

## Supplementary Information

### **A green and efficient process for the stepwise extraction of Cu, Ni, Co, Mn, and Li from hazardous waste with a novel solvent extraction system of D2EHPA-NNPA**

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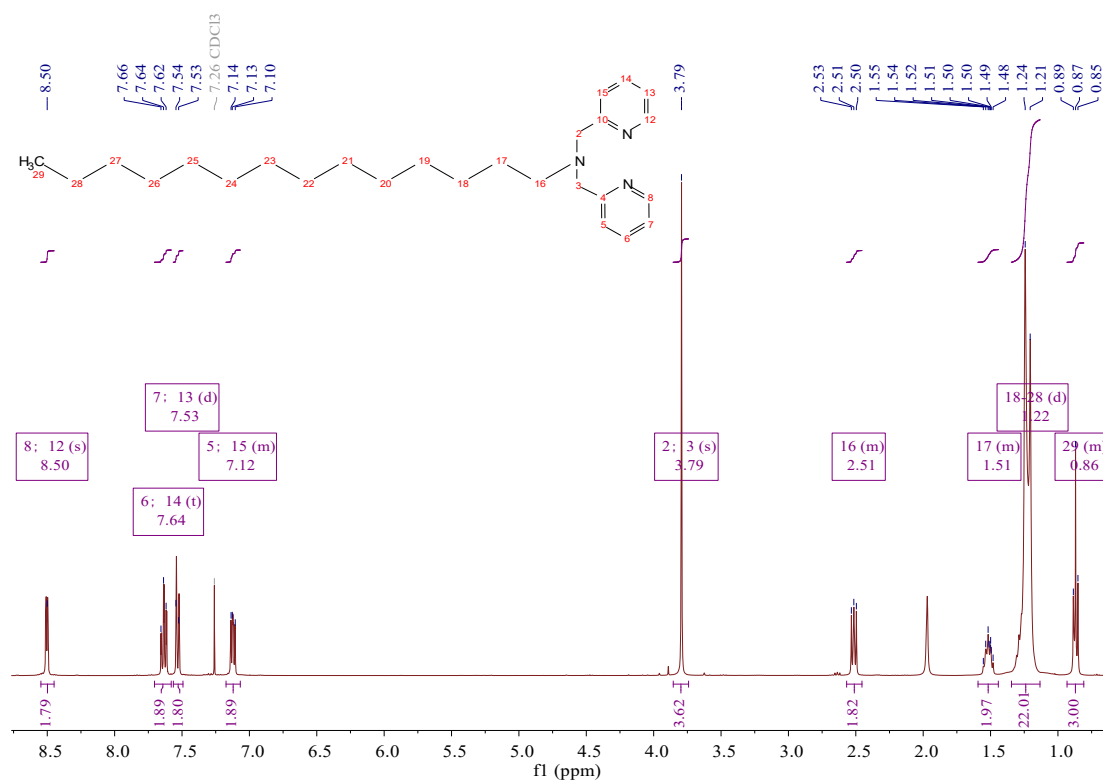


Fig. S1. <sup>1</sup>H NMR spectra of NNPA.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.50 (s, 2H), 7.64 (t,  $J = 7.6$  Hz, 2H), 7.53 (d,  $J = 7.9$  Hz, 2H), 7.17 – 7.07 (m, 2H), 3.79 (s, 4H), 2.57 – 2.45 (m, 2H), 1.59 – 1.44 (m, 2H), 1.22 (d,  $J = 14.8$  Hz, 22H), 0.93 – 0.81 (m, 3H).

### Removal of Fe and Al

NaHCO<sub>3</sub> neutralization was utilized to selectively precipitate almost all Fe along with some Al from the leaching solution obtained from Zhejiang Huayou Cobalt Co., Ltd. The resulting equilibrium pH of 3.3 at 90 °C facilitated the removal of over 99.93 % Fe and 61.73 % Al, while Ni, Co, Mn, and Li losses were approximately 1 %. The process involved heating 500 mL of the leaching solution to 90 °C, followed by the addition of NaHCO<sub>3</sub> solution (100 g/L) and 5 vol% H<sub>2</sub>O<sub>2</sub> solution at a feeding rate of 3.33 mL/min using a peristaltic pump. The pH of the solution was maintained at around 3.3 while stirring the mixture at 400 r/min for 3 hours. Subsequently, the Fe-removed solutions were obtained by filtration.

Likewise, using the NaHCO<sub>3</sub> neutralization method, almost all of the Al was precipitated from the raffinate of Ni and Co counter-current extraction process.

$$E = \frac{C_{\text{ORG}} \times V_{\text{ORG}}}{C_{\text{INI}} \times V_{\text{INI}}} \times 100\% \quad (\text{S1})$$

$$D = \frac{C_{\text{ORG}}}{C_{\text{AQ}}} \quad (\text{S2})$$

$$\beta_{\text{A/B}} = \frac{D_{\text{A}}}{D_{\text{B}}} \quad (\text{S3})$$

$$S = \frac{C_{\text{S}} \times V_{\text{S}}}{C_{\text{LOAD}} \times V_{\text{LOAD}}} \times 100\% \quad (\text{S4})$$

Concentrations (g/L) and volumes (mL) were denoted by C and V, respectively. Subscripts were used to differentiate the various phases, with “AQ” and “ORG” representing the aqueous and organic phases, respectively. “INI”, “S”, and “LOAD” were used to denote the initial state of the aqueous solution, the stripping solution, and the loaded organic phase, respectively.

$$\Delta E = \Sigma E (\text{products}) - \Sigma E (\text{reactants}) \quad (\text{S5})$$

$$\Delta G = \Sigma G (\text{products}) - \Sigma G (\text{reactants}) \quad (\text{S6})$$

The calculated total single point energy of products and reactants is denoted by E(products) and E(reactants), respectively. Similarly, G(products) and G(reactants) represent the calculated total Gibbs free energy (G) of products and reactants.

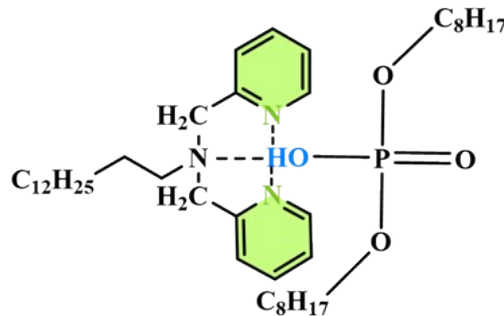


Fig. S2. Diagram of the combined form of NNPA and D2EHPA.

Table S1. Experimental data for the entire “extraction-scrubbing-stripping” process.

The “extraction-scrubbing-stripping” process for extracting Cu									
Feed solution 1 (leachate)									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	1.114	0.551	16.31	5.13	8.4	0.828	1.29	3.79
Raffinate 1									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	1.112	0.001	16.207	5.11	8.37	0.823	1.28	3.79
Scrubbing solution 1									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	0.206	0.016	20.01	4.02	2.997	1.01	1.998	~0
Strpping solution 1									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	26.91	0.001	0.002	~0	~0	~0	~0
The “extraction-scrubbing-stripping” process for extracting Ni-Co									
Feed solution 2 (raffinate 1)									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	1.112	0.001	16.207	5.11	8.37	0.823	1.28	3.79
Raffinate 2									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	1.009	~0	~0	0.001	7.37	0.763	1.19	3.73
Scrubbing solution 2									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	0.514	0.001	0.218	0.269	4.999	0.302	0.459	0.307
Strpping solution 2									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	0.002	40.37	12.59	0.004	~0	~0	~0
The “extraction-scrubbing-stripping” process for extracting Mn									
Feed solution 3 (raffinate 2)									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	~0	~0	0.001	7.37	0.763	1.19	3.73
Raffinate 3									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	~0	~0	~0	0.007	0.664	1.039	3.68
Scrubbing solution 3									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	~0	~0	~0	2.9	1.01	1.51	0.503
Strpping solution 3									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	~0	~0	0.005	35.35	~0	~0	~0

~0: the concentration of the metal ion in the loaded organic phase is below 0.5

ppm.

Table S2. Experimental data of the secondary cycle for the entire “extraction-  
scrubbing-stripping” process.

The “extraction-scrubbing-stripping” process for extracting Cu									
Feed solution 4 (leachate mixed with scrubbing solution 1)									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	1.105	0.546	16.346	5.119	8.346	0.83	1.297	3.79
Raffinate 4									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	1.103	~0	16.237	5.107	8.343	0.826	1.288	3.79
Scrubbing solution 4									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	0.204	0.041	10.89	1.2	0.307	0.401	1.004	~0
Strpping solution 4									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	27.28	0.001	0.001	~0	~0	~0	~0
The “extraction-scrubbing-stripping” process for extracting Ni-Co									
Feed solution 5 (raffinate 4 mixed with scrubbing solution 2)									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	1.005	~0	13.567	4.301	7.786	0.739	1.149	3.21
Raffinate 5									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	1.001	~0	~0	~0	6.714	0.6763	1.056	3.162
Scrubbing solution 5									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	0.514	~0	0.457	0.619	5.357	0.313	0.465	0.242
Strpping solution 5									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	~0	33.67	10.45	0.003	~0	~0	~0
The “extraction-scrubbing-stripping” process for extracting Mn									
Feed solution 6 (raffinate 5 mixed with scrubbing solution 3)									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	~0	~0	~0	6.367	0.706	1.097	2.965
Raffinate 6									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	~0	~0	~0	~0	0.604	0.939	2.916
Scrubbing solution 6									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	~0	~0	~0	2.9	1.021	0.792	0.497
Strpping solution 6									
Elements	Fe(III)	Al	Cu	Ni	Co	Mn	Ca	Mg	Li
Content (g/L)	~0	~0	~0	~0	~0	35.35	~0	~0	~0

~0: the concentration of the metal ion in the loaded organic phase is below 0.5 ppm.