Electronic Supporting Information-ESI-EM-ART-07-2013-000389: Verma et al.

Influences of different environmental parameters on sorption of trivalent metal ions on bentonite: Batch Sorption, Fluorescence, EXAFS and ESR Studies

P.K. Verma[1], P.N. Pathak[1*], P.K. Mohapatra[1], S.V. Godbole[1], R.M. Kadam[1]

A.A. Veligzhanin[2], Y.V. Zubavichus[2], S.N. Kalmykov[3]

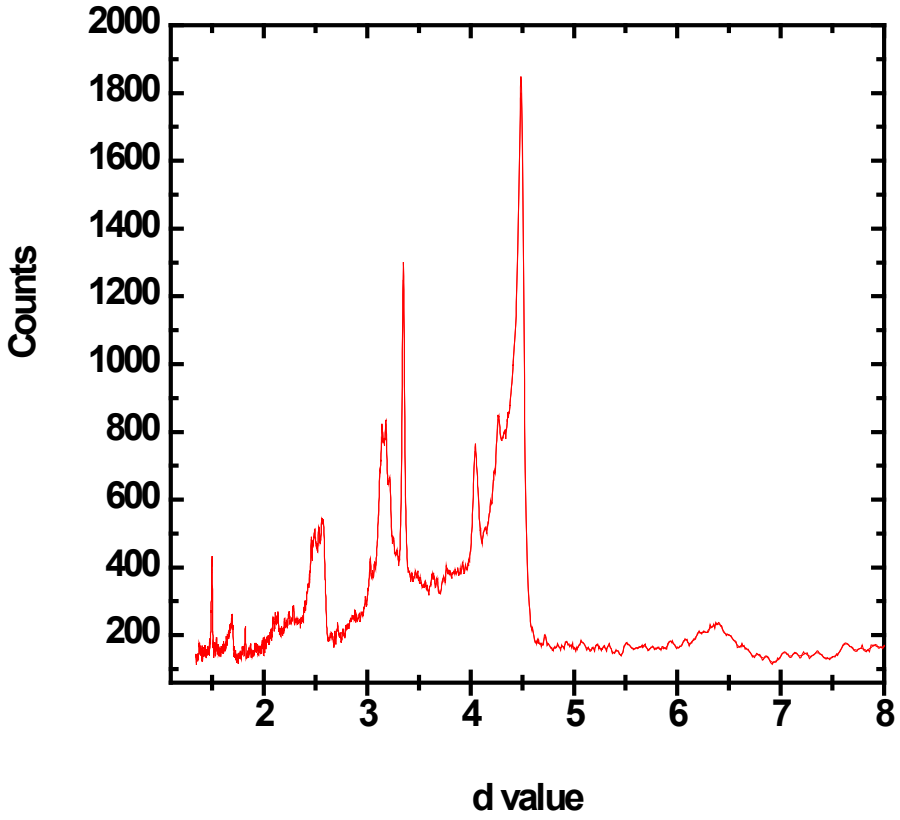
[1]Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai – 400 085, INDIA
[2]NRC "Kurchatov Institute", Acad. Kurchatov sq. 1, Moscow 123182, RUSSIA
[3]Radiochemistry Division, Chemistry Department of Lomonosov Moscow State University, Leninskie Gory, Moscow 119991, RUSSIA

ESI 1: Details of EXAFS facility, samples and measurements

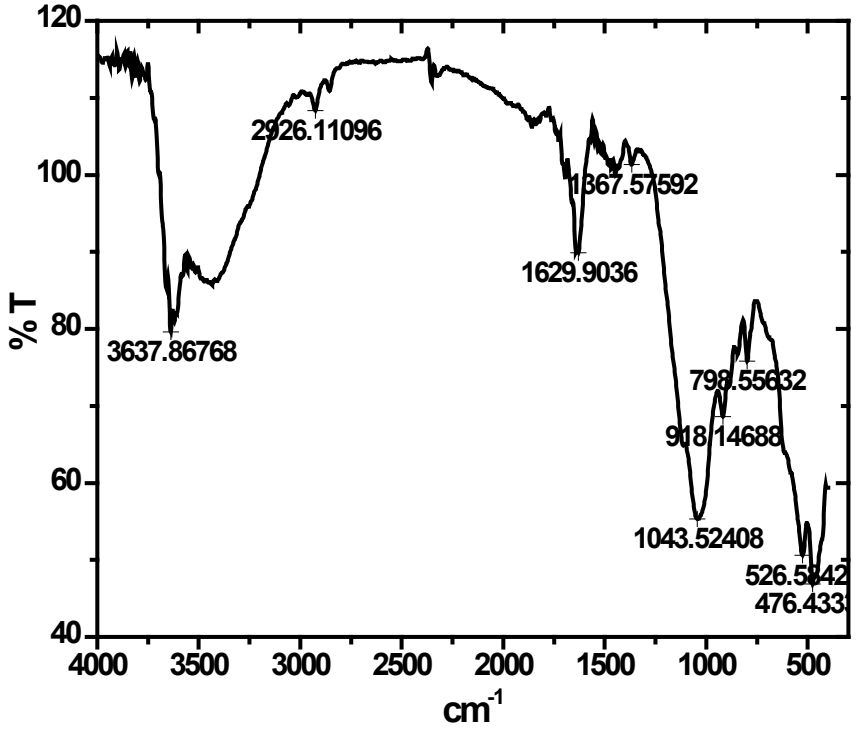
The measurements were performed in the fluorescence yield mode with a Si avalanche photodiode as a fluorescence detector and an ionization chamber as an incident beam intensity monitor. For the measurements, wet slurry of each bentonite sample was spread over an ash-less filter paper. The measurements were performed at the Eu L_2-edge (E_0~7617 eV) since Eu L_3-edge spectra (E_0~6977 eV) appeared to be spoiled by the occurrence of Fe K-edges (E_0~7120 eV) due to the presence of iron in bentonite. The series of samples measured included (a) $1x10^{-4}$ M Eu(III) in bentonite suspension (1 g/L) at pH 3, 5 and 8 and I = 0.01 M ($NaClO_4$), (b) $1x10^{-4}$ M Eu(III) + $1x10^{-4}$ M CA in bentonite suspension (1 g/L) at pH 4, and I = 0.01 M (NaClO4), and (c) $1x10^{-4}$ M Eu(III) + $1x10^{-4}$ M HA in bentonite suspension (1 g/L) at pH 4, and I = 0.01 M ($NaClO_4$). The EXAFS spectra were processed with Athena and Artemis software codes from the IFEFFIT package. The multisphere fitting of normalized EXAFS curves $\chi(k)$ was performed in the photoelectron wave number range k 2.0–10.0 $Å^{-1}$ (the range available is limited by the

occurrence of Eu L_1-edge) with the k^2 weighting scheme using the photo-electron theoretical phases and scattering amplitudes calculated by FEFF.

ESI 2: Characterization of raw bentonite by XRD (2(a)) and FTIR (2(b))



ESI 2(a): Powder XRD data (in d values) of raw bentonite



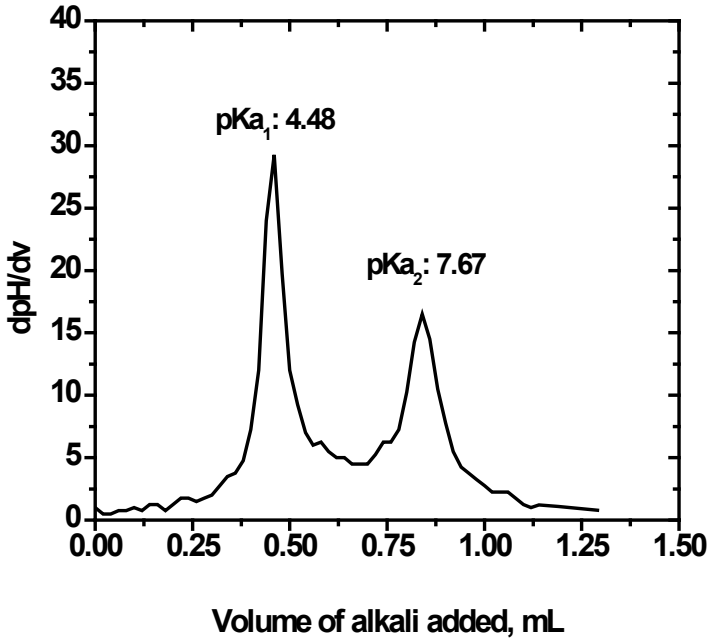
ESI 2(b): FTIR of raw bentonite in KBr pellet

Bond	Mode	Frequency, cm^{-1}	References
Quartz	---	459.07,798.56 (1085,797,778,694,511,460)	
Si-O-Si	Stretching	476.43	
Al-O-Si	Stretching	524.66	**[1-3]**
Al-Al-OH	Stretching	918.15	
Si-O	In plane bending	1043.52	
Si-O	Out of plane	1112.96	
H_2O	bending	1629.90	
H_2O in Benonite	Bending	3406.40	
H_2O in Benonite	Stretching	3637.86	

References:

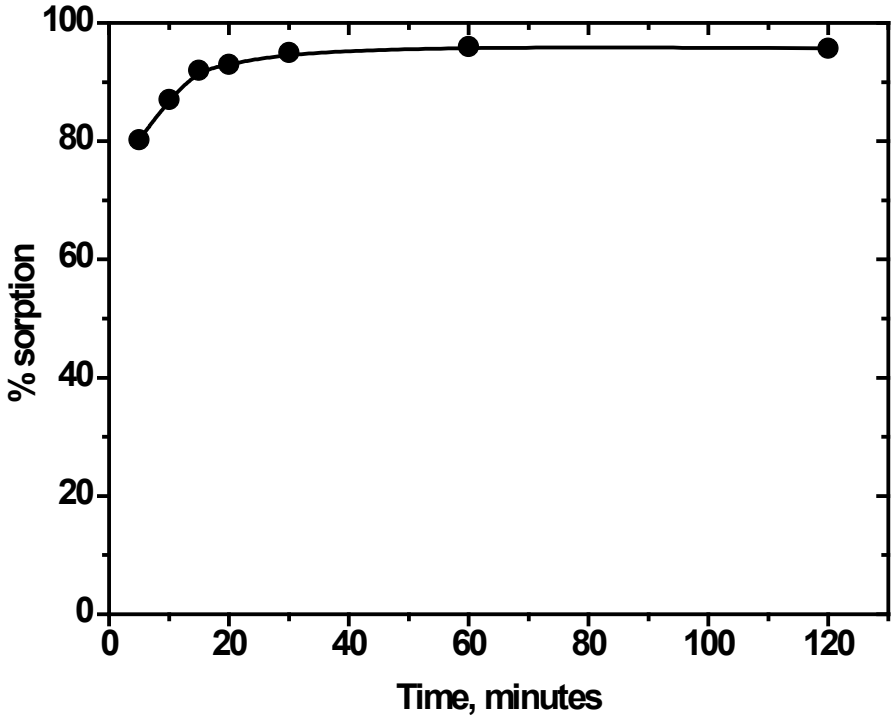
1. J. Madejova, FTIR techniques in clay mineral studies, *Vibrational Spectroscopy*. **2003**, 31, 1–10.
2. S. Wang, Y. Dong, Characterization of GMZ bentonite and its application in the adsorption of Pb(II) from aqueous solutions. *Applied Clay Science*. **2009**, 43, 164-171.
3. Lu Songsheng, Xu Hua, Sorption of Eu(III) on gaomiazi bentonite by batch technique as a function of pH, Ionic strength, and humic acid, *J. Radioanal. Nucl. Chem.* **2012**, 292, 889-895.

ESI 3: Potentiometric titrations of humic acid



ESI 3:Variation of pH of humic acid solution with the addition of stanadard alkali (0.067 M NaOH) *I* : 0.01 M $NaClO_4$;T - 298 K)

ESI 4: Sorption kinetics



ESI 4: Kinetics of sorption of Eu(III) on bentonite at pH = 4 +0.05; Bentonite = 1g/L; *I* = 0.01 M ($NaClO_4$); T = 298 K

ESI 5: Gran plot and calculation details

The values of the Gran function (G) were calculated as:[32] *(refers to 32 no. reference of manuscript)*

On the acidic side: $G_a = (V_0 + V_{at} + V_b) \cdot 10^{-pH} \cdot 100$ *(1)*

On the alkaline side: $G_b = (V_0 + V_{at} + V_b) \cdot 10^{-(13.8-pH)} \cdot 100$ *(2)*

where, V_0 is the initial volume of the bentonite suspension, and V_{at} and V_b are the total volumes of acid solution and of hydroxide ions (OH^-) added at the different titration points, respectively. As the bentonite suspension was acidified before the alkali titration, the OH^- added to the suspensions were consumed in the following three steps as shown in the Gran plot:

(a) neutralization of excess H^+ in the suspension (before V_{eb1}),

(b) reactions with the various surfaces active groups (between V_{eb1} and V_{eb2}), and

(c) contributing to the system pH (after V_{eb2}).

The specific volumes, V_{eb1} and V_{eb2}, could be obtained from the linear regression analysis of the Gran plots. The V_{eb1} could be considered as the point the zero titration (The point before which there were no surface reactions consuming OH^- except simple acid–base neutralization of additional protons). The 'TOTH' was calculated using the following relation:

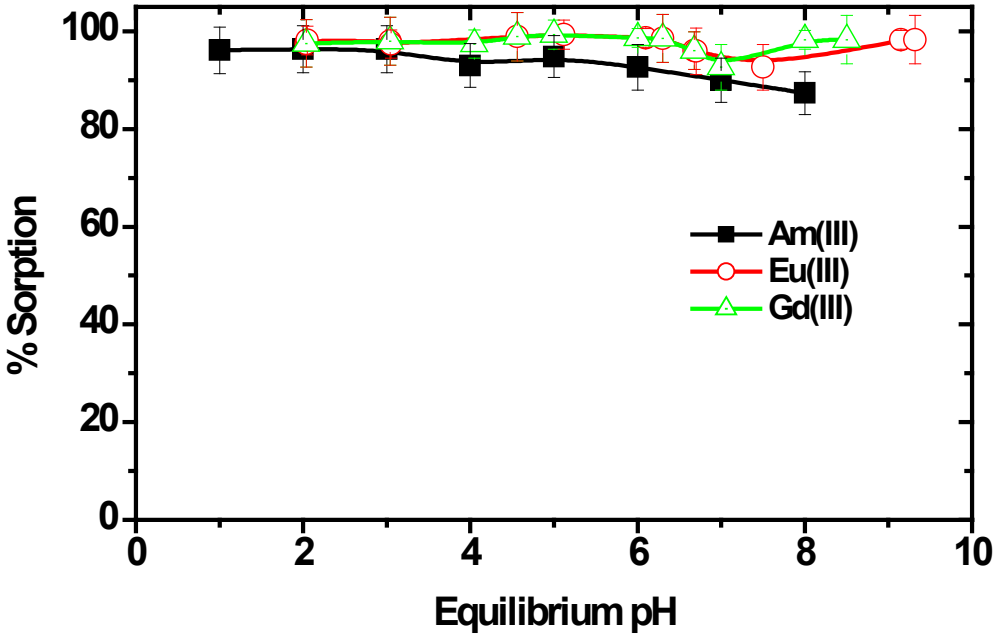
$$TOTH = -(V_b - V_{eb1}) \times C_b / (V_0 + V_{at} + V_b)\ (mol/L), \quad (3)$$

Where, C_b is the concentration of standard NaOH.

The data points from the hydroxide titration curve commencing after the point of zero charge calibration, were utilized in a nonlinear least-squares optimization program (FITEQL 4.0) to estimate the surface acidity constants.[34] The surface site concentration (H_S) was also derived from Gran plot using two equivalent points in the Gran plots, as given by the following equation:[32]

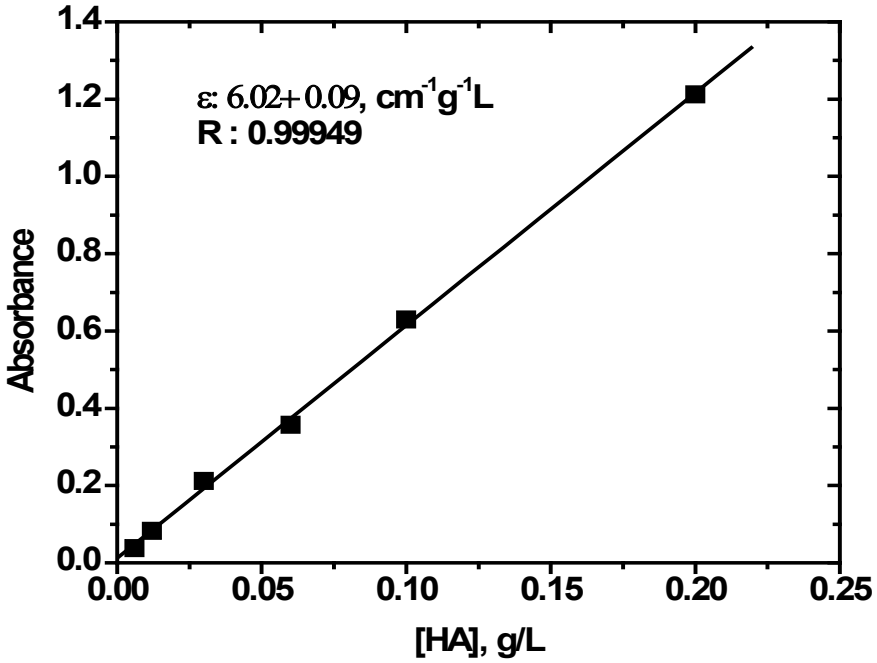
$$H_S = (V_{eb2} - V_{eb1})_{sample} \times C_b - (V_{eb2} - V_{eb1})_{blank} \times C_b \, V_0 \; (mol/L). \qquad (4)$$

ESI 6: Sorption profiles of different trivalent metal ions on to bentonite



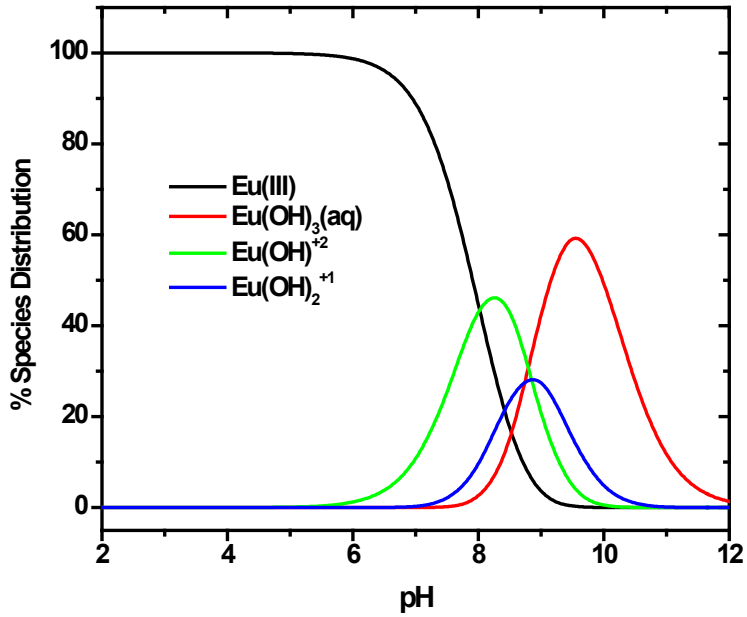
ESI 6: Sorption profile of tracer concentrations of different metal ions as a function of pH; [Bentonite]: 1 g/L; I: 0.01 M ($NaClO_4$); T: 298 K

ESI 7: Calibration plot for quantification of sorption of humic acid onto suspended bentonite

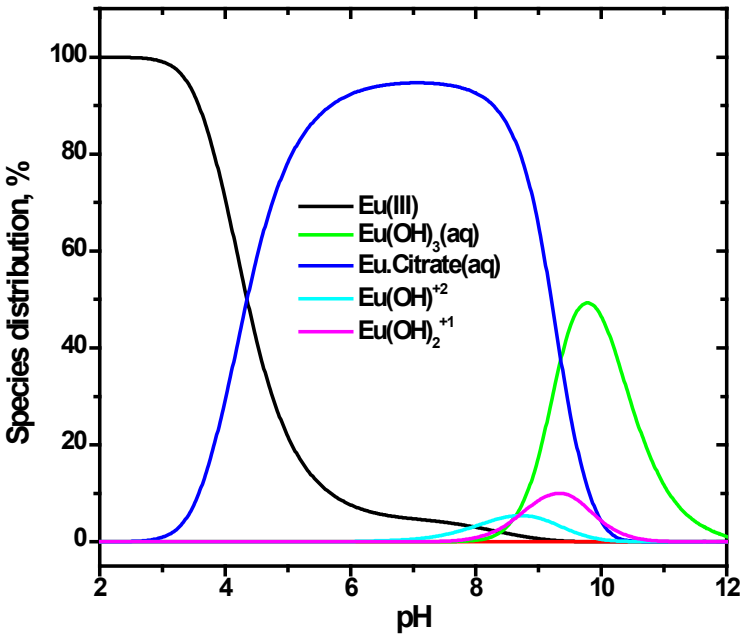


ESI 7: : Calibration plot for HA estimation by spectrophotometry ; λ_{max}: 400 nm

ESI 8: Species distribution of Eu(III) in the presence of citrate ion as a function of pH (curves generated by Visual Minteq 3.0 Software using inbuilt data base)

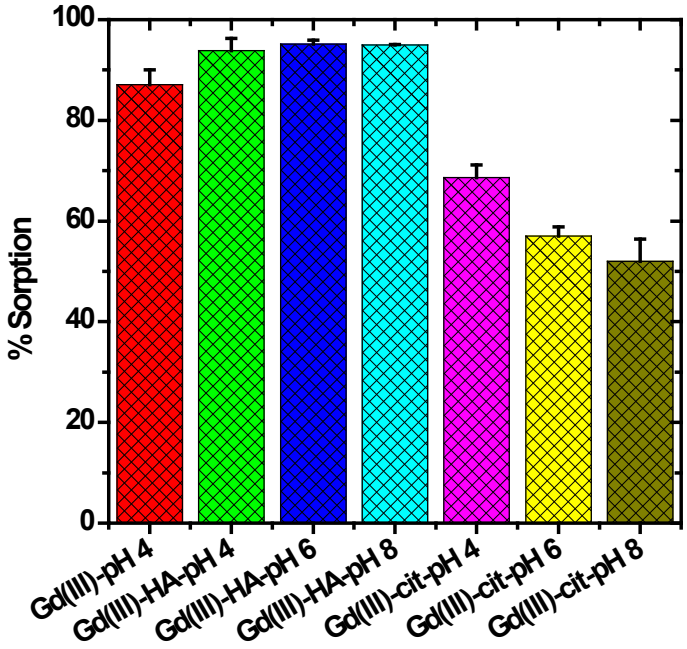


ESI 8(a): Speciation calculation of Eu(III) as a function of pH; [Eu(III)]: 10^{-5} M; I: 0.01 M ($NaClO_4$)



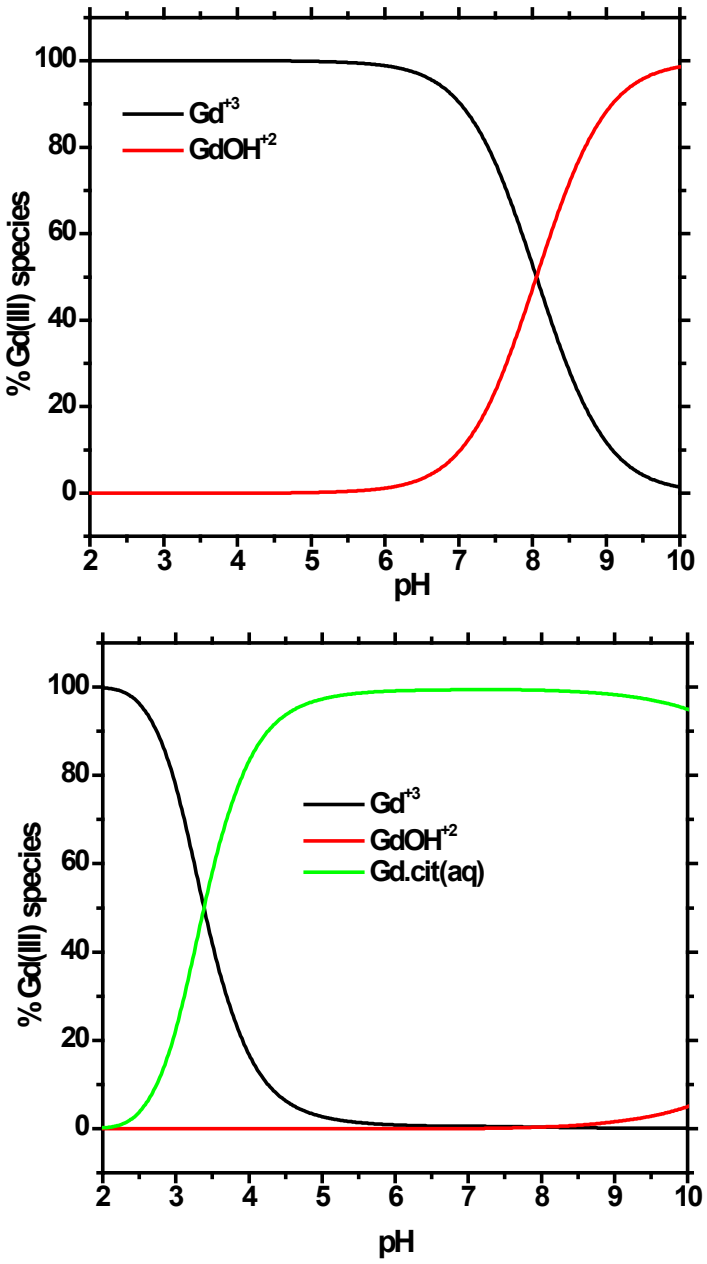
ESI 8(b): Speciation calculation of Eu(III) in the presence of citric acid; [Eu(III)]: 10^{-5} M; [cit]: 10^{-4} M; I: 0.01 M ($NaClO_4$)

ESI 9: Gd(III) sorption on bentonite in the presence of humic and citric acids



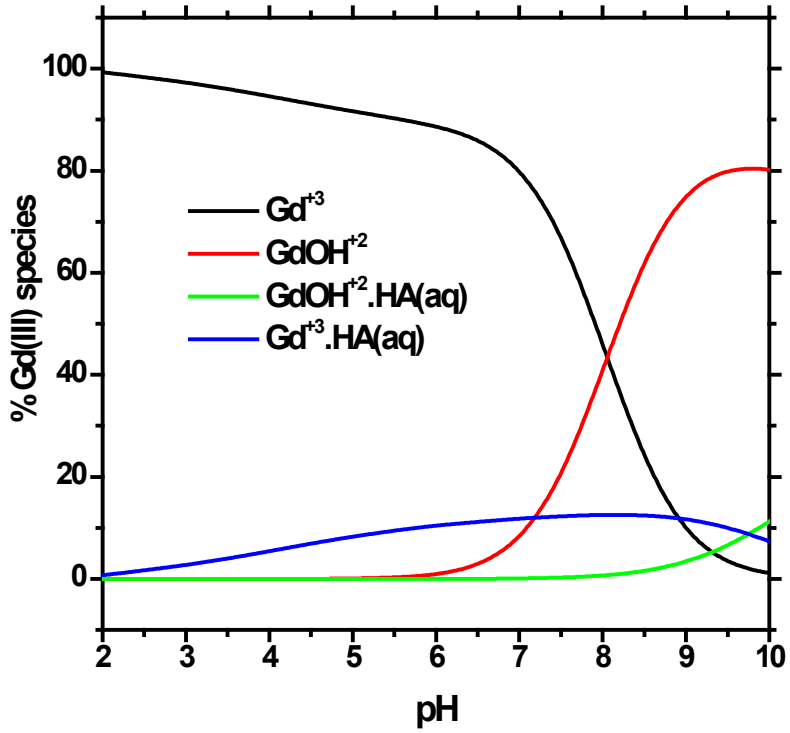
ESI 9: Sorption of Gd(III) on bentonite in the presence of diffrent ligands; [Gd(III)]: $1x10^{-4}$ M; [cit]: $1x10^{-4}$ M; [HA]: 10 mg/L; I: 0.01 M ($NaClO_4$)

ESI 10: Species distribution of Gd(III) in the absence/presence of citrate ion as a function of pH (curves generated by Visual Minteq 3.0 Software using inbuilt data base)



ESI 10: Speciation of Gd(III) in the absence and presence of CA; [Gd(III)]: 1x10^{-4} M; [cit]: 1x10^{-4} M; I: 0.01 M ($NaClO_4$)

ESI 11: Species distribution of Gd(III) in the presence of humic acid as a function of pH (curves generated by Visual Minteq 3.0 Software using inbuilt data base)



ESI 11: Speciation of Gd(III) in the absence and presence of HA; [Gd(III)]: $1x10^{-4}$ M; [HA]: 10 mg/L; I: 0.01 M ($NaClO_4$)