Simultaneous Recovery of Gold and Iodine from the Waste Rinse Water of the Semiconductor Industry Using Activated Carbon

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This research work focused on the simultaneous recovery of gold (40.5 mg/dm³) and iodine (748 mg/dm³) from the waste rinse water of the semiconductor industry using activated carbon. A batch study was conducted to optimize process parameters, such as contact time and carbon dose, for the recovery of gold and iodine from the waste water. The loading capacity of the activated carbon for adsorption of gold and iodine was found to be 33.5 mg Au/g carbon and 835 mg I₂/g carbon, respectively. Gold was found to exist on the activated charcoal surface in two forms: ionic gold and elemental gold. Aqua regia was used to convert metallic gold to its ionic form, and the iodine and the small amount of ionic gold were removed from the activated carbon by elution with aqua regia. Gold was recovered from the eluate by reduction with hydrazine. Iodine from the diluted aqua regia was then precipitated by adding sodium hydrosulfite (Na₂S₂O₄). A complete process flow sheet was developed to recover both gold and iodine from the waste water of the semiconductor industry, which conserves the resources while meeting environmental pollution requirements. [doi:10.2320/matertrans.M2012009]

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1. Introduction

Etching is an important process employed in the production of various electronic products. In this process, the etching of gold from a surface is performed using aqua regia, cyanide or iodide solutions. As the cyanides are very toxic, its application is strictly prohibited by Korean environmental regulations. Aqua regia is not stable; it needs to be freshly prepared before use.¹⁾ Iodine, which is relatively less toxic, is an effective etchant for dissolving gold. After gold electroplating of electronic devices, the plated material is etched with a solution of iodine (I₂/KI) to remove a portion of the electroplated gold and the exposed gold seed layer. Finally, water is used to wash the electroplated and etched components. The processing and rinsing generate large quantities of effluent containing gold (III) or gold (I) ions as [AuI₄]⁻ or [AuI₂]⁻ complexes, respectively; iodine and other anionic or cationic species. Their discharge to the environment and the sewage system contaminates the surface and ground water. Iodine is a necessary nutrient for the human body, but excess iodine causes an increase in the production of thyroid hormones due to its stimulating effect on the thyroid function, which may result in various complications such as weight loss, anxiety, an enlarged thyroid gland and insomnia.²⁻⁷⁾ To conserve resources and protect the environment from pollution, it is necessary to treat such effluents to recover the gold, a precious metal, and the iodine.

The hydrometallurgical processes involving ion exchange or adsorption have often been employed for the recovery of gold from non-cyanide solutions using various resins, such as Dowex 21K,⁸⁾ Dowex G-55,⁸⁾ Purolite A-500⁹⁾ and Amberlite XAD-7HP.¹⁰⁾ The strong anion exchange resins exhibit fast adsorption kinetics and high loading capacities,

but the elution of gold from the resin is more difficult due to high ionic adsorption strength. The non-ionic resin, Amberlite XAD-7HP, is effective for gold adsorption and has the advantage of easily eluting the loaded metal. However, the resin degrades in high acidity solutions; therefore, the solution pH should be maintained at a low level (approximately 0–1.0).⁹⁾ Under highly oxidizing conditions, most commercial resins are not stable,¹¹⁾ and the sorption capacity and life of the resins decrease with successive use and recycling.

Activated carbon is one of the best adsorbents for the recovery of gold from a solution because it has a large surface area, high porosity and low material cost, compared to strong-base resins. The chemistry of gold adsorption from non-cyanide solutions differs from adsorption from cyanide solutions¹²⁾ and is therefore, worth considering for further investigation. Several researchers have investigated the fundamentals of gold loading onto activated carbon from halide solutions under various conditions.¹³⁻¹⁵⁾ For an iodide solution, it has been found that gold deposits onto the activated carbon by the reduction of ionic gold (III) to metallic gold.^{11,13)} Gold from gold-iodide can also be found on activated charcoal in two main states: ionic and elemental gold.¹⁵⁾ A combined process of adsorption and reduction for gold uptake from iodide solutions onto activated carbon was suggested by Hiskey and Qi.¹⁶⁾ All the above researches were primarily concerned with investigating the use of activated carbon to recover gold from synthetic solutions, which may be considered to be ideal for gold recovery, unlike the complex nature of actual solutions.

Activated carbon has also been used for iodine adsorption. The degree of iodine adsorption from an aqueous solution of KI/I₂ has been reported as the iodine number. Studies have shown that only I₂ was adsorbed onto carbon from aqueous solutions containing I⁻, I₃⁻ and I₂ species.^{17,18)} During the adsorption process, iodine is a competitive adsorbate for the

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Table 1 Composition of waste rinse water.

Element	Concentration, $C/\text{mg}\cdot\text{dm}^{-3}$
Au^+	40.5
K^+	3552
Cu^{2+}	0.80
Ni^{2+}	0.66
I_2	748
I^-	3552
Cl^-	≤ 5
Br^-	≤ 2

gold complex. Although the adsorption of iodine and gold onto activated carbon has been investigated, the process for recovering both gold and iodine from waste solutions has not yet received much attention, mainly because the focus is on recovering gold, a more valuable material than iodine.

The present study is focused on using activated carbon for the simultaneous recovery of gold and iodine from the waste rinse water of the semiconductor industry. The effect of various process parameters such as contact time and activated carbon amount was investigated. All elemental gold was converted to its ionic form, and both iodine and ionic gold were removed from the carbon by elution with aqua regia. From the gold-enriched solution, metallic gold could be obtained by reduction with hydrazine, while iodine was precipitated from the diluted aqua regia using sodium hydrosulfite. A process flow sheet for the recovery of both gold and iodine from the waste solution is proposed.

2. Experimental

2.1 Materials

The waste rinse water generated during the manufacturing of semiconductors was supplied by a Korean semiconductor company. The waste solution contained the following metals: $40.5 \text{ mg}/\text{dm}^3$ Au, $3552 \text{ mg}/\text{dm}^3$ K, $0.8 \text{ mg}/\text{dm}^3$ Cu, $0.66 \text{ mg}/\text{dm}^3$ Ni (Table 1). The iodine content in the waste solution was determined by sodium thiosulphate titration using starch as the indicator. All of the chemicals used (sodium hydroxide, sodium thiosulphate, sodium hydrosulfite, starch, acetone, nitric and hydrochloric acid) were laboratory grade reagents. Activated carbon was supplied by Junsei Chemical Company, which was ground and sieved for size classification (listed in Table 2). The activated carbon used in this study had a surface area of $990.25 \text{ m}^2/\text{g}$ and particle sizes of 250–710 μm .

2.2 Methods

The adsorption experiments were performed by adding a known volume of waste rinse solution and a fixed dose of activated carbon to a stoppered conical flask. The mixture was equilibrated at 298 K for the desired time using a thermostatically controlled shaking water bath operating at a shaking speed of 140 rpm under ambient conditions. After the gold and iodine adsorption, the carbon was separated from the raffinate by filtration (Filter paper, Whatman no. 41). The aqueous raffinate and eluate were analyzed for gold content by atomic absorption spectroscopy (AAS) (AAnalyst 400,

Table 2 Characterization of activated carbon.

Particle size, $d/\mu\text{m}$	Pore size, d/nm	BET surface area, $S/\text{m}^2\cdot\text{g}^{-1}$
> 710	1.7–300	946.64
250–710	1.7–300	990.25
150–250	1.7–300	998.21

Fig. 1 Effect of contact time on the adsorption of gold and iodine onto activated carbon.

PerkinElmer Inc., USA), and the iodine content was determined by titration, using sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) in the presence of starch as the indicator. The oxidation–reduction potential (ORP) (E_h) of the waste solution was measured using a combined Pt and Ag/AgCl electrode (9678 BNWP, Thermo Orion, Beverly, MA, USA). The E_h values obtained after equilibration were corrected based on the standard hydrogen electrode (SHE). The activated carbon was characterized by the BET method (Micromeritics Tristar 3000, USA) for surface area and by scanning electron microscopy (SEM) (JSM-6380LA, Japan) for surface morphology.

3. Results and Discussion

3.1 Effect of contact time

The effect of contact time for the recovery of gold and iodine was investigated using 0.5 g of activated carbon and 25 cm^3 of the original waste solution in a different flask at 298 K. The adsorption percentage is plotted against time in Fig. 1. The results showed that the adsorption of gold and iodine onto activated carbon increased with increasing contact time. At 3,600 s, equilibrium was attained for the completion of gold and iodine adsorption. The amounts of K, Cu and Ni in the raffinate were analyzed by AAS, and the data obtained (not shown) indicated that the concentrations of these metals were the same as that in the feed aqueous solution. Therefore, the interference of these metal ions was negligible in the investigation of gold and iodine recovery using activated carbon.

3.2 Mechanism of gold reduction

The adsorption and reduction of gold using activated carbon has previously been reported.^{12,13,15} Like an electro-

Fig. 2 Relationship between the ORP of the solution and the amount of gold removal.

chemical reduction, there are two half cells formed on the activated carbon surface. At the cathode cell, auric iodide and aurous iodide anions can gain electrons to become metallic gold and iodide ions.

At the anode cell, electrons are released by the activated carbon:

The adsorption and reduction of gold can thus be expressed as:

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 \quad (6)$$

$$E_{\text{h}} = E_{\text{cell}}^0 + \frac{0.059}{n} \log \left(\frac{[\text{AuI}_2^-]}{[\text{I}^-]} \right) \quad (7)$$

For the reduction of the gold complex on the activated carbon, E_{cell}^0 in eq. (6) must be positive. From the given empirical data of eqs. (1), (2) and (3), E_{cell}^0 was calculated to be 0.35 and 0.368 V for the two gold iodide (tetra- and di-) species, respectively; therefore, the gold iodide reductions may be assumed to be spontaneous. The oxidation–reduction potential (ORP) of the waste solution was measured before and after contact with activated carbon. The ORP of the initial solution was found to be 423 mV, which indicated that the oxidizing solution contained mainly AuI_2^- complexes. Qi and Hiskey¹⁹⁾ reported that Au (I) was the predominant species at potentials < 0.5 V. Figure 2 shows that after contact with the activated carbon, the ORP of the solution decreased. The decrease in ORP may be explained in terms of eq. (7), which shows that the gold reduction converts AuI_2^- to metallic gold. Therefore, the decrease in the concentration of gold (iodide) complex caused a simultaneous decrease in the oxidation–reduction potential.

After adsorption, the characterization of activated carbon was performed by SEM. Figure 3(a) indicates that the gold reduction occurred to deposit gold on the activated carbon in the metallic (crystalline) form. This can be observed as an agglomerate in the center surrounded by small nuggets

(a)

(b)

Fig. 3 Scanning electron microscopy (SEM) images of gold and iodine on the activated carbon surface.

[Fig. 3(a)]. The SEM-EDS elemental mapping method was used to qualitatively and quantitatively detect the presence of elements on the sample. The elemental mapping image in Fig. 3(b) clearly reflected the high density distribution of iodine on the activated carbon.

3.3 Effect of activated carbon dose

The effect of the activated carbon dose on the adsorption of gold and iodine from the waste solution was studied, using a retention time of 3,600 s for mixing. The solution volume was 50 cm³, and the activated carbon dose was varied from 0.1 to 2 g (25 to 500 cm³ aqueous solution/g-carbon). Figure 4 indicates that the adsorption of gold and iodine increased with the increase in carbon dose. The adsorption of both gold and iodine increased to a limited extent beyond 0.5 g of carbon and reached a maximum at 1.0 g of adsorbent. As expected, increasing the adsorbent dose provided a larger surface area for gold and iodine adsorption, thus increasing the adsorption efficiency. The aqueous solution/carbon (A/C) ratio (v/mass) was selected to be 50 as an optimum parameter for the adsorption of gold and iodine using activated carbon.

Fig. 4 Effect of carbon dose on the adsorption of gold and iodine.

Fig. 6 Elution of adsorbed iodine using sodium hydroxide solutions.

Fig. 5 Loading capacity of activated carbon for gold and iodine adsorption.

3.4 Loading capacity

Studies were performed to determine the loading capacity of the activated carbon for gold and iodine recovery. For these studies, 0.5 g activated carbon was contacted with various volumes of waste rinse water at 298 K for 21,600 s in a conical flask. As mentioned in the Introduction, the solution contained three species (I_2 , I^- and I_3^-), but only I_2 was adsorbed onto the activated carbon. Therefore, the adsorption was considered to be a function of the free iodine concentration. Figure 5 indicates that the loading of both gold and iodine increased with increasing aqueous feed volume. The maximum loading capacity of the activated carbon (0.5 g) for the adsorption of gold (16.75 mg) and iodine (417.5 mg) was determined using 600 cm³ of waste solution. The maximum loading capacity of carbon for gold and iodine was thus measured to be 33.5 mg Au/g-carbon and 835 mg I_2 /g-carbon, respectively.

3.5 Elution of gold and iodine from the loaded carbon

The elution test was performed to remove the iodine loaded onto the activated carbon using a sodium hydroxide (NaOH) solution at an eluent to carbon ratio of 25 (v/mass). The NaOH solution concentration was varied from 0.05 to 0.5 mol/dm³. Figure 6 indicates that a 0.5 mol/dm³ sodium hydroxide concentration was suitable for eluting iodine

completely. The NaOH raffinate was then analyzed by AAS to determine the gold concentration in the solution. The results indicated that approximately 4% gold was eluted in the solution. This suggested that the ionic gold on the carbon surface was also removed by the NaOH eluent simultaneously with iodine. The surface morphology of the eluted activated carbon was observed by scanning electron microscopy (SEM). Figure 7(a) shows that the elemental gold was still present on the activated carbon after elution with sodium hydroxide, whereas iodine was not found, even in trace amounts, in the SEM-EDS elemental mapping [Fig. 7(b)].

As mentioned above (in Section 3.2), gold exists in two states: ionic gold and elemental gold. Ionic gold could be removed from the activated carbon surface by elution with NaOH solution. However, it would be complicated to recover the elemental gold. The recovery of the elemental gold from the activated carbon is difficult to achieve by desorption; an alternative approach is dissolution.¹²⁾ With the purpose of removing both gold and iodine from the carbon surface to the solution, the elution was performed using aqua regia in the subsequent studies. Experiments were performed with varying concentrations of freshly prepared aqua regia solution. Figure 8 shows that increasing the aqua regia concentration increased the dissolution of metallic gold. From these results, 50% aqua regia was found to be suitable for dissolving gold. Lower acid concentrations would also limit the generation of NO_x (toxic gases). The emission of such toxic gases should be handled separately by a standard absorption process. Gold was enriched nearly 8 times (320 mg Au/dm³) in the eluted solution, compared to that in the feed solution (waste rinse water—40.5 mg/dm³). In the elution process that used aqua regia, metallic gold was converted to AuCl₄⁻, and the adsorbed iodine was dissolved in the aqua regia solution.

In aqua regia, Cl₂ and NOCl gases are formed by eq. (8), and these gases may react with the adsorbed iodine.

The reduction of gold from the aqua regia solution was achieved using hydrazine to convert the ionic form to metallic gold.

Fig. 7 Scanning electron microscopy (SEM) images of gold and iodine on the activated carbon surface after elution using sodium hydroxide solutions.

Fig. 8 Elution and enrichment of gold from loaded activated carbon using various aqua regia concentrations.

The aqua regia was cooled at room temperature and placed in a centrifuge at 10,000 rpm for 600 s. The solution was then

Fig. 9 Precipitation of iodine from diluted aqua regia using sodium hydrosulfite.

filtrated to collect the precipitated gold metal. The NaOH solution was added to the solution depleted in gold to adjust the acidity to the desired litmus mark (pH = 5.0). A solution containing sodium hydrosulfite (2 mol/dm^3) was then added to precipitate the iodine. The solid iodine was filtered using a Büchner funnel and a cellulose acetate membrane.

The reduction of iodic acid by sodium hydrosulfite proceeds as follows:²⁰⁾

The amount of iodine estimated showed that 97% of the adsorbed iodine was removed from the activated carbon by elution with aqua regia. The precipitated iodine in its solid form is shown in Fig. 9.

3.6 Regeneration of activated carbon

The regeneration of activated carbon has been considered to improve the process economics.²¹⁾ In the present study, the solvent extraction process was employed to regenerate the carbon, as it is more effective than other methods such as a the thermal treatment or a chemical process.^{22,23)} Several solvents are used to remove adsorbates from activated carbon, including sodium hydroxide, ethanol, benzene and acetone. In this study, 0.5 mol/dm^3 sodium hydroxide solution was used to remove chloride, chlorine and small amounts of iodine remaining on the activated carbon surface. After eluting with acetone for 43,000 s, the remaining chlorine was washed with de-ionized water for 36,000 s and then dried in an oven at 353 K. The regenerated activated carbon was used for gold and iodine recovery. After each cycle, the batches of activated carbon were investigated to assess the loading capacity of the regenerated carbon.

Figure 10 shows that the adsorption capacity for gold and iodine decreased in every cycle. This was due to the decrease in the surface area of the carbon particles from an initial area of $990.3 \text{ m}^2/\text{g}$ to $975.0 \text{ m}^2/\text{g}$, $897.2 \text{ m}^2/\text{g}$ and $793.3 \text{ m}^2/\text{g}$ in the first, second and third cycles, respectively. The decrease

Fig. 10 Degradation of activated carbon after several cycles.

Fig. 11 Proposed process for recovering gold and iodine from waste rinse water using activated carbon.

in surface area may be attributed to the oxidation of activated carbon while in contact with strong chemical oxidation reagents (such as nitrosyl chloride, chlorine gas²⁴) and nitric acid²⁵) which formed C–Cl and C–O bonds. The excessive amount of tri-iodide oxidizer was also contributed to destroying the carbon surface and inhibiting the adsorption-reduction of gold-iodide.¹⁴ The adsorption efficiency of the regenerated carbon decreased significantly after 3 cycles, thereby limiting its recycling after this stage. The proposed process for using activated carbon to recover gold and iodine from the waste solutions of the semiconductor industry is presented in Fig. 11. The process can meet the objectives of resource recycling while reducing environmental degradation.

4. Conclusions

The adsorption studies using the waste rinse water from the semiconductor industry showed that activated carbon can be used for the effective recovery of both gold and iodine. The mechanism of gold adsorption with activated carbon was found to follow mainly the reduction process, as gold was present on the activated carbon in ionic and metallic forms. Aqua regia was used to remove all elemental gold, ionic gold

and iodine from the activated carbon by elution. The elution of gold from the activated carbon by aqua regia yielded a metal-enriched solution containing 320 mg Au/dm³, from which metallic gold was recovered by reduction with hydrazine. Approximately 97% of the iodine was also eluted by aqua regia. Solid iodine was obtained from the diluted aqua regia solution by a precipitation technique using sodium hydrosulfite. The solvent regeneration process for activated carbon showed the possibility to recover sorption capacity, which degraded in subsequent cycles. Based on the experimental results, a continuous, closed-loop industrial process has been established to recover gold and iodine from waste rinse solutions generated during the manufacturing of electronic products without affecting the environment.

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