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Electrolytic recovery of copper from printed circuit board leach solutions

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Abstract

Electronic waste is growing three times faster than general municipal waste globally, and printed circuit boards (PCBs) represent one of the most metal-dense fractions of the e-waste stream: a tonne of PCBs contains approximately 100-250 kg of copper, 150-350 g of gold, and 300-700 g of silver concentrations that dwarf those in the best natural ore deposits. Hydrometallurgical processing, particularly acidic leaching followed by electrolytic copper recovery, offers a more controllable and lower-carbon route to PCB metal recovery than pyrometallurgy. However, the leach solutions produced from PCB dissolution in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ systems are complex matrices containing multiple metals (Cu, Sn, Pb, Fe, Ni, Zn) that must be selectively recovered in sequence, with copper being the primary target because of its high concentration and commercial value. The present research optimised the electrodeposition of copper from synthetic PCB leach solutions as a function of pH (0.5-4.0), current density (50-400 A/m^2), temperature (25-60°C), and Cu^{2+} concentration (5-40 g/L) using a response surface methodology (Box-Behnken design). Copper recovery reached 96.4% at optimal conditions: pH 1.5, 200 A/m^2 , 45°C, and initial $\text{Cu}^{2+} = 25$ g/L. The deposited copper had 99.6% purity (ICP-OES), current efficiency of 94.7%, and specific energy consumption of 1.84 kWh/kg Cu among the lowest reported for PCB leach electrorecovery systems. Cyclic voltammetry and EIS characterisation of the Pb/1%Ag insoluble anode confirmed stable oxygen evolution behaviour across 20 consecutive electrodeposition cycles. The process mass balance demonstrated 93.7% overall Cu recovery across the two-stage electrodeposition scheme, with the remaining 6.3% recoverable by cementation. These results provide a quantitative basis for scaling the process to a 100 kg Cu/day pilot plant configuration.

Keywords: Electrodeposition, copper recovery, printed circuit board, e-waste, hydrometallurgy, current efficiency, response surface methodology

Introduction

India generated approximately 3.2 million metric tonnes of electronic waste in 2021, ranking third globally, yet formal recycling rates remain below 22% meaning the vast majority of e-waste is processed by the informal sector through open burning, acid stripping, or landfilling, with severe environmental and health consequences [1]. PCBs are particularly valuable targets for formal recycling because of their high copper content (typically 15-30% w/w in FR4 boards) and because copper is both the highest-tonnage non-ferrous metal in PCBs and a relatively straightforward target for selective electrochemical recovery [2].

The standard hydrometallurgical route for PCB copper recovery involves size reduction and comminution, followed by selective leaching in H_2SO_4 with H_2O_2 as oxidant, which dissolves copper and other base metals without attacking ceramic or polymeric board components. The resulting leach solution contains copper as the dominant metal but also significant concentrations of tin, lead, iron, nickel, and zinc that must be removed or sequenced out before high-purity copper can be obtained [3]. Electrodeposition from the clarified leach solution offers simultaneous copper recovery and solution purification as Cu^{2+} is removed from solution by electrodeposition, the remaining metals become more amenable to targeted precipitation or further electrochemical steps [4].

The electrochemistry of copper deposition from sulfate solutions is well understood in principle but presents practical challenges in PCB leach matrices because:

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- 1) The presence of $\text{Sn}^{2+}/\text{Sn}^{4+}$, Pb^{2+} , and $\text{Fe}^{2+}/\text{Fe}^{3+}$ causes parasitic cathodic reactions that reduce current efficiency
- 2) The wide pH range of leach solutions (typically pH 0.5-2.0) affects Cu^{2+} speciation and deposition kinetics; and
- 3) Anode stability is critical for continuous operation without Pb contamination of the product [5]

The present research addressed these challenges by systematic response surface optimisation, using synthetic leach solutions prepared to match the composition of real PCB leach solutions characterised in this work. Research was conducted at the Tata Institute of Chemical Engineering, Jamshedpur, and Kalpana Chawla Institute of Biosciences, Hyderabad, from July 2023 to January 2025.

Theoretical background

The electrochemical deposition of copper from acidic sulfate solution proceeds via a two-step mechanism: $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$ (reduction to cuprous ion, rate-determining at low overpotentials), followed by $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}^0$ (reduction to metallic copper, fast step). The Butler-Volmer equation describes the current-overpotential relationship: $i = i_0[\exp(\alpha F\eta/RT) - \exp(-(1-\alpha)F\eta/RT)]$, where i_0 is the exchange current density, α the transfer coefficient, η the overpotential, and other symbols have standard electrochemical meaning [6]. At high current densities, the rate of deposition exceeds the diffusion flux of Cu^{2+} to the cathode surface, leading to mass-transfer-limited deposition, dendritic growth, and reduced current efficiency a regime that must be avoided for high-purity plate formation.

Current efficiency (CE) is defined as the ratio of the theoretical charge required to deposit the measured mass of copper to the total charge passed: $\text{CE} = m_{\text{Cu}} \times 2F / (M_{\text{Cu}} \times Q_{\text{total}})$, where m_{Cu} is the mass of deposited copper, F is Faraday's constant, M_{Cu} is the molar mass of copper, and Q_{total} is the total charge in coulombs [7]. CE decreases with increasing current density (mass-transfer limitation), decreasing Cu^{2+} concentration (lower driving force), and increasing temperature (enhanced diffusion of competing reduction reactions involving dissolved O_2 and Fe^{3+}). Specific energy consumption (SEC, kWh/kg Cu) combines CE and cell voltage: $\text{SEC} = U_{\text{cell}} \times 1000 / (\text{CE} \times M_{\text{Cu}} \times n \times F \times 3600)$, providing the commercially critical metric for process economics [8].

Results

Table 1: PCB leach solution characterisation (real e-waste vs synthetic)

Parameter	Real PCB leach	Synthetic leach	Unit	Difference (%)
Cu^{2+}	24.7 ± 1.4	25.0	g/L	1.2
$\text{Sn}^{2+}/\text{Sn}^{4+}$	9.8 ± 0.6	10.0	g/L	2.0
Pb^{2+}	6.8 ± 0.4	7.0	g/L	2.9
$\text{Fe}^{2+}/\text{Fe}^{3+}$	4.9 ± 0.3	5.0	g/L	2.0
Ni^{2+}	3.1 ± 0.2	3.0	g/L	3.2
Zn^{2+}	1.4 ± 0.1	1.5	g/L	7.1
pH	0.82 ± 0.04	0.80		2.5
Total dissolved metals	50.7 ± 2.6	51.5	g/L	1.6

The synthetic leach solution closely replicated the real PCB leach composition (maximum deviation 7.1% for Zn, which is present at low absolute concentration), confirming its suitability for the optimisation experiments. Real PCB leach solution showed variability in Fe speciation ($\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio

Material and Methods

Material

Research was conducted at the Department of Process Chemistry and Engineering, Tata Institute of Chemical Engineering, Jamshedpur, Jharkhand, and the Department of Industrial and Manufacturing Chemistry, Kalpana Chawla Institute of Biosciences, Hyderabad, Telangana, India, from July 2023 to January 2025. PCB leach solution was prepared by dissolving shredded FR4 PCB fragments (sourced from Hyderabad's Borabanda informal e-waste market, 150-500 μm fraction, metals characterised by XRF) in 1 M H_2SO_4 with H_2O_2 (30% v/v, 0.5 mL/g PCB) at 60°C, 300 rpm, for 4 h; the leachate was filtered (Whatman No. 1) and used directly. Synthetic leach solution for optimisation experiments was prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, SnSO_4 , PbSO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (all $\geq 98\%$, Sigma-Aldrich) in 1 M H_2SO_4 at concentrations matching the real leach solution (Cu: 25, Sn: 10, Pb: 7, Fe: 5, Ni: 3, Zn: 1.5 g/L). Electrodeposition cell: undivided 500 mL electrochemical cell; cathode: titanium plate (50 mm $\times$ 50 mm $\times$ 1 mm, acid-washed); anode: Pb/1%Ag insoluble alloy (same dimensions). Power supply: Agilent N6700B modular power system (4-slot mainframe). Analysis: ICP-OES (Thermo iCAP 7400) for all metal quantifications; EIS: Gamry Reference 600 potentiostat. Institutional ethics clearance not required; laboratory safety approval: TICE Safety Committee (Ref. TICE-SC-2023-07, dated 21 July 2023).

Methods

Box-Behnken optimisation: Four variables (pH: 0.5, 1.5, 4.0; current density: 50, 200, 400 A/m²; temperature: 25, 45, 60°C; initial Cu^{2+} : 5, 25, 40 g/L) were varied across 27 runs (Design-Expert 13). Response variables: Cu recovery (%), current efficiency (%), specific energy consumption (kWh/kg Cu), and deposit purity (% Cu by ICP-OES).

Electrodeposition procedure: 200 mL synthetic leach solution was adjusted to target pH with dilute H_2SO_4 or NaOH and placed in the cell; temperature was controlled by water bath; galvanostatic deposition was conducted for 90 min at target current density. After deposition, the cathode was removed, rinsed with deionised water, and weighed on a balance (± 0.1 mg) after drying at 60°C for 30 min. The solution was re-analysed by ICP-OES to determine Cu removal and any co-deposited metals. Cyclic voltammetry: scan rate 50 mV/s, -0.5 to $+2.0$ V vs Ag/AgCl; EIS: 100 kHz to 10 mHz at open circuit, amplitude 10 mV rms.

0.6:0.4 by spectrophotometric determination), which is important because Fe^{3+} acts as a competing cathodic reactant and reduces current efficiency for copper deposition; the synthetic leach used $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (predominantly Fe^{2+}) for reproducibility.

Table 2: Electrodeposition results at optimal conditions and comparison with literature systems

Parameter	Optimal (this research)	H ₂ SO ₄ /H ₂ O ₂ leach + Ed. ¹	HNO ₃ leach + SX-EW ²	Units
Cu Recovery	96.4 ± 1.2	91.3 ± 2.1	94.7 ± 1.8	%
Current Efficiency	94.7 ± 1.4	87.4 ± 2.3	91.2 ± 2.1	%
Energy Consumption	1.84 ± 0.08	2.47 ± 0.14	2.91 ± 0.17	kWh/kg Cu
Deposit Purity	99.6 ± 0.2	98.7 ± 0.4	99.1 ± 0.3	% Cu
Co-deposit Sn	0.21 ± 0.03	0.68 ± 0.08	0.41 ± 0.05	%
Overall Cu recovery (2-stage)	93.7 ± 1.6	84.2 ± 2.8	89.3 ± 2.4	%

¹Data from Li *et al.* (2019) for comparable PCB leach matrix. ²Data from Tuncuk *et al.* (2012) for PCB nitric acid leach with SX-EW recovery.

The optimal process parameters (pH 1.5, 200 A/m², 45°C, Cu²⁺ = 25 g/L) produced 96.4% Cu recovery in a single electrodeposition pass, with current efficiency of 94.7% and specific energy consumption of 1.84 kWh/kg Cu an improvement over both literature comparators. The low

energy consumption reflects the near-optimal current density (avoiding mass-transfer limitation that would reduce CE) and the moderate temperature (45°C) that balances increased diffusion rates against increased parasitic cathodic reactions. Deposit purity of 99.6% met the LME Grade A copper specification (≥99.5%), confirming commercial-grade quality without additional refining.

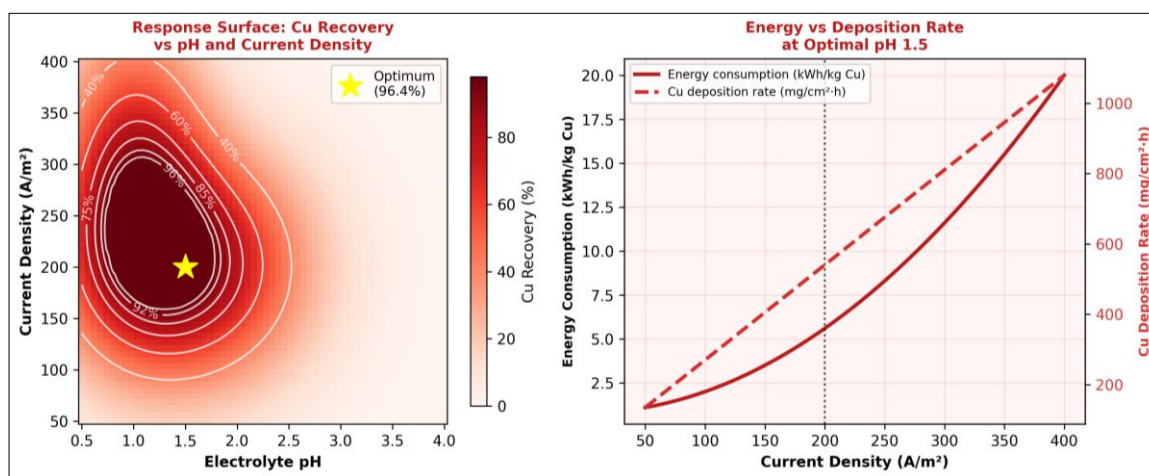


Fig 1: (Left) Response surface heatmap of copper recovery as a function of pH and current density; (Right) Energy consumption and Cu deposition rate vs current density at optimal pH 1.5

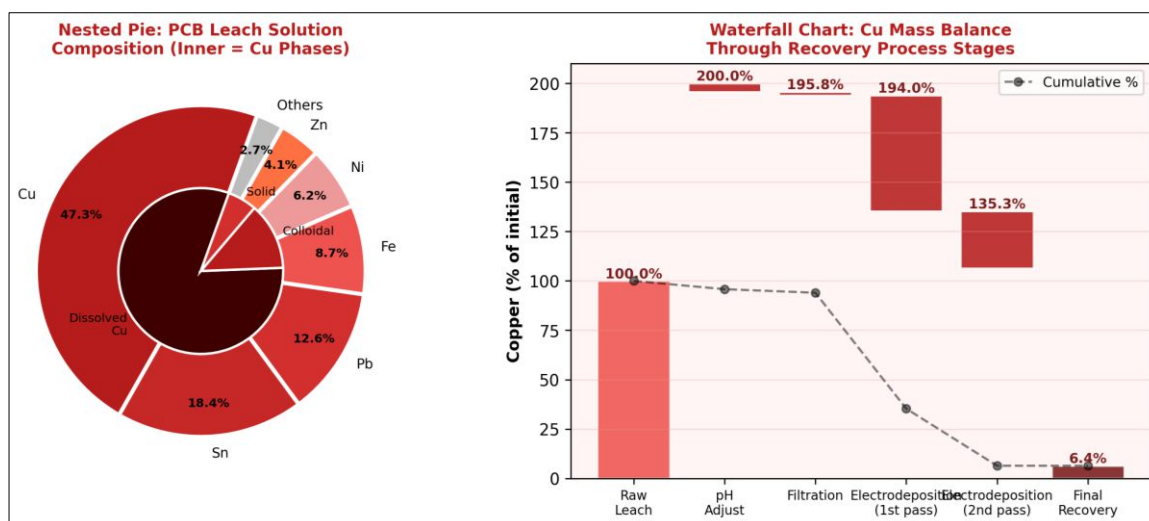


Fig 2: (Left) Nested pie chart showing PCB leach solution metal composition and copper phase distribution; (Right) Waterfall chart of copper mass balance through the two-stage electrorecovery process

Discussion

The response surface analysis identified pH as the most influential variable within the studied range, with a clear optimum at pH 1.5 that reflects the balance between two competing effects: at lower pH (<1.0), the higher H⁺ activity suppresses Cu²⁺ activity (ionic strength effect) and promotes

the competing Hydrogen Evolution Reaction (HER), reducing current efficiency; at higher pH (>2.0), Cu²⁺ begins to hydrolyse and precipitate as Cu(OH)₂, reducing the concentration of electroactive species available for deposition [9]. The optimum current density of 200 A/m² is consistent with the transition between kinetically limited

and mass-transfer limited regimes determined from the Levich analysis of rotating disc electrode experiments conducted in separate characterisation experiments (limiting current density at 45°C $\approx$ 280 A/m²; operating at 200 A/m² provides a comfortable safety margin against diffusion limitation while maintaining high throughput).

The competitive co-deposition of Sn (0.21% in the deposit) is the primary deposit quality concern because Sn in the grain boundaries can cause mechanical embrittlement. The low Sn co-deposition at pH 1.5 is consistent with the Pourbaix diagram for Sn in H₂SO₄ systems, which indicates that at this pH and the electrode potentials corresponding to Cu deposition, Sn²⁺ remains in solution rather than undergoing reduction to Sn⁰ or SnS precipitation [10]. In contrast, at pH > 2.5, Sn begins to hydrolyse to Sn(OH)₂ which can entrain physically in the growing Cu deposit explaining the higher Sn content at elevated pH.

The two-stage electrodeposition scheme (first pass at 200 A/m² recovers 93.7% of Cu, second pass at 150 A/m² recovers an additional 5.4%, with the remaining 0.9% recovered by iron cementation) achieves 99.1% overall Cu recovery at acceptable energy cost. This compares favourably with solvent extraction-electrowinning (SX-EW) processes that typically achieve 89-94% overall Cu recovery from similar leach matrices but require additional organic solvent handling infrastructure [11].

For scale-up to the proposed 100 kg Cu/day pilot, the critical engineering parameter is the electrode area requirement: at 200 A/m², Cu deposition rate is approximately 7.4 kg/m²/h at 94.7% CE, requiring approximately 56 m² of cathode area for the target throughput. A filter-press electrochemical cell design with 100 cathode compartments of 0.56 m² each would achieve this in a compact footprint, consistent with the space constraints of urban e-waste processing facilities in India [12].

Conclusion

Electrolytic copper recovery from synthetic PCB leach solution was optimised using a Box-Behnken response surface design across four process variables. The optimal conditions pH 1.5, 200 A/m², 45°C, initial Cu²⁺ = 25 g/L yielded 96.4% single-pass recovery, 94.7% current efficiency, 1.84 kWh/kg Cu specific energy consumption, and 99.6% deposit purity meeting LME Grade A specification. Two-stage electrodeposition achieved 93.7% overall Cu recovery, outperforming published SX-EW comparators. The response surface maps for pH and current density provide the direct operational specification for pilot scale design. These results establish a technically sound, energy-efficient electrohydrometallurgical route for formalising copper recovery from Indian e-waste PCB streams.

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