JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

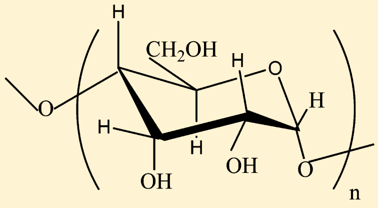
# An Assessment of Gold Recovery Processes Using Cross-Linked Paper Gel

Bimala Pangeni,[†] Hari Paudyal,[†] Katsutoshi Inoue,*[,†] Hidetaka Kawakita,[†] Keisuke Ohto,[†] and Shafiq Alam[‡]

[†]Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo 1, Saga 840-8502, Japan

[‡]Faculty of Engineering and Applied Science, Memorial University, St. John's, Newfoundland A1B 3X5, Canada

**ABSTRACT:** A novel type of adsorption gel was prepared from filter paper by treating it with concentrated sulfuric acid to investigate the efficient adsorption of Au(III) from aqueous acidic chloride media. Various parameters have been examined for the recovery of gold such as effects of hydrochloric acid concentrations, contact time, initial Au(III) concentrations, and temperature. The adsorption of gold was fitted with the Langmuir type adsorption model, and the maximum adsorption capacity of gold was evaluated as 5.05 $\text{mmol}\cdot\text{g}^{-1}$. The kinetics of gold adsorption was interpreted in terms of the pseudofirst-order kinetic model, and the activation energy was evaluated as 61.3 $\text{kJ}\cdot\text{mol}^{-1}$. The gold adsorbed by the paper gel was measured by means of X-ray diffraction spectrum, scanning electron microscope (SEM), and an optical microscope. The inferred mechanism for the adsorption of Au(III), followed by its reduction to elemental gold, was proposed based on the observation of infrared spectroscopic analysis. It was inferred that Au(III) was adsorbed by the coordination to oxygen atom of C−O−C linkage formed after the cross-linking with concentrated sulfuric acid, as well as the oxygen atoms of hydroxyl groups of pyranose rings of paper cellulose. The adsorbed gold can easily be recovered by the incineration method at elevated temperature.



## 1. INTRODUCTION

During the past decade, with the development of consumer-oriented electrical and electronic technologies, large amounts of electronic equipment have been provided to the market. The useful life of these devices is relatively short and has been decreasing as a result of rapid changes in equipment features and capabilities. The short useful life of these products brings about a large waste stream of obsolete electronic and electrical devices (e-waste).

Precious metals have a wide variety of applications in the manufacturing of electronic appliances, serving as contact materials due to their high chemical stability and good conducting properties.[1] Gold recovery from secondary sources such as electronic scraps and waste electroplating solutions is, therefore, remarkable technology.[2] Several studies reported that recovering precious metals from electronic scraps is one of the greatest economic profits for the recycling industry. The disposal e-wastes contain a higher proportion of precious metals than in the ore itself. Additionally, the purity of precious metals like gold in the printed circuit board (PCB) in e-waste is more than 10 times that of the corresponding minerals.[3]

Presently, many processes such as solvent extraction,[4] ion exchange,[5] and coprecipitation[6] have been available to separate and enrich the gold. However, these processes are only feasible for specially processed solutions containing high gold concentrations. These processes also suffer from various problems like low yields, operational difficulties, and environmental concerns. On the other hand, adsorptive separation, which is an efficient recovery process for gold from dilute solutions, also suffers from some problems such as insufficient selectivity. This gives a compelling reason for developing more efficient and more environmentally friendly methods for the recovery of precious metals, not only from mineral ores but also from waste materials such as e-waste.[7]

Bioadsorption is expected to be a promising technique for metal recovery since biomasses not only exhibit interesting adsorption behaviors for metal ions but also are environmentally friendly, biodegradable, and biocompatible. Therefore, they have attracted significant attention in recent years.

Cellulose, a polysaccharide made by most plants, is one of the most abundant organic compounds on earth. The chemical modification of polysaccharides is the most important route to modify the properties of the naturally occurring biopolymers, including cellulose, and to use this renewable resource in the context of sustainable development. This is because the hydroxyl groups in cellulose can coordinate with metal ions to form stable complexes.

In our previous studies, we had developed different kinds of adsorption gels for recovering precious metals such as dimethylamine-immobilized (DMA) paper gel, *p*-aminobenzoic (PAB) acid modified paper gel, and iminodiacetic acid (IDA) type of modified waste paper gel[8−10] from waste paper. These adsorption gels exhibited the maximum adsorption capacity for Au(III) as high as (4.6, 5.09, and 3.30) $\text{mmol}\cdot\text{g}^{-1}$ by DMA, PAB, and IDA type of modified waste paper gel, respectively. However, high costs are associated with the preparation of

**Received:** September 21, 2011
**Accepted:** January 12, 2012
**Published:** February 2, 2012

these adsorption gels from spent paper, one of cellulosic materials, though the feed material is cheap. In the present paper, we attempted to develop a more efficient adsorbent for the recovery of gold by means of a much more simple method at cheap cost from paper cellulose like filter paper.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Advantec quantitative ashless (5C, 150 mm) filter paper produced by Toyo Roshi Co., Ltd., Japan, was used as the feed material for the adsorption gel. Analytical grade chloride salts of zinc (Sigma Aldrich), iron, palladium (Wako, Japan), and copper (Katayama Chemical, Japan) were used to prepare the test solutions of respective metals. Analytical grade $HAuCl_4 \cdot 4H_2O$ and $H_2PtCl_6 \cdot 6H_2O$ (Wako, Japan) were used to prepare gold and platinum solutions, respectively. All other chemical reagents used for the preparation of adsorbent and for the adsorption tests were of analytical grade and used without further purification unless mentioned.

**2.2. Preparation of Adsorption Gel.** For the preparation of adsorption gel, first raw filter paper was cut into small pieces, and 10 g of paper was mixed together with 50 mL of 96 % concentrated sulfuric acid (Wako, Japan) in a round-bottom flask; the mixture was continuously stirred for 24 h at 373 K to enhance the cross-linking condensation reaction. During this condensation reaction, some of the hydroxyl groups in polymer chains of paper cellulose (shown in Figure 1) were dehydrated to form ether bonds as shown in Figure 2. Next, the mixture was cooled in room temperature and was neutralized with sodium bicarbonate. The insoluble cross-linked paper product was collected by vacuum filtration and washed several times with distilled water followed by hot water to remove the excessive acid from the gel. The gel was then dried in a convection oven for 24 h at 343 K. Then, the dried gel was sieved to produce a particle size fraction of between (75 and 100) $\mu$m; this is abbreviated as cross-linked paper (CP) gel hereafter.

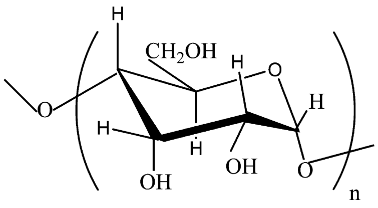


**Figure 1.** Structure of paper cellulose.

**2.3. Measurement and Analysis.** The metal concentrations before and after the adsorption were analyzed by using a Shimadzu model ICPS-8100 ICP/AES spectrometer and Shimadzu model AAS-6800 atomic absorption spectrophotometer. The total organic carbon (TOC) concentration generated during the preparation of the gel was measured by using a Shimadzu model TOC-VHS TOC analyzer. The scanning electron microscopy (SEM) analysis of the adsorbents was performed using the JEOL model JSM 5200 scanning microscope. Visual observation of elemental gold was recorded using KEYENCE model VHX/VH series optical microscope. Spectroscopic studies were performed by a JASCO model FT/IR-410 Fourier transform infrared spectrometer. The generation of elemental gold ($Au^0$) on the gels after the adsorption of Au(III) was elucidated by means of X-ray diffraction spectrum using a Shimadzu model, XRD-7000, X-ray diffractometer. Thermogravimetric analysis (TGA) of the sample before and after adsorption of gold was carried out using a TGA analyzer (Shimadzu model, simultaneous DTA-TG apparatus, DTG-60H).

**2.4. Batchwise Adsorption Tests.** The adsorption behaviors of the cross-linked paper gel for Au(III), Pd(II), Pt(IV), Fe(III), Cu(II), and Zn(II) were individually examined at varying hydrochloric acid concentrations. Each metal (0.2 mM) solution was prepared by varying the concentration of hydrochloric acid from (0.1 to 5) M. In typical runs, 10 mg of dried gel (CP) was shaken together with 10 mL of each metal solution using a thermostatted shaker maintained at 303 K for 24 h to attain equilibrium, which will be described later. After shaking, the mixture was filtered using Advantec filter paper (5C, 90 mm), and the filtrate was analyzed for residual metal concentrations.

Adsorption isotherms of Au(III) on CP gel were examined to evaluate the adsorption capacity of the adsorbent at four different temperatures ((298, 303, 313, and 323) K). A number of Au(III) solutions containing varying concentrations from (0.1 to 16) mM were prepared in 0.1 M hydrochloric acid solutions. Then, 10 mL aliquots of these solutions were mixed together with 10 mg of dried CP gel and were shaken at the four different temperatures for 96 h to ensure the complete equilibrium. All adsorption tests were repeated at least twice, and the obtained results reproduce the negligible differences.

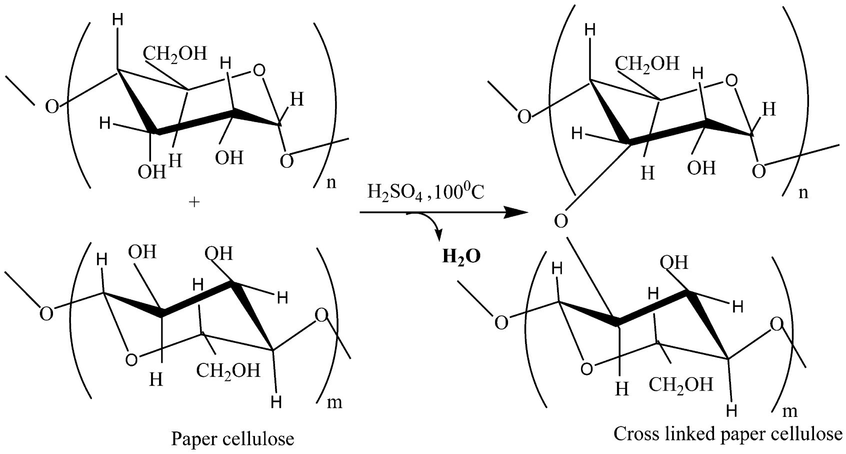


**Figure 2.** Preparation of cross-linked paper gel.

Adsorption kinetic studies were conducted using 200 mL (2 mM, that is, mM = mmol·L$^{-1}$) of Au(III) solution (which was prepared in 0.1 M hydrochloric acid solution) together with 200 mg of the dried CP gel at four different temperatures ((303, 308, 313, and 323) K), at varying contact times, to measure the adsorption rates at different temperatures and evaluate the apparent activation energy. The sample solution was taken at definite time intervals and analyzed for remaining Au(III) concentration after adsorption. The percentage adsorption of metal ions was calculated according to the following equation:

$$\%\ \text{adsorption} = \frac{(C_i - C_e)}{C_i}\cdot 100 \qquad (1)$$

where $C_i$ and $C_e$ are the initial and equilibrium concentrations of metal ions, respectively.

**2.5. Thermogravimetric Analysis (TGA).** TGA analysis of the sample before and after loading the gold was carried out using the TGA analyzer. Approximately 10 mg of samples before and after the gold loading was placed in the platinum (Pt) crucible for TGA measurement. The heating rate was maintained at 10 °C·min$^{-1}$ from (30 to 800) °C.

## 3. RESULTS AND DISCUSSION

**3.1. Product Yield and TOC Leak of CP Gel.** The product yield of CP gel was evaluated to be 73 % based on the weight of feed material employed according to eq 2. The total organic carbon (TOC) leaked during the preparation of CP gel, after washing with distilled water, was evaluated to be 26.2 mg of TOC/g of dry raw paper.

$$\%\ \text{yield} = \frac{(W_r - W_{cl})}{W_r}\cdot 100 \qquad (2)$$

where $W_r$ and $W_{cl}$ (g) are the weights of raw paper and CP gel, respectively.

**3.2. Effect of Hydrochloric Acid Concentration on the Adsorption of Metal Ions.** The adsorption behaviors of Au(III), Pt(IV), Pd(II), Zn(II), Fe(III), and Cu(II) on CP gel at varying hydrochloric acid concentrations (0.1 to 5 M), which was tested individually, is presented in Figure 3. As obvious from this figure, CP gel was found to be selective only for Au(III), and a significant extent of adsorption, that is, almost 100 % adsorption, was achieved over a wide range of the hydrochloric acid from (0.1 to 4) M, while the % adsorption of Au(III) was found to be lowered with further increasing the acid concentration beyond 4 M, the reason of which will be discussed in detail later in section 3.8. Such selective adsorption of Au(III) by CP gel is quite interesting because the gel is almost completely inert not only toward cupric, ferric, and zinc ions, which usually coexist with Au(III) ions, but also toward the Pt(IV) and Pd(II) ions. This means that CP gel prepared by a very simple method has the highest affinity for Au(III). To ensure the effect of other metal ions on the adsorption of Au(III), the mixture solution of Au(III), Cu(II), Fe(III), Pd(II), Pt(IV), and Zn(II) at 0.2 mM at varying hydrochloric acid concentrations was prepared to conduct the adsorption tests in a typical coexisting system. The results obtained were exactly the same as that for individual system; that is, similar adsorption was observed for Au(III), and negligible adsorption was observed toward other precious and base metals tested in the present study. On the basis of these results, further experiments were conducted only for Au(III).

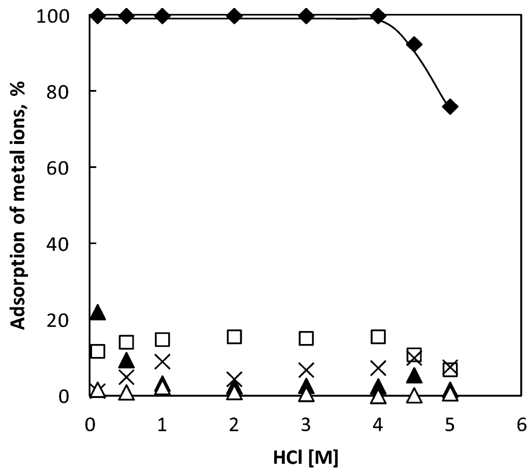


Figure 3. Adsorption of various metals by cross-linked paper gel at varying hydrochloric acid concentrations. Conditions: metal concentrations = 0.2 mM, volume of solution = 10 mL, weight of gel = 10 mg, shaking time = 24 h, temperature = 303 K. ◆, Au; □, Pt; ▲, Pd; ×, Fe; △, Cu.

**3.3. Adsorption Kinetic Studies.** The rate of Au(III) adsorption on CP gel was observed by varying the contact times at four different temperatures ((303, 308, 313, and 323) K). The initial Au(III) concentration was 2 mM, which was prepared in 0.1 M hydrochloric acid solution. A 200 mg of dried gel was shaken together with 200 mL of Au(III) solution at different time intervals, at which a 3.5 mL aliquot was sampled, and immediately filtered. The filtrate was analyzed for residual Au(III) concentration, from which the amount of Au(III) adsorption was calculated at each time. Figure 4a shows the time variation of the amount of adsorbed Au(III) at each temperature. From this figure, it is clear that the adsorption is increased with increasing the agitation time, and the equilibrium was approached within 4 h at 323 K, 8 h at 313 K, 28 h at 308 K, and 32 h at 303 K. Thus, the equilibrium time was increased with decreasing the temperature of the system. Hence, in the measurement of adsorption isotherms, the mixtures were shaken for 96 h to ensure the complete equilibrium. Also, the amount of adsorbed Au(III) was found to be increased with increasing temperature of the adsorption system. At different times, the amount of Au(III) adsorbed ($q_t$, mmol·g$^{-1}$) on CP gel was calculated from a mass balance principle as follows.

$$q_t = \frac{(C_i - C_t)}{W}\cdot V \qquad (3)$$

where $C_i$ and $C_t$ are the initial and residual concentration of Au(III) in the solution (mM), respectively. $V$ (L) is the volume of Au(III) solution, and $W$ (g) is the dry mass of CP gel used.

In this study, the kinetic data were analyzed on the basis of the Lagergren pseudofirst-order reaction model to investigate the details of the Au(III) adsorption on CP gel according to eq 4.

$$\ln\left(\frac{C_t}{C_i}\right) = -kt \qquad (4)$$

where $C_i$ and $C_t$ are the initial concentration and concentration of Au(III) at time $t$ (h) and $k$ is the pseudofirst-order rate constant (h$^{-1}$).

The plot of $\ln(C_t/C_i)$ versus time ($t$) is shown in Figure 4b. As seen in this figure, all of the plots for each temperature

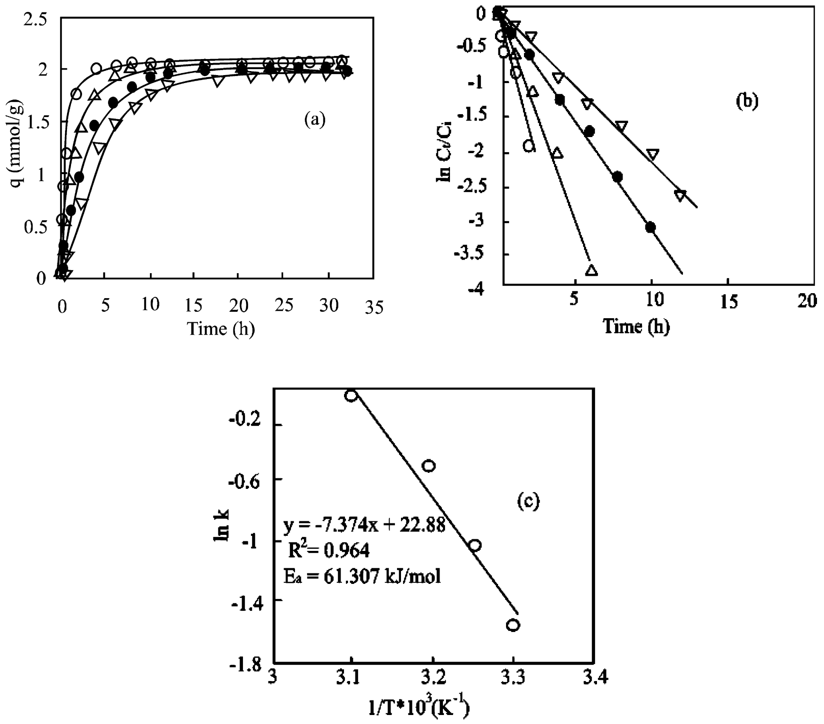


**Figure 4.** Adsorption kinetics of Au(III) by concentrated sulfuric acid cross-linked paper gel at different temperatures. (a) Experimental plot, (b) pseudofirst order plot, (c) Arrhenius plot. Conditions: volume of solution = 200 mL, weight of the dry gel added = 200 mg, concentration of Au (III) = 2 mM, HCl concentration = 0.1 M. ○, 323 K; △, 313 K; ●, 308 K; ▽, 303 K.

studied were found to lie on straight lines passing through the origin. From the slopes of these straight lines, the rate constants were evaluated for each temperature. The pseudofirst-order rate constants and corresponding correlations coefficients for four different temperatures are listed in Table 1. As shown in Table 1, the values of rate constants were increased with increasing temperature. Similar results have been observed for the Au(III) adsorption on cross-linked grape waste gel.[11] The rate constant, $k$, at different temperatures ((303, 308, 313, and 323) K) listed in Table 1 were used to calculate the activation energy for the present adsorption reaction according to the Arrhenius equation.

**Table 1. First-Order Rate Constants and Corresponding Correlation Coefficient for the Adsorption of Au(III) on Cross-Linked Paper Gel at Different Temperatures**

| $T$/K | rate constant/$h^{-1}$ | $R^2$ |
|---|---|---|
| 303 | 0.211 | 0.996 |
| 308 | 0.355 | 0.939 |
| 313 | 0.597 | 0.985 |
| 323 | 0.959 | 0.992 |

$$\ln k = \ln A - \frac{E_a}{RT} \tag{5}$$

where $R$ is the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$).

Figure 4c shows the plot of ln $k$ versus $1/T$. As expected from eq 5, the plots lie on a straight line in this figure. From the slope of this straight line, the activation energy ($E_a$) was evaluated as 61.3 $kJ \cdot mol^{-1}$. This value suggests that the adsorption of Au(III) onto CP gel is a chemical adsorption, which was confirmed from the fact that the values of $E_a$ for chemical adsorption is usually between (8.4 and 83.7) $kJ \cdot mol^{-1}$.[12] The positive value of $E_a$ suggests that an increase in temperature favors the adsorption of Au(III) by CP gel. This behavior of adsorption of Au(III) by CP gel was also supported by the value obtained from thermodynamic parameters, that is, a change in enthalpy which indicates a chemisorption process that is endothermic in nature (as described in detail later).

### 3.4. Adsorption Isotherms and Thermodynamic Investigation.

Figure 5a shows the adsorption isotherms of Au(III) at four different temperatures ((298, 303, 313, and 323) K). It is clear from this figure that, when increasing the concentration of Au(III) in the low concentration region, the amount adsorption of Au(III) was significantly increased. This figure also shows the plateau regions, observed at the high concentration region for each temperature, suggesting that the Langmuir-type adsorption takes places under the present experimental conditions. The result shows that the temperature has a great effect for the adsorption of Au(III) onto CP gel. All of the results of isotherm studies were replotted according to eq 6 on the basis of the Langmuir model as shown in Figure 5b, where all plots lie on straight lines corresponding to different temperatures.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}} \tag{6}$$

where $C_e$ (mM) is the concentration of Au(III) after adsorption, $Q_e$ ($mmol \cdot g^{-1}$) represents the equilibrium adsorption capacity, $Q_{max}$ ($mmol \cdot g^{-1}$) represents the maximum adsorption capacity, and $b$ ($L \cdot mmol^{-1}$) is the Langmuir constant or equilibrium constant related to the adsorption energy.

From the Figure 5b, the maximum adsorption capacities ($Q_{max}$) and Langmuir or equilibrium constant ($b$) were calculated from the slopes and intercepts respectively, for each temperature studied, and the evaluated values are listed

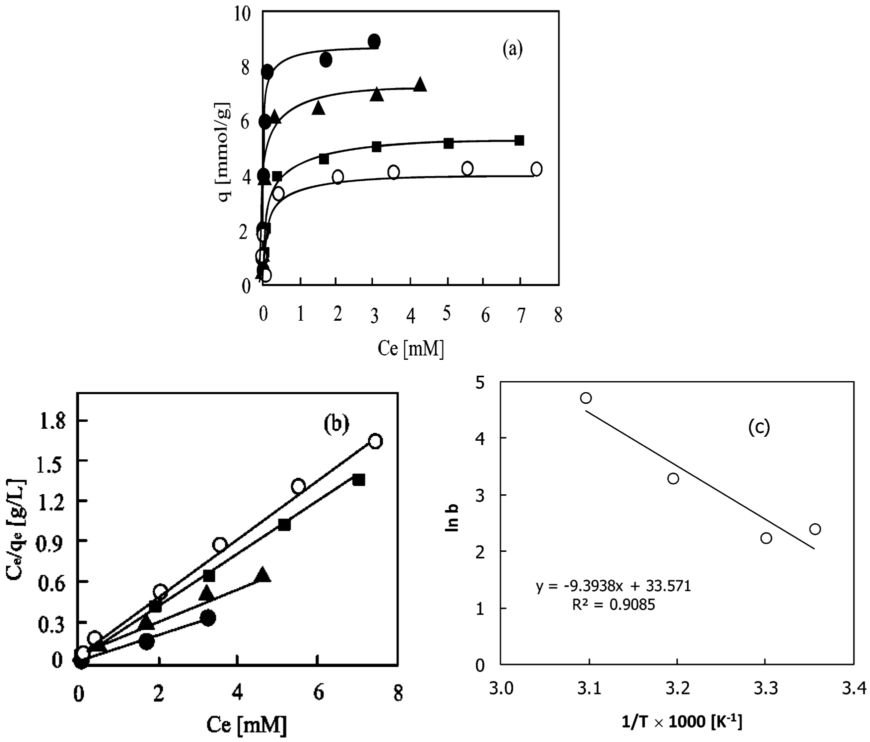


**Figure 5.** Adsorption isotherms of Au(III) on cross-linked paper gel at different temperatures. (a) Experimental plot, (b) Langmuir plot, and (c) van't Hoff plot. Conditions: dry weight of the gel = 10 mg, shaking time = 96 h, volume of the test solution = 10 mL, HCl concentration = 0.1 M. ●, 323 K; ▲, 313 K; ■, 303 K; ○, 298 K.

**Table 2. Thermodynamic Parameters for Au(III) by Cross-Linked Paper Gel**

|  | $b$ | $Q_{max}$ | $\Delta G°$ | $\Delta H°$ | $\Delta S°$ |  |
|---|---|---|---|---|---|---|
| $T$/K | L·mmol$^{-1}$ | mmol·g$^{-1}$ | kJ·mol$^{-1}$ | kJ·mol$^{-1}$ | J·K$^{-1}$·mol$^{-1}$ | $R^2$ |
| 298 | 11.05 | 4.524 | −5.953 |  |  | 0.997 |
| 303 | 9.42 | 5.050 | −5.653 | 78.0934 | 279.101 | 0.997 |
| 313 | 27 | 7.407 | −8.578 |  |  | 0.992 |
| 323 | 112 | 8.928 | −12.673 |  |  | 0.998 |

in Table 2. From Table 2, it is obvious that, with the increasing temperature of the system, the maximum adsorption capacity is increased; this suggests the endothermic nature of adsorption reaction of Au(III) on CP gel.

The Langmuir constant ($b$) can serve as an indicator which quantitatively reflects the affinity between the adsorbent and the adsorbate.[2] The applicability of the Langmuir constant or equilibrium constant ($b$) can be better understood for the determination of thermodynamic parameters. Different thermodynamic parameters such as change in Gibbs free energy ($\Delta G°$), change in enthalpy ($\Delta H°$), and change in entropy ($\Delta S°$) can be calculated using the following equations.

$$\Delta G° = -RT \ln b \tag{7}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

From eqs 7 and 8, the van't Hoff equation can be expressed as follows.

$$\ln b = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{9}$$

As shown in Figure 5c, the plot of ln $b$ versus $1/T$ gives a straight line with a slope of ($-\Delta H°/R$) (kJ·mol$^{-1}$) and an intercept of $\Delta S°/R$ (kJ·mol$^{-1}$·K$^{-1}$). The evaluated values of thermodynamic parameters are listed also in Table 2. As shown in this table, the negative increasing values of change in Gibbs free energy ($\Delta G°$) with increasing temperature indicates an increase in the feasibility and spontaneity of the adsorption at higher temperature. The positive value of change in enthalpy ($\Delta H°$) suggests that Au(III) adsorption is an endothermic process. Also, the positive value of change in entropy ($\Delta S°$) suggests that there is increased randomness at the solid−solution interface during the adsorption of Au(III) in aqueous solution on CP gel.

The comparative accounts for the maximum Au(III) adsorption capacity on various adsorbents listed in Table 3 shows the highest adsorption capacity of Au(III) onto CP gel among collected literature values. This account also supports the easy recovery and high efficiency of adsorption for Au(III) using CP gel.

### 3.5. Solid-State Analysis of Gel after the Adsorption of Au(III).

The presence of gold as Au(0) on CP gel was confirmed by XRD analysis. XRD patterns as shown in Figure 6 were compared to the reference database for metallic gold. No additional peaks, except those attributable to elemental gold, that is, Au(0), were detected, proving that CP gel has the ability to reduce Au(III) ions to metallic gold, that is, Au(0) crystals structure. The presence of well-defined sharp peaks at $2\theta$ values of 38.18, 44.28, 64.50, and 77.40 degrees is indicative of well-defined crystals of elemental gold. Similar results had been reported for persimmon peel gel.[13]

**Table 3. Comparison of Maximum Adsorption Capacities for Gold(III) on Different Adsorbents**

| adsorbents | maximum uptake capacity $\text{mmol}\cdot\text{g}^{-1}$ | condition | reference |
|---|---|---|---|
| cross-linked paper gel | 5.05 | 0.1 M HCl | present work |
| dimethyamine-paper | 4.6 | 1 M HCl | 8 |
| *p*-aminobenzoic acid-paper | 5.09 | 1 M HCl | 9 |
| iminodiacetic acid type of modified paper gel | 3.30 | 1 M HCl | 10 |
| alginate cross-linked with $CaCl_2$ | 1.47 | pH 2 | 14 |
| bayberry tannin-immobilized meso-porous silica | 2.20 | pH 2 | 15 |
| glutaraldehyde cross-linked chitosan (GCC) | 2.14 | pH 1.6 | 16 |
| persimmon waste | 4.95 | 0.1 M HCl | 17 |
| cross-linked lignophenol | 1.92 | 0.5 M HCl | 18 |
| primary amine-cross-linked lignophenol | 1.98 | 0.5 M HCl | 19 |
| ethylene diamine cross-linked lignophenol | 3.08 | 0.5 M HCl | 19 |
| glycine modified cross-linked chitosan | 0.86 | pH 2 | 20 |
| chemically modified chitosan with magnetic | 3.43 | pH 0.5 | 21 |

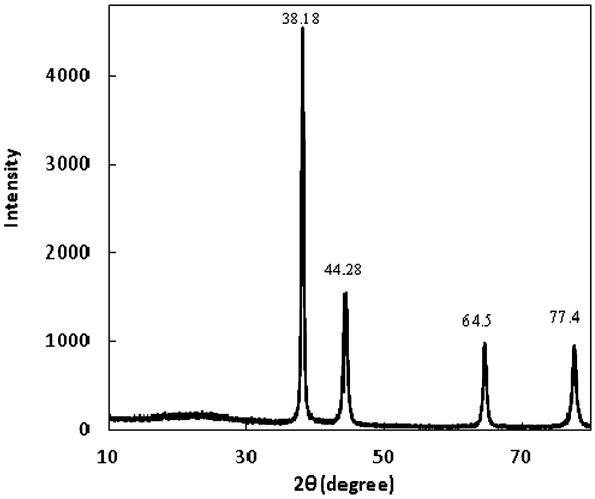


**Figure 6.** X-ray diffraction powder patterns of Au-adsorbed paper gel showing the presence of gold as Au(0).

By means of scanning electronic micrographs (SEM) of the adsorbent before and after the adsorption of Au(III), the surface morphology of the adsorbent, along with that of the gold particles on the surface, was elucidated as presented in Figure 7a,b.

From the visual observation, it was found that at low concentrations of Au(III), that is, 0.5 mM, fine gold particles were observed to float on the surface of the sample solution after 24 h of shaking time. On the other hand, after long time shaking (96 h) in the case of high concentrations of Au(III), these fine gold particles were found to form aggregates, resulting in the formation of large gold particles as shown in Figure 8. The high selectivity and loading capacity of CP gel for Au(III) may be attributed to the reduction of Au(III) to Au(0) during adsorption. From Figure 8, it can be inferred that fine gold particles formed by the reduction process on the gel surface may have a tendency to be detached from the gel surface, forming clear aggregates. Thus, the optical microscope and SEM images of gel after the adsorption of Au(III) provide a convenient and reliable visual indication of gold particle formation. Similar phenomena were observed in our previous study in the adsorption of Au(III) on chemically modified spent paper gel.[8]

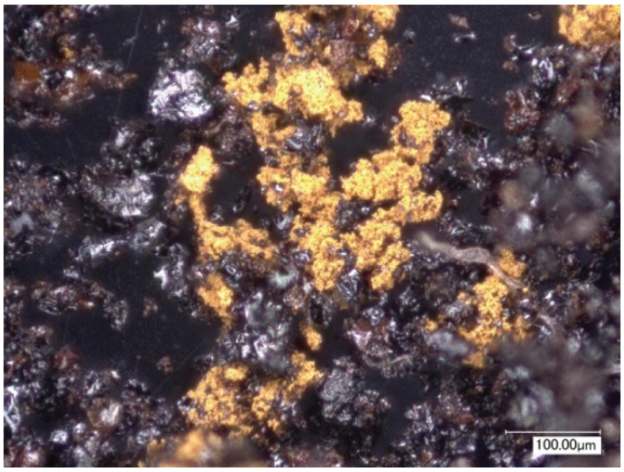


**Figure 8.** Optical microscope photograph of gold loaded cross-linked paper gel.

### 3.6. Fourier Transform Infrared (FTIR) Spectra.

Paper is one of the cellulose-rich biopolymers. Since hydroxyl groups (OH) are very abundant in polysaccharides, like cellulose, their participation in the adsorption followed by reduction process in

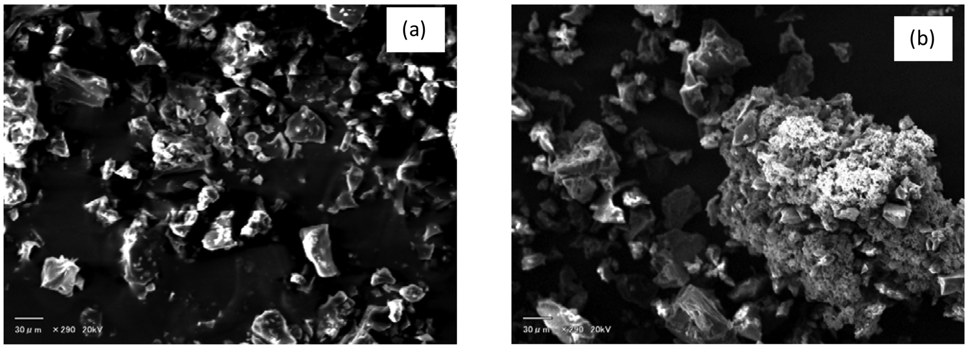


**Figure 7.** SEM micrographs of cross-linked paper gel (a) before and (b) after the adsorption of Au(III). 290× magnification, acceleration voltage = 20 kV, scale = 30 $\mu$m.

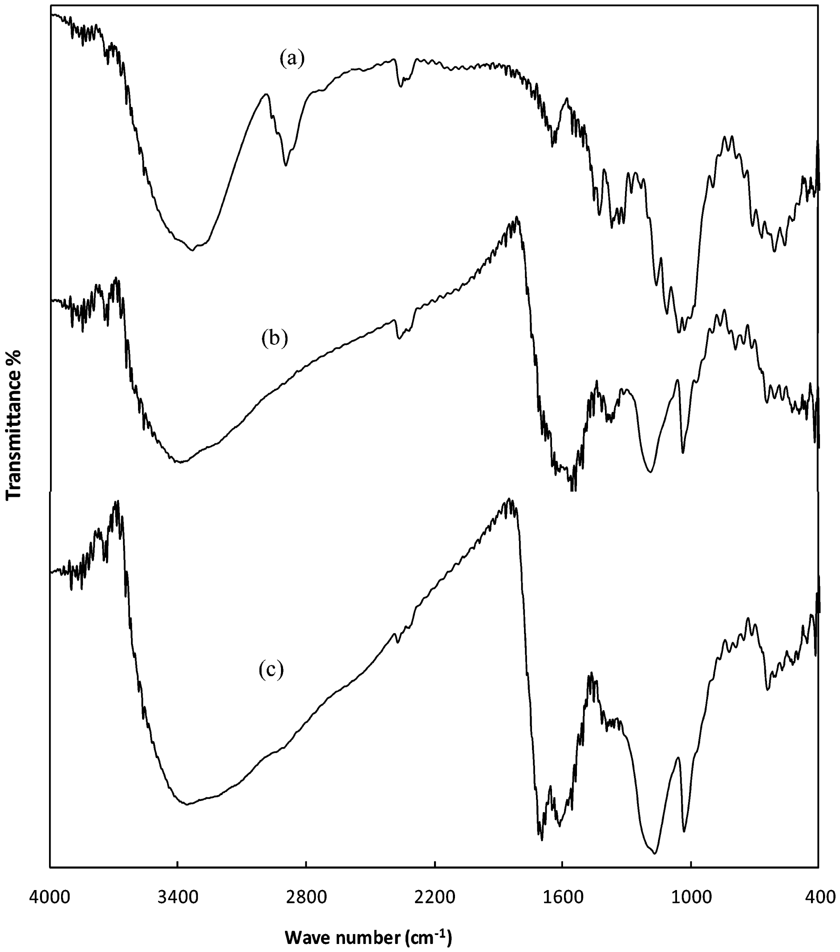


**Figure 9.** FTIR spectra of (a) crude, (b) cross-linked, and (c) gold-loaded paper gel.

the present system was confirmed by FTIR analysis of CP gel. The characteristic intermolecular and intramolecular O−H stretching vibration band of hydroxyl groups in the spectrum of crude paper was observed and displayed in Figure 9a, which is slightly less broad, showing the maximum intensity at around 3446 cm$^{-1}$. The corresponding band appeared in the spectrum of CP gel as presented in the Figure 9b at around 3417 cm$^{-1}$, which is broader compared to the crude paper band. This suggests that some of the OH groups in crude paper cellulose have been consumed in the cross-linking condensation reaction. The intense peak at 2913.91 cm$^{-1}$ in crude paper is due to the C−H stretching; the sharp peak at around 1716 cm$^{-1}$ is assigned to the C═O stretching vibration of carbonyl groups of paper cellulose, and a broad band centered at 1176 cm$^{-1}$ is due to the C−O stretching and O−H bending of alcoholic groups. Furthermore, a new peak appeared in CP gel at around 1215 cm$^{-1}$ which is due to the formation of C−O−C ether bond linkages, indicating strong evidence of the cross-linking condensation reaction by concentrated sulfuric acid. After the adsorption of the Au(III) ion, the broad band at 3417.24 cm$^{-1}$ has become broader, which is attributable to the coordination of the adsorbed Au(III) ion with an oxygen atom of the hydroxyl group because metal coordination weakens the O−H bond and absorption shifted toward the lower frequency region as depicted in Figure 9c. Similarly, the intensity of the peak at 1716 cm$^{-1}$ is increased after Au(III) adsorption. It is reasonably explained to be attributable to the oxidation of the hydroxyl groups to carbonyl group in CP gel which confirms the reduction of ionic gold to elemental gold.

### 3.7. Thermogravimetric Analysis of the Cross-Linked Paper Gel.

Very beautiful, shining, and twinkling gold aggregates attached on the surface of adsorbent were observed by optical microscope as shown in Figure 8. Such gold can easily be recovered in its pure form by incineration. Vanishing gel particles are shown in Figure 10, which shows the TG curves

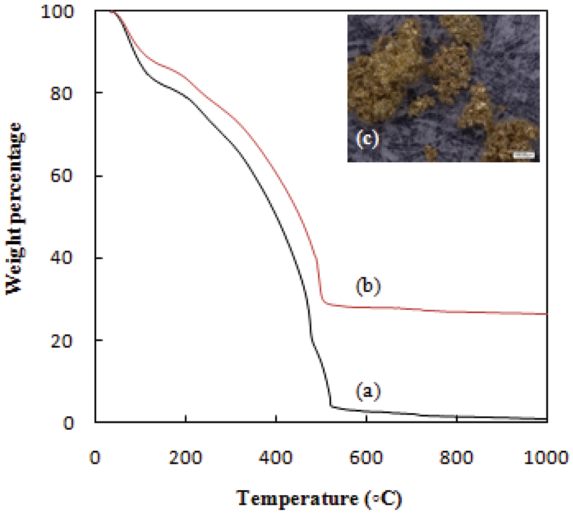


**Figure 10.** Thermogravimetric analysis of cross-linked paper gel (a) before gold loading, (b) after gold loading, and (c) recovered gold after incineration.

of the gel loaded and nonloaded with gold, the variation of the percentage of remained weight of the gels as a function of elevated temperature. As seen from Figure 10b, the gold-loaded CP gel was completely decomposed at temperature below 500 °C, leaving the weight of clear and pure gold aggregates as shown in Figure 10c while, in the case of nonloaded gel, the CP gel was completely decomposed, leaving very little weight at temperature below 520 °C. The weight loss at the temperature below 150 °C is due to the evaporation of adsorbed $H_2O$ molecules in both crude and gold loaded gel. The weight loss in the temperature range from (150 to 500) °C (gold loaded) and in that from (150 to 520) °C (nonloaded gel) is due to the decomposition of organic molecules by incineration reaction releasing $H_2O$ and $CO_2$ molecules.

Thus, 30 % of the initial weight is remained in the gold loaded gel, while the percentage weight remained in nonloaded gel is very small (0.75 %). Practically, the incineration process can be useful for recovering pure metallic gold in various industrial fields.

### 3.8. Proposed Mechanism for Adsorption Followed by Reduction of Au(III).

Several spectroscopic methods have been used to elucidate the mechanisms of gold adsorption and reduction processes. Most of the mechanism involved the reduction of ionic gold to metallic form. On the basis of FTIR analysis, Torres et al. suggested the involvement of carboxyl groups in binding followed by the reduction of Au(III) to Au(0) and Ag(I) to Ag(0), in the case of metal binding onto cross-linked calcium alginate beads.[14]

The main adsorption–reduction mechanism of Au(III) in the present system was investigated based on the structural changes observed in FTIR spectra for raw paper and CP gel. The reduction of ionic gold to elemental gold was proved by measuring the solid state analysis of the gel after adsorption by XRD, SEM, and optical microscope images. The polymeric structure of paper cellulose, in the presence of concentrated sulfuric acid, undergoes the condensation cross-linking reaction forming C–O–C ether bonds linkage (as observed in the FTIR studies) with the release of water molecules as shown in Figure 2. The majority of Au(III) ions in acidic chloride media exists predominantly as a tetra-chloro complex of $AuCl_4^-$. The adsorption of this complex takes place through the coordination with the oxygen atom of C–O–C linkage of ether bond and oxygen atoms of many other hydroxyl groups of pyranose ring of paper cellulose as shown in Figure 11.

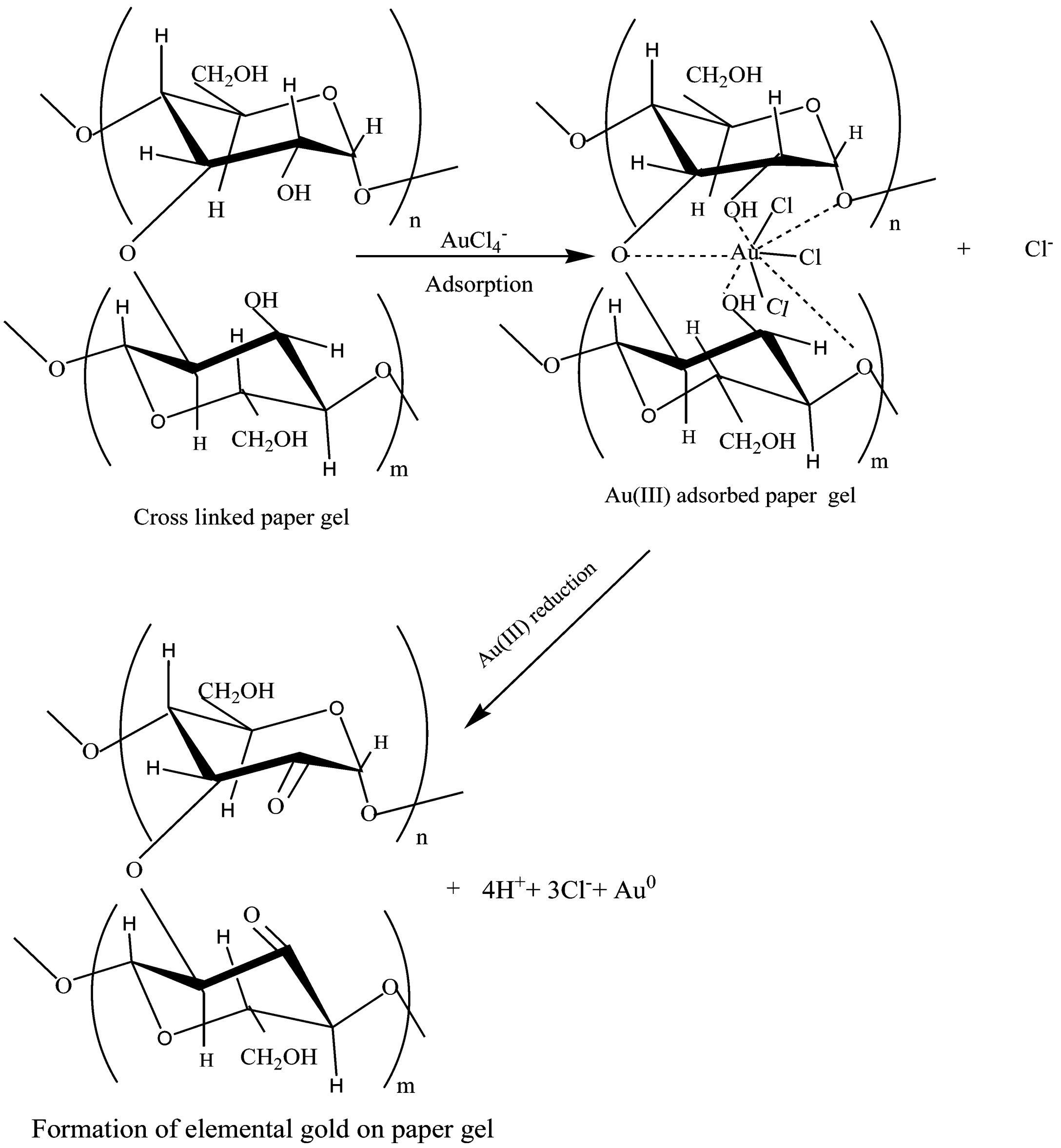


**Figure 11.** Inferred adsorption–reduction mechanism for Au(III) using cross-linked paper gel.

At this step of the adsorption, one chloride ion is released per unit ion of Au(III) into the aqueous solution, which results in the decrease in the adsorption of gold as observed in a high concentration range of HCl in Figure 3. Furthermore, during the adsorption, some hydroxyl groups are oxidized to carbonyl groups, leading to the reduction of Au(III) to Au(0) as discussed, concerning the changes in FTIR spectra. Thus, the very high adsorption capacity and selectivity of paper gel for Au(III) is attributable to the change in the structure of the polymer matrices of paper cellulose by a simple cross-linking reaction using concentrated sulfuric acid.

Another driving force for the reduction of Au(III) to Au(0) is the high oxidation−reduction potential (ORP) of $Au^{3+}$(1.0 V) in comparison to other metal ions like $Pd^{2+}$ (0.68 V) and $Pt^{4+}$ (0.62 V), which bring about selective reduction for Au(III). Thus, it is inferred that the mechanism of the adsorption of Au(III) on CP gel followed by the reduction to metallic gold is schematically depicted by Figure 11.

## 4. CONCLUSIONS

The applications of the paper cellulose for the recovery of gold have been investigated in terms of adsorption tests, spectroscopic analyses, and visual observations. Adsorption isotherms exhibited the Langmuir type of monolayer adsorption on the surface of the gel with a maximum adsorption capacity of 5.05 $mmol \cdot g^{-1}$ at 303 K. The values of thermodynamic parameters confirmed the spontaneous and endothermic reaction. Kinetic data were successfully interpreted in terms of the pseudofirst-order model with the activation energy of 61.3 $kJ \cdot mol^{-1}$. Thus, the high adsorption capacity and selectivity of the present gel toward Au(III) offers an ecological and economic alternative to the procedures currently used to treat mining and industrial effluents.

The present work suggests the possibility of very simple and new uses of cellulosic material, like paper, as a low-cost adsorbent for the effective recovery of gold(III) from various waste, especially from e-wastes, in its pure form.

## ■ AUTHOR INFORMATION

### Corresponding Author

*Fax: +81952288669. E-mail address: inoue@elechem.chem.saga-u.ac.jp.

### Funding

The present work was financially supported in part by a Grant-in-Aid for Scientific Research about Establishing a Sound Material-Cycle Society (K2131) from the Ministry of Environment of the Japanese Government.

## ■ REFERENCES

(1) Cui, J.; Zhang, L. Metallurgical recovery of metals from electronic waste: a review. *J. Hazard. Mater.* **2008**, *158*, 228−256.

(2) Ishikawa, S. I.; Suyama, K.; Arihara, K.; Itoh, M. Uptake and recovery of gold ions from electroplating wastes using eggshell membrane. *Bioresour. Technol.* **2002**, *81*, 201−206.

(3) Li, J.; Lu, H.; Guo, J.; Xu, Z.; Zhou, Y. Recycle technology for recovering resources and products from waste printed circuit boards. *Environ. Sci. Technol.* **2007**, *41*, 1995−2000.

(4) Akita, S.; Yang, L.; Takeuchi, H. Solvent extraction of gold(III) from hydrochloric acid media by nonionic surfactants. *Hydrometallurgy* **1996**, *43*, 37−46.

(5) Alguacil, F. J.; Adeva, P.; Alonso, M. Processing of residual gold(III) solutions via ion exchange. *Gold Bull.* **2005**, *38*, 9−13.

(6) Zhao, Y. Z. The enrichment and separation of trace gold, Pt and Pd from the ores based on co-precipitation. *Gold* **2006**, *27*, 42−44.

(7) Qu, R.; Sun, C.; Wang, M.; Ji, C.; Xu, Q.; Zhang, Y.; Wang, C.; Chen, H.; Yin, P. Adsorption of Au(III) from aqueous solution using cotton fiber/chitosan composite adsorbents. *Hydrometallurgy* **2009**, *100*, 65−71.

(8) Adhikari, C. R.; Parajuli, D.; Kawakita, H.; Inoue, K.; Ohto, K.; Harada, H. Dimethylamine modified waste paper for the recovery of precious metals. *Environ. Sci. Technol.* **2008**, *42*, 5486−5491.

(9) Adhikari, C. R.; Parajuli, D.; Inoue, K.; Ohto, K.; Kawakita, H.; Harada, H. Recovery of precious metals by using chemically modified waste paper. *New J. Chem.* **2008**, *32*, 1634−1641.

(10) Adhikari, C. R.; Parajuli, D.; Kawakita, H.; Chand, R; Inoue, K.; Ohto, K. Recovery and separation of precious metals using waste paper. *Chem. Lett.* **2007**, *36*, 1254−1255.

(11) Parajuli, D.; Adhikari, C. R.; Kawakita, H.; Kajiyama, K.; Ohto, K.; Inoue, K. Reduction and accumulation of Au(III) by grape waste: A kinetic approach. *React. Funct. Polym.* **2008**, *68*, 1194−1199.

(12) Li, Q.; Chai, L.; Yang, Z.; Wang, Q. Kinetics and thermodynamics of Pb(II) adsorption into modified spent grain from aqueous solutions. *Appl. Surf. Sci.* **2009**, *255*, 4298−4303.

(13) Parajuli, D.; Kawakita, H.; Inoue, K.; Ohto, K.; Kajiyama, K. Persimmon peel gel for the selective recovery of gold. *Hydrometallurgy* **2007**, *87*, 133−139.

(14) Torres, E.; Mata, Y. N.; Blázquez, M. L.; Muñoz, J. A.; González, F.; Ballester, A. Gold and silver uptake and nanoprecipitation on calcium alginate beads. *Langmuir* **2005**, *21*, 7951−7958.

(15) Huang, X.; Wang, Y.; Liao, X.; Shi, B. Adsorptive recovery of $Au^{3+}$ from aqueous solutions using bayberry tannin-immobilized mesoporous silica. *J. Hazard. Mater.* **2010**, *183*, 793−798.

(16) Arrascue, M. L.; Garcia, H. M.; Horna, O.; Guibal, E. Gold sorption on chitosan derivatives. *Hydrometallurgy* **2003**, *71*, 191−200.

(17) Xiong, Y.; Adhikari, C. R.; Kawakita, H.; Ohto, K.; Inoue, K.; Harada, H. Selective recovery of precious metals by persimmon waste chemically modified with dimethylamine. *J. Hazard. Mater.* **2009**, *100*, 4083−4089.

(18) Parajuli, D.; Adhikari, C. R.; Kuriyama, M.; Kawakita, H.; Ohto, K.; Inoue, K.; Funaoka, M. Selective recovery of gold by novel lignin-based adsorption gels. *Ind. Eng. Chem. Res.* **2006**, *45*, 8−14.

(19) Parajuli, D.; Kawakita, H.; Inoue, K.; Funaoka, M. Recovery of gold(III), palladium(II), and platinum(IV) by aminated lignin derivatives. *Ind. Eng. Chem. Res.* **2006**, *45*, 6405−6412.

(20) Ramesh, A.; Hasegawa, H.; Sugimoto, W.; Maki, T.; Ueda, K. Adsorption of gold(III), platinum (IV) and palladium(II) onto glycine modified crosslinked chitsosan resin. *Bioresour. Technol.* **2008**, *99*, 3801−3809.

(21) Donia, A. M.; Atia, A. A.; Elwakeel, K. Z. Recovery of gold(III) and silver (I) on a chemically modified chitosan with magnetic properties. *Hydrometallurgy* **2007**, *87*, 197−206.