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Sequential process of sorption and incineration for recovery of gold from cyanide solutions: Comparison of ion exchange resin, activated carbon and biosorbent

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ABSTRACT

This study evaluated the gold(I) sorption capacities of various types of sorbents such as ion exchange resin, granular activated carbon, and chemically modified biosorbent. The gold(I)-loaded sorbents were incinerated and the purity of gold in the ashes was compared. As a biosorbent, polyethylenimine modified biomass (PEIB) was prepared by cross-linking the biomass of *Corynebacterium glutamicum* with polyethylenimine. The sorption capacity of the sorbents of gold(I) ion from the gold(I)–cyanide complex solution were examined by the pH edge and isotherm experiments. The maximum uptakes of gold by ion exchange resin (Amberjet™ 4400), activated carbon, and PEIB were 427.77, 170.64 and 361.76 mg g^{-1}, respectively. To recover gold as a metallic form, the gold(I) sorbed sorbents were incinerated. The recovery efficiency of incineration process and purity of gold in the ash were estimated to be higher than 85.6% and 97.72% for the PEIB, 97.23% and 94.57% for activated carbon and 92.72% and 96.56% for the Amberjet™ 4400, respectively. These sorbent constituents could be burnt out and at the same time, the sorbed Au$^+$ could be reduced to Au^0. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) results indicated that the remaining ash contained metallic form of zero-valent gold. These results support that the sequential process comprising of sorption of gold ions followed by incineration of the loaded sorbents could be an alternative method for recovery of metallic zero-valent gold from gold–cyanide complex solution.

1. Introduction

Gold has been extensively used in jewelry and many high-tech industries and is experiencing increasing demand [1]. Recovery of gold from gold-containing waste solutions generated from ore processing and electroplating processes is an important technology. Attention has focused on developing highly efficient and environment friendly methods for gold recovery [2–5].

Hydrometallurgical and pyrometallurgical processes have been widely used to recover precious metals [1,3,6]. Gold has mostly been leached out from ores and gold containing electronic scraps by cyanidation [7]. The other leaching agents being used include aqua regia, thiourea, thiosulfate and halide. These solutions are then subjected to separation and purification procedures such as precipitation using zinc powder, solvent extraction using extractants such as hexanol, methyl-iso-butyl ketone, di-n-butyl ketone, tri-n-butyl phosphate (TBP) and cyanex 921, adsorption of gold onto activated carbon and ion-exchange to isolate and concentrate the gold. Consequently, the separated and purified solutions are treated by filtration, electrorefining process, gold reduction by saturated ferrous sulfate solution or concentrated sulfuric acid, hydrogen peroxide and oxalic acid mixture as a reduction agent, or crystallization for recovery of metallic gold [3,8]. This hydrometallurgical process has been utilized more often than the pyrometallurgical process. Pyrometallurgical processing, including incineration and smelting in a furnace or blast furnace at high temperatures, has become a traditional method to recover gold from ores and electronic wastes in the past two decades [3]. Compared with these processes, the hydrometallurgical method is more exact, predictable, and easily controlled. However, both of these recovery methods are very costly and require extensive labor and time. Furthermore, considerable quantities of secondary wastes are generated [9]. Therefore, there is a need to be replaced by low cost, environment friendly methods of recovery that generate little secondary waste.

Numerous biosorbents, such as bacteria, yeasts and fungi, have been reported in the literature as efficient vehicles for the adsorption of precious metals [2,5,10]. The use of biosorbent technology for metal-ion removal offers the advantage of solving the disposal

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problem for the large quantities of dead waste biomass generated from fermentation industries.

Corynebacterium glutamicum is widely used for the biotechnological production of amino acids. The use of waste biomass of *C. glutamicum* as a biosorbent is of great interest. This cell wall is composed of several functional groups, including carboxyl, phosphonate and amine groups [11,12]. These groups can bind to a variety of heavy metals. In particular, the excessive amine groups in *C. glutamicum* are known to be responsible for the binding of anionic metals. Thus, this waste biomass may be a possible sorbent for the anionic gold–cyanide complex.

Previous research has indicated that increasing the binding sites on the biomass surface via chemical modification would be an effective method to enhance the biosorption capacity [13–15]. Polyethylenimine (PEI), which is composed of a large number of primary and secondary amine groups in the molecule, exhibits a high sorption capacity for metals when it is grafted or cross-linked on the sorbent surface. In this study, PEI was cross-linked onto the biomass of *C. glutamicum* and used as a biosorbent [16].

This study investigates a sequential method of sorption and incineration to concentrate gold–cyanide complex ions and to convert sorbed gold(I) to zero-valent metallic gold, respectively. As sorbents, ion exchange resin (Amberjet^{TM} 4400), granular activated carbon, and chemically modified biosorbent were used. The gold(I) sorption capacity and recovery efficiency of the incineration process were compared with the sorbents. The purity and valence of gold in the incineration ash were also determined.

2. Materials and methods

2.1. Sorbents and gold(I)–cyanide solution

The fermentation waste (*C. glutamicum* biomass), was obtained in a dried powder form from the lysine fermentation industry (BASF-Korea, Kunsan, Korea). Prior to use, it was ground and sieved to obtain particle sizes in the range of 0.1–0.25 mm. The resultant biomass, referred to as raw biomass, was subsequently used in the biosorption experiments. For cross-linking the biomass with PEI, 50 g of the dried *C. glutamicum* biomass was suspended with 15 g of PEI in 500 mL distilled water for 24 h at a maintained temperature of 25 ± 2 °C according to our previous protocol [16]. Then 3 mL of glutaraldehyde (25%) solution was added and the suspension was stirred for 2 h. And then the suspension was centrifuged for solid–liquid separation and the solid biomass was washed four times with deionized water. Finally, the PEI modified biomass (PEIB) was freeze-dried and stored in a desiccator until used in the experiments.

Amberjet^{TM} 4400 resin (ROHM & HAAS, gel styrene, beads, exchange capacity: 1.4 meq-g L^{-1} and particle size: 0.58 ± 0.05 mm) was used as an ion exchange resin. This is a strong base anion exchange resin with uniform particle size and contains quaternary amines as functional groups.

The activated carbon used in this study was commercially available, coal-based carbons in granular form with a particle size range of 4–8 mesh (Daejung Chemical and Metals, Korea).

A 10,000 mg L^{-1} gold(I) stock solution was prepared using $KAu(CN)_2$. NaOH and HCl (0.1 M) were used for pH adjustment. All reagents, unless otherwise indicated, were of AnalaR grade and purchased from Sigma–Aldrich, Korea.

2.2. Equilibrium sorption experiments

The pH edge experiments were carried out with different initial concentrations of gold(I) (78.83 mg L^{-1} for raw biomass, 105.02 mg L^{-1} for PEIB, 113.25 mg L^{-1} for activated carbon and 471.69 mg L^{-1} for ion exchange resin) and 1 g L^{-1} of sorbents. The pH was intentionally altered by adding 0.1 M HCl or 0.1 M NaOH into the plastic bottles (high-density polyethylene). After 24 h of contact with the gold(I) solution, the sorbents were separated by centrifugation at 8000 rpm for 10 min. Preliminary kinetic study showed that 24 h was enough to reach the sorption equilibrium state. The gold(I) concentration in the supernatant was determined after appropriate dilution in inductively coupled plasma (ICP; SHIMADZU, ICP-7510, Japan).

To evaluate the sorption capacity of the sorbents, sorption isotherms experiments were conducted by bringing 0.03 g of sorbents into contact with 30 mL of gold(I) solution. The initial concentration was altered from 0 to 594.25 mg L^{-1}. The solution pH was controlled at the desired value during the experiments. All other conditions were the same as those used in the pH edge experiments. The pH edge and isotherm experiments were carried out twice, and the reported values were averages of duplicates. The gold(I) uptake was calculated from the mass balance, as follows;

$$Q_e = \frac{V(C_0 - C_f)}{M} \tag{1}$$

where, Q_e is the amount of gold(I) uptake (mg g^{-1}), C_0 and C_f the initial and final gold(I) concentration in the solution (mg L^{-1}), respectively, V the solution volume and M the mass of sorbents.

2.3. Experimental procedure for gold recovery

After sorption, the gold(I) loaded sorbent was incinerated in an electric furnace (LABTECH, LEF-115S, Korea) at 800 °C for 2 h and the resultant ash was weighed. The gold(I) loaded sorbent and porcelain boat were weighed before the burning experiment and after the incineration was completed the boat was pulled out and cooled down at room temperature and the weight of the ash was calculated by subtracting the weight of the boat from the total weight. Then, 10 mL of sodium cyanide was added and the solution was stirred for 24 h to dissolve the gold. The concentration of gold in this aqueous solution was then analyzed by ICP. The recovery efficiency of the incineration step was estimated by using Eq. (2). The purity of gold in the incineration ash was calculated from ICP-AES analysis using Eq. (3).

$$\text{Recovery efficiency}\,(\%) = \frac{\text{Weight of gold in ash}\,(\text{mg})}{\text{Weight of initially sorbed gold}\,(\text{mg})} \times 100 \tag{2}$$

$$\text{Purity}\,(\%) = \frac{\text{Weight of gold in ash}\,(\text{mg})}{\text{Weight of ash}\,(\text{mg})} \times 100 \tag{3}$$

2.4. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) pattern analysis

The oxidation state of the gold sorbed to the sorbents and the gold in the incineration ash was measured using X-ray photoelectron spectroscopy (XPS). The analysis was conducted using an AXIS-NOVA spectrometer (Kratos Analytical, Ltd., UK) with a monochromatic Al Kα as the X-ray source (1486.71 eV of photons) to determine the presence of Au, C, N, Cl and O atoms on the surface of the samples. The XPS instrument was calibrated at the Au $4f_{7/2}$ photopeak with a binding energy of 84.0 eV. During each measurement, the X-ray source was operated at a reduced power of 150 W and the base pressure in the analysis chamber was maintained at 8.8×10^{-8} Torr. All binding energies were referenced to the neutral C 1s peak at 284.6 eV to compensate for the surface charging effects. XPS spectra were collected by AXIS-NOVA spectrometer at Korea Basic Science Research Institute (KBSI), Jeonju Centre.

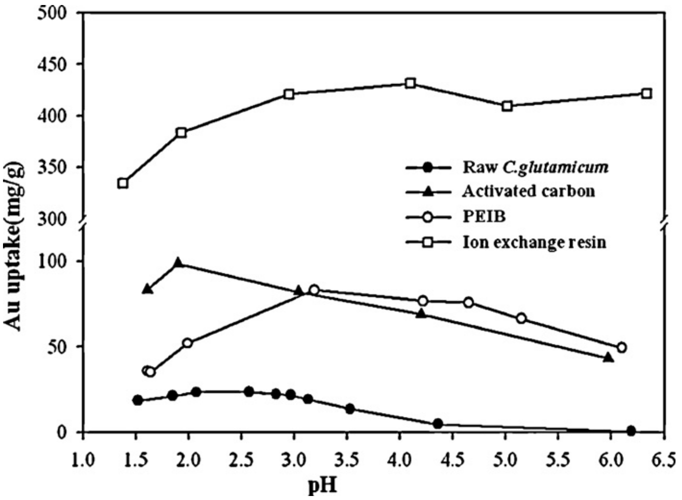

Fig. 1. Effect of pH on the sorption of gold(I) by raw *C. glutamicum* (●), activated carbon (▲), PEIB (○) and ion exchange resin (□). Gold(I) concentration: raw *C. glutamicum*: 78.83 mg L^{-1}, activated carbon: 113.25 mg L^{-1}, PEIB: 105.02 mg L^{-1}, ion exchange resin: 471.69 mg L^{-1}; adsorbent dose: 1 g L^{-1}; temperature: 25 ± 2 °C; contact time: 24 h.

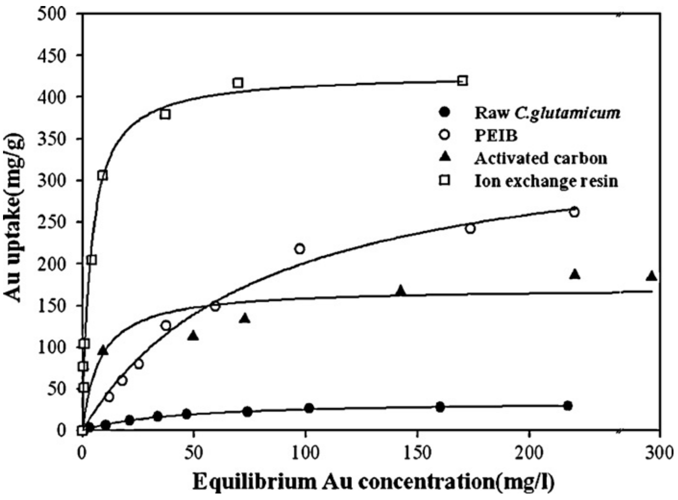

Fig. 2. Sorption isotherms at pH 3 for raw *C. glutamicum* (●), PEIB (○), activated carbon (▲) and ion exchange resin (□). Gold(I) concentration: 0–594.25 mg L^{-1}; adsorbent dose: 1 g L^{-1}; temperature: 25 ± 2 °C; pH: 3. Curves are predicted by the Langmuir model.

In order to confirm the crystallized form of gold in the ash, X-ray diffraction (XRD) spectra were obtained using a Rigaku D/max 2500 diffractometer equipped with a copper anode (k Cu Kα = 1.5406 Å) over a scanning interval (2θ) from 20° to 80°.

3. Results and discussion

3.1. Evaluation of sorption capacity

The pH of a gold(I) solution plays an important role in the whole sorption process, particularly in the sorption capacity. The variation in the sorption of gold(I) for each sorbent was studied within the pH range of 1–6, and the results are shown in Fig. 1. From this plot, the optimum pH for the uptake of gold(I) was an acidic condition of pH 3. With increasing pH, the uptake of gold(I) decreased for all sorbents, except the ion exchange resin. This resin is a strongly basic, anion exchange resin containing a quaternary amine functional group.

Our previous study identified the amino groups of raw *C. glutamicum* as being mainly responsible for reactive dye (negatively charged) biosorption [11,12]. The Fourier transform infrared absorption spectrum of raw biomass and PEIB has been reported previously [16], providing an evidence for the large number of amine groups in PEI introduced onto the biomass surface. Most common amino acids have isoelectric points in the pH range of 5–6. Thus, we expected that amino groups in the biomass will be protonated under acidic conditions, to afford a biomass with a net positive charge. On the other hand, gold–cyanide is negatively charged in aquatic solution, which will exhibit electrostatic attraction towards the positively charged cell surface. This could explain the maximum gold(I) uptake that occurred in the acidic pH range. The raw *C. glutamicum* biomass was chemically modified using PEI and the influence of the solution pH on the sorption of gold(I) was examined. The PEIB performed well at a strong acidic pH range, and its gold(I) uptake was higher than that of raw biomass, which was attributed to the increased amine groups.

Activated carbon is a highly porous carbonaceous material. The adsorption of gold(I)–cyanide complex ion on carbon is related to the electronic structure of the ion with the interaction related to the electron donation via the p orbital [17]. Hence, the adsorption capacity of gold(I)–cyanide complex on activated carbon is a function of the carbon porous structure.

The equilibrium sorption isotherm is of importance in the design of sorption systems. Experimental gold(I) sorption isotherms of different sorbents are presented in Fig. 2. The ratio between the gold(I) concentration remaining in the solution and that sorbed on the solid decreased when the solute concentration increased, generating a concave curve. These results indicated a progressive saturation of the solid. Modeling of the isotherm data was attempted using the Langmuir model [18]. The Langmuir parameters (Table 1) were estimated using the non-linear regression method. According to the Langmuir model, the PEIB achieved a maximum gold(I) uptake of 361.765 mg g^{-1}, which was higher than that of the raw biomass (35.149 mg g^{-1}). The Langmuir equilibrium constants (b) of the raw biomass and PEIB were 0.024 and 0.012 L mg^{-1}, respectively, indicating an affinity between gold(I) and the biosorbent. The ion exchange resin achieved the highest gold(I) loading of 427.771 mg g^{-1}.

Table 1
Isotherm constants for gold(I) sorption by the raw *C. glutamicum*, activated carbon, PEIB and ion exchange resin.

Isotherm models		Raw *C.glutamicum*	Activated carbon	PEIB	Ion exchange resin
Langmuir	Q_{max} (mg g^{-1})	35.149	170.642	361.765	427.771
	b (L mg^{-1})	0.024	0.126	0.012	0.267
	R^2	0.994	0.696	0.990	0.991
	ε (%)	0.824	37.143	9.987	16.848
Freundlich	K_F (L g^{-1})	3.531	68.720	17.061	135.753
	n	2.446	5.846	1.932	4.052
	R^2	0.956	0.961	0.962	0.911
	ε (%)	2.321	13.291	19.563	52.957

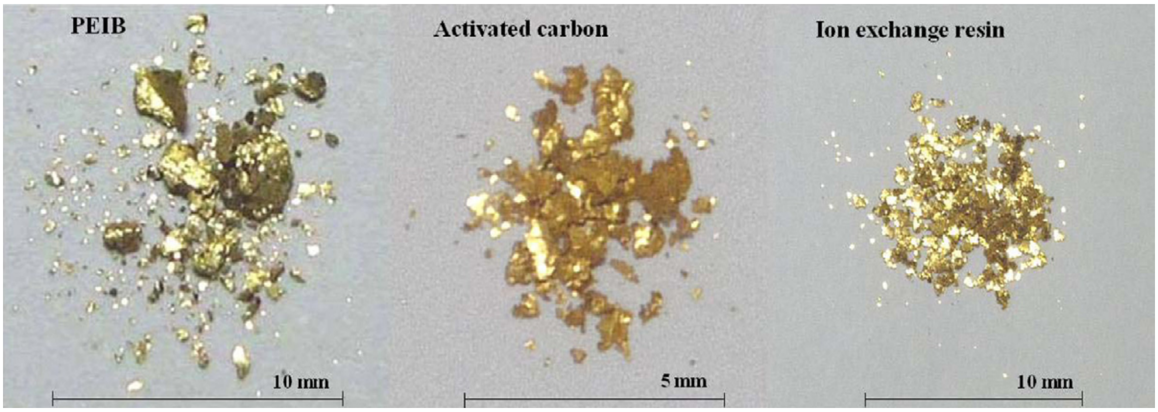

Fig. 3. Photograph of the incineration ashes of various sorbents.

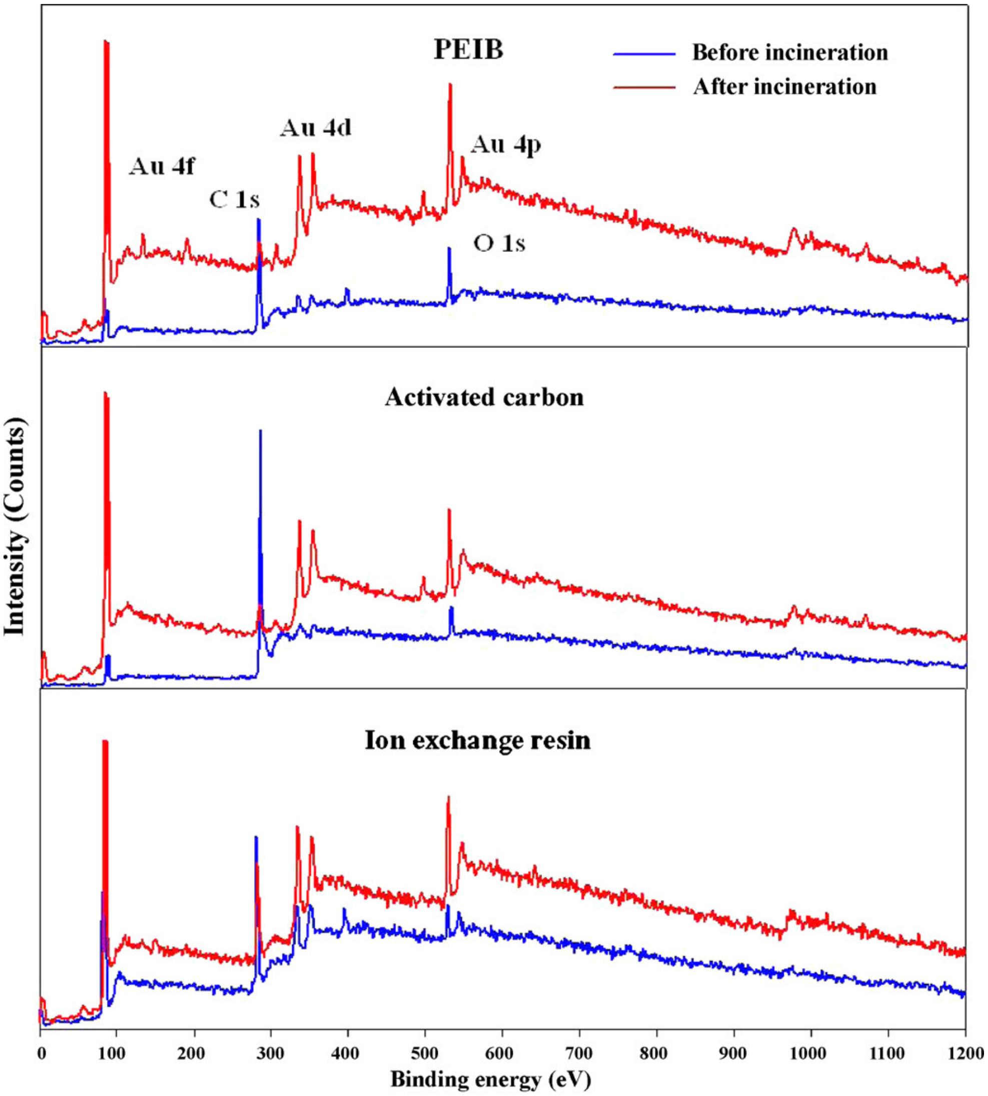

Fig. 4. XPS response of full survey of the gold(I) loaded sorbents: before (blue line) and after (red line) incineration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 2
Purity of gold in the ash generated from incineration of the gold loaded sorbents.

Sorbents	Gold uptake (mg g^{-1})	Removal efficiency (%)	Recovery efficiency (%)	Purity (%)
PEIB	277.77	54.35	85.60	97.72
Activated carbon	168.60	32.99	97.23	94.57
Ion exchange resin	434.31	84.98	92.72	96.56

Table 3
Relative surface distribution of gold species on the gold loaded sorbents (before and after incineration).

Sample	Condition	Au 4f binding energy (eV)	Surface Au Species (%[a])
Gold loaded PEIB	Before incineration	85.40 86.50	Au^{+3} (29.45) Au^{+3} (24.79)
	After incineration	83.70 87.38	Au^0 (45.76) Au^0 (54.24)
Gold loaded activated carbon	Before incineration	84.60 85.90	Au^{+1} (40.05) Au^{+3} (16.13)
	After incineration	83.74 87.43	Au^0 (55.21) Au^0 (41.39)
Gold loaded ion exchange resin	Before incineration	85.50 87.50	Au^{+3} (39.70) Au^{+1} (8.69)
	After incineration	83.70 87.38	Au^0 (46.09) Au^0 (53.91)

[a] Concentrations are expressed as a percentage of the total area of the Au 4f peak.

3.2. Recovery of gold

The gold(I) loaded sorbents were incinerated to remove organic constituents and to recover metallic gold. Complete incineration of the sorbents to afford metallic gold was attained with direct introduction to a furnace at 800 °C. Photographs of incineration ashes of various sorbents are shown in Fig. 3. As can be seen in Fig. 3, golden yellow ashes were left. To evaluate the recovery efficiency and purity of gold, the gold in the ashes were extracted with aqueous sodium cyanide. The concentration of gold in the extractant was then analyzed by ICP and the recovery efficiency and purity were calculated using Eqs. (2) and (3), respectively. The evaluated results are presented in Table 2. The recovery efficiencies ranged from 85.6% to 97.23%. Relatively low gold recovery efficiency of PEIB was estimated. In general, microbial biosorbents are basically small particles. Therefore, it often suffers from solid separation problem from liquid phase. The purities of gold in the ash were more than 96% in cases of biosorbents and ion exchange resins.

In this study, the incineration process was applied in order to directly recover zero-valent gold from the gold(I)-loaded sorbents. The sorbed gold ions can be easily obtained as a highly concentrated gold solution by elution (data not shown). However, the elution process does not give zero-valent solid-state metals but ionic form of metals contained in solution. The concentrated gold solution should be transformed into zero-valent form with reducing agents. Therefore, we suggest that the sequential process of sorption and incineration is possibly a simple and cost-effective means for recovery of metallic gold from cyanide solutions.

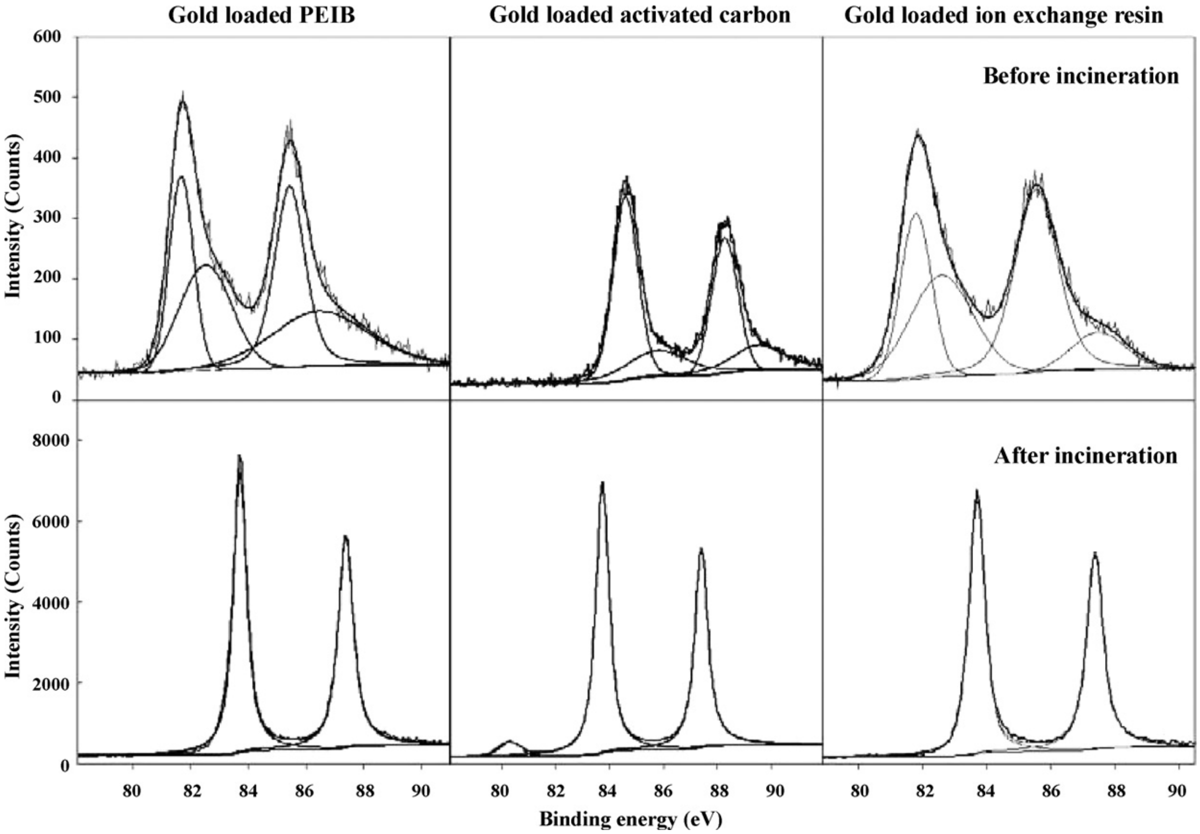

Fig. 5. XPS curve fitting of the Au 4f photoelectron peak in the gold(I) loaded sorbents (upper: before incineration, lower: after incineration).

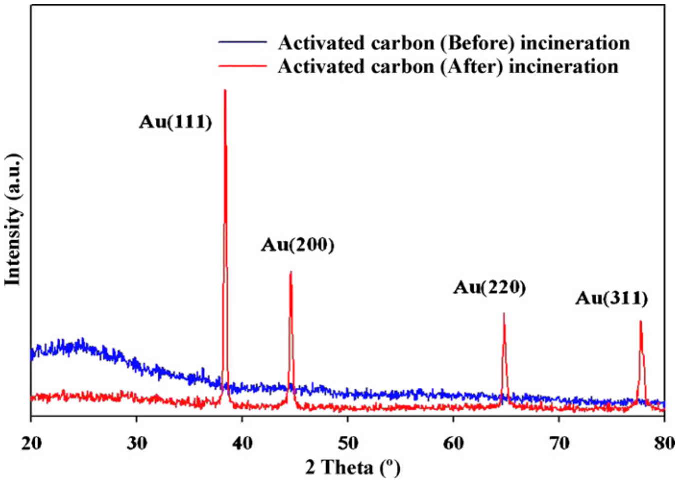

Fig. 6. X-ray diffractograms of the gold(I) loaded activated carbon (blue line) and after incineration (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.3. Identification of the forms of recovered gold

XPS analysis of the gold(I) loaded sorbents was performed to identify the forms of recovered gold existing in the ash after incineration. The XPS responses of the full survey of the gold(I) loaded sorbents (before and after incineration), presented in Fig. 4, clearly revealed the characteristic peaks of C 1s, N 1s, O 1s, Au 4f, Au 4d and Au 4p peaks for the gold(I) loaded sorbents (after incineration).

In all the gold(I) loaded sorbent, the Au 4f photoelectron peak is shown in Fig. 5 and the relative distribution of the Au species are examined in Table 3. The curve fitting of the Au 4f core-level spectrum is performed by using two spin–orbit split Au $4f_{7/2}$ and Au $4f_{5/2}$ components [19,20].

The Au 4f curve fitting of the gold loaded sorbents in Fig. 5 (before incineration) shows two Au $4f_{7/2}$ components at binding energies of 85.40 and 86.50 eV, which were assigned to Au^{+3} species (gold loaded PEIB), 84.60 and 85.90 eV, which were assigned to Au^{+1} and Au^{+3} species (gold loaded activated carbon) and 85.50 and 87.50 eV, which were assigned to Au^{+3} and Au^{+1} species (gold loaded ion exchange resin), respectively. No evidence of metallic gold particles was found in the gold loaded sorbents (before incineration).

The curve fitting of the Au 4f spectrum shown in Fig. 5 (after incineration) indicated Au $4f_{7/2}$ and Au $4f_{5/2}$ components at the following binding energies: 83.70 and 87.38 eV (gold loaded PEIB), 83.74 and 87.43 eV (gold loaded activated carbon) and 83.70 and 87.38 eV (gold loaded ion exchange resin). These were attributed to zero-valent gold.

Fig. 6 shows the XRD pattern of the gold remaining in the gold(I) loaded activated carbon ash. Four major diffraction peaks at 2θ of 38.0°, 44.2°, 64.4° and 77.4°, in the range of 20–80°, were observed in the case of the ash generated from the gold(I) loaded activated carbon, as shown in Fig. 6 (red line). No sharp peak was observed in the XRD diffraction pattern of the gold(I) loaded activated carbon (before incineration). The sharp peaks correspond to the diffraction from the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of the face-centered cubic structured Au (JCPDS 4-0784) [21]. These results indicated the existence of zero valent gold in the ashes.

4. Conclusions

The following conclusions were drawn from the present investigation into the recovery of gold from gold(I)–cyanide solution using ion exchange resin, activated carbon and chemically modified biosorbent:

- Through isotherm studies, the PEIB showed a maximum gold(I) uptake of 361.765 mg g^{-1}, which was much higher than that of the raw biomass (35.149 mg g^{-1}). The ion exchange resin achieved the highest gold(I) loading of 427.771 mg g^{-1}.
- The XPS and XRD analyses of the gold(I) loaded sorbents was performed to identify the forms of the recovered gold existing in the ash after incineration. No evidence of metallic gold particles was found in the gold loaded sorbents before incineration. However, after incineration, major form of recovered gold was of zero valent form.
- Complete incineration of gold(I) loaded sorbents to afford metallic gold was attained with direct introduction to a furnace at 800 °C. A high purity of gold above 95% was obtained for all the incinerated gold loaded sorbents.

Based upon the results of the present study, we claim that the sequential process of sorption and incineration can be simple and attractive means to recover zero-valent metallic gold from gold–cyanide solution.

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