Recycling of Copper and Gold from Waste Printed Circuit Boards by Leaching Followed by Solvent Extraction

Kamalesh Kumar Singh and Mudila Dhanunjaya Rao

Abstract This article presents a two-stage, eco-friendly hydrometallurgical route for the recovery of gold from the delaminated metallic layers of waste mobile phone Printed Circuit Boards (PCBs). The downsized PCBs were treated with an organic solvent dimethylacetamide (DMA) for the separation of metallic fraction from non-metallic glass fibre. The liberated metallic sheets are used for the selective dissolution of copper in an aqueous leaching reagent. Influence of various parameters such as type of leaching reagent, the concentration of the solution, temperature, time, and pulp density is optimized for the effective leaching (almost 100%) of copper. Results show that 3 M nitric acid is a suitable reagent for copper leaching but gold remained in solid residue. In the second stage, the separated residue is used for the recovery of gold by sulphuric acid with a combination of halide salt. Results have shown that almost 92% of gold is recovered at the optimized parameters. Solvent extraction with 0.1M tertiary amide reveled the selective and quantitative recovery of gold from gold leach solution.

Keywords Recycling · Secondary recovery · Hydrometallurgy · Extraction

Introduction

The rapid change in technology and the electronic gadgets are becoming obsolete at faster rate [1]. In turn, the quantity of electronic waste is growing at faster rate. In year 2019, the global e-waste generation crossed 53.6 million tonnes [2]. The lower recycling rate in developing countries makes the situation alarming [3–7]. The 100% recycling is still a distant dream to be achieved. The lower recycling rate is not only burdening the environmental load through toxic elements but also

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losing many valuable and scarce metals [8]. The printed circuit boards are most valuable component of any electronic gadget because it hosts as many as 60 elements including precious metals like gold, silver, platinum, and palladium and valuable metals like copper, tin, nickel, aluminium, and iron [9, 10]. The metallic content may be as high as 40% of the total weight of PCBs [10]. In the present paper, two-stage leaching and subsequent solvent extraction have opted for recovery of most valuable gold and abundantly present copper from WPCBs. Nitric acid dissolves the base metals present, and it becomes easier to extract those metals successfully by application of highly selective metal extractant [11]. In addition, for the dissolution of gold, halide leaching reagents at acidic conditions are more significant than the traditional processes [12–16]. Here, for copper extraction from leached solution hydroxyl oximes [17] are used whereas amides are used to recover gold [18].

Methodology

The printed circuit boards of mobile phones were collected from local vendors. The attached components and wires were removed from the circuit boards at a temperature below 200 °C by application of heat gun. The bare PCBs were cut into smaller pieces of the size 1 cm × 1 cm approximately with the help of shear cutter. These pieces were soaked into the solution of organic solvent N, N-dimethylacetamide (DMA) for 10 h to dissolve the resin of printed circuit boards to liberate the metallic components and the fibreglass present. The bare metallic fractions are subjected to hydrometallurgical extraction processes comprising acid leaching, solvent extraction, and stripping to recover gold and copper as shown in Fig. 1.

Results and Discussion

Chemical Analysis and Two-Stage Leaching

The metallic and non-metallic components were estimated through complete dissolution of the delaminated metallic components in *aqua regia*. One gram of sample was dissolved in 20 ml of aqua regia for 3 h at 50 °C at 500 rpm in a glass reactor fitted with stirring and heating facility. The solution was analysed through AAS/ICP-OES, and the obtained results are shown in Table 1.

It is clear that the major portion (84%) of the metallic values are copper followed by small quantities of nickel, zinc, tin, cadmium, aluminium, and lead and trace quantities of gold, silver, and palladium. The non-metallic plastics and glass fiber are separated manually from the metallic sheets.

Further, in next step, i.e. in stage-1 leaching, the metallic sheets of waste printed circuit boards are leached with 3 M nitric acid. However, some non-metallic fraction

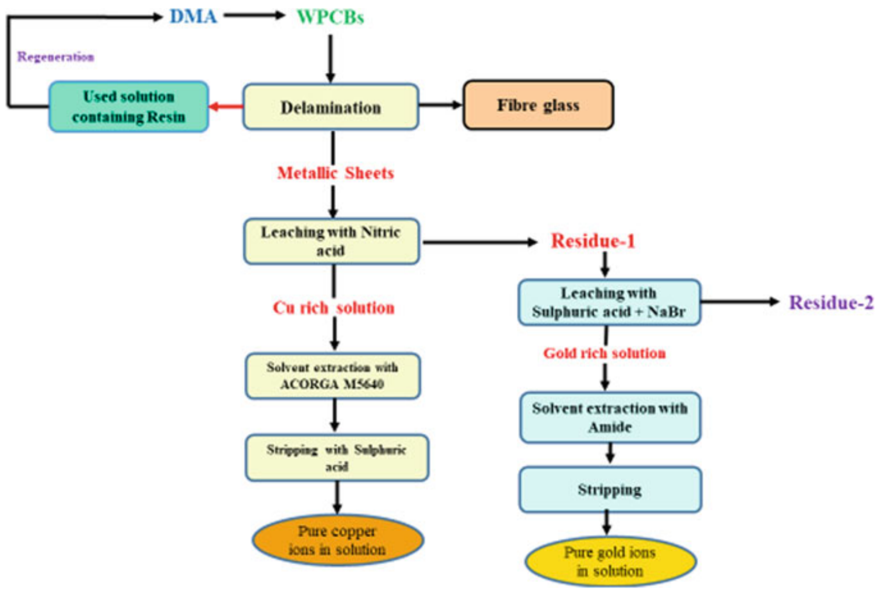

Fig. 1 Flow sheet of proposed process to recover copper and gold from WPCBs

Table 1 Chemical analysis of the sheared WPCB sample

Element	Wt%
Cu	84
Au	0.05
Ag	0.03
Sn	0.4
Pd	0.007
Ni	2.3
Zn	0.4
Pb	0.1
Cd	0.3
Al	0.2
Plastic and glass fiber	12.2

(12 wt%) is also still availed with the metallic fraction. The leaching conditions are optimised and carried out at the temperature 30 °C for 2 h with the pulp density 50 g/L. The stirring speed was maintained at 500 rpm. AAS/ICP-OES analysis data are given below in Table 2, which shows that precious metals gold, silver, and palladium have not entered the solution whereas other metals except copper also leached in very small quantity. This stage of leaching is able to extract more than 97% of copper.

Table 2 Chemical analysis of the first stage leached solution

Element	Wt%
Cu	97.3
Au	0
Ag	0
Sn	0.4
Pd	0
Ni	0.8
Zn	0.6
Pb	0.5
Cd	0.4
Al	0

Table 3 Chemical analysis of the second stage leached solution

Element	Wt%
Cu	0.2
Au	7
Ag	3
Sn	89

Table 4 Extraction of copper and gold after leaching from 5 g initial WPCB sample

Metal	Extracted wt	Extraction (%)
Copper	4.99 g	99.96%
Gold	0.0025 g	95.28%

Precious metals such as gold and silver have been observed in the residue of stage-1 leaching along with a non-metal fraction.

The residue with non-metallic fraction obtained after the first stage of leaching is subjected to second stage of leaching with sodium bromide in presence of sulphuric acid. The optimised conditions are maintained at 3M sulphuric acid with 3M sodium bromide at the temperature of 70 °C for 1 h and at the same stirring speed of 500 rpm. AAS/ICP-OES analysis of stage-2 leached samples is given in Table 3. The collected residue after stage-2 leaching consists of non-metallic fraction in a minor quantity.

After completion of two-stage leaching from 5 g initial PCB sample, stage-1 and stage-2 leachates comprise 4.99 g copper and 0.0025 g gold individually as shown in Table 4. Further purification process is required for stage-2 leach solution to separate gold from silver and tin. For that, solvent extraction process is used with an amide as an extractant.

Solvent Extraction of Gold

The recovery of Au(III) was observed using solvent extraction with an organic amide diluted in toluene as an extractant by leaving other elements in the raffinate. The protonation of an amide plays a crucial role in the selective extraction of Au(III) into the organic phase. Combination of the protonated and neutral amide with $[AuBr4]^-$ through hydrogen bonding and electrostatic interactions creates a neutral assembly and transport into the organic phase. The process of Au(III) extraction with primary amide as an extractant diluted in toluene is shown in Fig. 2.

From the analysis of the organic phase, it is evident that the amount of gold extracted into the organic phase increased from $\mathbf{L^1}$ (80%) to $\mathbf{L^2}$ (98%) and $\mathbf{L^3}$ (99%). In addition to gold, a proportion of tin (16–20%) is also extracted by all amides as shown in Table 5. However, no silver and copper are seen. Therefore, tertiary amide has been chosen for the maximum extraction of gold.

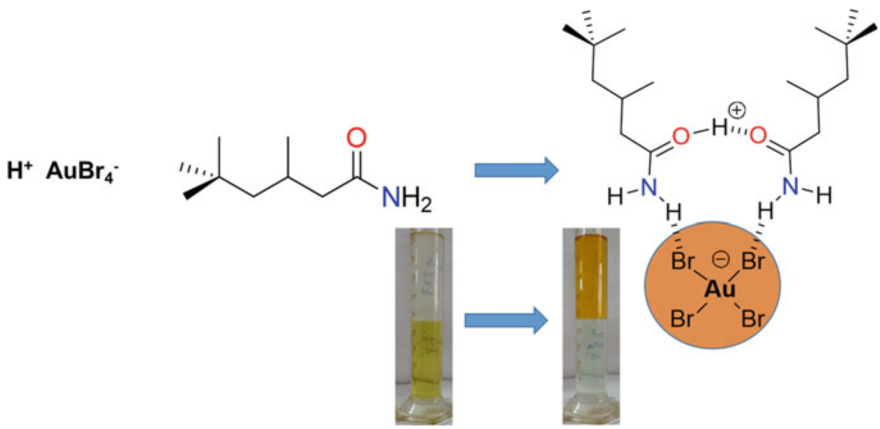

Fig. 2 Summary of the process involved in the extraction of Au(III) from an aqueous leach solution into an organic phase containing primary amide

Table 5 Transport of gold from the stage-2 leach liquor into a toluene solution of 0.1 M primary ($\mathbf{L^1}$), secondary ($\mathbf{L^2}$), or tertiary amide ($\mathbf{L^3}$) [Conditions: o/a 1:1; 1 h; 20 °C]

Amide	Au (% recovery)	Sn (% recovery)
$\mathbf{L^1}$	80	20
$\mathbf{L^2}$	98	18
$\mathbf{L^3}$	99	16

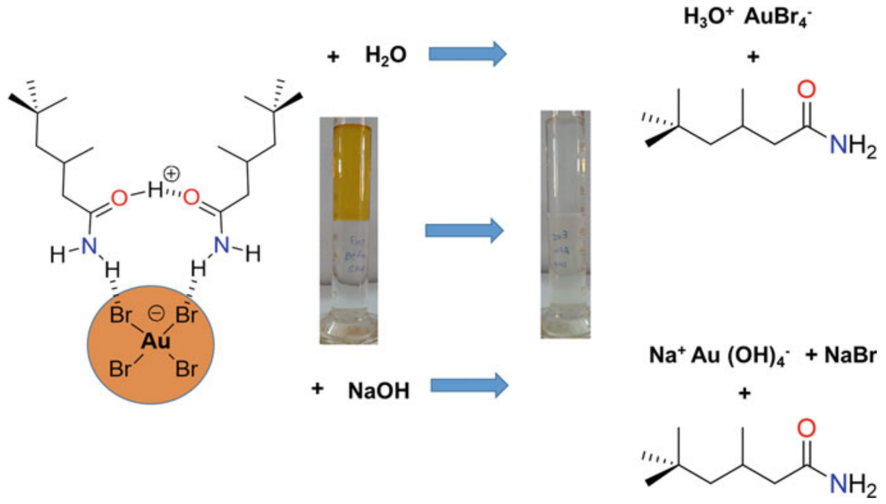

Fig. 3 Summary of the process involved in the back extraction of Au(III) from primary amide complex into an aqueous (water or sodium hydroxide) solution

Stripping

Back extraction of $[AuBr4]^-$ from the amide neutral complex into an aqueous phase is also essential for the generation of pure gold solution and the re-generation of free extractant for another extraction cycle. The process of back extraction or stripping with either water or sodium hydroxide is also shown in Fig. 3

From ICP-OES analysis, it is observed that no gold is stripped into water from extraction solutions of $\mathbf{L^1}$ and $\mathbf{L^2}$, and 10% of gold is stripped with water from metal-loaded toluene solutions of **L3**. Using 0.1 M NaOH solution as the stripping reagent, gold stripping increased from $\mathbf{L^1}$ (40%), $\mathbf{L^2}$ (78%) to $\mathbf{L^3}$ (82.6%). In contrast, when 1 M NaOH is used as the stripping reagent, almost all gold recovery is achieved from all amide extractions as shown in Table 6. Therefore, 1 M sodium hydroxide was chosen for the back extraction of gold from either secondary or tertiary amides.

In addition to gold stripping, tin is also stripped from the organic solutions to some extent and gradually decreases from $\mathbf{L^1}$ to $\mathbf{L^3}$ with water and sodium hydroxide as

Table 6 Effect of reagent on stripping of gold from the organic phase, using 0.1 M $\mathbf{L^{1-3}}$ in toluene as the extracting agent [Conditions: o/a 1:1; 1 h; 20 °C]

Amide	% recovery of gold with water stripping	% recovery of gold with 0.1 m NaOH stripping	% recovery of gold with 1 m NaOH stripping
L^1	0	40	95
L^2	1	70	98
L^3	10	80	99

Table 7 Effect of reagent on stripping of tin from the organic phase, using 0.1 M $\mathbf{L^{1-3}}$ in toluene as the extracting agent [Conditions: o/a 1:1; 1 h; 20 °C]

Amide	% recovery of tin with water stripping	% recovery of tin with 0.1 m NaOH stripping	% recovery of tin with 1 m NaOH stripping
$\mathbf{L}^1$	10	40	60
$\mathbf{L}^2$	8	35	22
$\mathbf{L}^3$	5	17	9

shown in Table 7. It shows that traces of tin (9%) were only found with 1 M sodium hydroxide as a stripping reagent from tertiary amide. The repetition of extraction cycles can reduce tin contamination. After completion of solvent extraction from 5 g initial PCB sample, strip solution comprises 0.0024 g gold. The strip solution consists of 480 ppm of gold.

Conclusions

The two-stage metal leaching process selectively dissolves copper from delaminated WPCBs in stage-1 leaching to leave a gold-rich solid residue for the subsequent extraction of gold in stage-2 leaching. Selective leaching of copper was achieved when using 3 M nitric acid at 30 °C, over a 2 h resident time, for 50 g/L pulp density, and 500 rpm agitation speed. Importantly, no gold was dissolved using these conditions. In the stage-2 leaching, selective extraction of gold is observed with bromide leaching with 3 M sulfuric acid with 3 M sodium bromide at 70 °C, over a 1 h time and 500 rpm agitation speed. The use of 0.1 M tertiary ($\mathbf{L^3}$) amide is efficient for the transportation of Au(III) into toluene solution. In addition, fraction of tin was also co-extracted. The extracted Au(III) was stripped from the toluene solution, with 99% recovered, with 1 M NaOH as stripping reagent.

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