Supplementary materials

Mesoporous Nano-titania with Grafted Amino Phosphonate Functions, its Molecular Structure and Potential for Extraction of Rare Earth Elements

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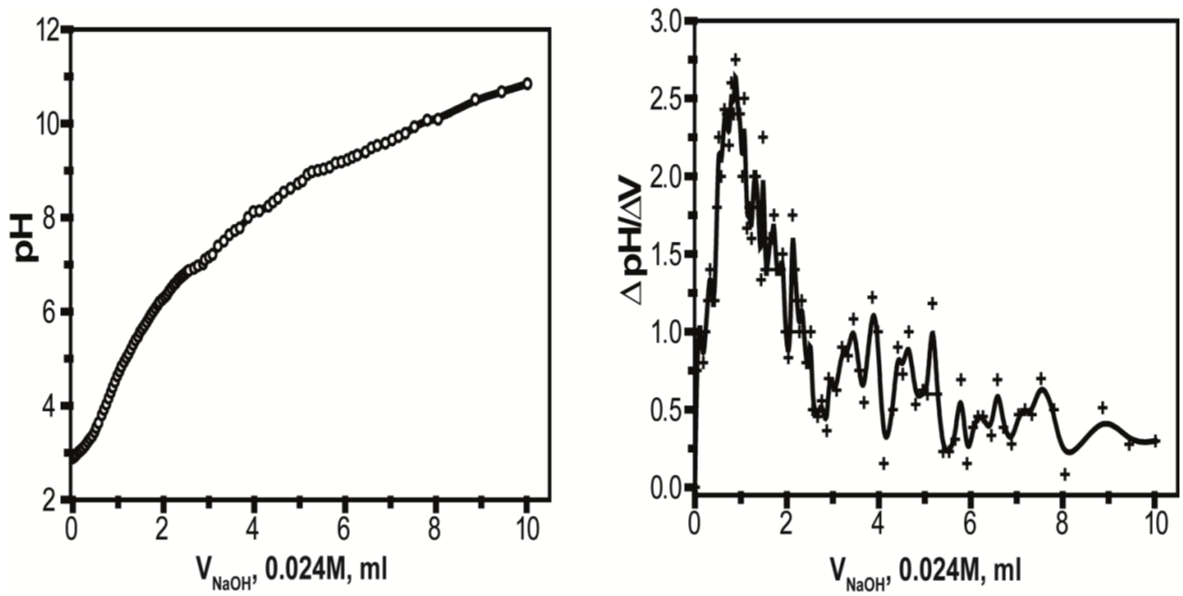
Table TS1 EDX analysis, L:Ln^{3+} ratio, SSC and the distribution coefficient (Q, as calculated from sorption isotherms)

Sample	Content of chemical elements (%, wt.)		Funct.gr./Ln^{3+}	SSC mg/g	Q cm^3/g
	P	Ln			
TiO_2-IMPA/Y	2.7	0.9	4.3	16	1480
TiO_2-IMPA/La	2.2	2.3	2.1	32	2420
TiO_2-IMPA/Nd	3.5	3.8	2.1	30	2400
TiO_2-IMPA/Dy	3.0	5.4	1.5	39	2350
TiO_2-AEPA/Y	1.1	0.1	31.5	4	400
TiO_2-AEPA/La	0.4	0.85	2.1	8	400
TiO_2-AEPA/Nd	0.8	1.1	3.3	9	400
TiO_2-AEPA/Dy	0.7	1.2	3.1	14	1430

Figure FS1 The curve of potentiometric titration (a) and differential curve (b) of TiO_2-IMPA sample (0.024M NaOH; ion background – 0.1M $NaNO_3$).



The caution has to be taken even considering the data of potentiometric titration, which has been carried out for both the individual ligands (amino phosphonic acids) and for the samples with grafted ligands on the surface. It is important to note that amino phosphonic acids exist in solution apparently in the form of salts resulting from self-protonation – the proton transfer from the acidic function to the basic center existing due to the presence of an NH_2 or NH groups in the structure.

The AEPA ligand is characterized by relatively low acidity (pH = 3.96 for 0.008 M solution) making the results of potentiometric measurements uncertain. In contrast, IMPA has two phosphonic acid functions per one NH-center in its molecule, granting lower pH for its water solution, 2.18 for 0.008 M concentration, which facilitates the measurements. However, even in this case it turned quite difficult to estimate the number of available functional groups as no distinct steps otherwise typical for titration of weak acids could be clearly identified in this case (Figure FS1a). The more apparent equivalence point can be deduced from the differential curve

(Figure FS1b), which permits to evaluate the content of acidic functions to be 0.3 mmol/g. Assuming that the surface grafting should enhance the acidity of two phosphonate functions this result was divided by 2 to obtain the ligand content displayed in **Tab. 2** for the TiO_2-IMPA sample (0.15 mmol/g).

Figure FS2 ^{31}P NMR spectra of TiO2-AEPA adsorbent in free and Y- and La-bound forms respectively

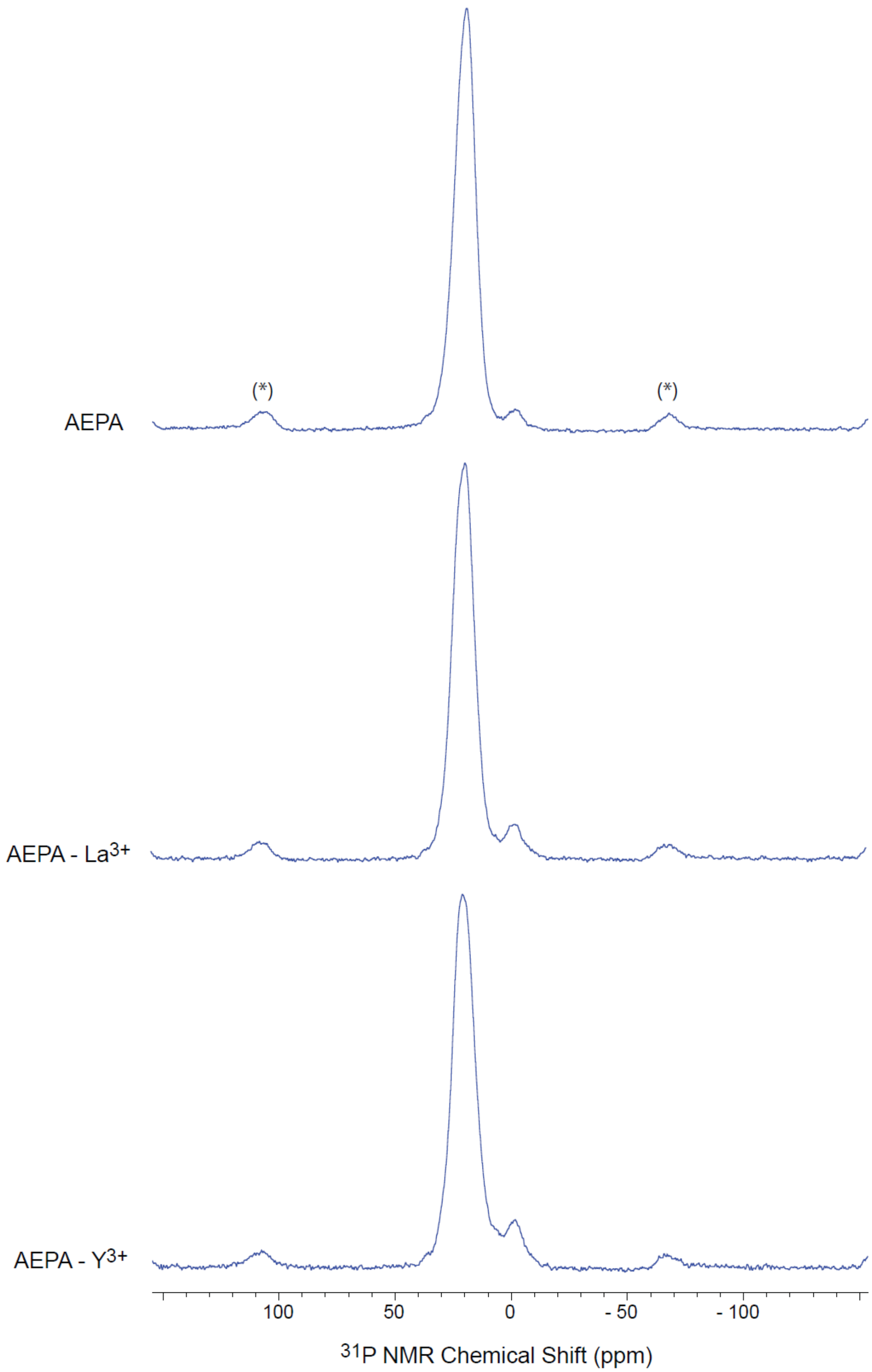


Figure FS3 ^{31}P NMR spectra of TiO2-IMPA adsorbent in free and Y- and La-bound forms respectively

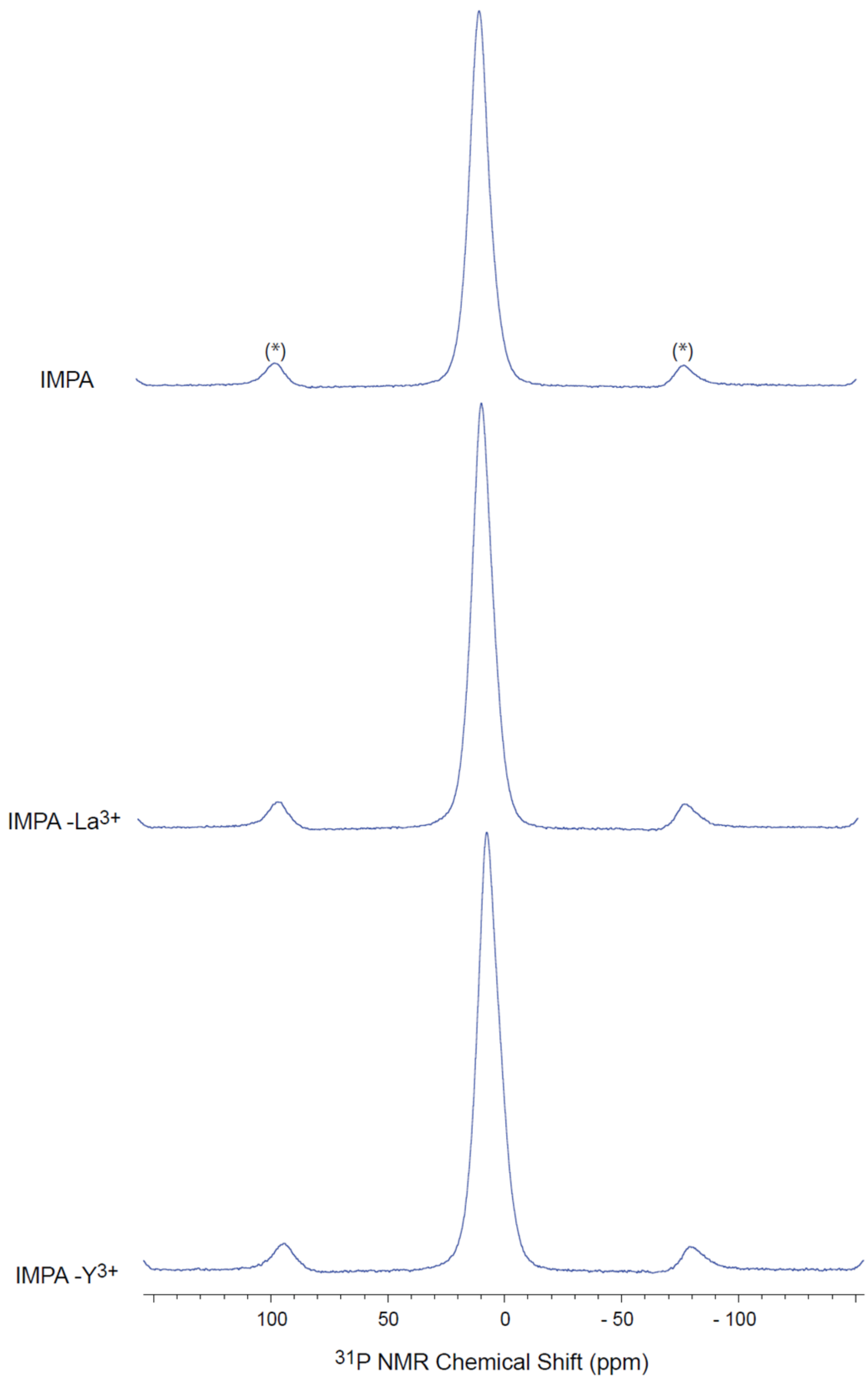


Figure FS4 Comparison of the ^{31}P NMR spectra of TiO_2-AEPA and TiO_2-IMPA

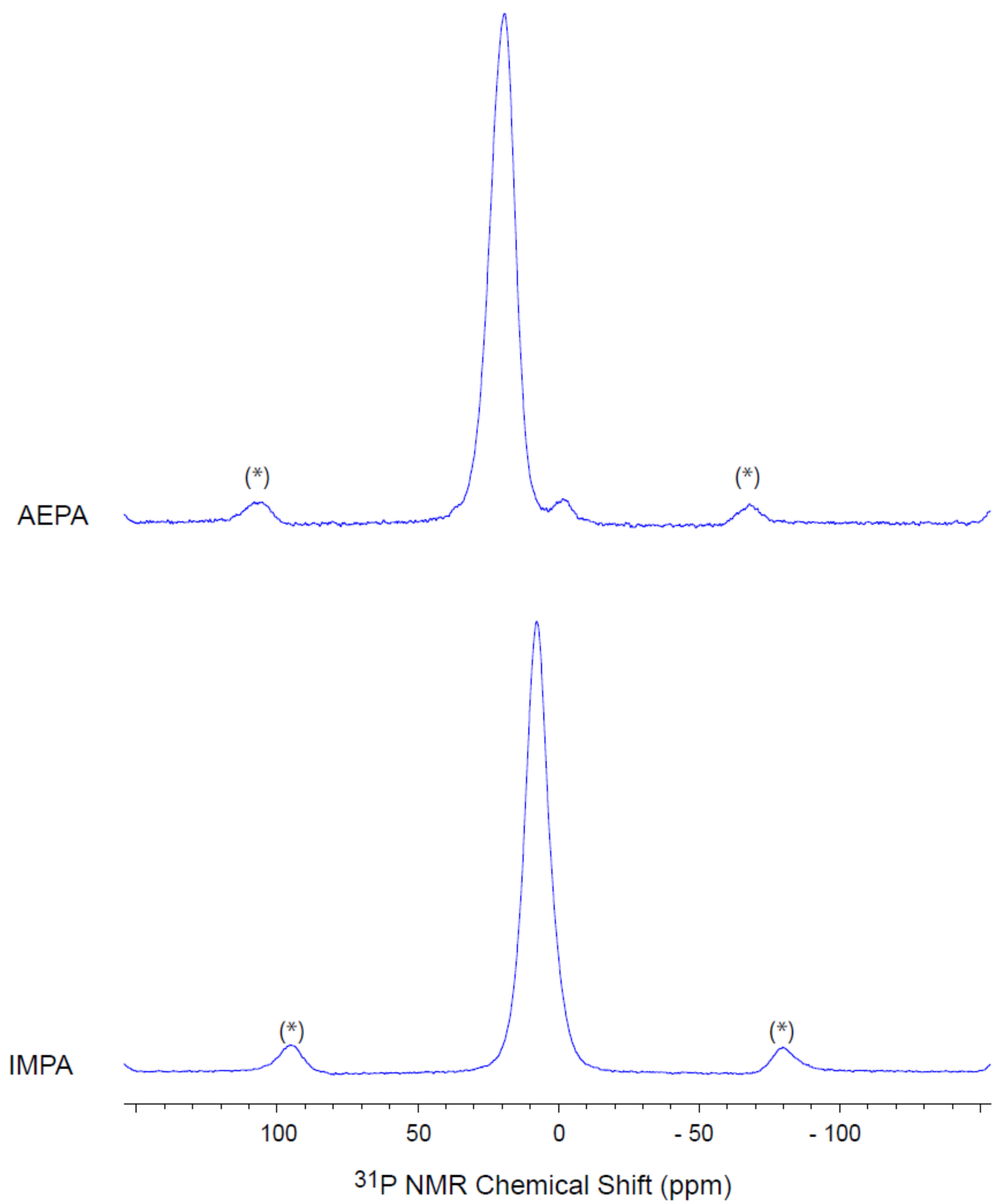


Figure FS5 Solution ^{31}P spectrum of $Ti_4O(OEt)_{12}(O_3P^tBu)$ (1)

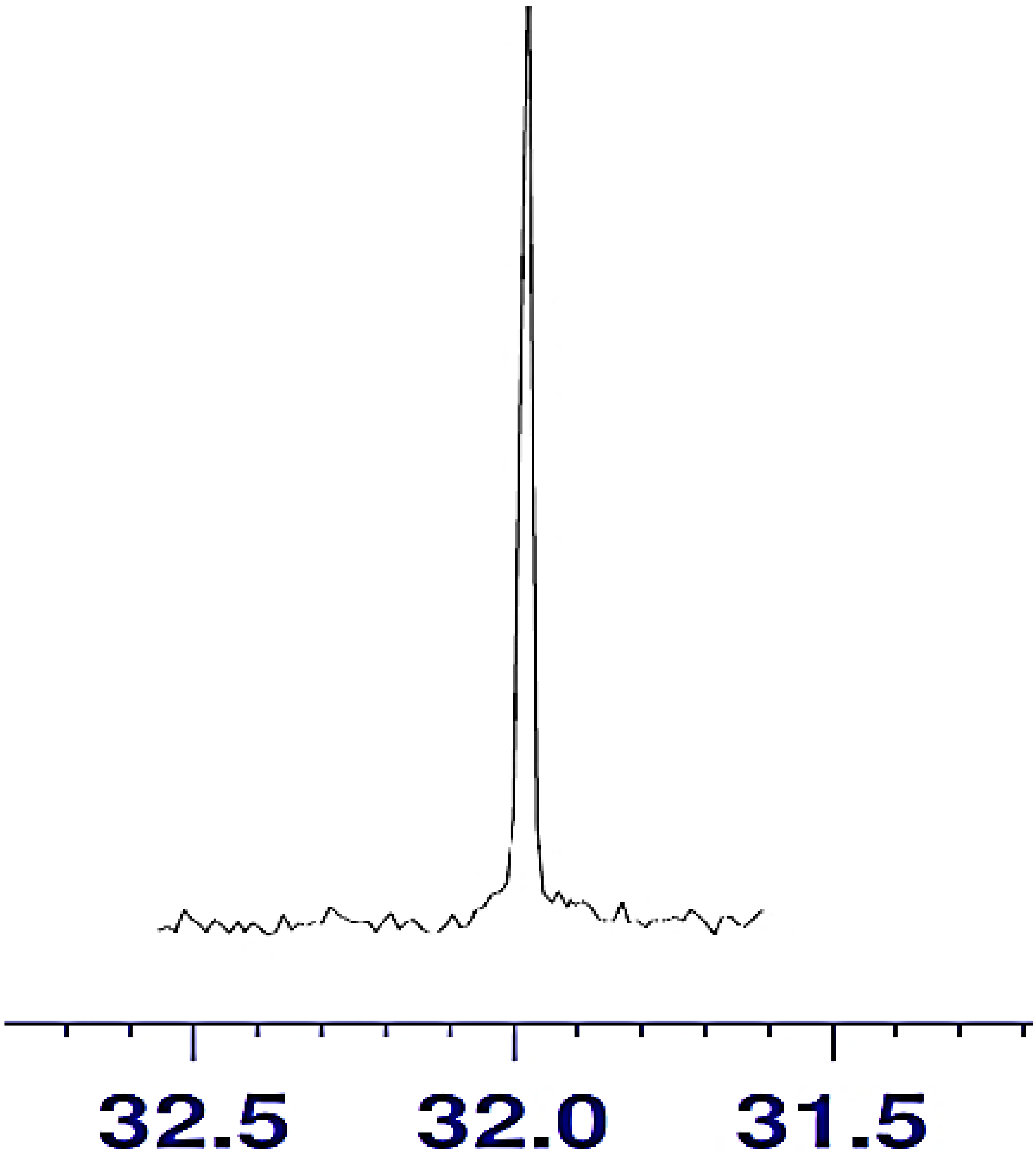


Table TS2. Sorption of Ln^{3+} ions by TiO_2-IMPA sample

No Point	C_M before sorption, mmol/l	C_M after sorption, mmol/l	M^{3+} adsorbed, mmol/g (mmol/l)	pH after sorption	C_{H^+} after sorption, mmol/l	$C_{H^+} : M^{3+}_{adsorbed}$	$M^{3+}_{adsorbed} : C_{f.g.}$
Nd^{3+}							
1	0.1	0	0.04 (0.1)	3.05	0.89	8.9	0.24
2	0.175	0.025	0.06 (0.15)	3	1	6.7	0.35
3	0.25	0.025	0.09 (0.23)	2.96	1.09	4.9	0.53
4	0.325	0.075	0.1 (0.25)	2.91	1.23	5.0	0.59
5	0.475	0.1	0.15 (0.38)	2.84	1.45	3.9	0.88
6	0.925	0.425	0.2 (0.5)	2.79	1.62	3.2	1.18
7	1.375	0.8625	0.21 (0.51)	2.77	1.7	3.3	1.24
8	1.85	1.325	0.21 (0.52)	2.72	1.9	3.6	1.24
Dy^{3+}							
1	0.09	0	0.03 (0.09)	3.06	0.87	10.1	0.18
2	0.172	0.025	0.06(0.15)	3.02	0.95	6.5	0.35
3	0.215	0.05	0.07(0.17)	2.96	1.09	6.6	0.41
4	0.279	0.075	0.08(0.21)	2.96	1.09	5.3	0.47
5	0.43	0.075	0.14(0.36)	2.88	1.32	3.7	0.82
6	0.86	0.363	0.20(0.50)	2.85	1.41	2.8	1.18
7	1.29	0.713	0.23(0.58)	2.8	1.58	2.7	1.35
8	1.72	1.125	0.24(0.59)	2.79	1.62	2.7	1.41
Y^{3+}							
1	0.09	0.025	0.03 (0.06)	3.12	0.76	12.1	0.18
2	0.176	0.0375	0.06(0.14)	3.04	0.91	6.6	0.35

3	0.22	0.0375	0.07(0.18)	3.01	0.98	5.4	0.41
4	0.286	0.075	0.08 (0.21)	3.02	0.95	4.5	0.47
5	0.418	0.125	0.12(0.29)	2.96	1.09	3.7	0.7
6	0.858	0.5	0.14 (0.36)	2.86	1.38	3.9	0.82
7	1.32	0.888	0.17(0.43)	2.83	1.48	3.4	1.0
8	1.716	1.263	0.18(0.45)	2.85	1.41	3.1	1.06
La^{3+}							
1	0.088	0	0.04(0.09)	3.13	0.74	8.4	0.24
2	0.176	0.025	0.06 (0.15)	3.08	0.83	5.5	0.35
3	0.22	0.0375	0.07(0.18)	3.07	0.85	4.7	0.41
4	0.286	0.0625	0.09(0.22)	3	1	4.5	0.53
5	0.418	0.125	0.12(0.29)	3	1	3.4	0.7
6	0.858	0.4	0.18(0.46)	2.9	1.26	2.8	1.06
7	1.32	0.775	0.22(0.55)	2.86	1.38	2.5	1.29
8	1.716	1.138	0.23 (0.58)	2.89	1.29	2.2	1.35

Table TS3. Sorption of Ln^{3+} ions by TiO_2-AEPA sample.

No Point	C_M before sorption, mmol/l	C_M after sorption, mmol/l	M^{3+} sorbed, mmol/g (mmol/l)	pH after sorption	C_{H^+} after sorption, mmol/l	C_{H^+} : M^{3+}_{sorbed}	M^{3+}_{sorbed} : $C_{f.g.}$
Nd^{3+}							
1	0.05	0.013	0.015(0.037)	4.36	0.044	1.2	0.07
2	0.1	0.025	0.03(0.075)	4.38	0.042	0.6	0.14
3	0.13	0.05	0.03(0.075)	4.16	0.07	0.96	0.14
4	0.17	0.087	0.035(0.083)	4.02	0.095	1.1	0.17

5	0.25	0.138	0.045(0.112)	3.98	0.1	0.9	0.21
6	0.5	0.363	0.055(0.137)	3.88	0.13	0.95	0.26
7	0.75	0.6	0.06(0.15)	3.78	0.17	1.15	0.29
8	1.0	0.844	0.062(0.156)	3.8	0.16	1.02	0.3
Dy^{3+}							
1	0,0645	0	0,026(0,065)	4,53	0.03	0.47	0.12
2	0,086	0,0125	0,029(0,074)	4,19	0.06	0.82	0.14
3	0,129	0,025	0,042(0,1)	4,08	0.08	0.77	0.2
4	0,172	0,0375	0,054(0,135)	3,99	0.1	0.74	0.26
5	0,258	0,1125	0,058(0,146)	3,85	0.14	0.96	0.28
6	0,516	0,3	0,086(0,216)	3,8	0.16	0.74	0.41
7	0,753	0,5375	0,086(0,215)	3,74	0.18	0.84	0.41
8	0,989	0,77375	0,086(0,215)	3,67	0.21	0.98	0.41
Y^{3+}							
1	0.044	0.025	0.008(0.019)	4.51	0.031	1.63	0.04
2	0.088	0.038	0.028(0.051)	4.37	0.043	0.85	0.13
3	0.132	0.075	0.023(0.057)	4.29	0.051	0.89	0.11
4	0.176	0.088	0.035(0.089)	4.18	0.066	0.75	0.17
5	0.264	0.163	0.041(0.102)	4.13	0.074	0.73	0.2
6	0.506	0.4	0.042(0.106)	4.02	0.095	0.9	0.2
7	0.77	0.663	0.043(0.108)	3.94	0.11	1.02	0.2
8	0.99	0.875	0.046(0.115)	3.91	0.12	1.04	0.22
La^{3+}							
1	0.044	0.025	0.008(0.019)	4.59	0.026	1.37	0.04

2	0.088	0.0375	0.02(0.051)	4.43	0.037	0.74	0.1
3	0.132	0.075	0.023(0.057)	4.33	0.047	0.83	0.11
4	0.176	0.0875	0.035(0.089)	4.33	0.047	0.54	0.17
5	0.264	0.175	0.036(0.089)	4.18	0.066	0.75	0.17
6	0.506	0.3625	0.057(0.144)	4.05	0.089	0.63	0.27
7	0.77	0.625	0.058(0.145)	4.07	0.085	0.59	0.27
8	0.99	0.84375	0.059(0.146)	4.05	0.089	0.61	0.28