Delineating influence of picolinic acid on Eu (III) sorption by γ-alumina

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Supporting Information

SI Table 1. Assignment of vibrational frequencies of aqueous Picolinc acid (PA) at different pH which is in conformity with the assignment given by Loring et. al. [40]

Assignments	pH 3.5	pH 5.5	pH 8.5
Pyridine ^{v}(CC, CN)	*	1600	*
Carboxylate $^{vas}(CO_2)$	1603	1560	1566
Pyridine ^{v}(CC, CN)	1529	1438	1437
Pyridine ^{v}(CC, CN)	1457	*	*
Carboxylate $^{vs}(CO_2)$	1387	1392	1390
Pyridine $^{\delta}$(CH)	1298	1301	1293
Pyridine $^{\delta}$(NH)	1234	1243	*
Pyridine $^{\delta}$(CH)	1172	1172	*
Pyridine $^{\gamma}$(CH)	1024	1002	1002
Carboxylate $\delta(CO_2)$	832	838	845

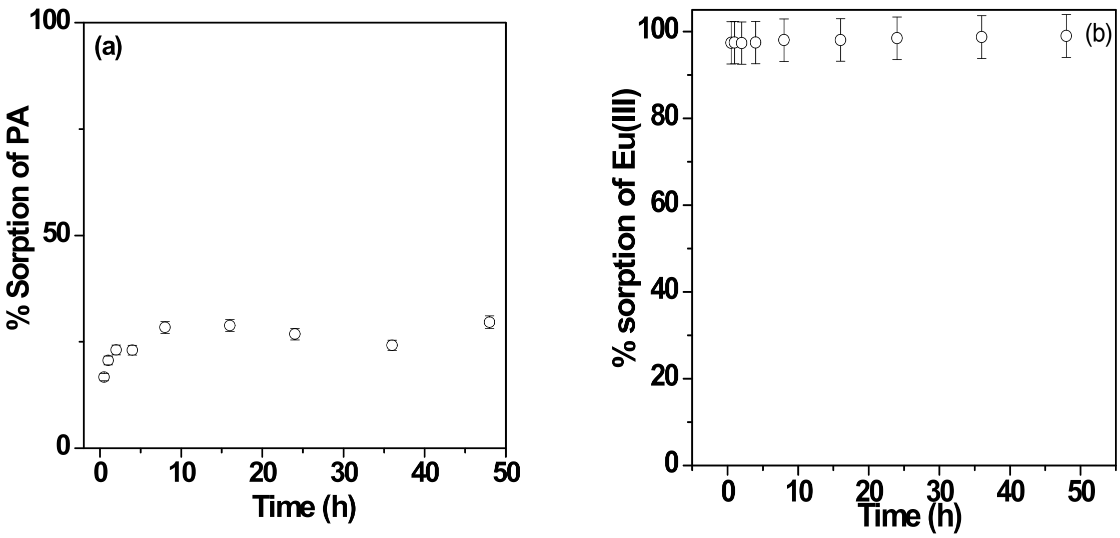
SI Table 2. Aqueous thermodynamic data (I = 0; T = 298.15 K)[35,49,50]

Formation	**log K⁰**	**Source**
$Eu^{3+} + H_2O \leftrightarrow Eu(OH)^{2+} + H^+$	-7.64	[55]
$Eu^{3+} + 2H_2O \leftrightarrow Eu(OH)_2^+ + 2H^+$	-15.1	[55]
$Eu^{3+} + 3H_2O \leftrightarrow Eu(OH)_3 + 2H^+$	-23.7	[55]
$Eu^{3+} + 4H_2O \leftrightarrow Eu(OH)_4^- + 4H^+$	-36.21	[55]
$Eu^{3+} + Cl^- \leftrightarrow EuCl^{+2}$	1.10	[54]
$Eu^{3+} + 2Cl^- \leftrightarrow EuCl_2^+$	1.50	[54]
$PA^- + 2H^+ \leftrightarrow H_2PA^+$	6.45	[54]
$PA^- + H^+ \leftrightarrow HPA^0$	5.44	[54]
$Eu^{3+} + PA^- \leftrightarrow Eu(PA)^{2+}$	4.63	[54]
$Eu^{3+} + 2PA^- \leftrightarrow Eu(PA)_2^+$	6.55	[54]
$Eu^{3+} + 3PA^- \leftrightarrow Eu(PA)_3^0$	8.37	[54]
$Al^{3+} + PA^- \leftrightarrow Al(PA)^{2+}$	4.49	[40]
$Al^{3+} + 2PA^- \leftrightarrow Al(PA)_2^+$	8.42	[40]
$Al^{3+} + 3PA^- \leftrightarrow Al(PA)_3^0$	12.3	[40]
$Al^{3+} + H_2O + 2PA^- \leftrightarrow Al(OH)(PA)_2 + H^+$	3.83	[40]

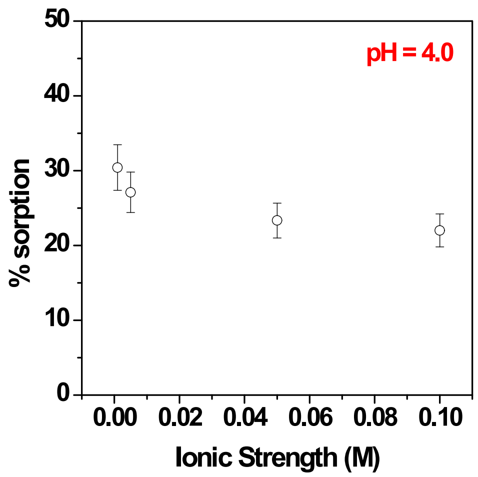
SI Table 3. Surface characteristics of γ-alumina (taken from Kumar et al. [30]

Site types	Site capacities
Specific surface area	203 m^2/g

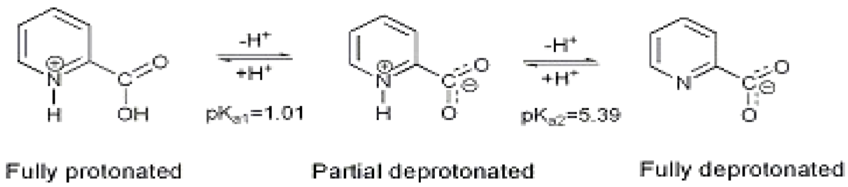
$\equiv XOH$	1.36×10^{-5} mol/l
$\equiv YOH$	6.66×10^{-4} mol/l
Protolysis reaction	log $K_{protolysis}$
$\equiv AlOH + H^{+} \leftrightarrow \equiv AlOH_{2}^{+}$	7.2 ±0.2
$\equiv AlOH - H^{+} \leftrightarrow \equiv AlO^{-}$	-9.1 ±0.1



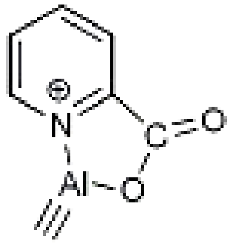
SI. Figure1. (a) Kinetics of PA sorption on γ-alumina,(b) kinetics of Eu(III) sorption in presence of PA (Eu and PA coaddition); [PA] = 5x10-4 M, [Eu(III)] = 1.72 x10-8 M, S/L = 5 g L-1, I= 0.1 M NaCl.



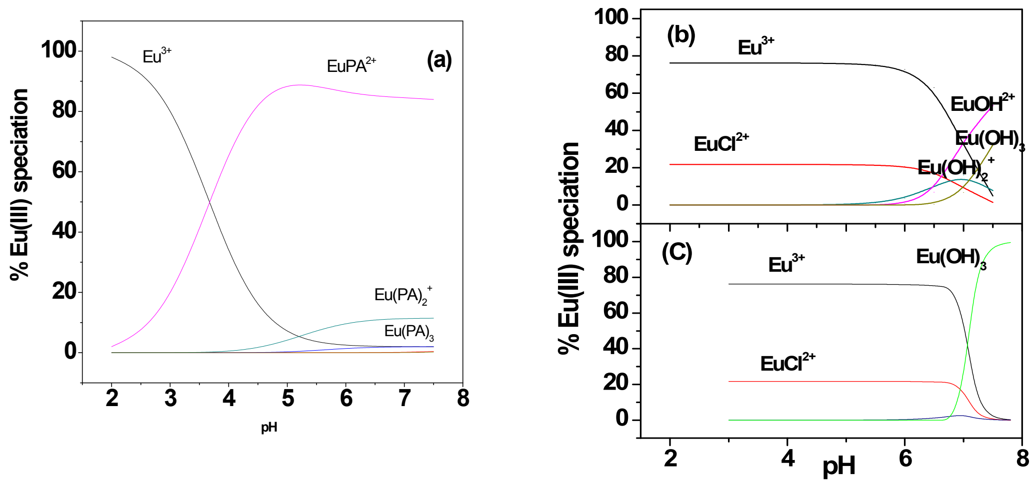
SI. Figure 2. (a) Effect of ionic strength on PA sorption by γ-alumina.[PA] = 5x10-4 M, S/L = 5 g L-1, I= 0 to 0.1 M NaCl.



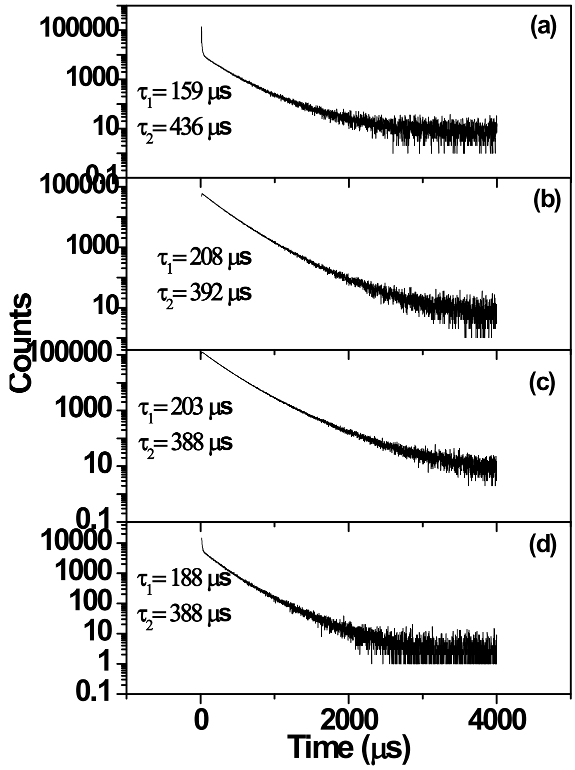
SI Figure 3. Aqueous Solution Forms and pKa of PA



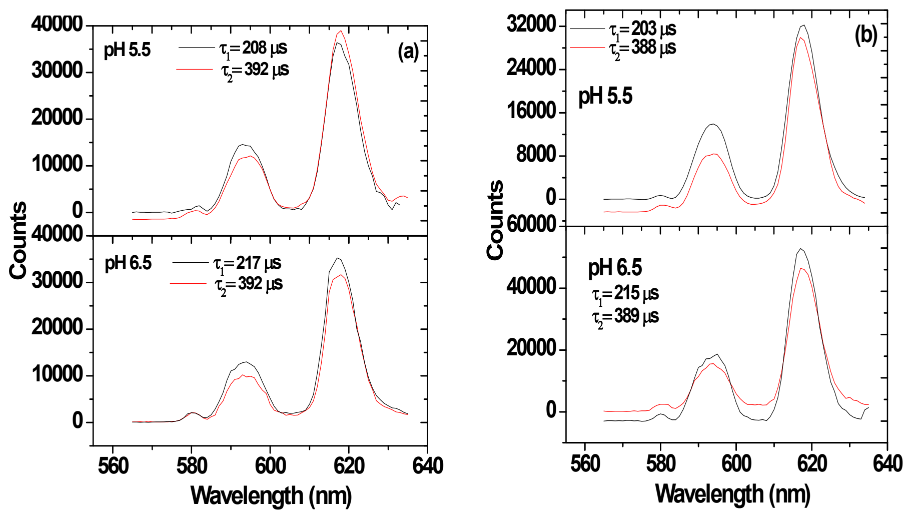
SI Figure 4. Proposed surface complexation structure formed between surface hydroxyl group of γ-alumina and PA.

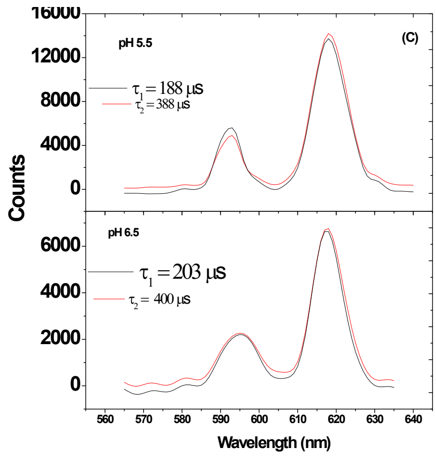


SI Figure 5. Europium speciation in aqueous solution, in presence (a) and absence (b, c) of PA, [Eu(III)]; (a) [Eu(III)] = 5 x 10^{-4} M, [PA] = 5 x 10^{-3}, (b) [Eu(III)] = 1.72 x 10^{-8} M (taken from reference 29), (c) [Eu(III)] = 5 x 10^{-5} M (taken from reference 29), I = 0.1 M NaCl.



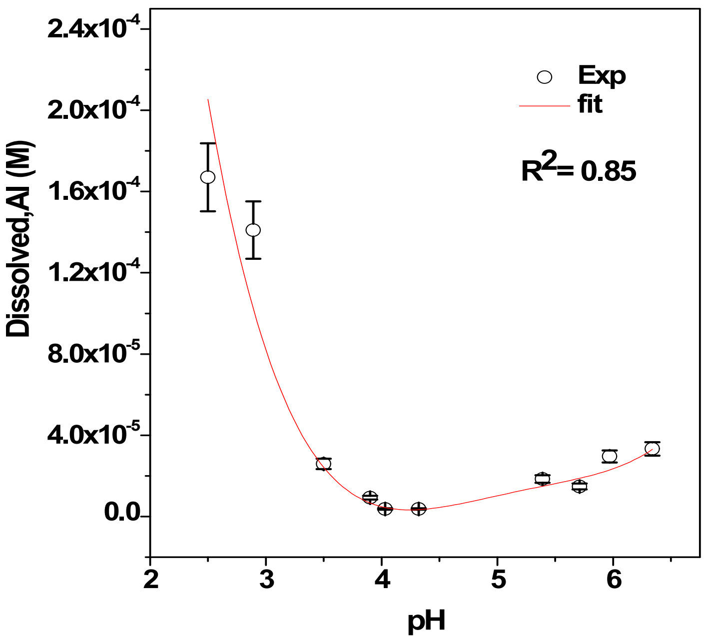
SI Figure 6. Fluorescence decay curve of Eu(III) sorbed on alumina in presence and absence of PA at pH = ~ 5.5, (a) Al-Eu, (b) Al-Eu+PA, (c) Al-Eu-PA, (d) Al-PA-Eu; [Eu(III)] = 5 x 10^{-5} M , [PA] = 5 x 10^{-4}, S/L = 5 g L^{-1}, I = 0.1 M NaCl.



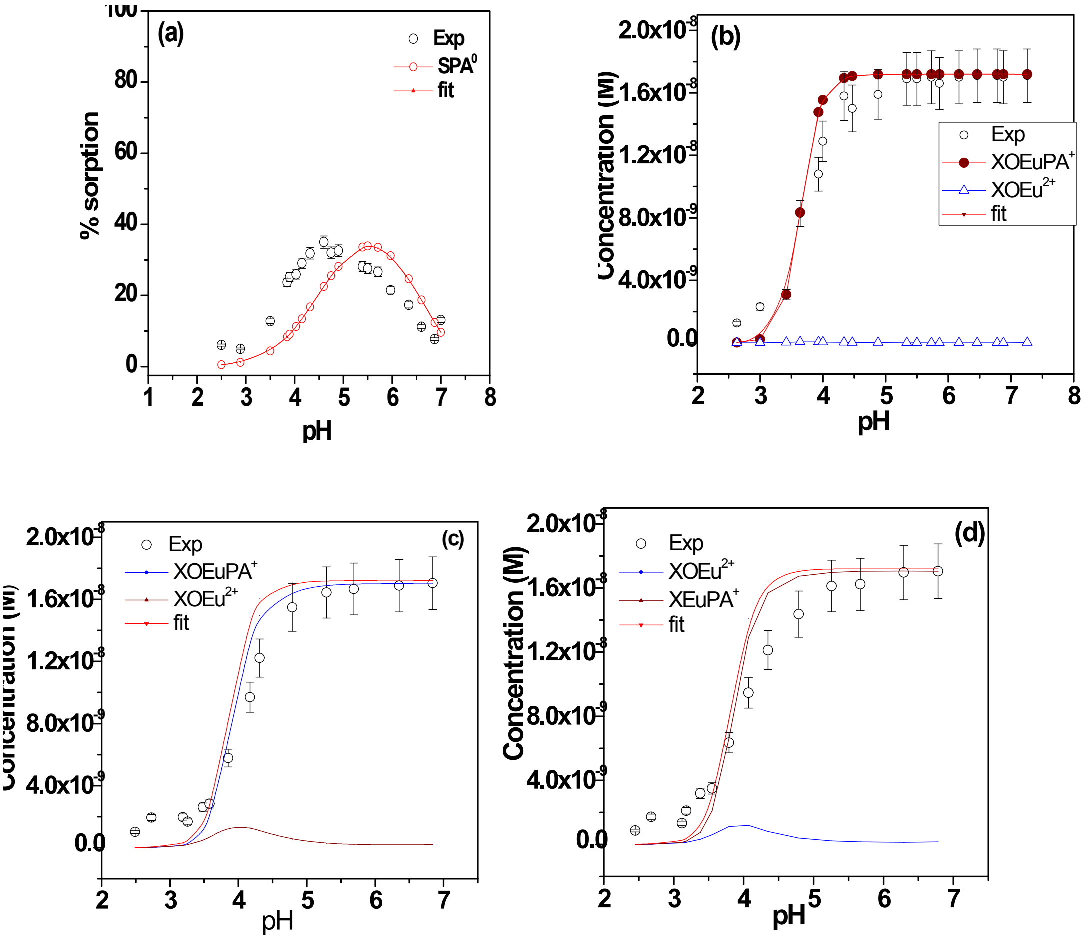


SI Figure 7. Time Resolved Spectra corresponding to the two lifetime components τ_1 and τ_2 for Eu(III) sorption in presence of PA. (a) Al-Eu+PA, (b) Al-Eu-PA, (c) Al-PA-Eu; [Eu(III)] = 5 x 10^{-5} M , [PA] = 5 x 10^{-4}, S/L = 5 g L^{-1}, I = 0.1 M NaCl. TRES recorded using fluorescence measurements was sliced to obtain emission spectra corresponding to the two lifetime components τ_1 and τ_2.

The γ-alumina dissolution has been estimated by determining dissolved aluminium in supernatant of γ-alumina suspensions. The γ-alumina suspensions have been equilibrated with PA for the period of 24 hours. The decrease in γ-alumina dissolution with pH signifies proton promoted dissolution. Therefore as the pH increases dissolution profile tends to achieve a plateau. The comparable dissolution in absence and presence of PA depicts that PA does not facilitate ligand promoted dissolution of γ-alumina.



SI Figure 8. Dissolution of γ- alumina as a function of pH, I = 0.1 M NaCl; S/L = 5 gL^{-1}; equilibration time = 24 h; solid line represent the fitted data.



SI Figure 9. Modeling of sorption data. (a) PA sorption by γ-alumina , (b) Eu(III) sorption by γ-alumina in presence of PA (Eu and PA co-added (Al-Eu+PA), (c) Eu preceeded by PA (Al-Eu-PA), (d) PA preceeded by eu (Al-PA-Eu), [Eu(III)] = 5 x10-5 M [PA] = 5 x10-4 M, S/L = 5 gL--1, I= 0.1 M NaCl.

References:

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