



UNIVERSITÀ DEL PIEMONTE ORIENTALE

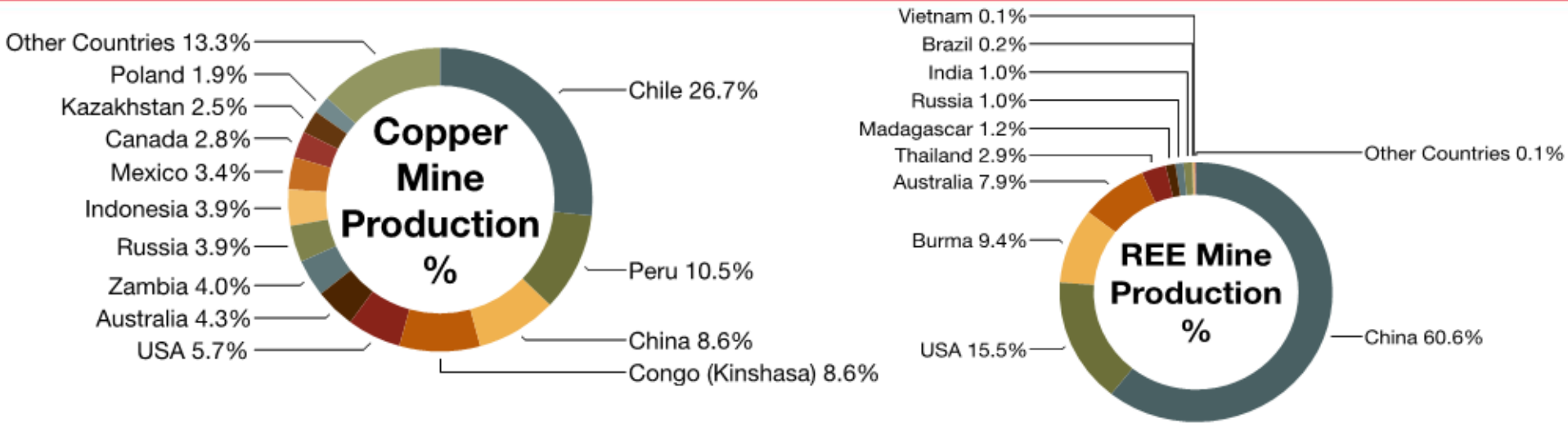
DTPA-Functionalized silica-based Monoliths for the removal of transition and lanthanide ions from aqueous phase

Gioele Ancora

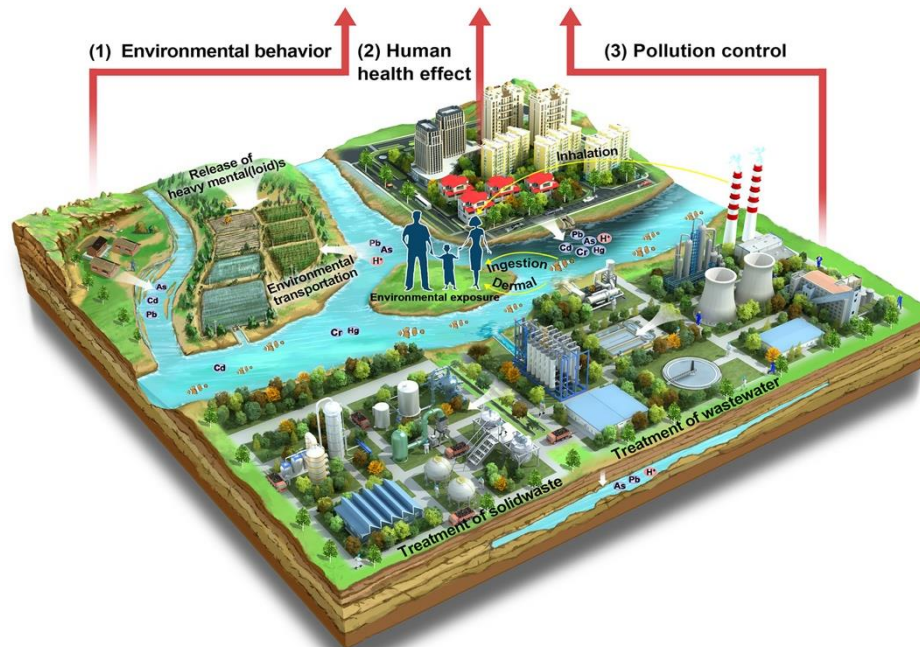
Stefano Marchesi

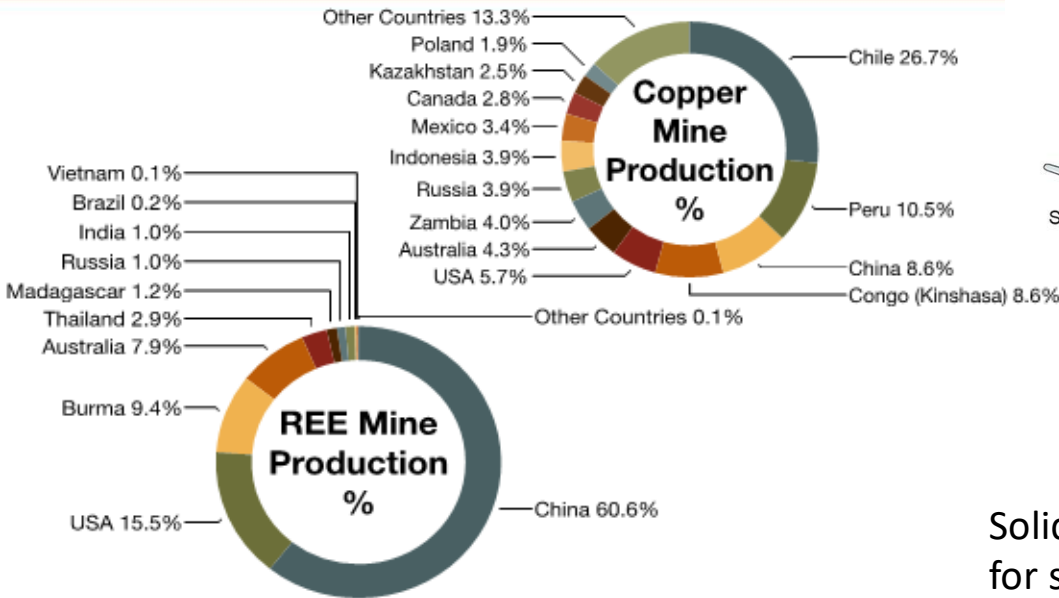
Fabio Carniato

Chiara Bisio

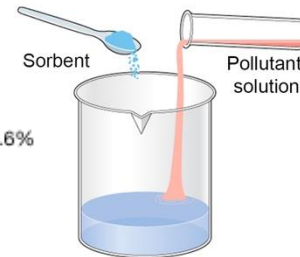


Full life-cycle processes of heavy metal(loid)s





SLE Solid-Liquid Extraction



- ✓ Waste reduction
- ✓ Few operational steps
- ✓ Low quantities of solvents for disposal
- ✓ Extraction capacity

Solids can be **functionalized** with organic moieties for specific purposes

Full life-cycle processes of heavy metal(loid)s



SBA-15



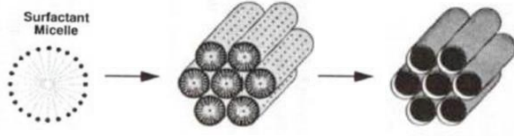
Silica Monoliths

Wastewater treatment **easier with massive solids**

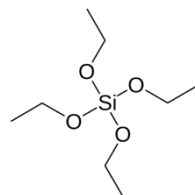
Silica monoliths: Sol-gel Synthesis

1. Formation of the siliceous framework :

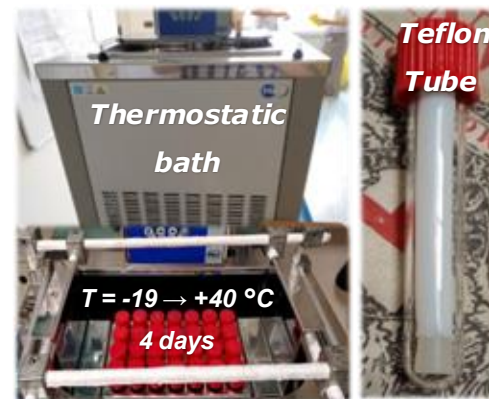
PEO
H₂O
HNO₃
(0 °C)



Polyethylene oxide (PEO) as a templating agent



+ TEOS



Sol-gel Transition

2. Consolidation of mesoporous structure:

Basic Treatment

Drying and Calcination

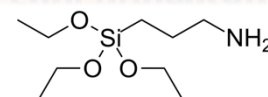
Functionalization



NH₃ 40°C
(0.1 M) 24 h

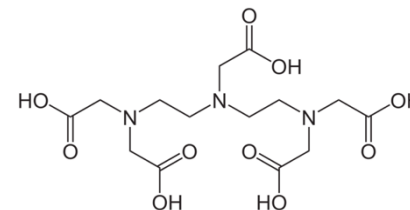


Drying (RT, 3 days)
Calcination in O₂
(550°C, 6 h, 3°C/min)



APTS

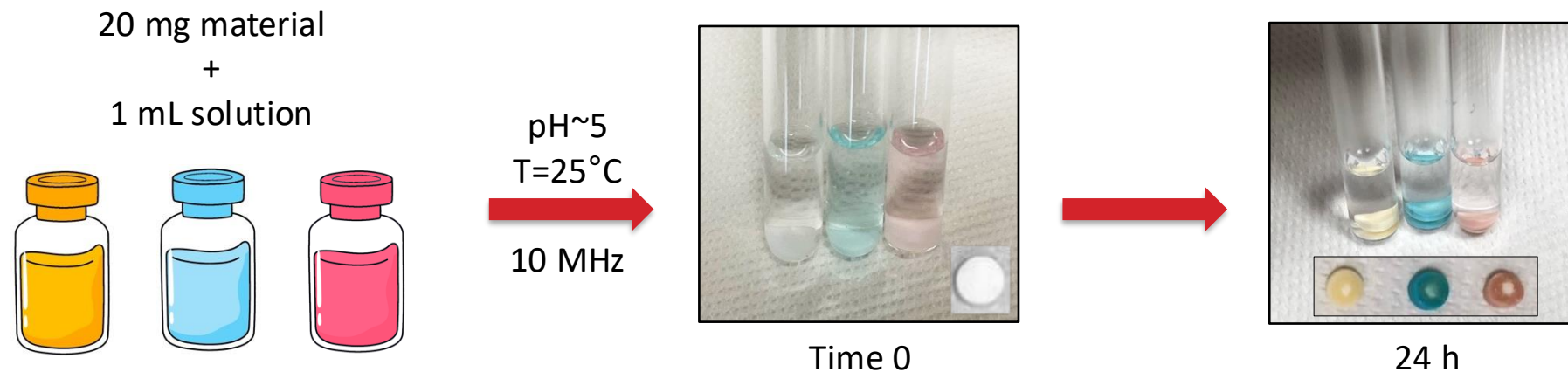
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DTPA

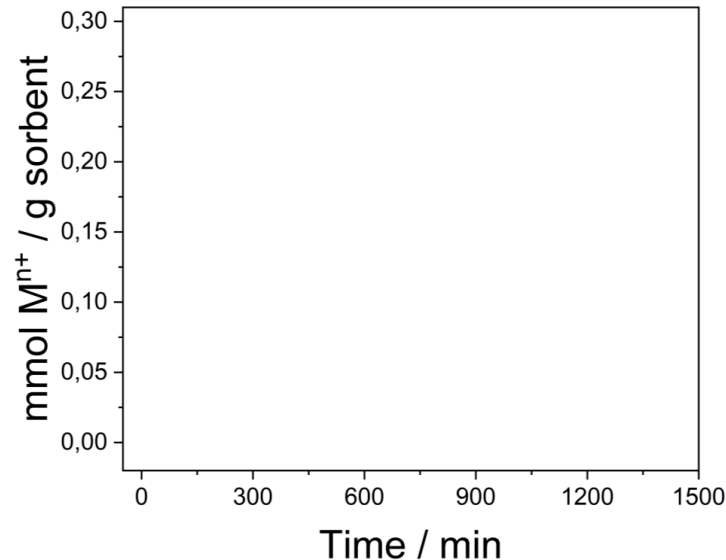
Functionalization with
diethylenetriaminopentaacetic acid (DTPA)

Real-time measurement of **paramagnetic** ion concentration in solution by ^1H -NMR Relaxometry

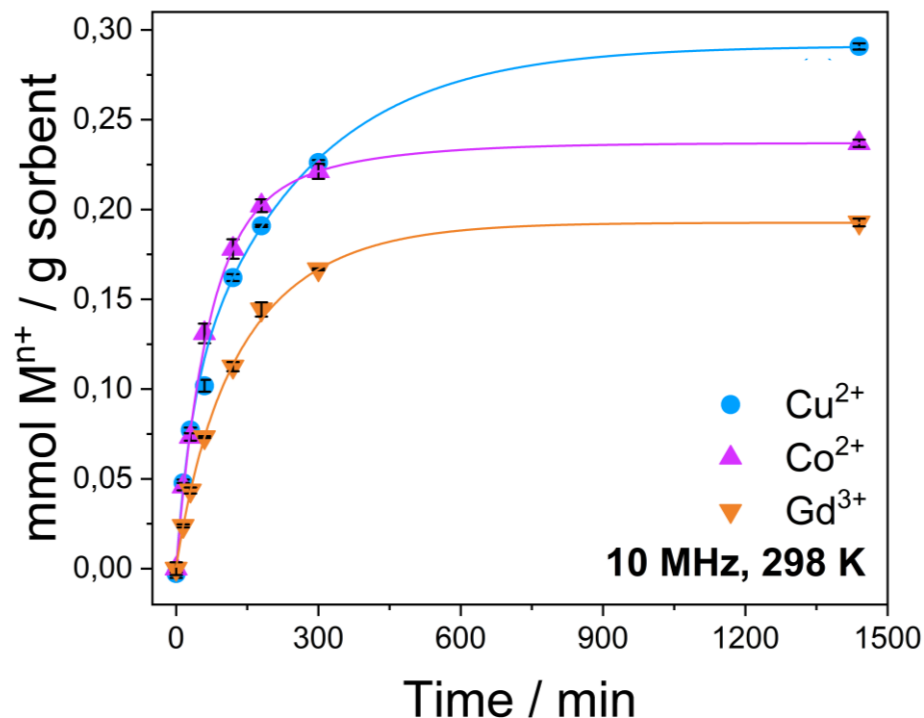


$$r_1 = \frac{R_1^{obs} - R_1^d}{[M^{n+}]}$$

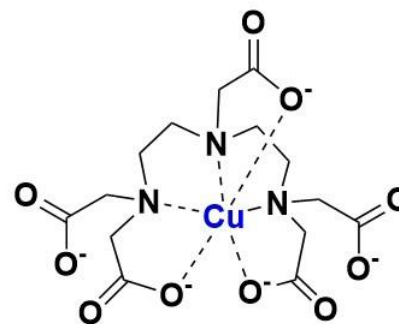
- R_1^{obs} (s^{-1}) = Longitudinal relaxation rate of the ^1H proton of the paramagnetic solution;
- R_1^d (s^{-1}) = diamagnetic contribution of pure water (0.38 s^{-1} at 298 K and 10 MHz);
- r_1 ($\text{mM}^{-1} \text{ s}^{-1}$) = relaxivity.



Increase in the concentration of metal captured by the material



Copper is the most highly sequestered metal, and the amount of captured metal is comparable with the amount of ligand present on the material surface

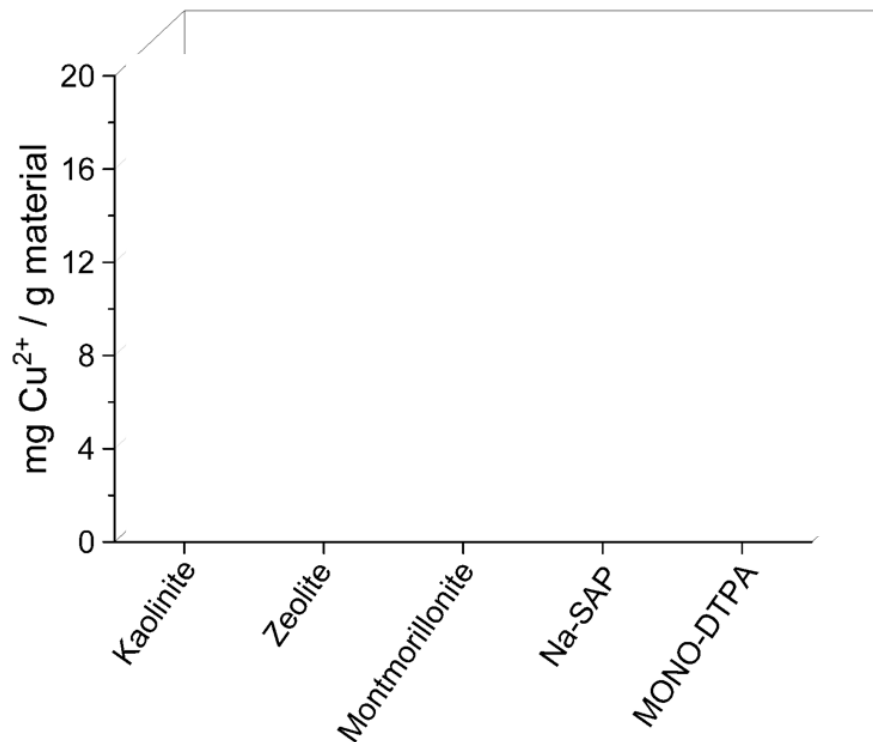


1 : 1 ligand : metal interaction

Sample	mmol M^{n+} / g sorbent	Captured M^{n+} [a] %	mg M^{n+} / g sorbent	[DTPA] (mmol / g)
MONO-DTPA + Cu^{2+}	0.29 ± 0.01	62.7 ± 0.3	18.48 ± 0.11	0.31 ± 0.01
MONO-DTPA + Co^{2+}	0.24 ± 0.01	49.2 ± 0.4	13.96 ± 0.12	0.31 ± 0.01
MONO-DTPA + Gd^{3+}	0.19 ± 0.01	40.0 ± 0.4	30.31 ± 0.34	0.31 ± 0.01
[a] = in reference to the initial concentration value of each metal solution used (10 mM)				

MONO-DTPA showed better performances than those of clay materials commonly used as cation exchangers.

However, the former occur as massive solids and are therefore easier to use, while the latter occur as powders.



Ö. Yavuz, Y. Altunkaynak and F. Güzel, *Water Res.*, 2003, **37**, 948–952.

M. Šljivić, I. Smičiklas, S. Pejanović and I. Plečaš, *Appl. Clay Sci.*, 2009, **43**, 33–40.

C. O. Ijagbemi, M.-H. Baek and D.-S. Kim, *J. Hazard. Mater.*, 2009, **166**, 538–546.

S. Marchesi, S. Nascimbene, M. Guidotti, C. Bisio and F. Carniato, *Dalton Trans.*, 2022, **51**, 4502–4509.

Sample	mmol M ⁿ⁺ / g sorbent	Captured M ⁿ⁺ [a] %	mg M ⁿ⁺ / g sorbent	[DTPA] (mmol / g)
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Thanks for your kind attention