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Simple Recycling of Copper by the Synergistic Exploitation of Industrial Wastes: A Step towards Sustainability†

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Experimental

Materials

One of the solid waste samples, Si-sludge (composition given in Table 1a), generated in the EMCs processing was obtained from a Korean semiconductor giant. The other waste acid solution (Table 1b), generated during sputter cleaning was received from a small scale company of South Korea. Organic extractants di-2-ethylhexyl phosphoric acid (D2EHPA, purity 95%) and LIX 84-I (purity > 93%) were supplied by Sigma Chemical Co. (USA) and BASF (Germany), respectively; whereas the kerosene used as diluent was supplied by Junsei Chemical Co., Japan. Solution of the both NaOH and H_2SO_4 (supplied by Junsei Chemical Co., Japan) were prepared in deionized water to be used for the pH adjustment during extraction and for the back-extraction of copper, respectively. All the reagents were used without further purification.

Methods

Leaching. All the leaching experiments were carried out in 500 mL scale using a Pyrex reactor fitted with water bath (Lab. Companion CW-10G) and a mechanical agitator. A known amount of sludge (maintaining the desired pulp density, PD) was charged under stirring condition (180 rpm) into the preheated waste acid solution at the fixed temperature. After completion of the leaching, the solid-liquid separation was done using a Buckner funnel under vacuum. Leaching efficiency of the metals was determined by the chemical analysis of residue, and was calculated as:

$$\%\,Leaching = \left(\frac{Metal\,in\,feed\,-\,Metal\,in\,residue}{Metal\,in\,feed}\right) * 100 \qquad (S1)$$

Solvent extraction. All the solvent extraction experiments were performed at room temperature (298±2K), unless otherwise mentioned. Except the phase ratio variation, 25mLvolume of each aqueous and organic phase was contacted into a separating funnel (cap. 60 mL) for 5 minutes at a fixed equilibrium pH. After the phase separation, metal contents in the aqueous phase was analyzed after the proper dilution with 5 vol.% of HCl. Extractability of metal ions (M) in terms of distribution ratio (*D*) and %extraction was calculated using Eqs. (S2) and (S3), respectively:

$$D = \frac{[M]_{org.}}{[M]_{aq.}} \qquad (S2)$$

$$\%\,Extraction = \left(\frac{[M]_{org.}}{[M]_{org.} + [M]_{aq.}}\right) * 100 \qquad (S3)$$

where $[M]_{org.}$ and $[M]_{aq.}$ are metal concentrations in the organic and aqueous phase, respectively.

Instrumentation. The acidity of aqueous solutions were measured by a digital benchtop pH meter (ORION 3 STAR, Thermo Electron Corp., USA) provided with a combined glass electrode. The XRD patterns of as-received Si-sludge and water washed leach residue were measured by Rigaku D/Max 2200PC (Japan) diffractometer using Cu-Kα target at a slow scan speed of 2 degree·min^{-1}. To analyze the metal contents in aqueous phase an Inductively Coupled Plasma-Atomic Emission Spectroscopy (Model: iCAP6000 series, Thermo Scientific) was used. The infrared spectra of the organic phase (before and after extraction) were recorded using Fourier Transform Infrared Spectroscopy (Model: NICOLET 380 FT-IR, Thermo Electron Corp.). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-500 and calibrated by using un-deuterated chloroform (δ_H = 7.29 ppm) and $CDCl_3$ (δ_C = 77.16 ppm) as internal references. The following abbreviations are used to designate the multiplicities: br s = broad singlet, m = multiplet.

Energy computation.

Pump power (Lw in kg·m·sec^{-1}) = γ(in kg·m^{-3}) × H(in m) × Q(in m^3·sec^{-1}) (S4)

= γHQ / 102 kW (S5)

Where, 1kW : 102 kg·m·sec^{-1}, 1 kg = 9.8 N, 1 W = 1 J·sec^{-1} = 1 N·m·sec^{-1}

Putting the above values in Eq. (2) it comes as:

Lw = 1000 × H × Q × (1kW / 102 kg·m·sec^{-1})

= 9.8 Q H kW (S6)

In the case of water discharge

Lw = 1000 × H × Q × (1kW / 102 kg·m·sec^{-1}) × 1min/60sec

= 0.163 Q H kW (S7)

Hence, Lw = 0.0085 L·h^{-1} × (1/60 h·min^{-1}) * 0.163 kw * 5 m

= 0.00011546 kW

It is known that

1 kW = 1000 J·sec^{-1} = 1000 N·m·sec^{-1} × (1kg / 9.8N) = 102 kg·m·sec^{-1}

= 102 kg·m·sec^{-1} × 1 kcal / 427 kg·m^{-1} × 3600 sec·h^{-1}

= 860 kcal·h^{-1}

Hence, 1 kWh = 860 kcal

Total pump efficiency (η) = water horse power/ shaft horse power (S8)

Power consumption of mixing impellers (Po) = Np X ρ X N^3 X d^5 (S9)

Where, Np: power number, d: impeller dia.(m), N : rotation speed (RPS), ρ : density(kg·m^{-3}) and it is assumed that d = 1/2 D, N = 10, paddle type impeller. The diagram of Re no. vs. power number (Np) can be calculated as:

$Np = A/Re + B\{(10^3 + 1.2Re^{0.66})/(10^3 + 3.2Re^{0.66})\}^p \times (H/D)^{(0.35+b/D)} (\sin Dr)^{1.2}$ (S10)

Where, $A = 14+(b/D)\{670(d/D-0.6)^2 + 185\}$; $B = 10^{1.3-4(b/D-0.5)2 - 1.14(d/D)}$ and

$P = 1.1 + 4(b/D) - 2.5(d/D-0.5)^2 - 7(b/D)^4$

In absence of baffle, Re= d^2 X N X De/Vi (S11)

Fig. S1: XRD pattern for the as received Si-sludge sample, indicating for the presence of Si (JCPDS file no. 99-0092) and Cu_2O (JCPDS file no. 99-0041)

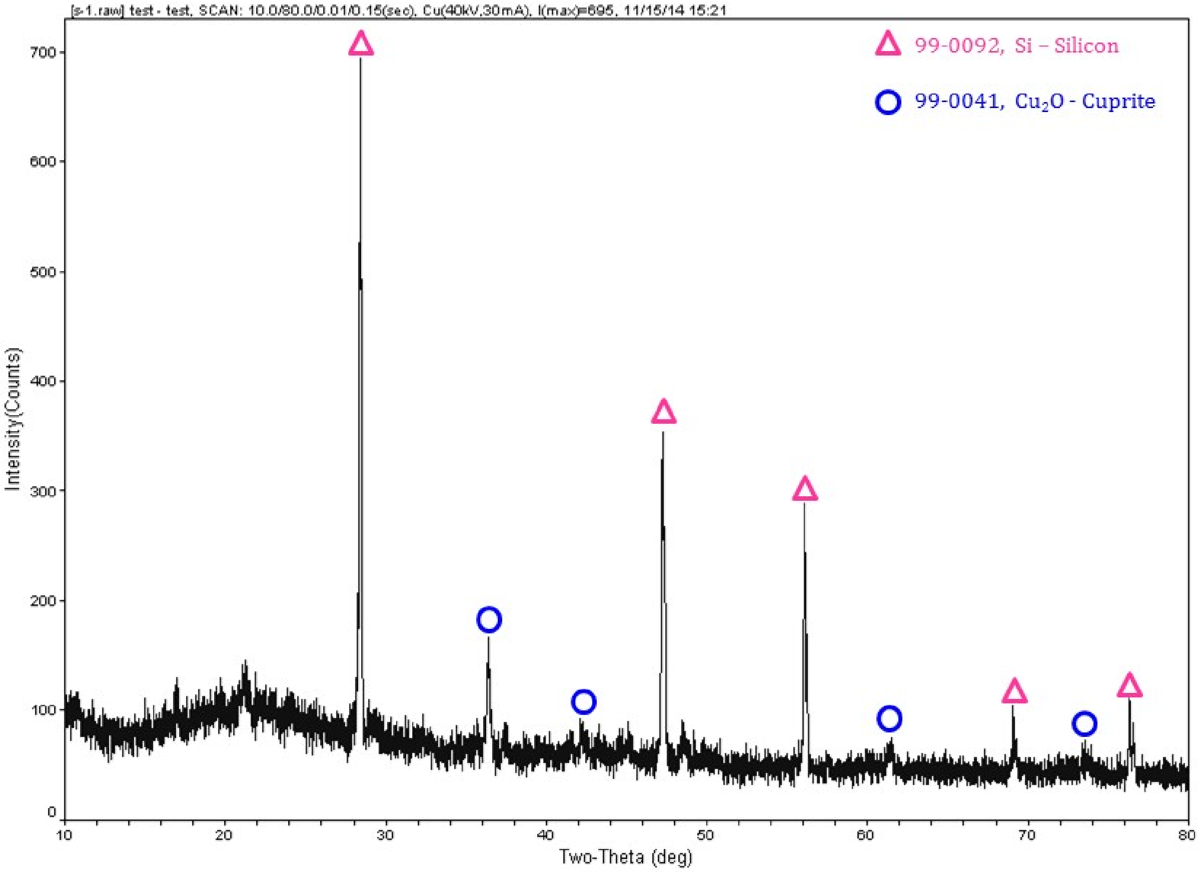


Fig. S2: The comparative extraction of copper from Si-sludge leached in waste nitric acid solution (containing 95.5 g·L^{-1} Cu^{2+} used in the present study) and in synthetic nitric acid solution (without any Cu^{2+} in lixiviant), showing the autocatalytic behaviour of Cu^{2+}-ions in copper leaching; (condition: PD = 10%, temperature = 298 K, agitation speed = 180 rpm).

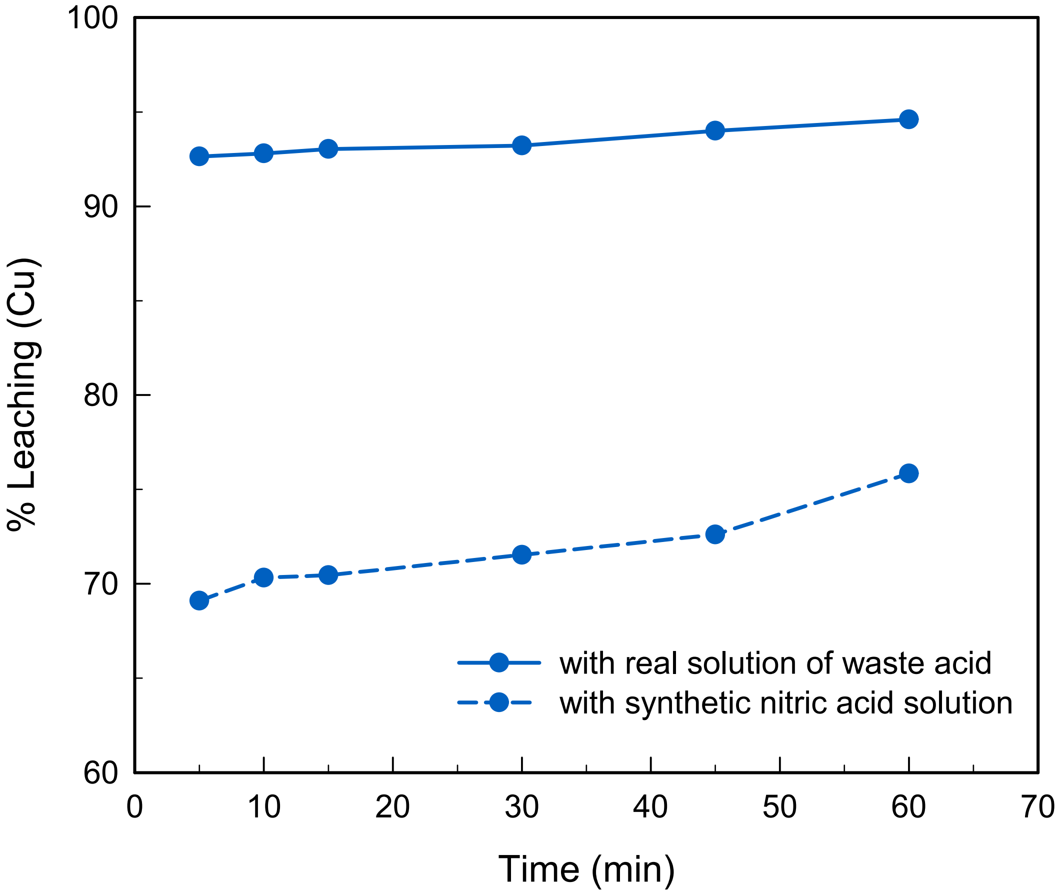


Fig. S3: XRD pattern for the leach residue. The appeared peaks only of Si (JCPDS file no. 99-0092) indicating for the efficient leaching of Cu_2O under the condition of: 25% PD, temperature 363 K, duration 30 min.

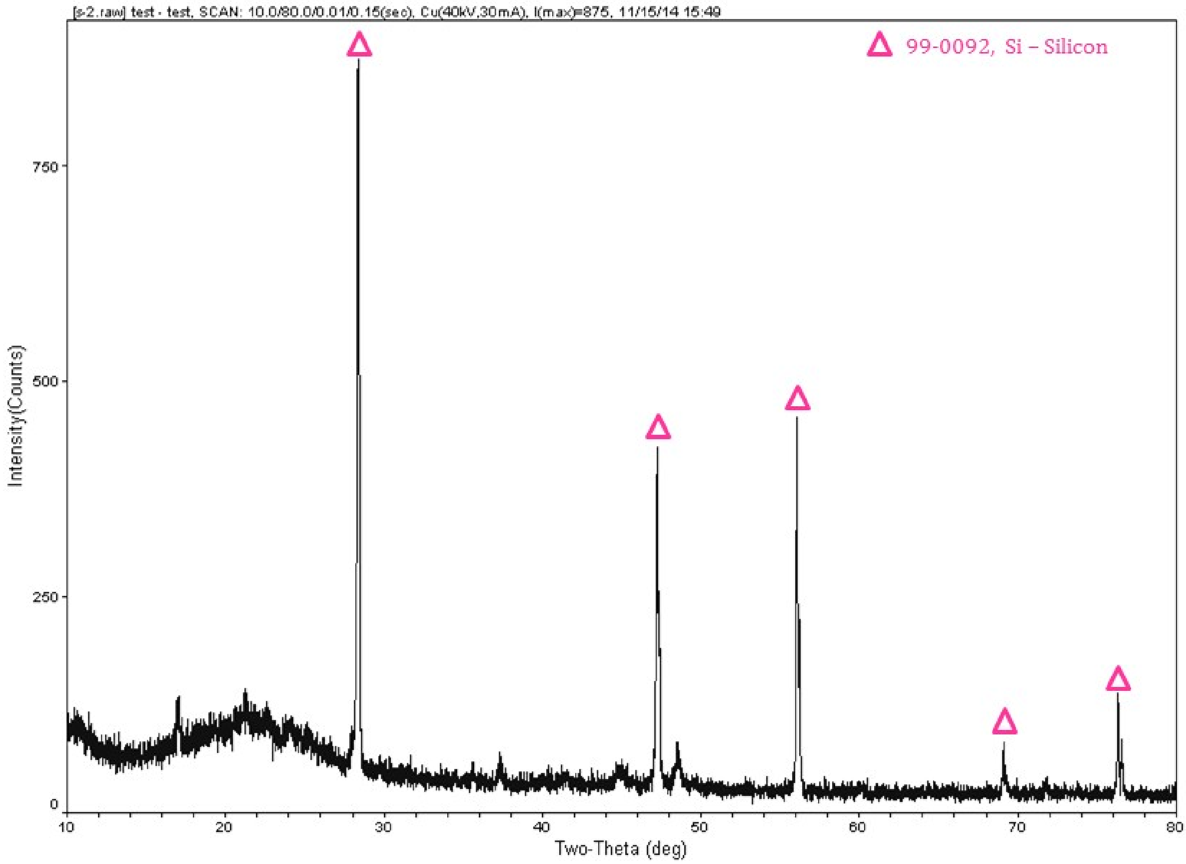


Fig. S4: The IR-transmittance spectra of fresh organic solvent LIX 84-I and metal loaded organic for the saturated complex between Cu^{2+} and LIX 84-I.

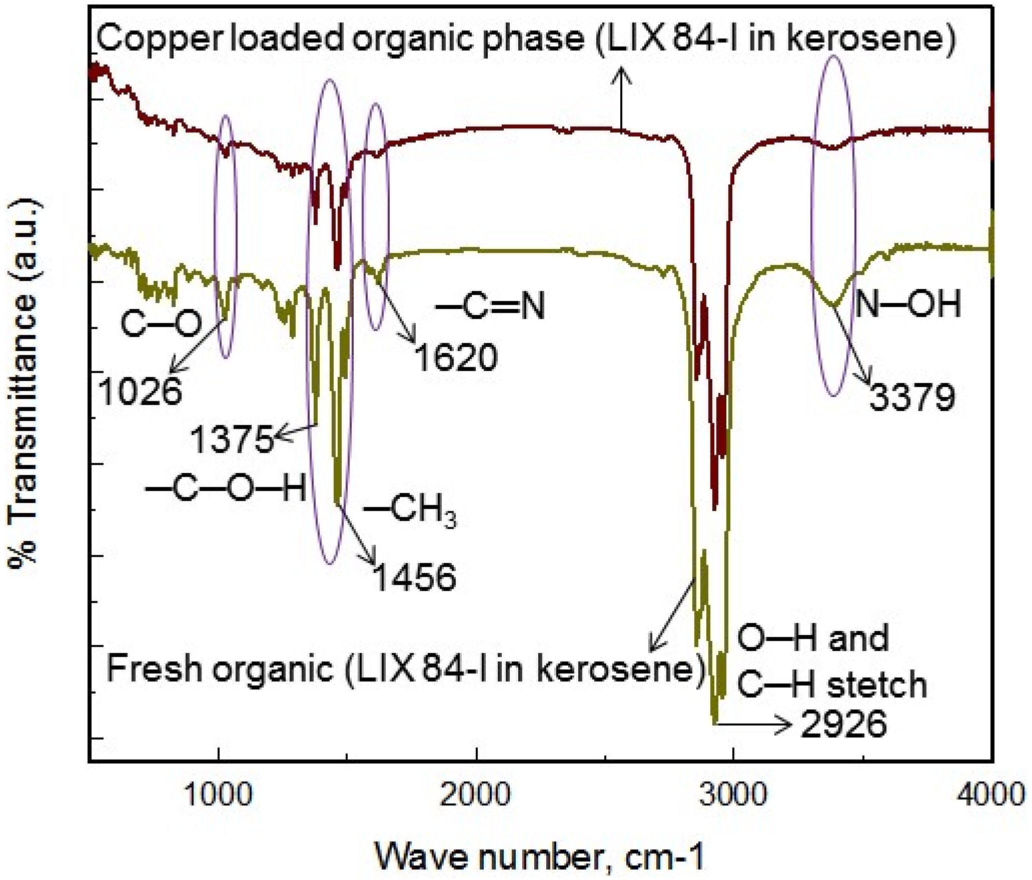


Fig. S5a: ^{1}H NMR spectra of the organic extractant LIX 84-I (before copper extraction): [δ_H (500 MHz; $CDCl_3$; Me_4Si) 0.86–0.93 (9 H, m, alkyl), 1.24–1.32 (10 H, m, alkyl), 2.39–2.40 (3 H, m, Me), 6.93–6.94 (1 H, m, Ar-H), 7.20–7.24 (1 H, m, Ar-H), 7.27–7.33 (1 H, m, Ar-H), 10.98 (1 H, br s, OH)].

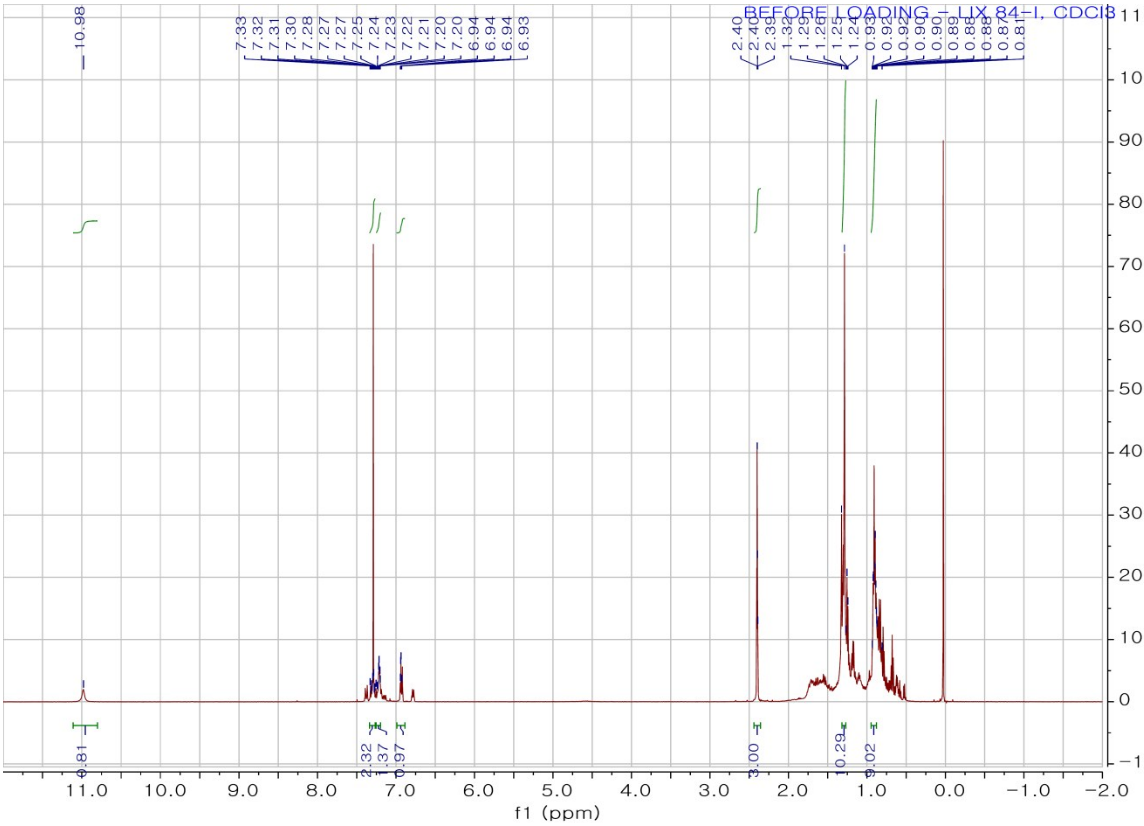


Fig. S5b: ^{1}H NMR spectra of the metal-loaded organic phase (after copper extraction with LIX 84-I): [δ_H (500 MHz; $CDCl_3$; Me_4Si): 0.86–0.93 (9 H, m, alkyl), 1.24–1.32 (10 H, m, alkyl), 2.39–2.40 (3 H, m, Me), 6.93–6.94 (1 H, m, Ar-H), 7.20–7.24 (1 H, m, Ar-H), 7.27–7.33 (1 H, m, Ar-H).

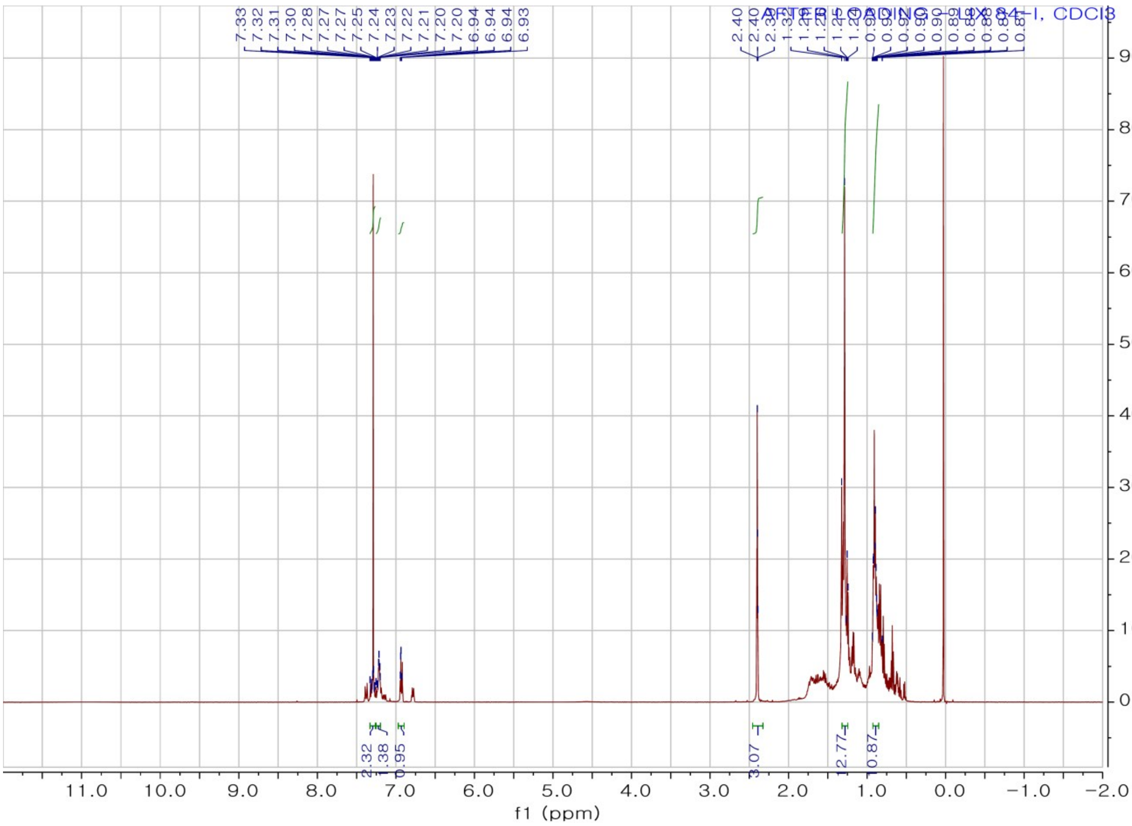


Fig. S5c: ^{13}C NMR spectra of the organic extractant LIX 84-I (before copper extraction): ^{13}C NMR (CDCl$_3$; 100 MHz; Me$_4$Si) δ 159.74 (C –OH), 154.83 (C ═NOH), 138.53, 128.54, 124.83, 116.54, 114.63, 44.43, 32.44, 30.67, 29.26, 23.45, 14.37, 10.85 (Me).

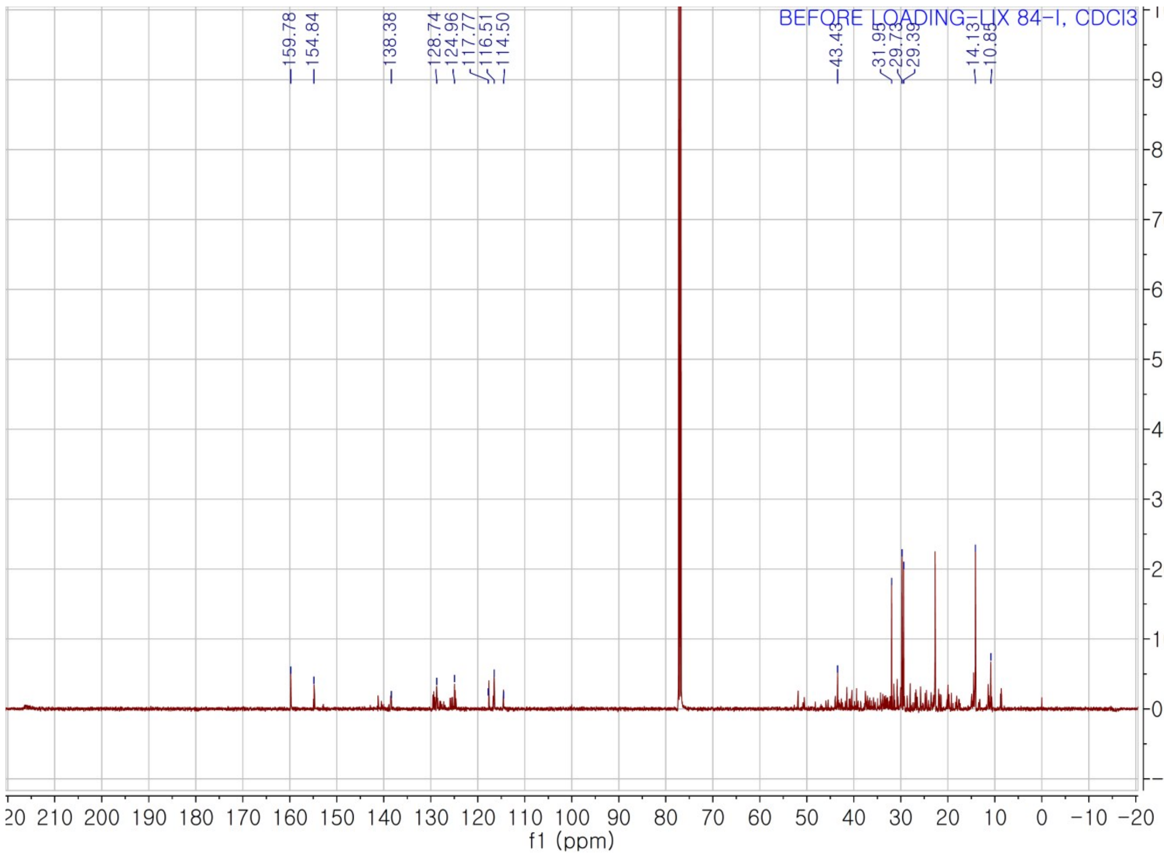


Fig. S5d: ^{13}C NMR spectra of the metal-loaded organic phase (after copper extraction with LIX 84-I): ^{13}C NMR ($CDCl_3$; 100 MHz; Me_4Si) δ 159.74 (C –OH), 154.83 (C ═NOH), 138.53, 128.54, 124.83, 116.54, 114.63, 44.43, 32.44, 30.67, 29.26, 23.45, 14.37, 10.85 (Me).

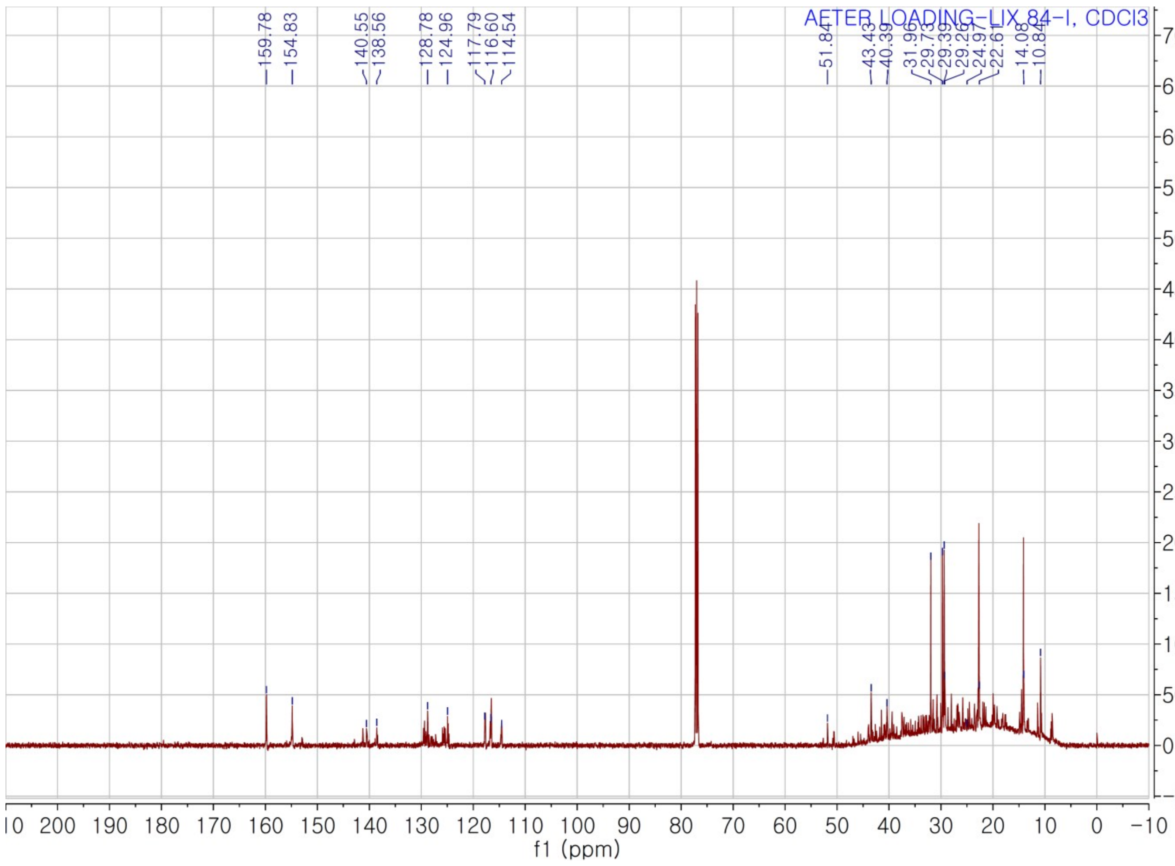
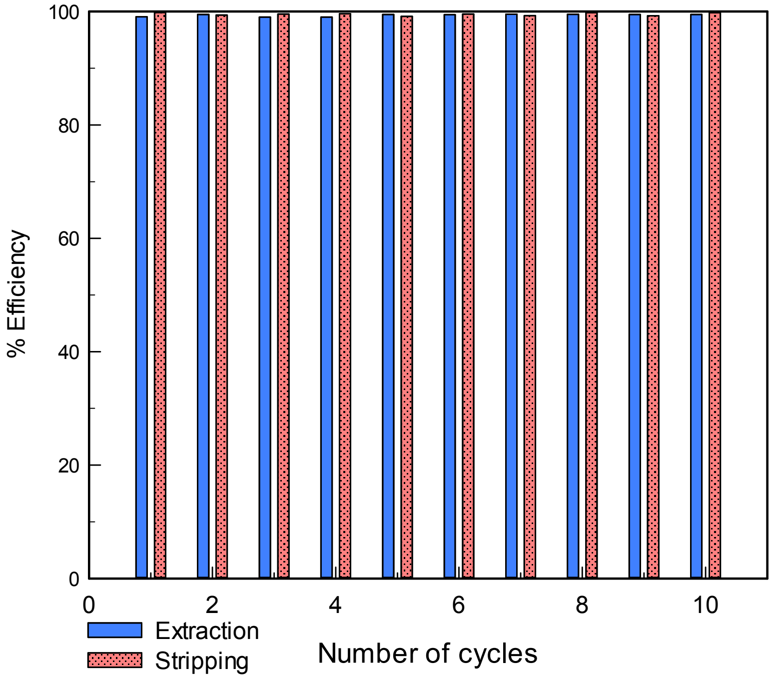


Fig. S6: The cycles for copper extraction with LIX 84-I (condition: aqueous feed = 5.7 g·L^{-1} Cu^{2+}, 0.7 g·L^{-1} Ca^{2+}, 0.2 g·L^{-1} Al^{3+}; 0.5 mol·L^{-1} LIX 84-I in kerosene; O/A = 1; temperature = 298 K; contact time = 5 min) followed by back-extraction with sulfuric acid (condition: metal loaded organic contacted with 3.6 mol·L^{-1} H_2SO_4 on each cycle of stripping at an O/A = 1; temperature = 298 K; contact time = 5 min). The result has established the reusability of extractant to be applicable in nitric acid medium.



Computation of energy consumptions in various unit operations during copper extraction (leaching-Solvent extraction-electro winning):

Table S1: Summary of the materials charged into leaching operation

Si-sludge	**Waste acid solution**
1 kg·h^{-1}	4 L·h^{-1}
0.0928 Cu kg·h^{-1}	0.382 Cu kg·h^{-1}
2.2272 Cu -kg/day	9.182 Cu-kg/day

Table S2: Summary of energy consumption in each stages of leaching operation

Leaching			**Filtration**		
In heating	In mixing	Total	Residue generation	Leach liquor generation	Total
9.616279 kW·h^{-1}	0.194022 kW·h^{-1}	9.810301 kW·h^{-1}	0.8104 kg·h^{-1}	3.25 L·h^{-1}	0.259242 kW·h^{-1}

Table S3: Summary of energy consumption during solvent extraction of iron

Fe-extraction from leach liquor (flow 6.5 L·h^{-1} at O/A = 1:1)		**Fe-stripping from loaded organic (flow 6.5 L·h^{-1} at O/A = 1:1)**	
In mixer	In pump	Mixer	pump
0.00155466 kW·h^{-1}	0.00004415 kW·h^{-1}	0.00155466 kW·h^{-1}	0.00004415 kW·h^{-1}

Table S4: Summary of energy consumption during solvent extraction of copper

Cu-extraction from Fe-depleted solution (flow 24 L·h^{-1} at O/A = 1:1.1)		**Cu-stripping from loaded organic (flow 12.22 L·h^{-1} at O/A = 4.5:1)**	
Mixer	Pump	Mixer	Pump

0.001722085 kW·h^{-1}	0.00032600 kW·h^{-1}	0.01148056 kW·h^{-1}	0.00032600 kW·h^{-1}

Table S5: Summary of energy consumption during copper electro-winning

In electro-winning cell house	**In pumping**
2.5 kW·h^{-1}·kg^{-1} Cu	Flow: 8.5 L·h^{-1}

Table S6: Overall summary for the energy consumption of the entire process on 24 h basis

Unit operation	**Unit of measurement**	**Energy consumed in Cu production**
Leaching heating	kWh	9.616279
Leaching mixing	kWh	0.194022
Filtering pump	kWh	0.259242
Fe extraction– mixer	kWh	0.037312
Fe extraction– pump	kWh	0.00106
Fe stripping – mixer	kWh	0.037312
Fe stripping – pump	kWh	0.00106
Cu extraction– mixer	kWh	0.4133
Cu extraction–pump	kWh	0.007824
Cu stripping – mixer	kWh	0.275534
Cu stripping– pump	kWh	0.007824
Cu EW– current	kWh	28.488
Cu EW– pump	kWh	0.00277
Total energy consumed	kWh	39.3415

Recovery of Cu	kg	11.3952