Cleaner synthesis of silylated clay adsorbents for the durable recovery of ions (Co^{2+} and Sr^{2+}) from aqueous solutions

Thomas Thiebault^{†,‡,§,}, Jocelyne Brendlé^{†,‡}, Grégoire Augé^Φ and Lionel Limousy^{†,‡}*

[†]Université de Haute-Alsace; IS2M, CNRS, UMR 7361, 3b Rue Alfred Werner, F68100, Mulhouse, France

[‡]Université de Strasbourg, France

[§]EPHE, PSL University, UMR 7619 METIS (SU, CNRS, EPHE), 4 Place Jussieu, F75005, Paris, France

^ΦONET Technologies, 36 Boulevard de l'Océan, CS 20280, 13258, Marseille Cedex 09, France

To whom correspondence should be addressed. E-mail: thomas.thiebault@ephe.psl.eu Phone: +33(0)144275997

Supporting Information

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Experimental Techniques

X-ray powder diffraction (XRD) patterns of the different samples were recorded on a PANanalytical X'Pert Pro MPD diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and Θ - 2Θ mounting (Bragg-Brentano geometry). Measurements were achieved for 2Θ angles values between 2 and 70° , step $0.17^\circ 2\Theta$, on powdered samples.

Fourier transform infrared (FTIR) measurements in the range $400\text{--}4000 \text{ cm}^{-1}$, were recorded using a Bruker 55 FT-IR spectrometer equipped with Nd:YAG laser operating at 1064 nm and a Ge detector. The analyses were performed in transmission mode and each spectrum was the average of 256 scans collected at 2 cm^{-1} resolution. About 0.01 g of material was mixed with 0.99 g of potassium bromide (KBr) and pelletized with a hydraulic press at 10 kPa during 5 minutes.

Thermogravimetric (TG) analyses were performed on a TG Mettler Toledo STARe apparatus under air flow with a heating rate of 2°C min^{-1} from 30 to 900°C . All samples were air-dried during 48 hours in order to obtain comparable hydration state.

Solid-state ^1H ($I = 1/2$) magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were performed at room temperature on a Bruker Avance II 400 spectrometer operating at $B_0 = 9.4 \text{ T}$ (Larmor frequency $\nu_0 = 400.17 \text{ MHz}$). Single pulse experiment was recorded with a double channel 2.5 mm Bruker MAS probe, a spinning frequency of 30 kHz , a $\pi/2$ flip angle, pulse duration of $3.5 \mu\text{s}$ and a recycling delay of 35 s .

^1H decoupled ^{29}Si MAS and ^1H - ^{29}Si cross polarization (CP)MAS Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance II 400 spectrometer ($B_0 = 9.4 \text{ T}$) operating at 79.460 and 100.484 MHz respectively. Samples were packed in a 7 mm diameter cylindrical zirconia rotor and spun at a spinning frequency of 4 kHz . A $\pi/6$ flip angle, pulse duration of $6.5 \mu\text{s}$, recycle delay of 80 s was used for ^1H decoupled ^{29}Si MAS NMR,

whereas a $\pi/2$ flip angle, pulse duration of 6.5 μ s, contact time of 4 ms and a recycle delay of 10 s were used for CP MAS.

Decompositions of the NMR spectra to extract the proportion of the corresponding species were performed with the DMfit software.¹

Sorption Modeling

The fit of the resulting adsorption isotherms with Langmuir, Freundlich and Dubinin-Radushkevich (DR) equation models drives to numerous thermodynamic parameters allowing one to precisely quantify the affinity of contaminants with the sorbent. Briefly, Langmuir model is expressed by the following equation (Eq.1):

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad \text{Eq.1}$$

Where q_e is the equilibrium amount adsorbed on sorbent (mmol.g⁻¹), C_e the equilibrium concentration in the supernatant (mmol.L⁻¹), q_{max} the adsorption capacity of the sorbents (mmol.g⁻¹) and K_L is the Langmuir adsorption constant (L.mol⁻¹) which is related to the adsorption free energy (ΔG°). The linear Freundlich model equation (Eq.2) is written as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Eq.2}$$

where K_F (L.g⁻¹) and n are the Freundlich constants indicating the extent of the adsorption and the degree of nonlinearity between contaminants and the adsorbent respectively.

The linear expression of the DR model (Eq.3) used to adjust our experimental data is expressed as:

$$\ln q_e = \ln q_{max} + \beta \varepsilon^2 \quad \text{Eq.3}$$

where ε corresponds to the Polanyi potential of which relation including C_e the equilibrium concentration could be found elsewhere. The constant β corresponds to the activity coefficient associated to the mean free energy E (kJ.mol⁻¹) by the equation (Eq.4):

$$E = (2\beta)^{-1/2} \quad \text{Eq.4}$$

This parameter gives information whether the adsorption mechanism involves a chemisorption or physical adsorption. Indeed, if the magnitude of E is below 8 kJ.mol^{-1} , physisorption is envisaged, while for $E > 8 \text{ kJ.mol}^{-1}$ the adsorption process is supposed to follow chemisorption.

Reference: (1) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Calvé, S. L.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. Modelling One- and Two-Dimensional Solid-State NMR Spectra. *Magnetic Resonance in Chemistry* **2002**, *40* (1), 70–76. <https://doi.org/10.1002/mrc.984>.

Table S1. General information about grafting agent, 3-aminopropyltriethoxysilane (APTES)

Structure
Formula	C₉H₂₃NO₃Si
CAS-Number	919-30-2
Molar mass	221.37 g mol ⁻¹

Table S2. Quantitative data of APTES grafted on Lap extracted from TG curves (Fig. S1)

Samples	OM content %	APTES content mmol.g ⁻¹	Grafting yield %	Edge-site occupation CE _{edges}
Gly30	3.5	0.31	35.3	0.86
Gly60	3.8	0.32	36.2	0.88
Gly90	4.3	0.36	41.5	1.01
Phe30	1.5	0.13	14.4	0.35
Phe60	7.2	0.59	67.8	1.65
Phe90	7.6	0.62	70.7	1.72

Table S3. Intensity ratios obtained from the deconvolution of ^{29}Si NMR spectra

Material	Q^3/Q^2	T^3/T^2	ΣT	$\Sigma Q/\Sigma T$
Lap	10.2	-	0	-
Gly30	23.2	0.22	10.1	8.9
Gly60	24.5	0.22	7.1	13.1
Gly90	30.5	0.22	6.4	14.6
Phe30	21.1	0.07	3.3	28.9
Phe60	51.0	0.46	13.1	6.6
Phe90	95.2	0.70	11.2	7.9

Table S4. Single-solute (S) and Bi-solute (B) adsorption model parameters derived from Langmuir, Freundlich and D-R equations for the adsorption of Sr^{2+} and Co^{2+} onto silylated Lap in various synthesis conditions

			Langmuir				Freundlich			Dubinin-Radushkevich		
			$Q_{\max}$ mmol.g^{-1}	K_L L.mmol^{-1}	ΔG° kJ.mol^{-1}	r^2	n	K_F L.g^{-1}	r^2	$Q_{\max}$ mmol.g^{-1}	E kJ.mol^{-1}	r^2
Co^{2+}	Gly30	S	0.547	2.949	-19,47	0.941	5.441	0.474	0.963	0.419	8.771	0.704
		B	0.527	12.76	-23,04	0.970	9.208	0.422	0.875	0.333	18.26	0.835
	Gly60	S	0.841	37.97	-25,70	0.996	3.045	0.845	0.751	0.952	8.452	0.893
		B	0.603	81.28	-27,55	0.993	2.441	0.416	0.974	0.834	8.639	0.832
	Gly90	S	0.493	17.33	-23,79	0.999	12.17	0.441	0.933	0.458	11.18	0.919
		B	0.567	15.48	-23,51	0.987	9.363	0.453	0.861	0.502	6.868	0.877
	Phe30	S	0.642	2.160	-18,71	0.881	4.179	0.493	0.969	0.434	7.071	0.812
		B	0.529	16.73	-23,70	0.883	6.998	0.454	0.924	0.369	12.91	0.750
	Phe60	S	0.898	11.66	-22,82	0.994	12.14	0.747	0.953	0.857	18.26	0.907
		B	0.816	176.1	-29,44	1.000	6.527	1.054	0.948	0.786	14.14	0.907
	Phe90	S	0.740	10.75	-22,62	0.994	12.27	0.617	0.937	0.621	15.81	0.812
		B	0.661	63.04	-26,94	0.997	12.90	0.608	0.892	0.627	11.04	0.942
Sr^{2+}	Gly30	S	0.455	3.107	-19,60	0.961	4.488	0.350	0.954	0.336	6.250	0.930
		B	0.241	19.39	-24,06	0.998	6.954	0.227	0.781	0.235	7.071	0.886
	Gly60	S	0.563	8.233	-21,97	0.998	2.525	0.444	0.922	0.497	5.608	0.979
		B	0.348	13.32	-23,15	0.974	2.941	0.900	0.865	0.222	8.771	0.933
	Gly90	S	0.508	4.797	-20,66	0.993	4.331	0.375	0.997	0.423	5.300	0.906
		B	0.283	19.13	-24,03	0.998	4.929	0.257	0.948	0.265	6.041	0.979
	Phe30	S	0.392	2.303	-18,87	0.910	3.971	0.315	0.907	0.299	5.717	0.970
		B	0.201	5.016	-20,77	0.976	6.266	0.165	0.999	0.205	3.748	0.798
	Phe60	S	0.703	4.700	-20,61	0.997	3.293	0.514	0.957	0.000	4.683	0.915
		B	0.483	7.586	-21,77	0.998	2.970	0.431	0.970	0.426	5.051	0.951
	Phe90	S	0.624	4.746	-20,63	0.997	3.640	0.456	0.986	0.520	4.880	0.901
		B	0.361	9.581	-22,34	1.000	3.477	0.330	0.933	0.344	5.077	0.992

Figure S1. TG curves of Lap and silylated-Laps for different synthesis solvents and temperatures.

Figure S2. FTIR spectra of Lap and silylated Lap for different synthesis solvents and temperatures for wavenumbers between 400 and 1600 cm^{-1} (B) and between 2500 and 3700 cm^{-1} (A).

Figure S3. Bi-solute adsorption isotherms of Sr^{2+} onto silylated-Laps synthesized in different conditions, dashed dark lines marks the Langmuir fits.

Figure S4. Bi-solute adsorption isotherms of Co^{2+} onto silylated-Laps synthesized in different conditions, dashed dark lines marks the Langmuir fits.

Figure S5. Adsorbed amount of Co²⁺ (orange circles) and Sr²⁺ (blue circles) in single solute adsorption experiments as a function of the APTES content of adsorbent derived from TG analyses.