

Supplementary Information: Selective Recovery of Copper from Multi-Component Waste Streams Using the Thiourea-Functionalised Ion Exchange Resin Puromet MTS9140.

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Nitric Acid Elution of Cu from Puromet MTS9140

To quantify the extent to which nitric acid could act as a suitable eluent for Cu-loaded thiourea resin, a 5 mL column of S914 was loaded dynamically (Figure S1), after which aliquots of the 5 mL bed volume were used for subsequent elution experiments. Integration of the area above the loading curve suggested a total of 29.03 mg Cu adsorbed to the column, equating to a loading of 5.81 mg Cu/mL S914 for this batch of resin.

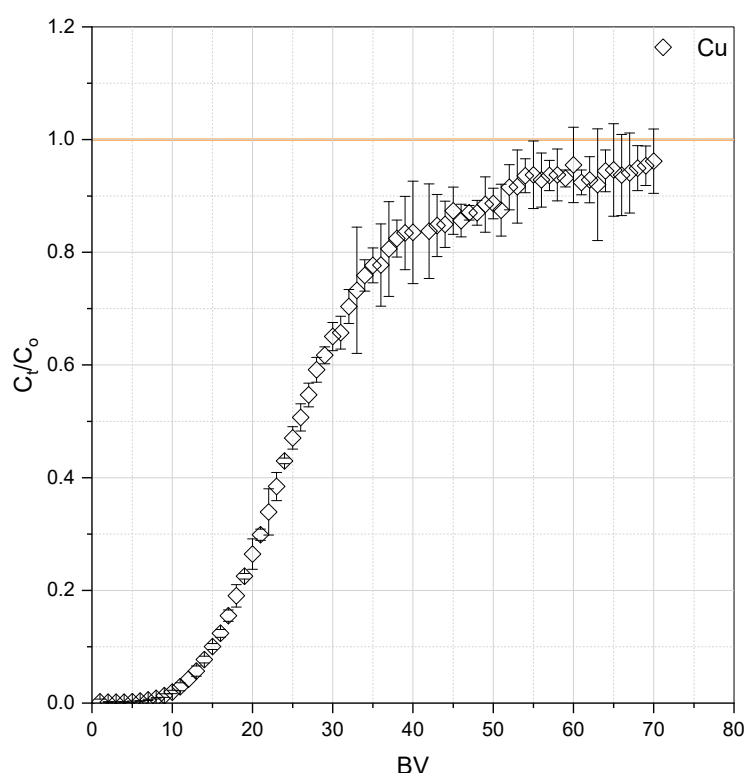


Figure S1. Breakthrough curve of Cu from MTS9140 (5 mL BV, 5 BV/h, 400 mg/L Cu, pH 1.55).

Figure S2 presents three elution profiles of Cu from S914 using a 3 M HNO_3 solution as an eluent. The first elution profile (labelled Elution 1) occurred at 27 mL throughput (31 BV) and was very sharp, with a maximum Cu concentration of 2853.6 mg/L (2.85 g/L). Prior to the elution peak, Cu concentrations are negligible in effluent solutions, as is the case for effluent solutions following the elution peak. The 1.6 mL BV column was calculated to be loaded with 9.29 mg Cu, with analysis of elution peak area suggesting a 109% Cu recovery. While recovery beyond 100% is an impossibility, such a result is attributed to the loading procedure, whereby variation in the loading profile within the 5 mL column may cause discrepancy between the calculated loading of the larger column and the smaller aliquots. Nevertheless, given the sharpness and magnitude of the profile it is assumed that a near-total recovery was achieved.

Inconsistencies in sample collection were observed, with the bed volume immediately prior to Cu elution being overfilled, and empty 'missed' fractions during the Cu elution stage (hence the low data resolution during the Elution 1 in Figure S2). This was

initially attributed to equipment malfunction, and so the elution was repeated using a separate aliquot of Cu-loaded S914.

Repetition of Cu elution with 3 M HNO₃ also yielded a sharp and highly concentrated elution peak (Elution 2 in Figure S2), yet this occurred sooner than during the first elution attempt with peak Cu concentration reached after 11 mL throughput. Peak concentration was also much higher; 5208 mg/L compared to 2853 mg/L. As for the previous elution, the issue of 'missed' and overfilled fractions surrounding the elution peak was encountered, but in this case was observed to be due to the formation of gas during the elution cycle which caused an airlock within the small column used.

Given the inconsistencies of previous elution experiments, the 3 M HNO₃ elution experiment was repeated once more using a batch-loaded resin (loaded to 8.64 mg Cu/mL resin), the results of which are also presented in Figure S2 as Elution 3. In this instance, peak Cu elution occurred at 10 mL throughput at a concentration of 5400 mg/L, comparable to Elution 2. Again, the formation of gas bubbles within the column and tubing caused the airlock issues previously encountered and resulted in low data resolution during the Cu elution event. Comparison of the three elution peaks concurrently clearly exhibits the variation in peak position and magnitude, despite comparable recoveries (Table S1).

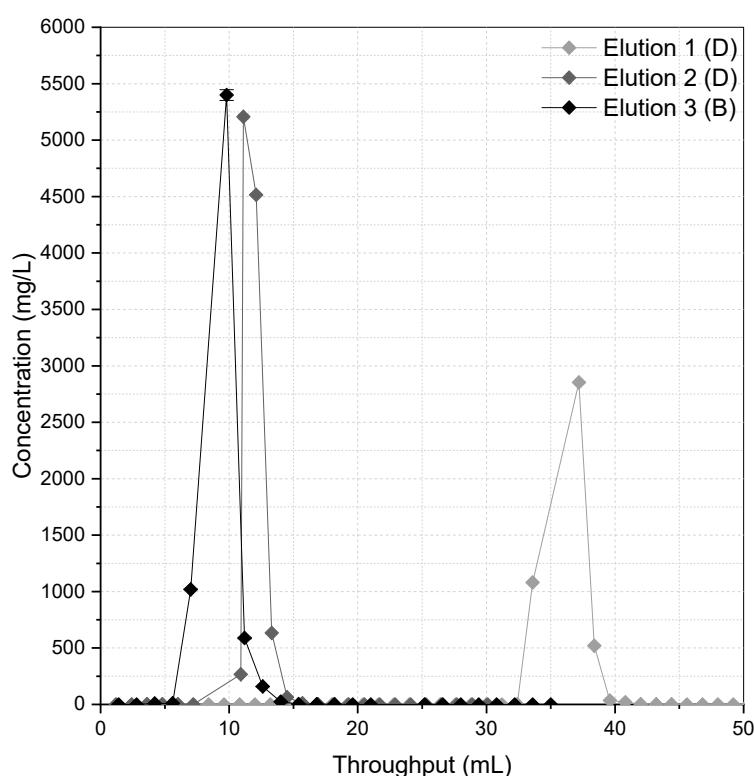


Figure S2. Comparison of Cu elution profiles from MTS9140 using 3 M HNO₃ at 2 BV/h (D = dynamically-loaded resin, B = batch-loaded resin).

Table S1. Details of Cu elution investigations using HNO₃ (FWHM provided for comparison of peak widths).

	[HNO ₃]	Loading Method	Cu loading mg/mL	Bed Vol- ume mL	Total Cu available mg	Cu recovered mg	FWHM mL	Recovery efficiency %
Elution 1	3 M	Dynamic	5.805	1.6	9.289	10.142	3.6	109.2
Elution 2	3 M	Dynamic	5.805	1.6	9.289	9.465	1.7	101.9
Elution 3	3 M	Batch	8.641	1.6	13.825	14.580	2.5	105.5
Elution 4	1 M	Batch	8.641	1.4	12.097	0.837	-	6.92

The use of lower concentration nitric acid was investigated to attempt to minimise the gas formation issues encountered. Elution was repeated using 1 M HNO₃ and a fresh

aliquot of batch loaded MTS9140 packed in to a 1.4 mL BV column. The resulting Cu elution profile indicated poor potential of this eluent for Cu recovery (Figure S3). Despite an initial spike, Cu concentrations remained relatively low over the experimental run, with no complete elution profile captured over a 75 BV period. Analysis of the curve suggested recovery of under 7% over the studied period (Table S1). While it is anticipated that given enough time, a higher recovery efficiency would be achieved, the relatively low definition of the elution peak when compared to peaks presented in Figure S2 suggested that 1 M HNO₃ would not be a suitable eluent for effective resource recovery given the lower concentration product stream that would result from such an elution profile.

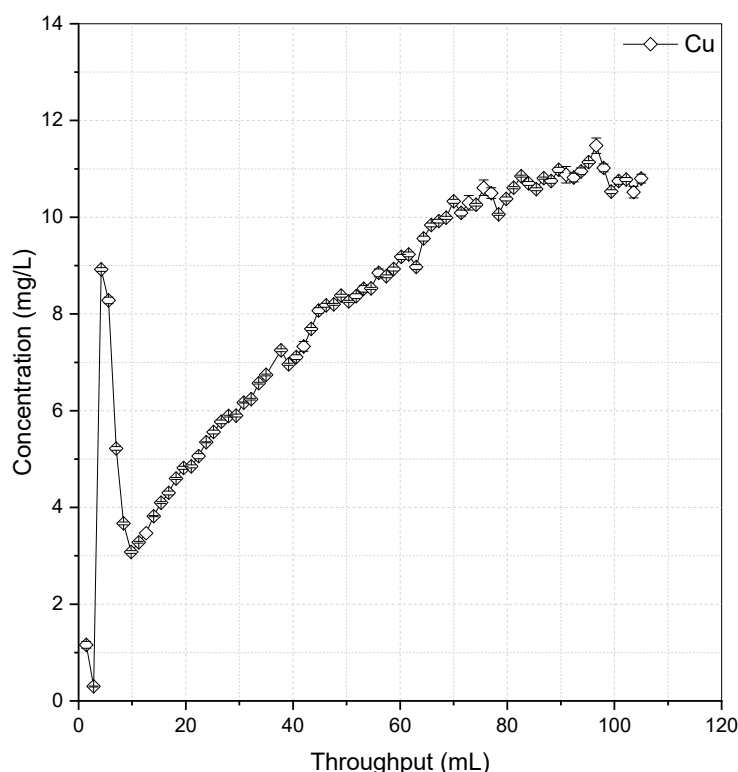
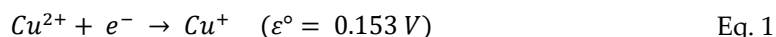


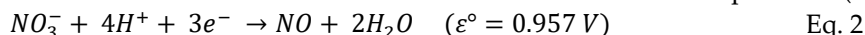
Figure S3. Elution of Cu from MTS9140 using 1 M HNO₃ at 2 BV/h.

The formation of gas within the column was likely a product of the redox interaction between nitrate and Cu(I). The half-reactions for the reduction of Cu(II) and nitrate, and standard reduction potentials (ϵ°) are provided in Equations 1 and 2.

Equation 1. Reduction half-reaction of Cu(II) to Cu(I) and standard reduction potential (V).

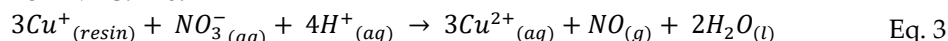


Equation 2. Reduction half-reaction of nitrate and standard reduction potential (V).



When Equation 1 and Equation 2 are combined, with Cu(I) being oxidised to Cu(II), and NO₃ being reduced, the resulting balanced redox reaction is formed, requiring three moles of cuprous ions per mole of nitrate (Equation 3).

Equation 3. Proposed redox reaction between Cu⁺ and NO₃⁻ during the HNO₃ elution of Cu from MTS9140.



Considering the products of Equation 3, nitric oxide (NO) gas was likely responsible for the airlock problems encountered in columns when using 3 M HNO₃ as an eluent. Electrochemical nitrate reduction by copper has been reported elsewhere, particularly in acidic media where the products were NO and NH₄⁺ [1]. The reduction of nitrate cannot be initiated by Cu metal or Cu(II) ions, but the catalytic effect of Cu(I) ions does allow nitrate to reduce and form NO gas [2], further suggesting that this was the case during 3

M HNO₃ elution. It was also likely that the nitric acid oxidised not only the Cu(I) loaded to the resin but also the thiourea functional groups. At high acidity it is known that thiourea may be completely oxidised by HNO₃ to form NO gas [3], which may also have contributed to the observed behaviour.

References

- [1] E. Pérez-Gallent, M. C. Figueiredo, I. Katsounaros and M. T. M. Koper, "Electrocatalytic reduction of Nitrate on Copper single crystals in acidic and alkaline solutions," *Electrochimica Acta*, vol. 227, pp. 77-84, 2017.
- [2] E. V. Filimonov and A. I. Shcherbakov, "Catalytic Effect of Copper Ions on Nitrate Reduction," *Protection of Metals*, vol. 40, no. 3, pp. 280-284, 2004.
- [3] J. Kirchnerova and W. C. Purdy, "The mechanism of the electrochemical oxidation of thiourea," *Analytica Chimica Acta*, vol. 123, no. 1, pp. 83-95, 1981.