Supplementary Information

Metal ion - humic acid nanoparticle interactions: role of both complexation and condensation mechanisms

Raewyn M. Town[*a] and Herman P. van Leeuwen[b]

[a] Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense, Denmark. Email: raewyn.town@sdu.dk

[b] Physical Chemistry and Soft Matter, Wageningen University & Research, Stippeneng 4, 6708 WE Wageningen, The Netherlands.

Table S1. Parameters defining the bulk and intraparticulate metal speciation in highly charged, soft nanoparticulate complexants[a]

M(II) species	Bulk aqueous medium	Intraparticulate double layer	Donnan volume	Governing physicochemical features
Free M	$c_{M,f}^{*}$	$c_{M,f}^{DL} = \overline{f}_{B,M}^{DL} c_{M,f}^{*}$	$c_{M,f}^{D} = \overline{f}_{B,M}^{D} c_{M,f}^{*}$	Donnan
Condensed M		$c_{M,cond}^{DL} = \overline{f}_{C} c_{S}^{DL}$	$0^{(b)}$	Counterion condensation
Inner-sphere MS[c]		$c_{MS} = \overline{K}_{int} c_{S} c_{M,f}$		Covalent binding
Total particle-associated M	$c_{MHA}^{*} = \overline{K}_{app} c_{S}^{*} c_{M,f}^{*}$			

[a] The concentrations are denoted by: superscript * for smeared-out bulk solution concentration; superscript D or DL for local intraparticulate concentrations in the pertaining part of the particle volume; no superscript for the average intraparticulate concentration. The condensation limit for **2+** counterions in the DL with $\rho = \overline{\rho}_{DL}$ is denoted by $\overline{f}_{C}$. See main text for definitions of all symbols.

[b] in the high charge density regime, with $\kappa_{p} r_{p} \gg 1$, counterion condensation is confined to the intraparticulate double layer shell.

[c] see eqn (8) in main text.