

Electronic Supporting Information (ESI)

**Recovery of cobalt from dilute aqueous solutions using activated
carbon – alginate composite spheres impregnated
with Cyanex 272**

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Table S1: Reported wavelengths and view mode (AX/RAD) for the ICP-OES measurements.

Element	Wavelength (nm)	Axial (AX) or radial (RAD)
Ca	317.933	RAD
Co	228.616	RAD
Cu	327.393	RAD
Fe	238.204	RAD
Mn	257.610	RAD
Ni	231.604	RAD
P	214.914	RAD
Sc	361.383	RAD
Zn	206.200	RAD

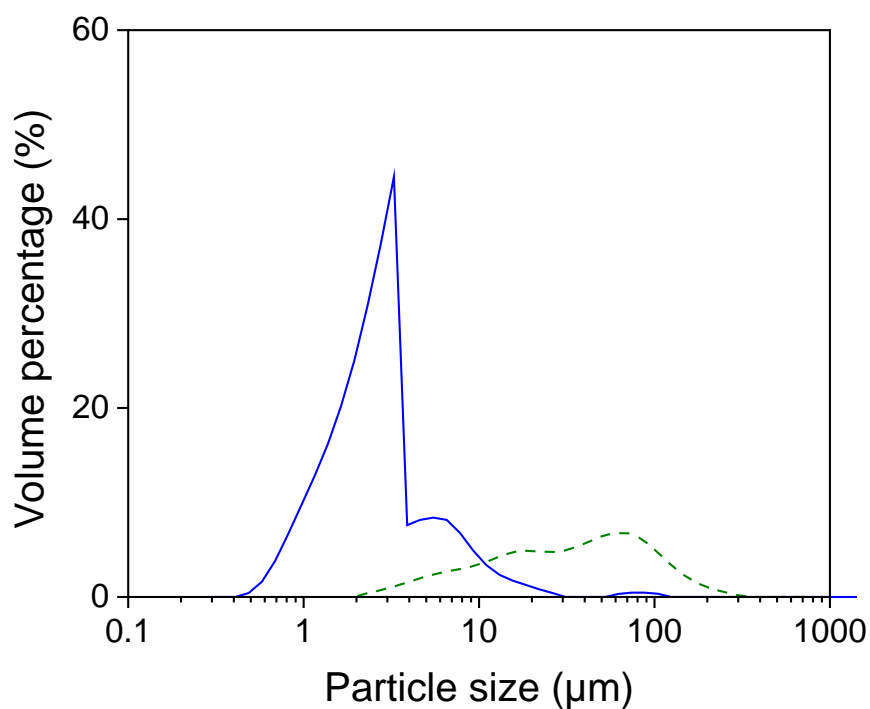


Figure S1: Particle size distribution of the AC powder before (green, dashed lines) and after (blue, full lines) milling.

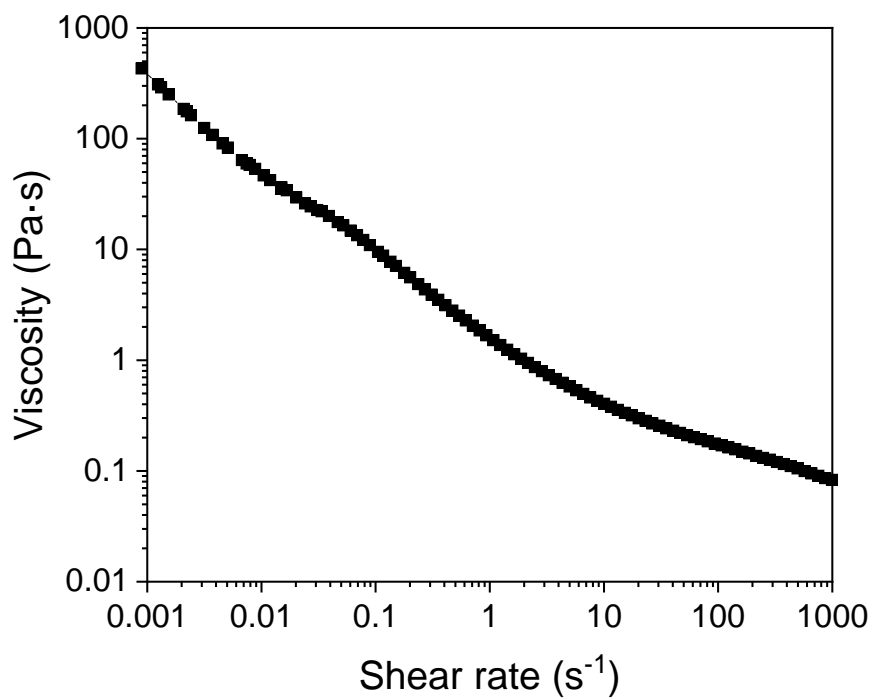


Figure S2: Viscosity of the AC-ALG suspension as a function of the shear rate.

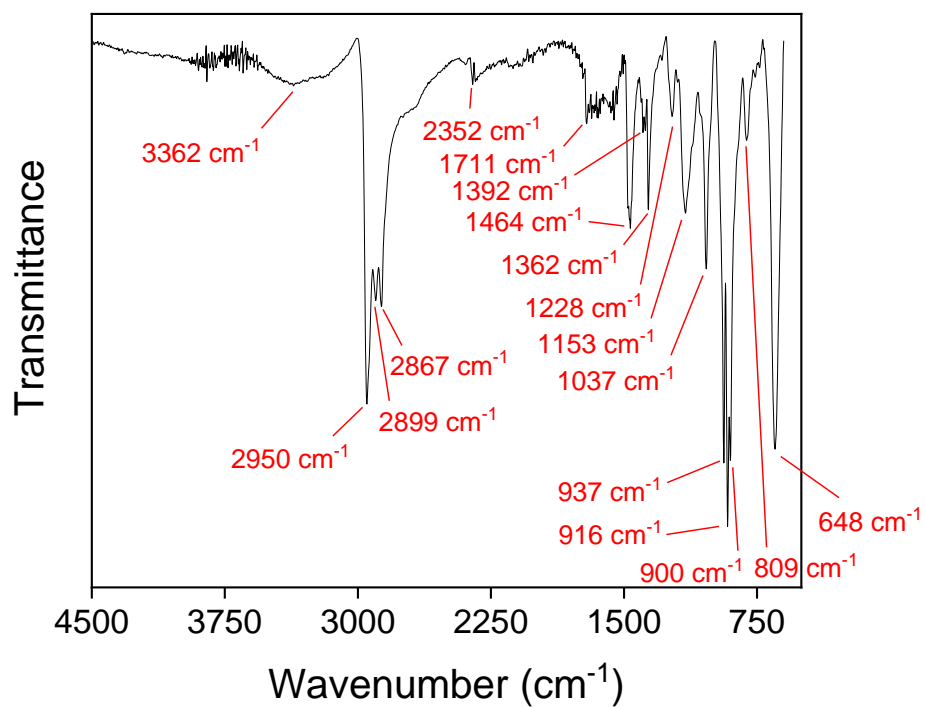


Figure S3: FTIR spectrum of the AC-ALG-C272 spheres.

Adsorption of cobalt(II) from a synthetic, multi-element solution:

To check the performance of AC-ALG-C272 for recovering cobalt(II) from more complex metal mixtures, the influence of the pH on the adsorption of metals from a synthetic multi-element solution was studied. First, a blank experiment was performed to determine the precipitation of the different metal ions cobalt(II), nickel(II), manganese(II), zinc(II), iron(III) and copper(II) from the mixture upon increasing the pH. As shown in Figure S4, the removal of metal ions from solution was very limited, except of iron(III). At pH 5.2, already a significant amount of iron(III) was removed as iron(III) hydroxide by hydrolysis. Subsequently, the same mixture was contacted with AC-ALG-C272 under the same conditions at various pH levels (Figure S5). The same selectivity was observed as previously reported for Cyanex 272 in liquid-liquid extraction: iron(III) > zinc(II) > manganese(II) > cobalt(II) ~ copper(II) > nickel(II).¹ The high affinity for iron(III) might cause issues when using AC-ALG-C272 for the adsorption of the more valuable elements such as cobalt(II) because it is often present in relatively high concentrations and might easily saturate the adsorbent spheres. In this case, the possibility of removing iron(III) by precipitation, as shown in Figure S4, could be exploited to first remove iron(III) from solution prior to the addition of AC-ALG-C272.

The stability of complexes of divalent first-row transition metal ions formed by certain ligands generally follow a trend according to the so-called Irving–Williams series.² However, the data shown in Figure S5 does not completely follow this trend. Some extractants are able to alter the order within this series due to various reasons. Cyanex 272, for instance, is able to preferentially extract cobalt(II) in the presence of nickel(II), which is an alteration of the Irving–Williams trend.³ This has been ascribed to the destabilisation of the octahedral nickel(II) complexes which results from the greater steric hindrance of the ligands with alkyl groups attached directly to the phosphorus atom.⁴

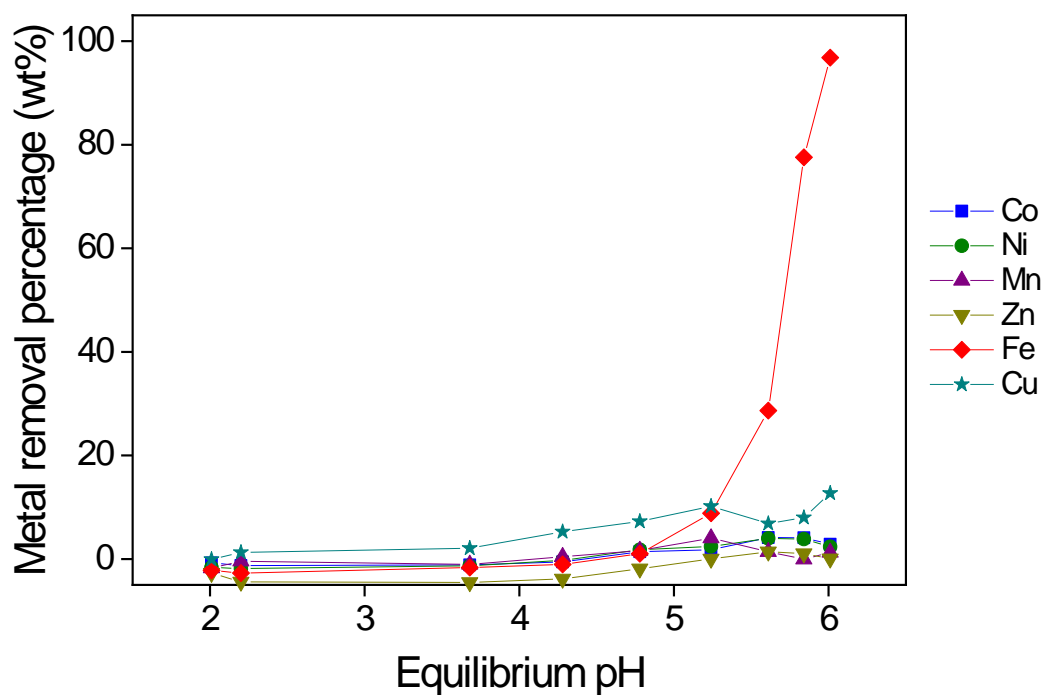


Figure S4: pH influence on the removal of metals out of a multi-element solution without the addition of adsorbent (= blank) (10 mL solution, $0.48 \text{ mmol}\cdot\text{L}^{-1}$ cobalt(II), $0.48 \text{ mmol}\cdot\text{L}^{-1}$ nickel(II), $0.47 \text{ mmol}\cdot\text{L}^{-1}$ manganese(II), $0.47 \text{ mmol}\cdot\text{L}^{-1}$ zinc(II), $0.35 \text{ mmol}\cdot\text{L}^{-1}$ iron(III), $0.50 \text{ mmol}\cdot\text{L}^{-1}$ copper(II), $0.25 \text{ mol}\cdot\text{L}^{-1}$ acetate buffer, 0 mg of AC-ALG-C272, 4 h adsorption, pH 2–6).

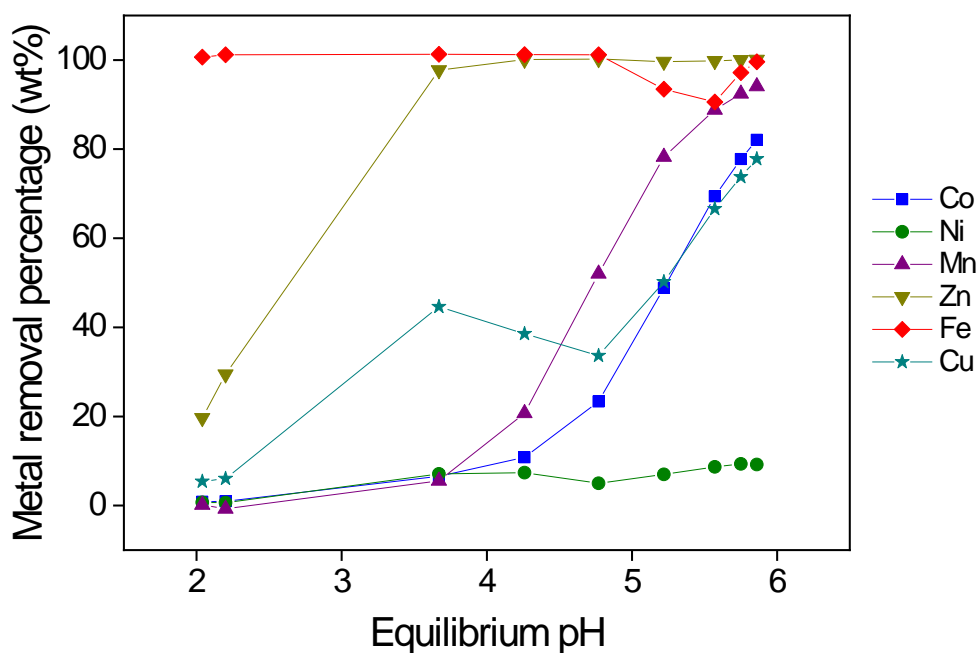


Figure S5: pH influence on the removal of metals out of a multi-element solution with the addition of adsorbent (10 mL solution, $0.48 \text{ mmol}\cdot\text{L}^{-1}$ cobalt(II), $0.48 \text{ mmol}\cdot\text{L}^{-1}$ nickel(II), $0.47 \text{ mmol}\cdot\text{L}^{-1}$ manganese(II), $0.47 \text{ mmol}\cdot\text{L}^{-1}$ zinc(II), $0.35 \text{ mmol}\cdot\text{L}^{-1}$ iron(III), $0.50 \text{ mmol}\cdot\text{L}^{-1}$ copper(II), $0.25 \text{ mol}\cdot\text{L}^{-1}$ acetate buffer, 50 mg of AC-ALG-C272, 4 h adsorption, pH 2–6).

Stripping of cobalt(II) from a synthetic, multi-element solution:

After adsorption from the multi-element solution with the AC-ALG-C272 spheres, the loaded spheres were contacted with stripping solutions containing various concentrations of sulphuric acid. The results are shown in Figure S6, where the total recovery (a combination of the adsorption and stripping) is presented. Since iron(III) was removed by hydrolysis precipitation prior to the adsorption, iron(III) is not shown in the figure. It became clear that by changing the acidity of the stripping solution, the elements could be recovered in a selective way. The only elements that appeared to be a challenge, are cobalt(II) and manganese(II). However, as mentioned before, this problem could be overcome by applying a column setup as this enhances separation and total recovery.

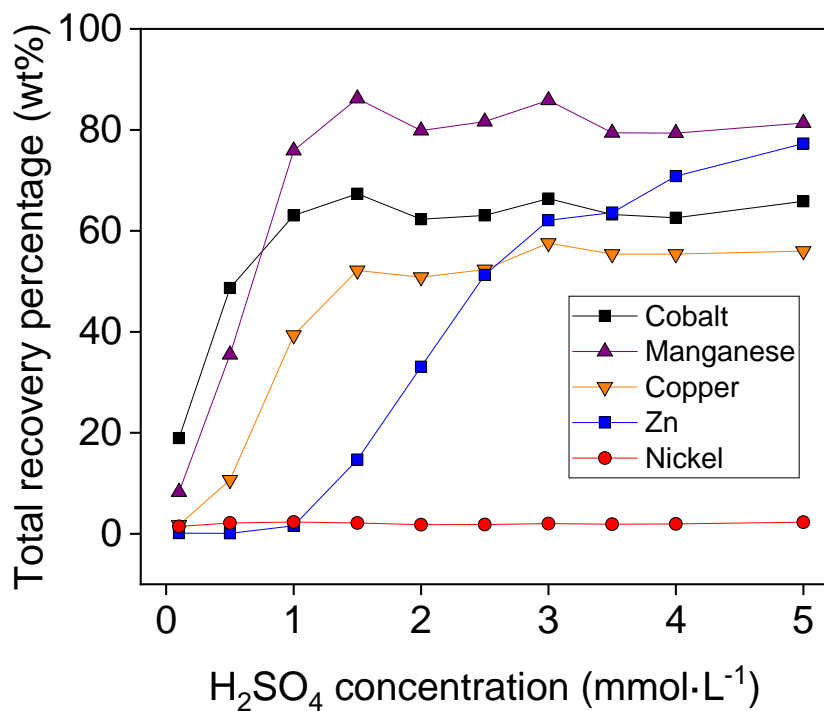


Figure S6: Influence of the sulphuric acid concentration on the total recovery efficiency using a multi-element solution (50 mg AC-ALG-C272 loaded with 3.8 mg·g⁻¹ cobalt(II), 4.6 mg·g⁻¹ manganese(II), 3.5 mg·g⁻¹ copper(II), 6.2 mg·g⁻¹ zinc(II) and 0.6 mg·g⁻¹ nickel(II) under optimal adsorption parameters, 10 mL stripping solution, 4 h stripping, 0.1–5 mmol·L⁻¹ stripping solution concentration).

REFERENCES

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4. P. A. Tasker, P. G. Plieger and L. C. West, in *Comprehensive Coordination Chemistry II*, eds. J. A. McCleverty and T. J. Meyer, Pergamon, Oxford, 2003, DOI: <https://doi.org/10.1016/B0-08-043748-6/09011-3>, pp. 759-808.