction are suitable for the recovery from solutions of high concentration, while adsorption and ion-exchange are suitable from those of low or trace concentration.

During long operation, solvent extraction reagents, adsorbents, and ion-exchangers gradually deteriorate and finally they are discarded. For example, in the cases of ion-exchange resins, they deteriorate through the formation of many cracks and clogging of micropores of the resins by fine particles present in actual solutions, both of which impede smooth operation using packed columns.

For the effective separation and concentration in hydrometallurgical processes, high selectivity and high loading capacity for targeted metals are strongly required for solvent extraction reagents and adsorbents. However, the selectivity exhibited by a majority of commercially available ion-exchange resins including chelating resins has not been always satisfactory.

Ion-exchange resins are plastic beads produced from petroleum. In recent years, environmental pollutions by microplastics have been deeply worried all over the world and big expectations are placed on biodegradable plastics. However, their high production costs prevent their actual employments in various fields.

In our recent studies, we found that adsorption gels prepared from various kinds of biomass materials including various biomass wastes, i.e., bioadsorbents, exhibit high selectivity and high loading capacity for targeted metals such as hazardous heavy metals and valuable metals. These are prepared from waste wood [1–4] and straws of rice and wheat [5], spent papers [6–10], cotton [11], waste seaweeds [12, 13], persimmon tannin [14–16] or wastes of persimmon [17, 18] and grape [19, 20] rich in tannin compounds, wastes of citrus such as orange [21] and lemon [22], and residue of microalgae after extracting biofuel [23, 24].

In the present chapter, we introduce the adsorptive recovery of gold from printed circuit boards (PCBs) of spent mobile phones, a typical e-waste, and actual gold ore, a primary resource of gold, as well as that of trace concentration of gold from simulated spent cyanide solutions using some of these bioadsorbents.

2. Preparation of bioadsorbents for gold recovery

The bioadsorbents for gold recovery can be easily prepared in a simple manner as schematically shown in Figure 1. Pieces of feed materials of biomass are stirred in
boiling concentrated sulfuric acid for about 24 h, where hydroxyl groups contained in the biomass undergo dehydration condensation reactions and polymer chains of the biomass are cross-linked via ether bonds. The solid materials are neutralized using dilute alkali solution and water-washed and then, they are dried in a convection oven and pulverized. Finally, they are sieved to uniform the particle size. The final products are black powder, the particle size of which are less than 0.1 mm.

3. Adsorption behaviors of bioadsorbents for metal ions

All of the bioadsorbents prepared by the method mentioned above exhibited extraordinary high selectivity only to gold(III) in the adsorption from hydrochloric acid solutions. For example, Figure 2 shows the % adsorption of some metal ions onto bioadsorbent prepared from orange waste (orange juice residue) from various concentrations of hydrochloric acid solution [21], where the % adsorption denotes the percentage of metal ion adsorbed on the adsorbent from aqueous solution and defined by the following equation.

\[
\% \text{Adsorption} = \frac{\text{Mass of metal ion adsorbed on the adsorbent}}{\text{Mass of metal ion initially present in the aqueous solution}} \times 100
\]

\[
= \left\{ \frac{\text{initial concentration of the metal ion} - \text{concentration of the metal ion after adsorption}}{\text{initial concentration of the metal ion}} \right\} \times 100
\]

As seen in this figure, only gold(III) is quantitatively adsorbed over the whole concentration range of hydrochloric acid tested, while other metal ions, not only precious metals such as palladium(II) and platinum(IV) but also base metals such as

![Figure 2. Percentage adsorptions of some metal ions on bioadsorbent prepared from orange waste by treating in boiling concentrated sulfuric acid [21].](image)
copper(II) and zinc(II), are not practically adsorbed. Similar phenomena were also observed also for all bioadsorbents prepared by the method using boiling concentrated sulfuric acid.

Figure 3 shows the similar plots in the case of the adsorption on the bioadsorbent of orange waste prepared by means of carbonization at 800°C, for comparison. Although gold(III) is quantitatively adsorbed over the whole concentration range of hydrochloric acid also on this bioadsorbent, considerable amount of platinum(IV) and palladium(II) is also adsorbed at low concentration range in particular; i.e., the selectivity of the carbonized bioadsorbent to gold(III) is inferior to that prepared by using boiling concentrated sulfuric acid.

Figure 4 shows the adsorption isotherm of gold(III), i.e., the relationship between the amount of adsorption of gold(III) and its concentration present in the aqueous solution (0.1 mol/L hydrochloric acid solution) at equilibrium at 30°C, on the adsorbent prepared from orange waste. The amount of adsorption increases with increasing concentration of gold(III) at low concentration range, while it tends to approach a constant value at high concentration range, suggesting the typical Langmuir-type adsorption isotherm. From the constant value, the maximum adsorption capacity for gold(III) on this adsorbent was evaluated as 10.5 mol/kg ( = 2.07 kg gold(III)/kg adsorbent), which is an extraordinarily high value, greater than the weight of the adsorbent. Similarly, very high values of adsorption capacity for gold(III) were observed also for other adsorbent prepared from different kinds of biomass materials. Table 1 shows the maximum adsorption capacities for gold(III) on the adsorbent prepared from various biomass materials and those on other adsorbents reported in some literatures, for comparison.

As seen in this table, some of bioadsorbents exhibit much higher adsorption capacity for gold(III) than commercially available adsorbents such as activated carbon and chelating resins.
Figure 5 shows the image of optical microscope of the bioadsorbent prepared from residue of microalgae after biofuel extraction after adsorption of gold(III). In this photograph, aggregates of elemental gold particles are observed as brilliant yellow lumps, while black particles are bioadsorbents of microalgae. The formation of elemental gold was confirmed also from the observation by X-ray diffraction (XRD) analysis. Similar phenomena were observed also for other bioadsorbents we prepared. From these results, it can be concluded that the adsorbed gold(III) was reduced into elemental gold on the surface of the bioadsorbent and that the extraordinary high adsorption capacity for gold(III) is attributable to the formation of elemental gold particles on these bioadsorbents. Furthermore, it can be concluded that the high selectivity for gold(III) over other metal ions is attributed to the higher oxidation-reduction potential (ORP) for gold(III) than other metal ions; e.g., those of some metal ions are as follows. Au(III): 1.52 V, Pd(II): 0.915 V, Cu(II): 0.340V, Ni(II): −0.257 V, Zn(II): −0.763 V.

The mechanism of adsorptive reduction of gold(III) is shown in Figure 6. Gold (III) present in aqueous solution is adsorbed on the surface of the bioadsorbents and reduced into elemental gold as follows.

1. Interaction of positively charged gold(III) ion with oxygen atoms of hydroxyl groups and other oxygen atoms of polysaccharide molecules or tannin compounds contained in bioadsorbents followed by adsorption forming stable five-membered chelate rings. Here, by the cross-linking reactions using boiling concentrated sulfuric acid, structures of polymer chains of polysaccharide and tannin molecules are transformed into those suitable for forming stable five-membered metal chelates.
2. Reduction of the adsorbed gold(III) ions into elemental or metallic gold particles by the aid of hydroxyl groups that take part in the interaction with the gold(III) ions, releasing hydrogen ions, where the hydroxyl groups are oxidized into carbonyl groups.

3. Protonation of the carbonyl groups followed by returning back to hydroxyl groups which function again as the adsorption sites.

4. Aggregation of elemental gold particles into bigger lumps followed by isolation from surface of the bioadsorbents.

| Adsorbent                                           | Maximum adsorption capacity (g/kg) | Reference |
|----------------------------------------------------|-----------------------------------|-----------|
| Cross-linked lignophenol prepared from sawdust of cedar | 374                               | [3]       |
| Cross-linked lignocatechol prepared from sawdust of cedar | 472                               | [3]       |
| Cross-linked lignopyrogallol prepared from sawdust of cedar | 374                               | [3]       |
| Cross-linked lignophenol prepared from rice straw    | 552                               | [5]       |
| Cross-linked lignophenol prepared from wheat straw   | 217                               | [5]       |
| Cross-linked cellulose                               | 1491                              | [25]      |
| Cross-linked dextran                                 | 1418                              | [25]      |
| Cross-linked alginic acid                            | 1111                              | [25]      |
| Cross-linked pectic acid                             | 946                               | [25]      |
| Cross-linked paper                                   | 1005                              | [10]      |
| Cross-linked cotton                                  | 1221                              | [11]      |
| Persimmon extract powder (PT powder, feed material of CPT) | 1162                              | [14]      |
| Cross-linked persimmon tannin (CPT)                  | 1517                              | [14]      |
| Cross-linked persimmon peel waste (PP)               | 985                               | [17]      |
| Cross-linked orange juice residue (OJR)              | 1970                              | [21]      |
| Cross-linked lemon peel                              | 1300                              | [22]      |
| Cross-linked chestnut pellicle                       | 2100                              | [26]      |
| Cross-linked grape waste                             | 1962                              | [19]      |
| Cross-linked microalgal residue (CMA)                | 650                               | [23]      |
| Microalgal residue, feed material of CMA             | 79                                | [23]      |
| Commercially available wood-based activated carbon   | 493                               | [3]       |
| Rice husk carbon                                     | 150                               | [27]      |
| Barley straw carbon                                  | 290                               | [27]      |
| Wattle tannin cross-linked using formaldehyde        | 8000                              | [28]      |
| Chitosan cross-linked using glutaraldehyde           | 566                               | [29]      |
| Commercially available chelating resin containing thiol functional groups (Duolite GT-73) | 114                               | [30]      |

Table 1. Maximum adsorption capacities for gold(III) on bioadsorbents we prepared and those reported in some literatures.
The surface of polysaccharides and tannin compounds cross-linked by the aid of boiling concentrated sulfuric acid functions as catalysts for the reduction reaction of gold(III) ions into elemental gold(0) under acidic conditions.

Figure 5.
*Image of optical microscope of the bioadsorbent prepared from residue of microalgae after biofuel extraction after adsorption of gold(III).*

Figure 6.
*Mechanism of the cross-linking between polymer chains of cellulose molecules by the aid of concentrated sulfuric acid and that of reductive adsorption of gold(III) on the cross-linked cellulose [25].*
Figure 7 shows the effect of pH on the adsorption of gold(III) on the bioadsorbent prepared from orange waste by treating in boiling concentrated sulfuric acid. Although gold(III) is quantitatively adsorbed at pH less than 6 (acidic condition), no adsorption of gold(III) takes place at pH higher than 8 (basic condition) in accordance with the mechanism mentioned above.

Figure 8 shows the relationship between the concentration of gold(III) remained in the aqueous solution after the adsorption on bioadsorbent prepared from orange waste by treating in boiling concentrated sulfuric acid and solid/liquid ratio, the ratio of dry weight of the added adsorbent to volume of aqueous solution.
Figure 8 shows the effect of solid/liquid ratio, the ratio of dry weight of the added adsorbent to volume of aqueous solution, on the concentration of gold(III) remained in the aqueous solution after the adsorption from 0.25 mol/L hydrochloric acid solution containing 1.05 mg/L gold(III) on bioadsorbent prepared from orange waste by treating in boiling concentrated sulfuric acid. As seen in this figure, the concentration of gold(III) is lowered down to as low as 0.02 mg/L (20 ppb) by this bioadsorbent; i.e., about 98% recovery was achieved from such trace concentration of gold(III) solution.

The elution or desorption of the adsorbed gold(III) is difficult or nearly impossible using usual elution agents. In such cases, as will be mentioned in the latter section, gold-loaded adsorbents are incinerated leaving solid gold particles in the incineration residues. The bioadsorbents prepared from biomass materials are easy to be incinerated at relatively low temperature compared with commercially available ion-exchange resins, plastic beads produced from petroleum, which is another advantage of bioadsorbents.

Figure 9 shows the thermogravimetric curves (relationship between percentage decrease in the weight of materials and temperature) of bioadsorbent of microalgae residue after biofuel extraction before (blue line) and after (red line) the adsorption of gold(III) [23].

4. Recovery of gold from printed circuit boards of spent mobile phones

As an example of the use of bioadsorbents we prepared, recovery of gold from printed circuit boards (PCBs) of spent mobile phones is introduced in this section.
Spent home appliances such as mobile phones are dismantled by hand work into various parts to recover various valuables for their reuses as shown in Figure 10.

Of these dismantled parts, gold and other precious metals such as palladium and platinum are contained in PCBs; i.e., PCBs of spent electronics are typical secondary resources of precious metals. According to the conventional recovery process of precious metals from complex feed materials such as anode slimes of copper and nickel generated in electrowinning processes of these metals which contain many kinds of metals such as gold, silver, palladium, platinum and base metals, they are recovered by repeating dissolution using aqua regia followed by precipitation for many times, which needs tedious long-time operations and high labor costs. In early 1970s, new recovery process was developed and commercialized by INCO [31]. In this process, the feed materials are totally dissolved in hydrochloric acid into that chlorine gas had been blown, abbreviated as chlorine-containing HCl, hereafter. Here, the chlorine gas dissolved in hydrochloric acid solution is converted into hypochlorous acid (HClO) according to the following reaction:

$$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{HCl} \quad (2)$$

Thus, formed hypochlorous acid functions as a strong oxidation agent, converting solid metals into metal ions, dissolving into hydrochloric acid solution, where the metal ions give rise to stable chloro-complexes interacting with chloride ions; e.g., gold(III) is present as AuCl$_4^-$, anionic species. However, because the hypochlorous acid formed by the abovementioned reaction is unstable and is easily converted into hydrochloric acid, the metal recovery from such solutions is actually the same with that from hydrochloric acid solutions.

In the present work, the sample of spent PCBs was treated in the similar manner using chlorine-containing HCl as schematically shown in Figure 11.

They are incinerated at first at 750°C to extinguish epoxy resin boards on which various parts are placed. Then, the residues are leached using nitric acid solution to remove silver, which impedes the recovery of gold and other precious metals in the latter steps, together with some base metals. The residue of the nitric acid leaching was calcined at 750°C again and leached using chlorine-containing HCl to recover gold and other precious metals. In the present work, the sample of such metal-loaded leach liquor was kindly donated by Shonan Factory of TANAKA.
KIKINZOKU KOGYO Co. Ltd., Hiratsuka, Japan. The metal concentrations of this sample solution measured by ICP-AES were as follows (mg/L): Au(100), Pd(8), Pb(342), Fe(314), Cu(250), Ni(411), and Zn(41). The total acid concentration measured by acid-base titration was around 3.0 mol/L.

Figures 12 and 13 show the effect of solid/liquid ratio, the ratio of amount (dry weight) of added bioadsorbent to unit volume of sample leach liquor, on % adsorption of each metal in the case of adsorptive recovery using bioadsorbents of orange waste and cotton prepared by treating in boiling concentrated sulfuric acid, respectively. As seen from these figures, although gold is nearly quantitatively adsorbed, other metals are not practically adsorbed on these bioadsorbents.

Figure 11.
Flow sheet for the treatment of spent PCBs in the present work.

Figure 12.
Effect of solid/liquid ratio on the % adsorption of various metals from leach liquor of chlorine-containing HCl using the bioadsorbent prepared from orange waste by treating in boiling concentrated sulfuric acid.
5. Recovery of gold from Mongolian gold ore

At present, majority of gold has been recovered from gold and silver ores by means of cyanide process developed at the beginning of twentieth century as schematically shown in Figure 14. In this process, pulverized ores are leached using alkaline cyanide solution to extract gold as gold(I)-cyanide complexes according to the following reaction:

$$4\text{Au} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{AuCN}_2^- + 4\text{OH}^-$$  \(3\)

The extracted gold(I) as anionic species, \(\text{AuCN}_2^-\), is adsorbed onto activated carbon or strongly basic anion exchange resins, which are termed as CIP and RIP.

![Figure 13.](image)

*Effect of solid/liquid ratio on the % adsorption of various metals from leach liquor of chlorine-containing HCl using the bioadsorbent of cotton prepared by treating in boiling concentrated sulfuric acid.*

![Figure 14.](image)

*Flow sheet of conventional gold recovery process from gold ores using alkaline cyanide solutions.*
processes, respectively. Because it is difficult to desorb the gold adsorbed onto these adsorbents, these are incinerated at high temperature to recover metallic gold.

This cyanide process has suffered from some problems as follows:

1. Strong toxicity of cyanide, which causes serious environmental problems and, consequently, needs some costs for safe operation and environmental protection.

2. Interference by other coexisting metals or low selectivity over other metals.

3. Slow dissolution of gold as shown in Table 2 that shows the comparison of dissolution rate of gold by some lixiviants.

As alternatives to cyanide leaching, some noncyanide leaching processes such as those using hypochlorous acid, bromine, thiosulfate, and thiourea have been proposed. However, these new processes also suffer from their own drawbacks as follows. Thiourea is known as carcinogen and, additionally, it is expensive and chemically unstable compared to cyanide, while it has a big advantage of much faster dissolution rate of gold than cyanide; that is, it was reported that the dissolution rate of gold using the mixture of 1% thiourea in 0.5% sulfuric acid containing 0.1% ferric ion is over 10-folds faster than that using the mixture of 0.5% sodium cyanide and 0.05% calcium oxide [33].

Following the recovery of gold from spent PCBs, a typical secondary resource, we attempted to apply the bioadsorbents we prepared to noncyanide leach liquor of actual gold ore (one example of typical primary resources). The sample of the ore was kindly donated by Western Mongolian Metals Co. Ltd., Ulaanbaatar, Mongolia. It was fine powder, the particle size of which was around 75–150 μm and the metal contents (mg/g) were as follows: gold 0.046, platinum 0.018, aluminum 0.694, iron 64.75, cobalt 0.008, nickel 0.040, copper 0.779, and zinc 0.069.

In the present work, the recovery of gold from the abovementioned gold ore was investigated by means of leaching using acidothiourea solution consisting of 0.1 mol/L thiourea and 0.05 mol/L sulfuric acid followed by adsorption using bioadsorbent of cotton. Figure 15 shows the effect of liquid/solid ratio (ratio of volume of the leach liquor to unit dry weight of the sample of ore powder) on the leached amount of gold and platinum from the ore sample. From this result, 30 mL/g appears to be the most suitable liquid/solid ratio for extracting gold and platinum from the ore sample; i.e., addition of about 0.23 g of thiourea and 0.15 g of sulfuric

| Reagents or mixtures                                      | Operating condition | Dissolution rate (g/cm² h) |
|-----------------------------------------------------------|---------------------|---------------------------|
| 32 wt.% HCl + MnO₂(s)                                     | 100°C, atm          | 0.137                     |
| 32 wt.% HCl + MnO₂(s)                                     | 90°C, 639 kPa       | 0.25                      |
| 6 mmol/dm³ NaCN + 4 mmol/dm³ Ca(OH)₂ + air               | 30°C, atm           | 0.7                       |
| 0.45 mol/dm³ NaCN + 0.2 mol/dm³ NaOH + air               | 30°C, atm           | 1.5                       |
| 6 mol/dm³ HCl + 0.22 mol/dm³ H₂O₂                         | 50°C                | 4                         |
| 6 mol/dm³ HCl + saturated Cl₂ (typical chlorine-containing HCl) | 40°C, atm           | 180                       |
| 3 HCl + HNO₃ (6 mol/dm³) (aqua regia)                     | 80°C, atm           | 1800                      |

Table 2. Comparison of dissolution rates of gold using some lixiviants [32].
Acid is necessary for complete extraction of gold and platinum from unit gram of the ore sample.

**Figure 15.**
Effect of liquid/solid ratio on the leaching amount of gold and platinum from the Mongolian gold ore sample using acidothiourea consisting of 0.1 mol/L thiourea and 0.05 mol/L sulfuric acid.

**Figure 16.**
Effect of solid/liquid ratio on the adsorption of gold using cotton adsorbent from the leach liquor of the Mongolian gold ore.

Acid is necessary for complete extraction of gold and platinum from unit gram of the ore sample.

**Figure 16** shows effect of solid/liquid ratio (ratio of dry weight of the added adsorbent to unit volume of the leach liquor containing gold(III)) on the adsorption of gold using bioadsorbent of cotton prepared by treating in boiling concentrated sulfuric acid from the leach liquor of Mongolian gold ore. This figure indicates that addition of at least 3 g of bioadsorbent of cotton is necessary for quantitative adsorption of gold(III) from this leach liquor.

**Figure 17** shows the XRD pattern of the bioadsorbent of cotton after adsorption of gold(III). Four sharp peaks in this figure obviously evidence the presence of solid...
elemental gold, suggesting that gold was recovered as elemental gold particles also in this system.

6. Recovery of gold from simulated spent cyanide solutions using bioadsorbents

As mentioned earlier, cyanide solution has been extensively employed for a long time in gold mining and also in plating applications because of its special complexing capabilities in aqueous solutions, creating the soluble \(^{\text{Au(CN)}_2^-}\) complex. Also as mentioned in the preceding section, such \(^{\text{Au(CN)}_2^-}\) complex is recovered by means of adsorption on activated carbon or strongly basic anion-exchange resin. However, such adsorptive recovery of gold is not always quantitative and trace concentrations of gold still remain in the cyanide solution. Spent cyanide solutions generated after the recovery of gold are treated for cyanide decomposition before discharging in environments according to the following processes [34]:

1. Oxidative decomposition using sulfur dioxide (INCO process)

In this process, cyanide ion is decomposed by the aid of sulfur dioxide and oxygen gasses blown into the cyanide solution catalyzed by cupric sulfate according to the following reaction:

\[
\text{CN}^- + \text{SO}_2 + \text{O}_2 + \text{H}_2\text{O} = \text{OCN}^- + \text{SO}_4^{2-} + 2\text{H}^+ \tag{4}
\]

where \(\text{OCN}^-\) ion is unstable and easily hydrolyzed into ammonium bicarbonate. The sulfur dioxide gas can be replaced by sulfurous acid or sodium pyrosulfite (\(\text{Na}_2\text{S}_2\text{O}_5\)).

2. Oxidative decomposition using hydrogen peroxide

Cyanide ion is decomposed by the aid of hydrogen peroxide also catalyzed by cupric sulfate according to the following reaction:
\[ \text{CN}^- + \text{H}_2\text{O}_2 = \text{OCN}^- + \text{SO}_4^{2-} + 2\text{H}^+ \] (5)

3. Decomposition using Caro’s acid

Cyanide is decomposed using Caro’s acid, which is formed by interacting hydrogen peroxide with sulfuric acid according to the following reaction:

\[ \text{CN}^- + \text{H}_2\text{SO}_5 = \text{OCN}^- + \text{SO}_4^{2-} + 2\text{H}^+ \] (6)

4. Decomposition by the aid of microorganisms

Cyanide is decomposed by microorganisms according to the following reaction:

\[ \text{CN}^- + 2\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + \text{Bac} = \text{HCO}_3^- + \text{NH}_3 \] (7)

5. Decomposition by the aid of sodium hypochlorite

Cyanide is decomposed by the aid of sodium hypochlorite in alkaline media according to the following reaction [15]:

\[ 2\text{NaCN} + 5\text{NaClO} + \text{H}_2\text{O} = 2\text{NaHCO}_3 + \text{N}_2 + 5\text{NaCl} \] (8)

The recovery of trace concentrations of gold remaining in spent cyanide solutions has been difficult due to relatively high processing costs as well as other various technical problems. However, the recovery of such trace concentration of gold has become highly attractive from an economical point of view due to the high price of gold in recent years. Consequently, we attempted to recover such trace concentration of gold(I) from waste cyanide solutions.

However, since gold(I) cyanide solutions are very toxic and its use is prohibited in our laboratory, a sodium salt of gold(I) sulfite, i.e., sodium gold(I) sulfite, \( \text{Na}_3[\text{Au(I)(SO}_3\text{)}_2] \), was employed for the adsorptive recovery test of gold(I) in the present work as a simulated solution of cyanide solutions to obtain the fundamental information for exploring the feasibility for the recovery of gold(I) [35]. The use of the gold(I) sulfite complex for gold plating had been known since 1842 [36] and has

Figure 18.

Effect of sodium hypochlorite concentration on the adsorption of some metal ions on bioadsorbent of pure cellulose prepared by treating in boiling concentrated sulfuric acid [35].
been currently employed in noncyanide gold plating. The trace amount of Au(I) is also exhausted from such gold sulfite-based plating baths.

In the adsorption of gold(I) in the absence of hypochlorite, only negligible adsorption of gold(I) was observed regardless of pH values. However, by adding sodium hypochlorite to the gold(I) solution in hydrochloric acidic media, the adsorption was drastically improved as shown in Figure 18, suggesting that the addition of sodium hypochlorite provides suitable chemical changes for gold(I). Additionally, a high selectivity to gold(I) was also observed over other metals similar to the case of the adsorption of gold(III) from hydrochloric acid solution as shown in Figure 2, for example.

It is considered that gold(I) was oxidized into gold(III) by the aid of sodium hypochlorite according to the following reaction and adsorbed onto the bioadsorbent of pure cellulose.

\[
\text{NaClO} + \text{HCl} \rightarrow \text{HOCl} + \text{NaCl} \quad (9)
\]

\[
2\text{Au}^{+} + 3\text{HOCl} + 3\text{H}^{+} + 5\text{Cl}^{-} \rightarrow 2\text{AuCl}_{4}^{-} + 3\text{H}_{2}\text{O} \quad (10)
\]

Here, the sample solution of sodium gold(I) sulfite, Na₃[Au(SO₃)₂], was colorless. But, after the addition of excess amount of sodium hypochlorite in the presence of hydrochloric acid, the color was changed to pale yellow, the color of AuCl₄⁻, i.e., Au(III) solution, which visually evidence the oxidation reaction.

Figure 19 shows the effect of solid/liquid ratio, the ratio of added amount (dry weight) of bioadsorbent of cellulose prepared by treating in boiling concentrated sulfuric acid to unit volume of the test solution, on the concentration of gold(I) remained in the aqueous solution after the adsorption from the aqueous solution initially contained 0.3 mmol/L gold(I) in 0.1 mol/L sodium hypochlorite [35].

![Figure 19](image)

**Figure 19.** Effect of adsorbent dose on the concentration of gold(I) remained in the aqueous solution after the adsorption on bioadsorbent of cellulose at pH = 3 where the test aqueous solution initially contained 0.3 mmol/L gold(I) in 0.1 mol/L sodium hypochlorite [35].

7. Prospects for the application of bioadsorbents to actual cyanide processes

As mentioned in the preceding section, gold(I) can be quantitatively recovered by means of adsorption using bioadsorbents under acidic conditions similar to gold
(III) after oxidizing gold(I) into gold(III) by the oxidation treatment using sodium hypochlorite, for example.

Also as mentioned earlier, the main hydrometallurgical process for gold and silver ores is cyanide leaching followed by gold recovery by means of adsorption on strongly basic anion exchange resins and activated carbon or by means of cementation using zinc powder. In the adsorption process, the adsorbed gold is recovered by incinerating these loaded adsorbents because the elution of gold adsorbed on these adsorbents is difficult. On the other hand, the cementation using zinc powder also suffers from some problems, one of which is severe control of oxygen or air, except for which it would consume too much amount of zinc powder and cause redisolution of the resulted elemental gold powders. The major gold plating process is also that using cyanide plating solution, in which gold is recovered by the same processes. In these processes, after the recovery of gold, spent cyanide solutions are discharged into environment after the decomposition of cyanide using sodium hypochlorite, for example, as mentioned in the preceding section.

However, by means of the adsorption using bioadsorbents as mentioned above, more economical and more environmental benign process can be proposed as schematically depicted in Figure 20.

In the new process shown in Figure 20, trace concentration of gold(I) contained in cyanide solution will be able to be quantitatively recovered using bioadsorbents, which are easy to be incinerated at comparatively low temperature consuming less amount of energy leaving only gold powder as shown in Figure 9, for example.

A number of processes for recovering cyanide from gold plant barren solutions or pulps also have been developed [32]. For example, the acidification, volatilization and reneutralization (AVR) process as schematically depicted in Figure 21 was practiced at Pachuca silver mine in Mexico and at Flin Flon mine in Canada more than 60 years ago and still now is under operation. Further, it has been recently installed at several other mines around the world.

In this process, by adding acid to the barren solution after recovering gold, cyanide is converted into HCN gas, which is scrubbed using caustic solution, returning into cyanide for reuse again. For this process, more economical and more

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**Figure 20.**

New recovery process of gold from cyanide solutions using bioadsorbents.
An environmentally benign process using bioadsorbents can be proposed as shown in Figure 22 only by changing the order of the step of acidification.

Further, a more recent advancement is the sulfidization, acidification, recycling, and thickening of precipitate (SART) process schematically shown in Figure 23 developed for ores containing high content of copper, which consumes large
amount of cyanide, making worse of the economy of gold recovery. In this process, sulfides are added during the acidification by which pH is lowered from about 10 to 4.5. Under such conditions, the copper present as cyanide complex, \( \text{Cu(CN)}_4^{3-} \), is completely converted into the mineral chalcocite, \( \text{Cu}_2\text{S} \), releasing hydrogen cyanide, HCN gas. However, because selectivity of both strongly basic anion exchange resins and activated carbon to gold(I) cyanide are inferior, large amount of copper (I) cyanide are also adsorbed onto these adsorbents together with gold(I) cyanide, which results in tedious posttreatments.

Also for this process, more economical and more environmentally benign new process using biomass adsorbents can be proposed as schematically depicted in Figure 24. In this proposed process, cyanide leach liquor is acidified by adding

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**Figure 23.**
Flow sheet for the recovery of gold by means of cyanide leaching followed by recycling of cyanide by means of SART process.

**Figure 24.**
Modification of SART process using bioadsorbents.
hydrochloric acid, not after the recovery of gold but before the gold recovery step. During the acidification, gold(I) and copper(I) are spontaneously oxidized into gold (III) and copper(II) by oxygen in air. From such acidified liquor containing gold (III) and copper(II), gold(III) can be quantitatively and highly selectively recovered over copper(II) using the bioadsorbents as metallic gold in a simple manner, leaving copper(II) in the raffinate, which can be easily recovered by means of solvent extraction using hydroxime reagents or, more simply, by means of precipitation using sodium sulfide as the precipitates of copper sulfide.

8. Conclusion

Bioadsorbents for gold recovery were prepared from various biomaterials including biomass wastes such as orange juice residue in a simple manner only by treating in boiling concentrated sulfuric acid. These bioadsorbents exhibited extraordinary high loading capacity and high selectivity for gold in the adsorption from acidic chloride media, which were elucidated to be attributable to the reduction reaction of gold(III) into gold(0), elemental gold, due to the highest oxidation-reduction potential of gold(III), catalyzed by the surface of the bioadsorbents prepared by condensation reaction using concentrated sulfuric acid.

It was confirmed in the recovery tests of gold from printed circuit boards of spent mobile phones, Mongolian gold ore, and simulated spent cyanide solutions containing trace concentration of gold(I) that satisfactory gold recovery was achieved by using these bioadsorbents. Some new gold recovery processes using bioadsorbents were proposed for actual cyanide processes.

By using other types of bioadsorbents, it is possible to recover other precious metals such as palladium and platinum and hazardous materials such as heavy metals.

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