

ELECTRONIC SUPPLEMENTARY INFORMATION

Application of NMR relaxometry for the real-time monitoring of the removal of metal ions from water by synthetic clays

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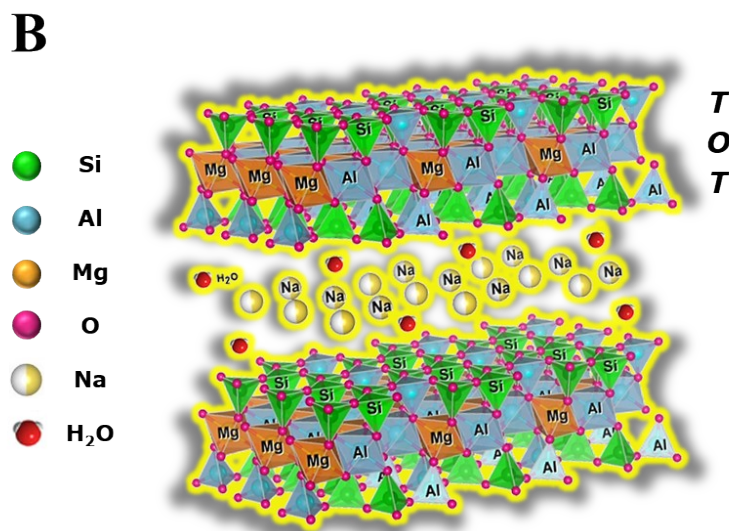
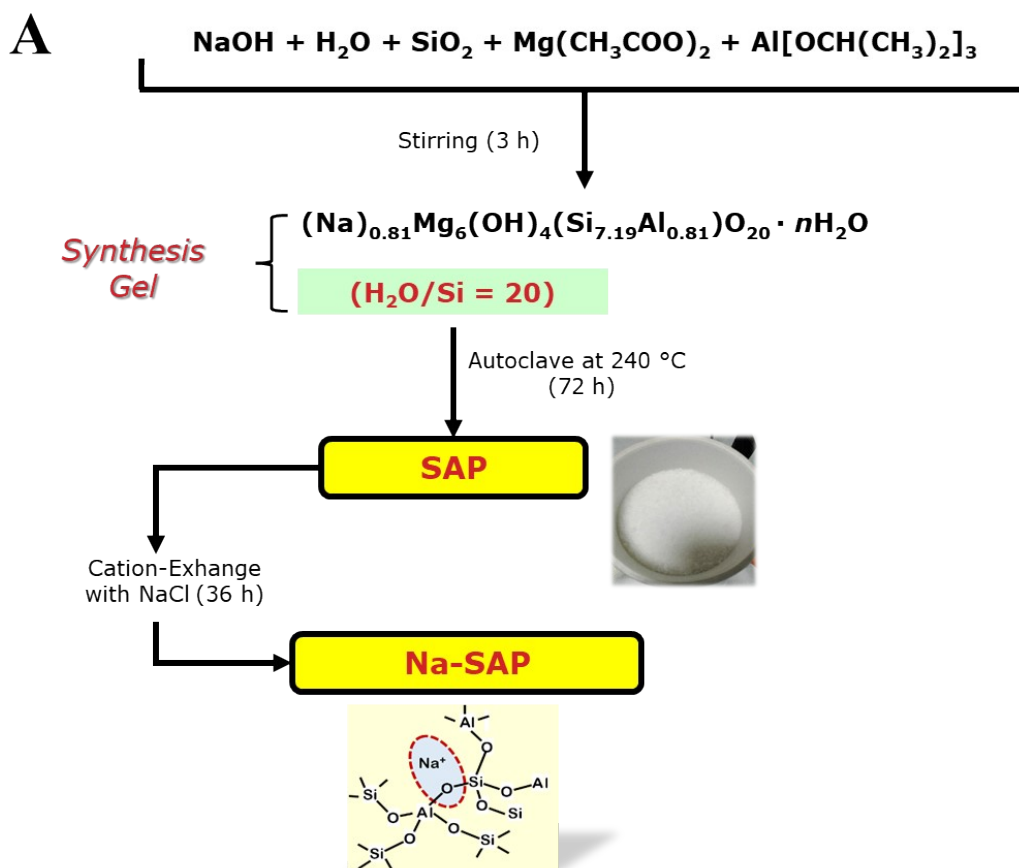
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1) FIGURES



Scheme S1. Schematic view of the hydrothermal procedure for the preparation of the Na⁺-exchanged synthetic saponite clay (Na-SAP) (A) and the related structure (B).

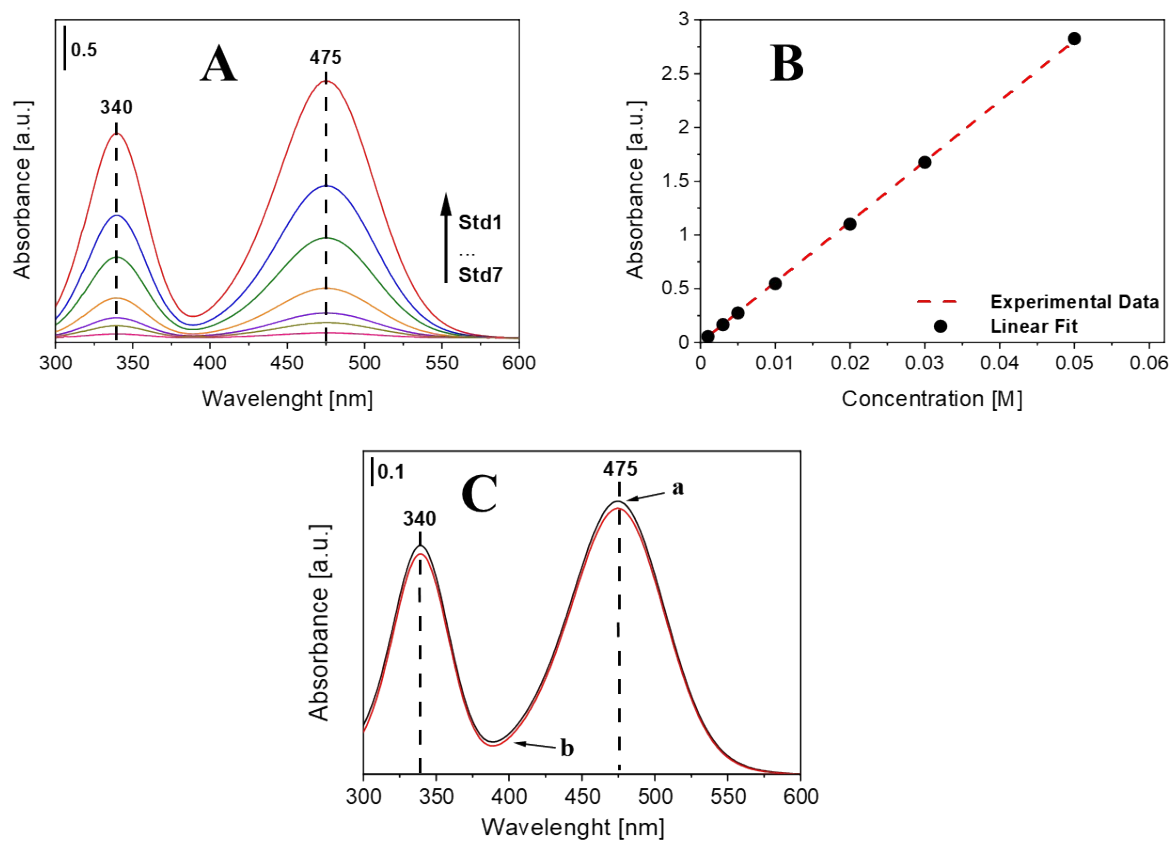


Fig. S1. A) UV-Vis spectra of $[\text{Co}(\text{NH}_3)_6]^{3+}$ standard aqueous solutions at room temperature, in the concentration range of 0.05-0.005 M, used for the calibration curve. B) Calibration curve obtained by UV-Vis spectra of the standards solutions ($\lambda_{\text{abs}} = 475$ nm). C) UV-Vis spectra of the supernatants of Na-SAP (a) and acid-treated Na-SAP (b) samples, obtained after treatment of the solids in 0.02 M $[\text{Co}(\text{NH}_3)_6]^{3+}$ aqueous solution at room temperature for 60 h.

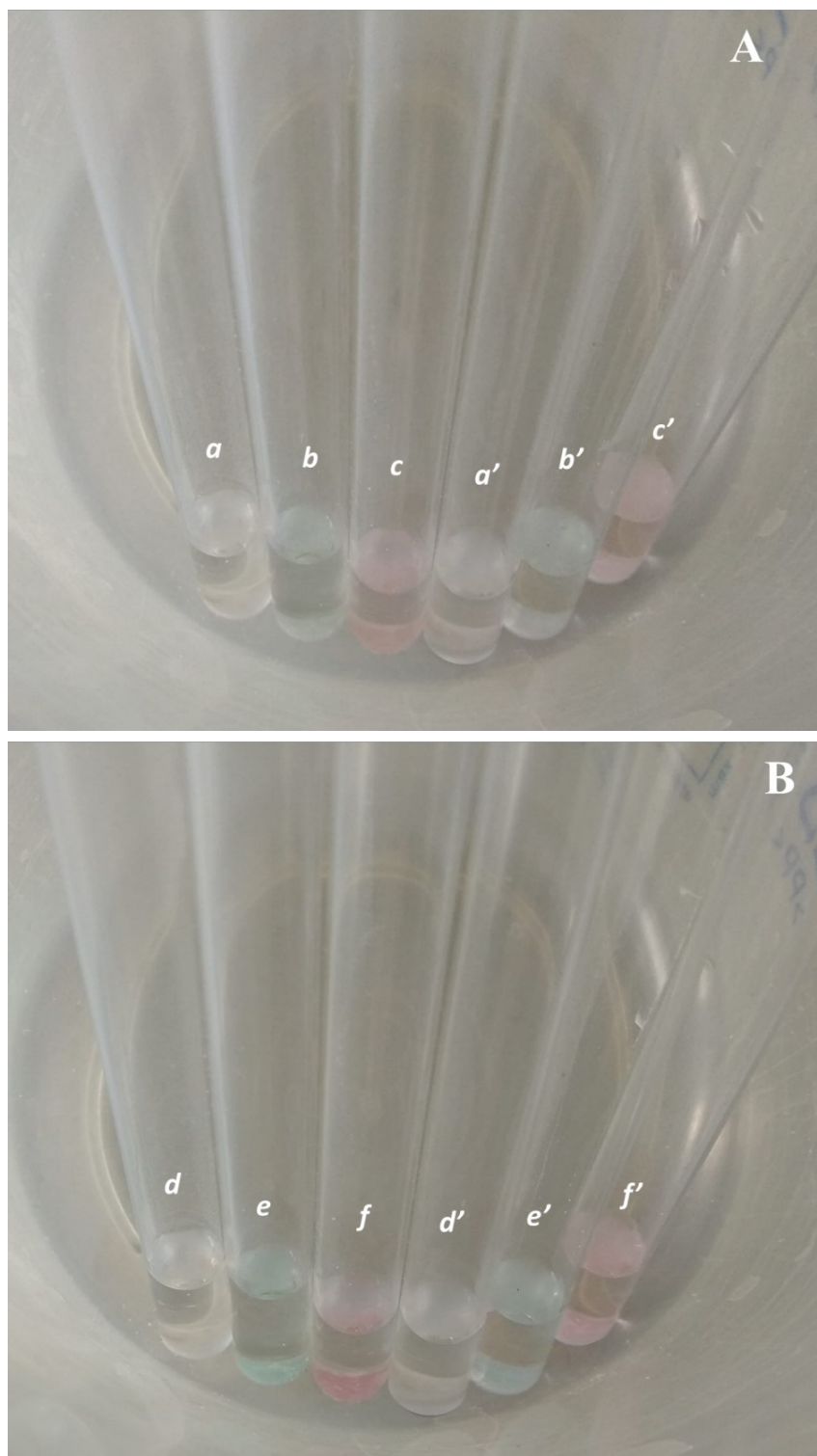


Fig. S2. (A) 10mM paramagnetic aqueous solutions after few seconds of contact with Na-SAP in the NMR tubes: Gd^{3+} (a), Cu^{2+} (b) and Co^{2+} (c) at pH = 5.5, Gd^{3+} (a'), Cu^{2+} (b') and Co^{2+} (c') at pH = 3.0. (B) The same solutions after 24 h of contact with the solid: Gd^{3+} (d), Cu^{2+} (e) and Co^{2+} (f) at pH = 5.5, Gd^{3+} (d'), Cu^{2+} (e') and Co^{2+} (f') at pH = 3.0.

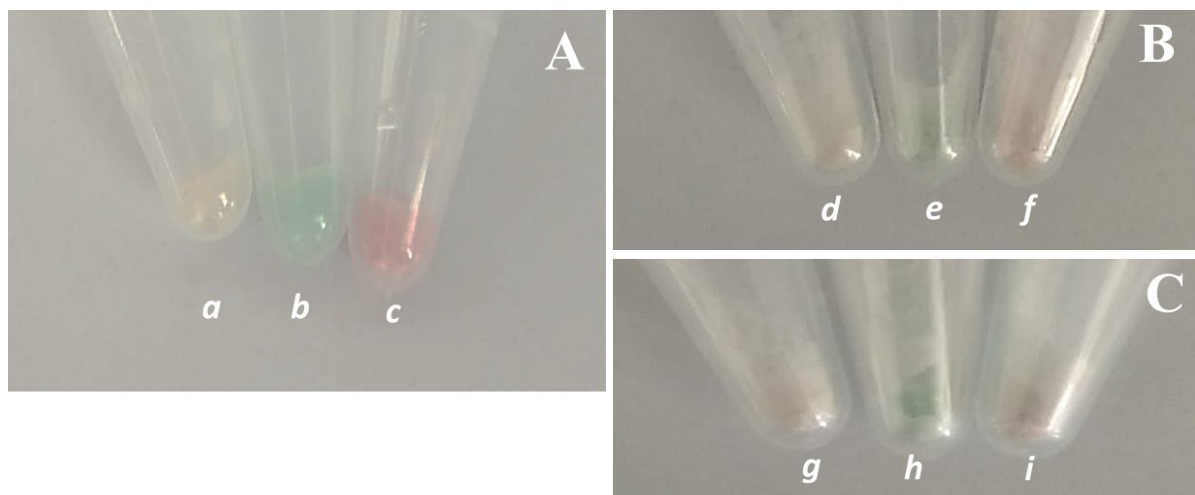


Fig. S3. (A) Na-SAP solids after 24 h of contact with 10 mM solutions of Gd^{3+} (a), Cu^{2+} (b) and Co^{2+} (c) at pH = 5.5. (B) Saponite samples after regeneration tests in saturated NaCl solutions at pH = 5.5, for Gd^{3+} (d), Cu^{2+} (e) and Co^{2+} (f). (C) Solids after regeneration at pH 2.5 for Gd^{3+} (g), Cu^{2+} (h) and Co^{2+} (i).

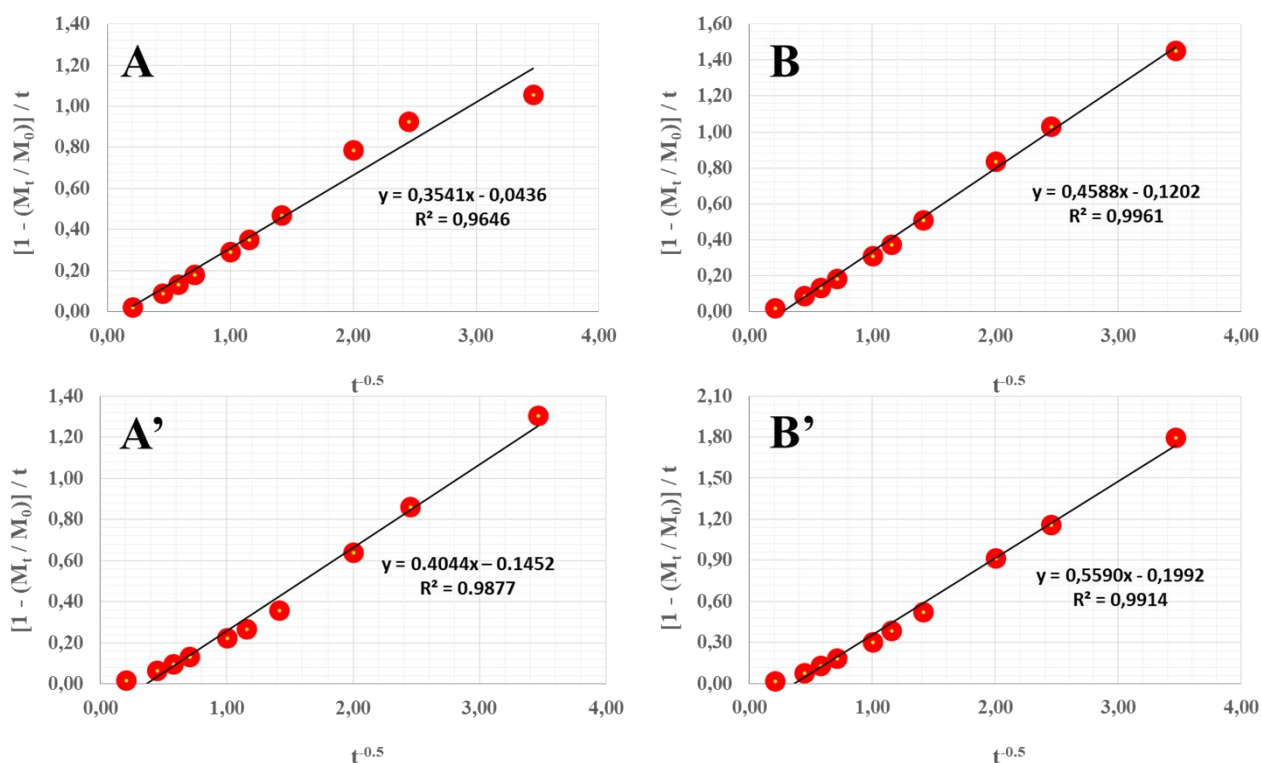


Fig. S4. Fitting of the data obtained by ^1H -NMR relaxometric analysis with a parabolic diffusion kinetic model¹ for the sorption on Na-SAP of Cu^{2+} at pH = 5.5 (A) and 3.0 (A'), and of Co^{2+} at pH = 5.5 (B) and 3.0 (B').

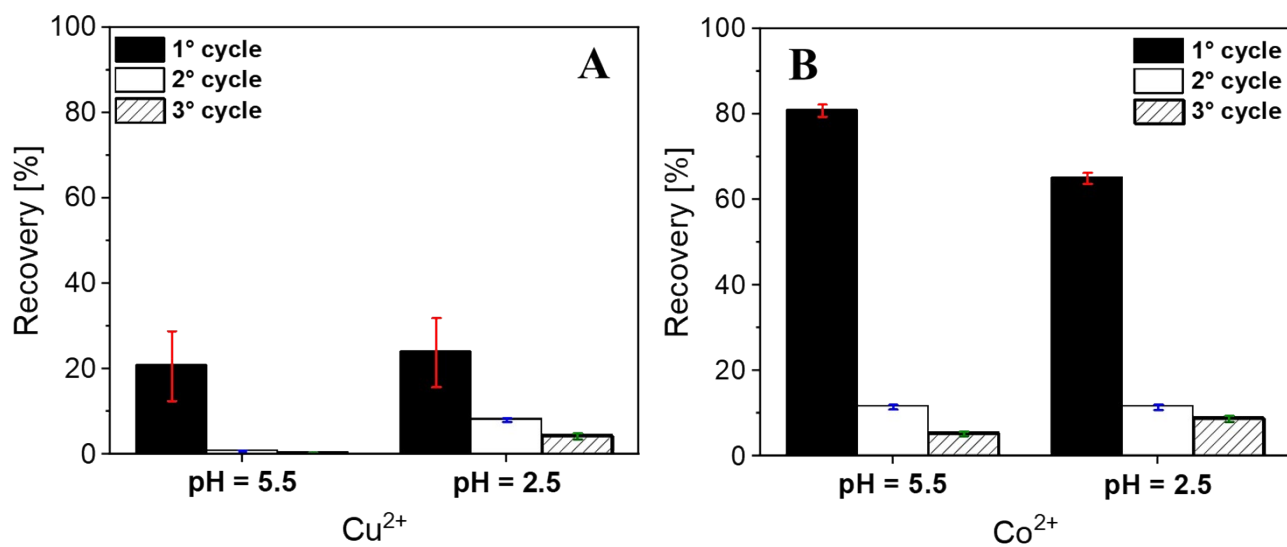


Fig. S5. Cu^{2+} (A) and Co^{2+} (B) release (%) from paramagnetic Na-SAP. The regeneration test was repeated for 3 cycles in saturated NaCl solutions at pH = 5.5 and 2.5.

2) TABLES

pH	Metal Ion	NMR Relaxometry			ICP-OES		
		Uptake [%]	Uptake [mM]	Uptake [mg/g]	Uptake [%]	Uptake [mM]	Uptake [mg/g]
5.5	Gd ³⁺	43.55 ± 2.05	4.19 ± 0.20	32.28 ± 1.52	42.33 ± 2.02	4.11 ± 0.20	31.63 ± 1.50
	Cu ²⁺	51.38 ± 2.49	4.64 ± 0.23	14.57 ± 0.71	55.91 ± 3.01	4.91 ± 0.28	15.42 ± 0.87
	Co ²⁺	51.93 ± 1.61	5.33 ± 0.17	15.41 ± 0.48	58.39 ± 2.98	5.91 ± 0.27	17.07 ± 0.83
3.0	Gd ³⁺	35.18 ± 2.03	3.44 ± 0.20	26.48 ± 1.53	40.04 ± 3.51	3.90 ± 0.34	30.06 ± 2.60
	Cu ²⁺	41.37 ± 3.62	3.88 ± 0.34	12.01 ± 1.05	41.06 ± 3.73	3.82 ± 0.35	11.84 ± 1.09
	Co ²⁺	41.61 ± 1.80	4.27 ± 0.19	12.34 ± 0.53	44.13 ± 4.82	4.52 ± 0.46	13.07 ± 1.40

Tab. S1. Uptake values after 24 h of Gd³⁺, Cu²⁺ and Co²⁺ ions obtained from NMR relaxometric and ICP-OES elemental analyses, expressed as % (respect to the starting concentration of each metal solution), mM and mg/g.

Metal Ion	Ionic Radius (Å)
Gd ³⁺	1.05
Cu ²⁺	0.73
Co ²⁺	0.65

Tab. S2. Ionic radii values of Gd³⁺, Cu²⁺ and Co²⁺ ions.²

	Metal Ion	Total Recovery [%]
Regeneration tests in saturated NaCl solution at pH = 5.5	Gd³⁺	50.6 ± 8.5
	Cu²⁺	22.1 ± 9.8
	Co²⁺	97.9 ± 1.4
Regeneration tests in saturated NaCl solution at pH = 2.5	Gd³⁺	60.2 ± 7.7
	Cu²⁺	36.7 ± 9.0
	Co²⁺	85.6 ± 0.9

Tab. S3. Recovery (%) values for Gd³⁺, Cu²⁺ and Co²⁺ at pH 5.5 and 2.5, calculated by ¹H NMR relaxometry analyses carried out at 10 MHz and 298 K. The regeneration tests were performed in saturated NaCl solutions at pH = 5.5 and 2.5.

3) REFERENCES

1. H. Zhang, D. Pan, X. Duan, *J. Phys. Chem. C*, 2009, **113**, 12140-12148.
2. A) R. D. Shannon, *Acta Cryst.*, 1976, **A32**, 751-767; B) Shriver and P. Atkins, *Inorganic Chemistry* (5th Ed.), Oxford University Press, New York, 2010.