

SUPPORTING INFORMATION

Sustainable hydrophobic terpene-based eutectic solvents for the extraction and separation of metals

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Tables

Table S1. Densities and viscosities of the menthol:carboxylic acid and thymol:carboxylic acid hydrophobic eutectic systems at 60 °C. The mole fraction (x) and the predicted (PC-SAFT equation of state) melting temperatures (T_m) of each mixture are displayed (Martins et al., 2018).

	x_{Terpene}	$x_{\text{Carboxylic Acid}}$	T_m (°C)	Viscosity (cP)	Density (g·cm ⁻³)
Menthol					
Caprylic acid	0.60	0.40	-1.82	3.88	0.8735
Capric acid	0.60	0.40	8.86	4.58	0.8705
Lauric acid	0.75	0.25	21.23	5.40	0.8677
Myristic acid	0.80	0.20	26.62	5.89	0.8665
Palmitic acid	0.85	0.15	33.18	6.09	0.8666
Stearic acid	0.90	0.10	37.88	6.27	0.8662
Thymol					
Caprylic acid	0.42	0.58	6.68	2.83	0.9020
Capric acid	0.50	0.50	18.86	3.70	0.9031
Lauric acid	0.55	0.45	24.83	4.42	0.8992
Myristic acid	0.75	0.25	38.16	4.34	0.9126
Palmitic acid	0.80	0.20	41.22	4.53	0.9140
Stearic acid	0.90	0.10	46.22	4.06	0.9240

Table S2. Starting compounds description for HES.

Compound	Supplier	CAS	Purity wt% ^a
L(-)-menthol	Acros	2216-51-5	99.7
Thymol	Sigma	89-83-8	≥99.5
Caprylic acid	Sigma	124-07-2	≥99
Capric acid	Sigma	334-48-5	99-100
Lauric acid	Sigma	143-07-7	≥99
Myristic acid	Sigma	544-63-8	≈95
Palmitic acid	Aldrich	57-10-3	≥98
Stearic acid	Merck	57-11-4	≥97

^aAs declared by the supplier.

Table S3. Speciation of the chemical components present in the aqueous phase prior to extraction calculated using the Visual MINTEQ program at the following conditions: pH=4.9, $T=20^{\circ}\text{C}$, $[\text{Na}_2\text{SO}_4]=0.1\text{M}$, $[\text{CuSO}_4]=0.0175\text{M}$ (Gustafsson, 2018).

Component	% of total concentration	Species name
SO_4^{-2}	76.4	SO_4^{-2}
	21.3	NaSO_4^-
	2.2	CuSO_4 (aq)
Cu^{+2}	9.7	Cu^{+2}
	1.0	CuOH^+
	0.1	$\text{Cu}_2\text{OH}^{+3}$
	18.6	$\text{Cu}_2(\text{OH})_2^{+2}$
	55.6	$\text{Cu}_3(\text{OH})_4^{+2}$
	15.1	CuSO_4 (aq)
Na^{+1}	87.5	Na^{+1}
	12.5	NaSO_4^-
	76.4	SO_4^{-2}

Table S4. Cu(II) distribution in HES ($x_{\text{CapricAcid}}=0.7$) and classic solvent extraction with xylene as diluent ($[\text{Capric acid}]=0.5\text{M}$) as a function of pH ($T=20^{\circ}\text{C}$, $[\text{Na}_2\text{SO}_4]=0.1\text{M}$). Data used in Figure 2 of the manuscript, σ is the standard deviation.

pH	HES (Menthol) $\pm \sigma$	HES (Thymol) $\pm \sigma$	Capric acid - Xylene $\pm \sigma$
1.07	0.02 \pm 0.01	0.03 \pm 0.00	-
1.52	0.02 \pm 0.01	0.03 \pm 0.01	-
2.05	0.04 \pm 0.02	0.09 \pm 0.03	-
2.38	-	-	0.00 \pm 0.01
2.47	0.09 \pm 0.00	0.14 \pm 0.05	-
2.90	0.13 \pm 0.02	0.21 \pm 0.06	-
3.44	0.21 \pm 0.05	0.35 \pm 0.04	0.08 \pm 0.04
3.78	-	-	0.19 \pm 0.06
4.01	0.49 \pm 0.03	0.48 \pm 0.03	-
4.05	-	-	0.32 \pm 0.03
4.20	-	-	0.65 \pm 0.04
4.51	0.75 \pm 0.01	0.61 \pm 0.06	1.13 \pm 0.10
4.71	-	-	1.42 \pm 0.27
5.01	0.86 \pm 0.00	0.77 \pm 0.03	1.47 \pm 0.09
5.25	0.83 \pm 0.03	0.85 \pm 0.05	1.51 \pm 0.21

Methodology

Chemicals

Information on the starting compounds used in the formation of hydrophobic eutectic solvents (HES) and their structure is summarized in Table S2 and Figure S1, respectively. The pure components were used as received without further purification. The purity of the terpenes was evaluated by ^1H and ^{13}C NMR spectra and GC-MS. Additional information on these compounds can be found elsewhere (Martins et al., 2018). The menthol stereochemistry is omitted in the manuscript. The mixtures preparation is described in a previous publication (Martins et al., 2018). Based on the purity of the starting compounds (Table S2) and the composition of the used HES, the minimal purity of the menthol- and thymol-based HES is of 99.2%. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (>99% purity), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (>99% purity), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (>99.5% purity), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (>99% purity), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (>99.5% purity) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (>99% purity) were obtained from Merck; $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (>98% purity) and $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ (>98% purity) were obtained from Panreac and Fluka respectively. The various aqueous phase sodium salt additives used during solvent extraction are: Na_2SO_4 (>99% purity from Merck), NaCl (99.9% purity from BDH Chemicals), NaNO_3 (>99% purity from Analar), $\text{NaC}_2\text{H}_3\text{O}_2$ (99.9% purity from VWR), $\text{Na}_2\text{C}_4\text{H}_4\text{O}_5$ (>98% purity from Sigma Aldrich), $\text{NaC}_7\text{H}_5\text{O}_3$ (>99.5% purity from Sigma Aldrich). Sulfuric acid (95 %) was acquired from Sigma-Aldrich. NaOH (98 % purity) was purchased from Eka. Ultrapure, double distilled water, passed through a reverse osmosis system and further treated with a Milli-Q plus 185 water purification apparatus, was used for all experiments.

Instrumentation

Viscosities were measured at atmospheric pressure and in the temperature range (25 to 80) °C using an automated SVM 3000 Anton Paar rotational Stabinger viscometer–densimeter. An 831 KF Coulometer (Metrohm) was used to determine the water content of the HES phase. Qualitative ^1H -NMR was performed in a 300 MHz Bruker Avance III spectrometer using DMSO as deuterated solvent. Solution pH were monitored using a SevenExcellence multiparameter pH and conductimeter (Mettler Toledo). Single metal Cu(II) solution concentration before and after extraction was obtained by quantitative UV-Vis analysis (Biotek Synergy HT microplate reader) of the aqueous phase at $\lambda=800\text{nm}$. Other single metal solution [Fe(III) , Ni(II) , Co(II) , Mn(II) and Zn(II)] as well as metal concentration in multi-element solutions was determined by inductively couple optical emission spectroscopy (ICP-OES, Jobin Yvon Activa spectrometer) analysis of the aqueous phase after metal extraction.

Metal extraction

The mechanisms dictating metal extraction into the terpene-based HES are determined based on the study of a single metal CuSO_4 solution depending on multiple factors including carboxylic acid chain length at a fixed composition, change in composition for a given carboxylic acid, pH, Cu(II) concentration and counter anion selection. Unless otherwise stated, the following standard conditions were employed: 0.015M CuSO_4 concentration, 0.1M aqueous solution ionic strength adjusted with Na_2SO_4 , pH of 4.2 and an organic to aqueous phase volume ratio of 1 for a total volume of 2 mL. All tests were performed by mixing the compounds for 5 min in a temperature controlled thermostatic bath and left to phase separate for 15 min. A mixing time of 5 min was deemed sufficient to attain the extraction equilibrium (*cf.* Figure S2) due to the low viscosity of the HES. The concentration of Cu(II) was determined by quantitative UV-Vis analysis of the aqueous phase and extrapolating the results to determine the organic phase concentration. The pH was adjusted using 0.1M H_2SO_4 and 0.1M NaOH . At the optimised system conditions of $x_{\text{Capric Acid}}=0.7$ and $x_{\text{Thymol}}=0.3$, $T=20$ °C, $\text{pH}=4.9$ (for divalent

metals) or pH=3 (for trivalent metals) and O:A=1, an identical procedure as that described for Cu(II) extraction and analysis was followed for the determination of 0.01M Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Zn(II) partition in HES and the separation of 0.01M Cu(II) from 0.1M Co(II) and Ni(II) respectively. Metal concentrations in this system were determined by ICP-OES analysis of the aqueous phase after extraction. The extraction efficiency (%EE), distribution ratio (D_M) and Cu(II) separation factors ($\alpha_{Cu/M}$) for a given metal (M) were calculated using Equations (1) to (3),

$$\%EE = \frac{([M]_{aq,i} - [M]_{aq,f})}{[M]_{aq,i}} \times 100 \quad (1)$$

$$D_M = \frac{[M]_{HES,f}}{[M]_{aq,f}} = \frac{\%EE}{100 - \%EE} \quad (2)$$

$$\alpha_{(Cu/M)} = \frac{D_{Cu}}{D_M} \quad (3)$$

where the subscript *HES* and *aq* denote the phase and *i* and *f* the time frame (*i* – before extraction and *f* – after extraction). Due to the negligible mutual solubilities during extraction, the phase volume ratio remained practically unchanged. All tests were performed in triplicate being the average value reported.

Figures

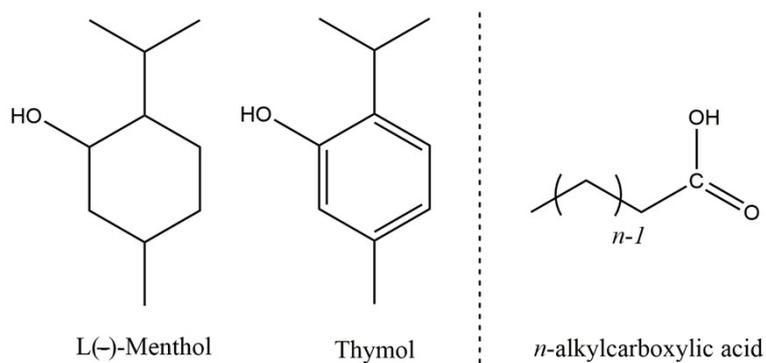


Figure S1. Chemical structure of the hydrophobic eutectic components.

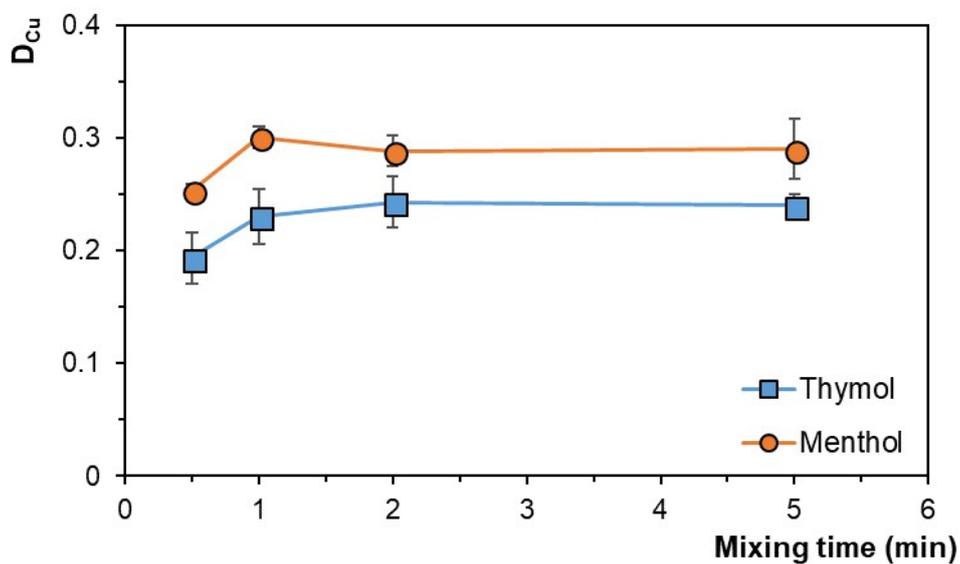


Figure S2. Cu(II) distribution ratio in menthol:capric acid (0.3:0.7) and thymol:capric acid (0.3:0.7) HES as a function of mixing time ($[Cu]=0.02M$, $[Na_2SO_4]=0.1M$, $T=20\text{ }^{\circ}C$, $pH=4.9$).

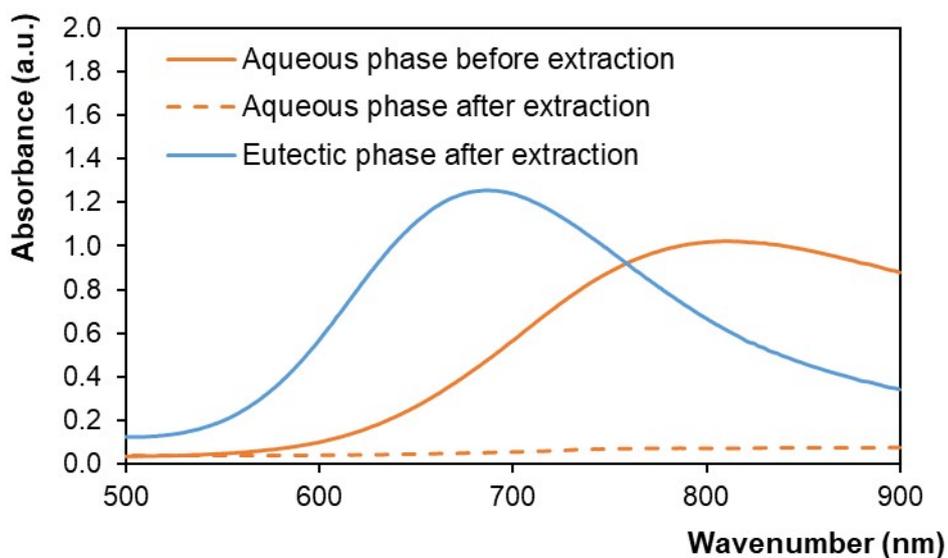


Figure S3. UV-Vis analysis of the aqueous phase before and after extraction, and the mixture thymol:capric acid (0.3:0.7 molar ratio) after extraction (containing 0.01M Cu(II)).

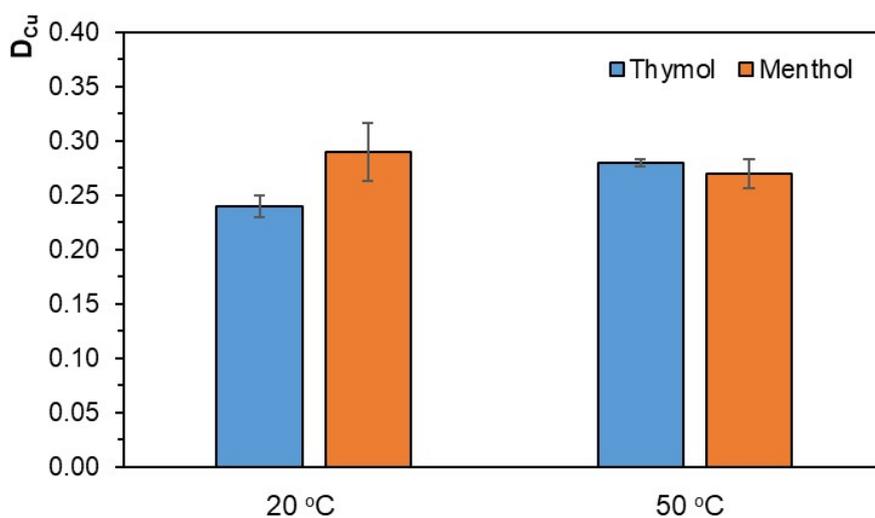


Figure S4. Cu(II) extraction in menthol:capric acid (0.3:0.7) and thymol:capric acid (0.3:0.7) HES as a function of temperature ($[Cu]=0.02M$, $[Na_2SO_4]=0.1M$, $pH=4.9$).

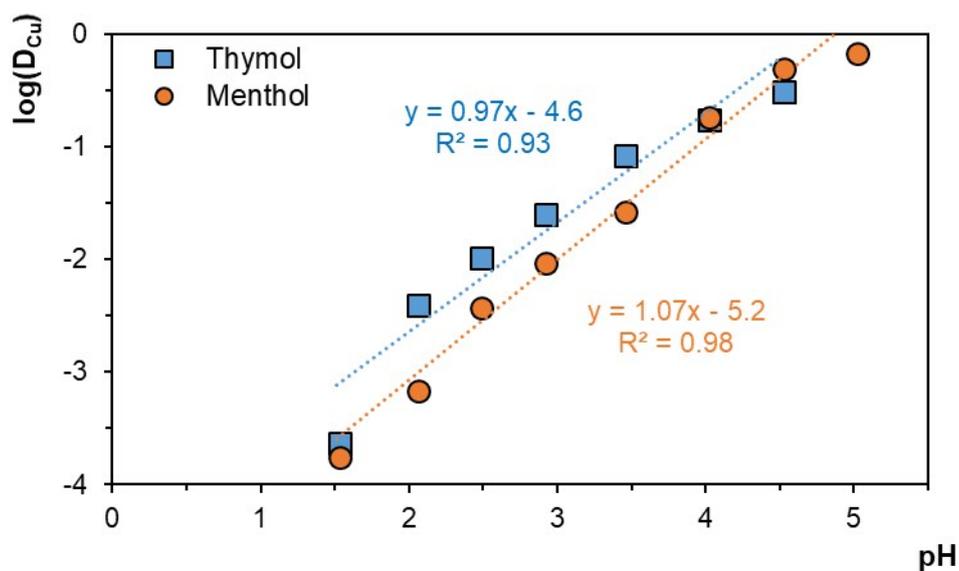


Figure S5. Slope analysis of $\log(D_{Cu(II)})$ as a function of pH based on the data reported in Figure 2 in the manuscript ($x_{\text{CapricAcid}}=0.7$, $T=20$ °C, $[Cu]=0.0175M$).

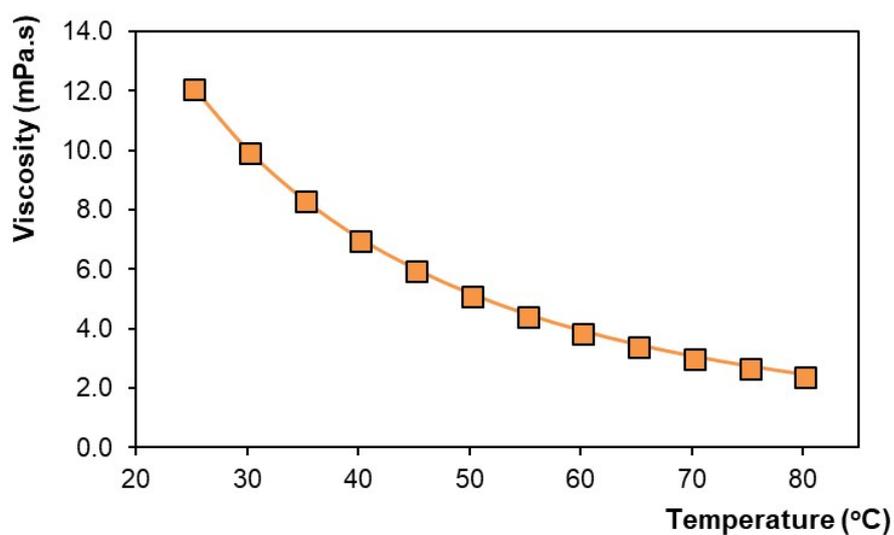


Figure S6. Viscosity of thymol:capric acid HES (0.3:0.7 molar ratio) after Cu(II) extraction at pH 4.9 as function of temperature.

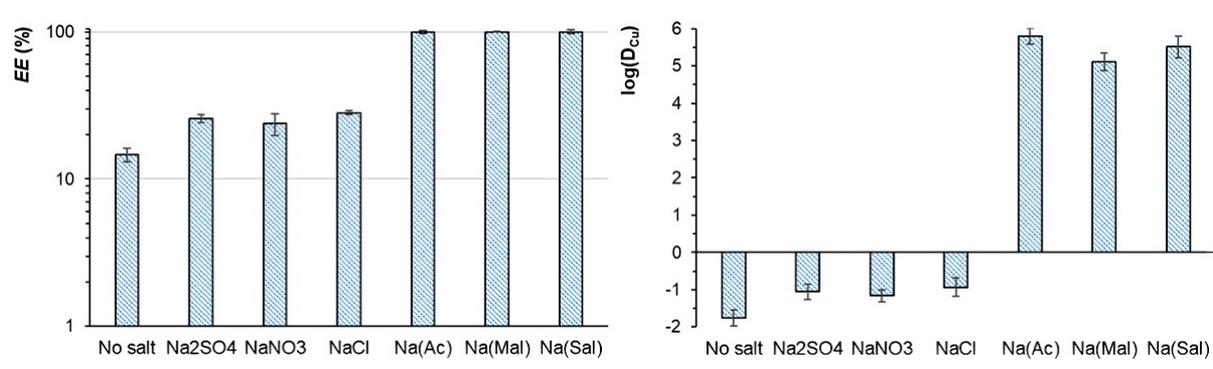


Figure S7. Effect of 0.1M sodium salt addition on the extraction efficiency of 0.02M CuSO₄ (pH 4.9, T=20 °C) by thymol:capric acid HES (0.3:0.7 molar ratio) (Ac – acetate; Mal – maleate; Sal – salicylate).

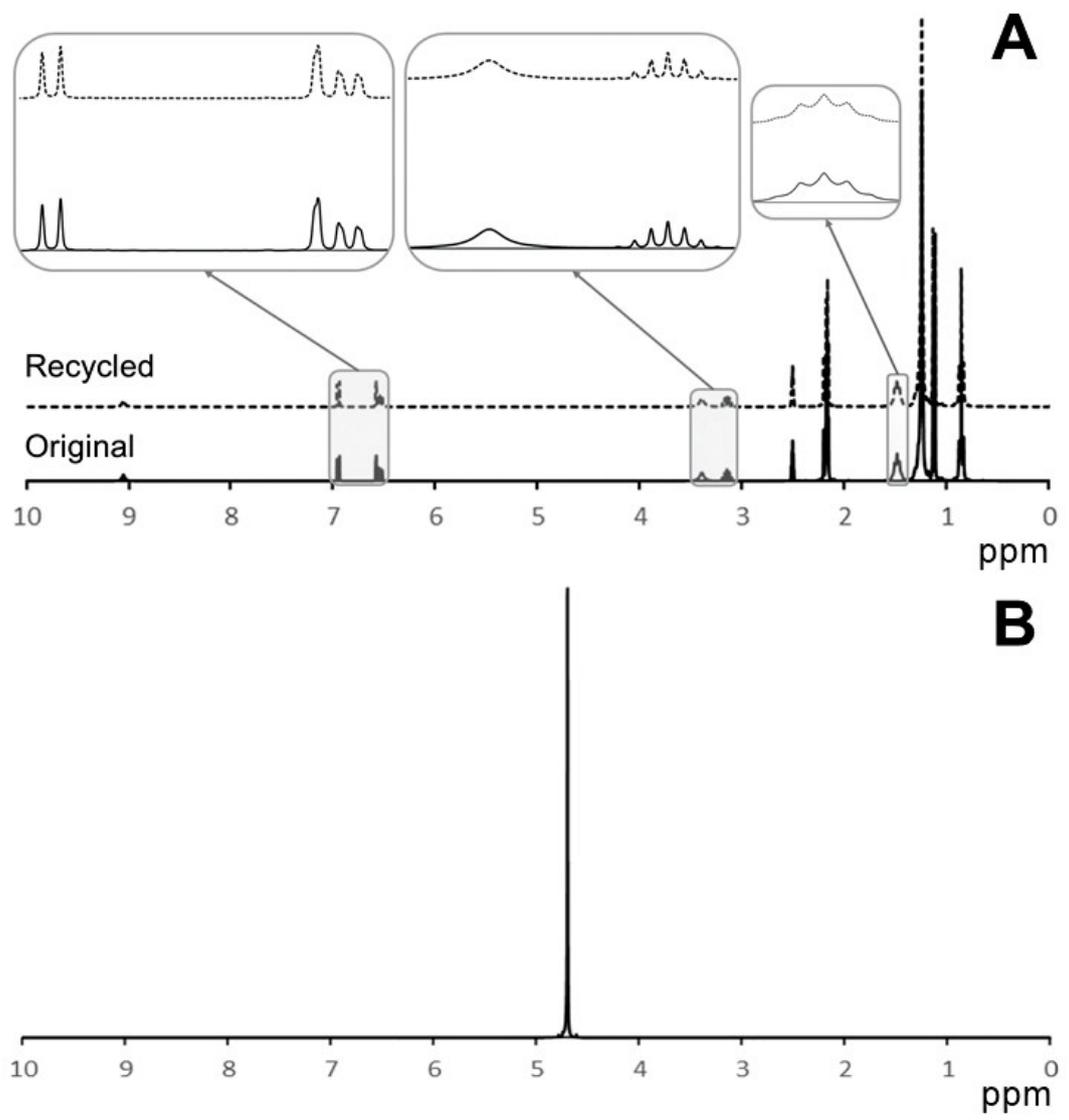


Figure S8. ¹H-NMR spectra of (A) original and five time recycled thymol:capric acid HES (0.3:0.7 molar ratio) and (B) aqueous phase after extraction of 0.01M Cu(II).

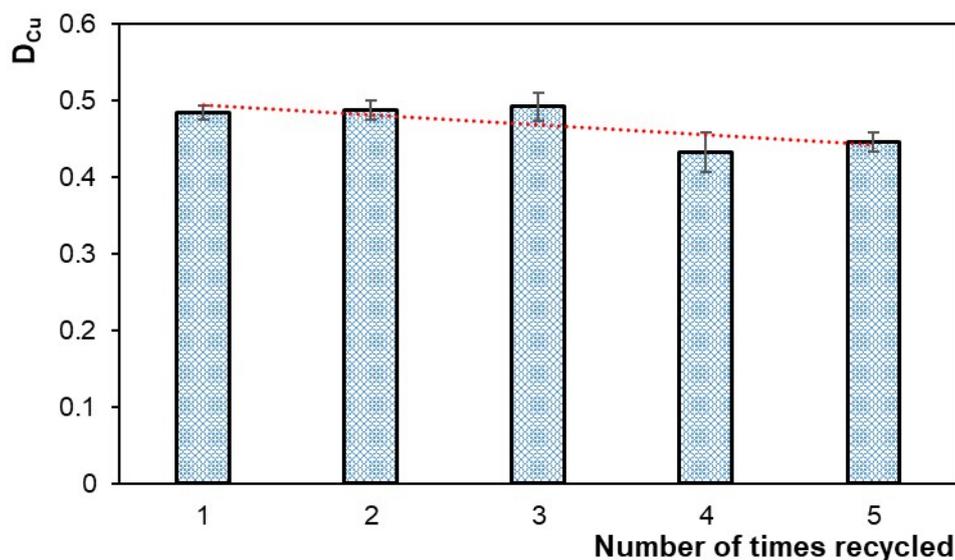


Figure S9. Extraction efficiency of 0.0175M Cu(II) over multiple recycling stage using thymol:capric acid HES (0.3:0.7 molar ratio, pH=4.9, $T=20\text{ }^{\circ}\text{C}$).

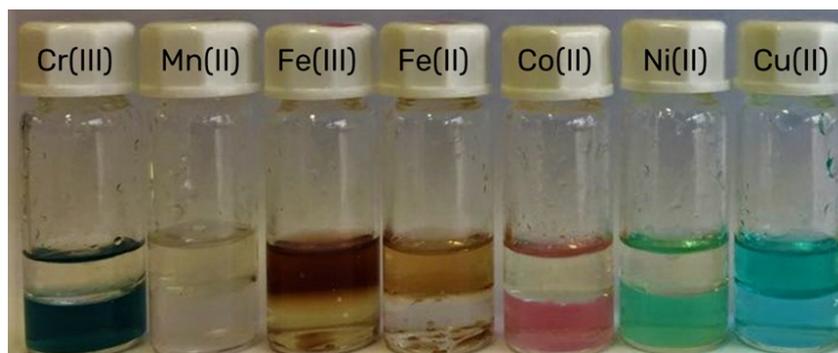


Figure S10. Extraction of sulphate salts of Cr(III), Mn(II), Fe(III), Fe(II), Co(II), Ni(II) and Cu(II) by thymol:capric acid HES (0.3:0.7 molar ratio) at $T=20\text{ }^{\circ}\text{C}$. A concentration of 0.05M was used for the transition elements and the ionic strength of the solution was adjusted to 0.1M using Na_2SO_4 . Although Fe(II) could be extracted, UV-Vis analysis of the HES phase indicates a change from Fe(II) to Fe(III) in the HES. Mg(II), Ca(II) and Zn(II) is not presented as the solution is colourless.

References

Gustafsson, J. P. Visual MINTEQ, version 3.1 (2018), <https://vminteq.lwr.kth.se/> (accessed 10 June 2018).

M.A.R. Martins, E.A. Crespo, P.V.A Pontes, L.P. Silva, M. Bülow, G.J. Maximo, E.A.C. Batista, C. Held, S.P. Pinho, J.A.P. Coutinho. Tunable Hydrophobic Eutectic Solvents Based on Terpenes and Monocarboxylic Acids. ACS Sustain. Chem. Eng. (2018), doi: 10.1021/acssuschemeng.8b01203