

Article

Cadmium Sorption on Alumina Nanoparticles and Mixtures of Alumina and Smectite: An Experimental and Modelling Study

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1. S1. Cadmium speciation and surface complexation constants

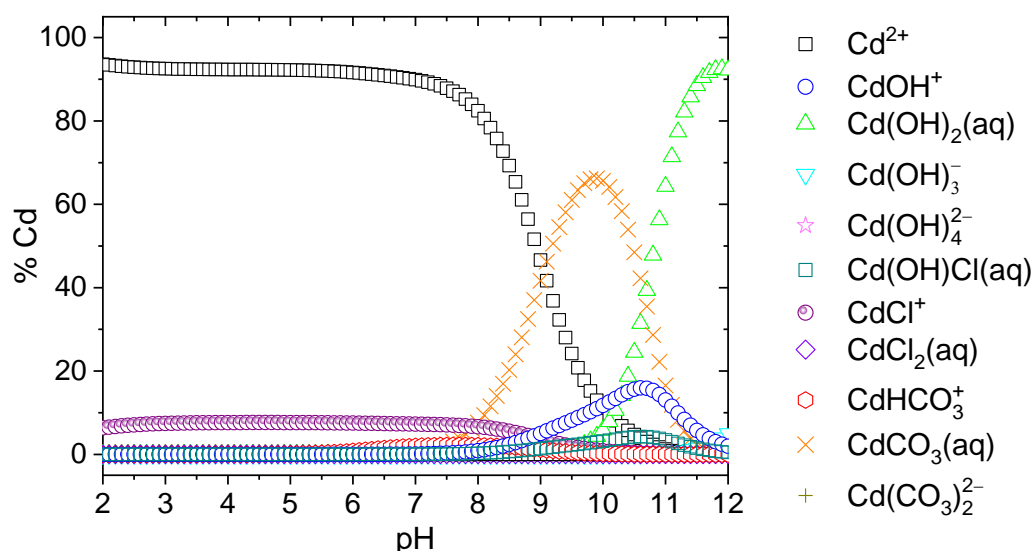


Figure S1. Cadmium species distribution (% Cd) as a function of pH. The speciation was calculated considering the thermodynamic constants in Table 4 for a $[Cd^{2+}]_0 = 4.6 \cdot 10^{-8}$ M, $[NaClO_4] = 1 \cdot 10^{-1}$ M, $[HCO_3^-] = 1 \cdot 10^{-3}$ M, and $[NaCl] = 1 \cdot 10^{-3}$ M.

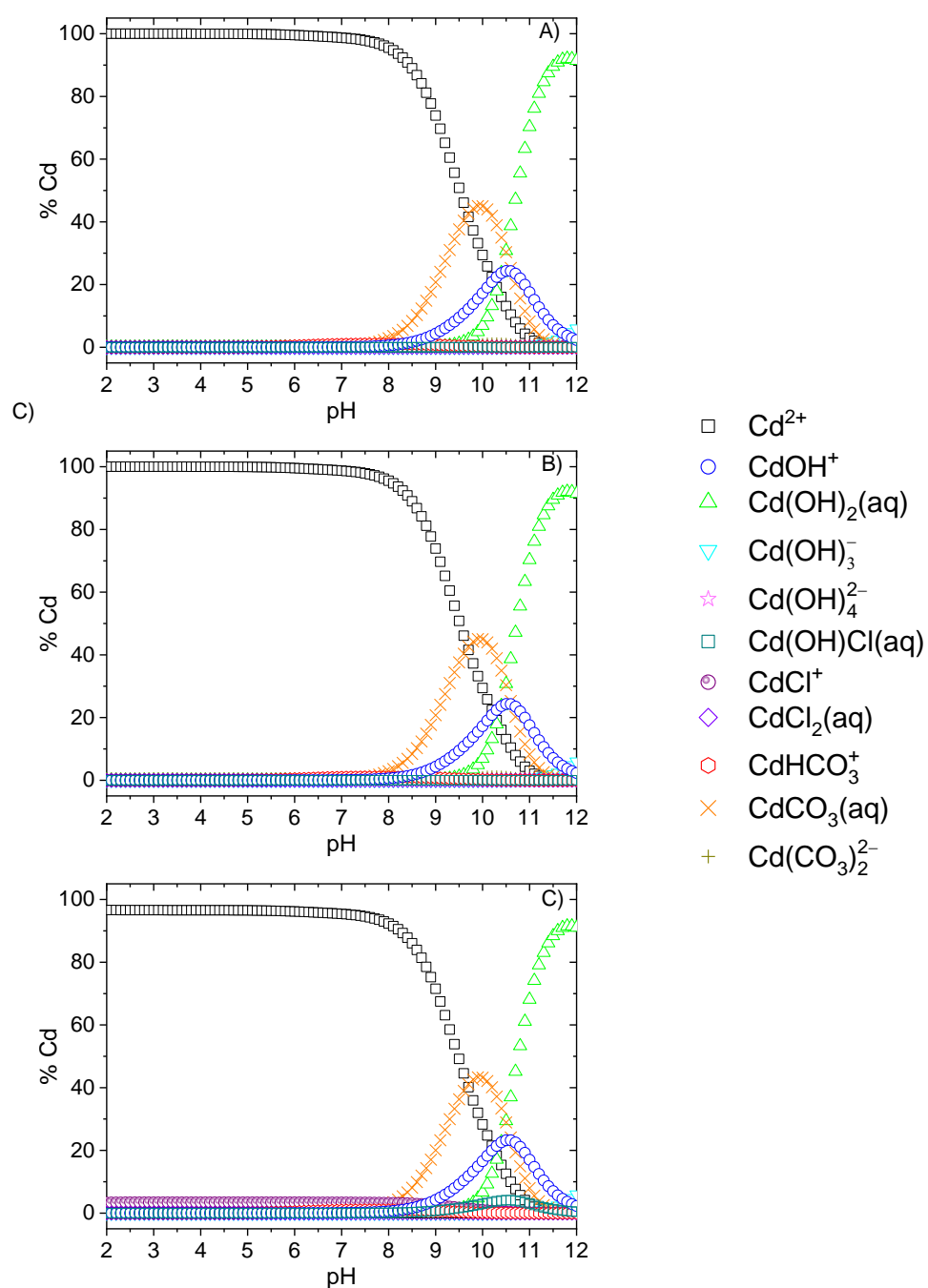


Figure S2. Cadmium species distribution (% Cd) as a function of pH. The speciation was calculated considering the thermodynamic constants in Table 4 for a $[\text{Cd}^{2+}]_0 = 4.6 \cdot 10^{-8}$ M, $[\text{NaClO}_4] = 1 \cdot 10^{-1}$ M, $[\text{HCO}_3^-] = 1 \cdot 10^{-3}$ M and A) $[\text{NaCl}] = 0$ M, B) $[\text{NaCl}] = 1 \cdot 10^{-8}$ M, and C) $[\text{NaCl}] = 1 \cdot 10^{-3}$ M.

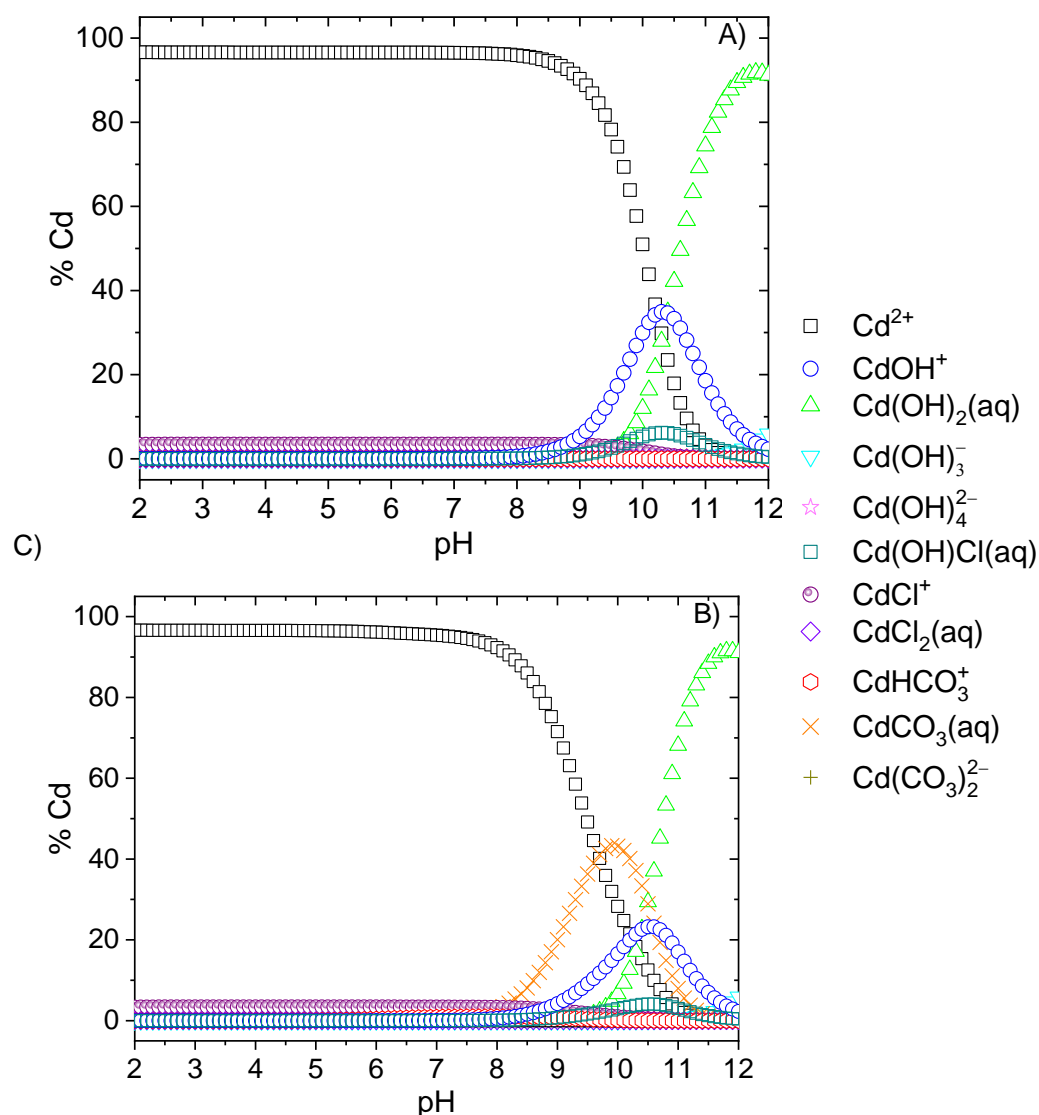


Figure S3. Cadmium species distribution (% Cd) as a function of pH. The speciation was calculated considering the thermodynamic constants in Table 4 for a $[\text{Cd}^{2+}]_0 = 4.6 \cdot 10^{-8} \text{ M}$, $[\text{NaClO}_4] = 1 \cdot 10^{-1} \text{ M}$, $[\text{NaCl}] = 1 \cdot 10^{-3} \text{ M}$ and A) $[\text{HCO}_3^-] = 0 \text{ M}$, and B) $[\text{HCO}_3^-] = 1 \cdot 10^{-3} \text{ M}$.

Cd^{2+} is the dominant species from pH 2.0 to pH 8.0. At pH > 8.0, the Cd-carbonate ($\text{CdCO}_3(\text{aq})$) and Cd hydroxo species (CdOH^+ , Cd(OH)_2) are dominant. The precipitation of Cd species is not predicted under the chemical conditions used for the calculation of Figure S1. According to the saturation index of the Cd solid species, otavite (CdCO_3) controls Cd solubility for higher Cd ($[\text{Cd}] > 1 \cdot 10^{-4} \text{ M}$) at pH > 6.0.

2. S2. Additional figures reproducing cadmium sorption on alumina nanoparticles

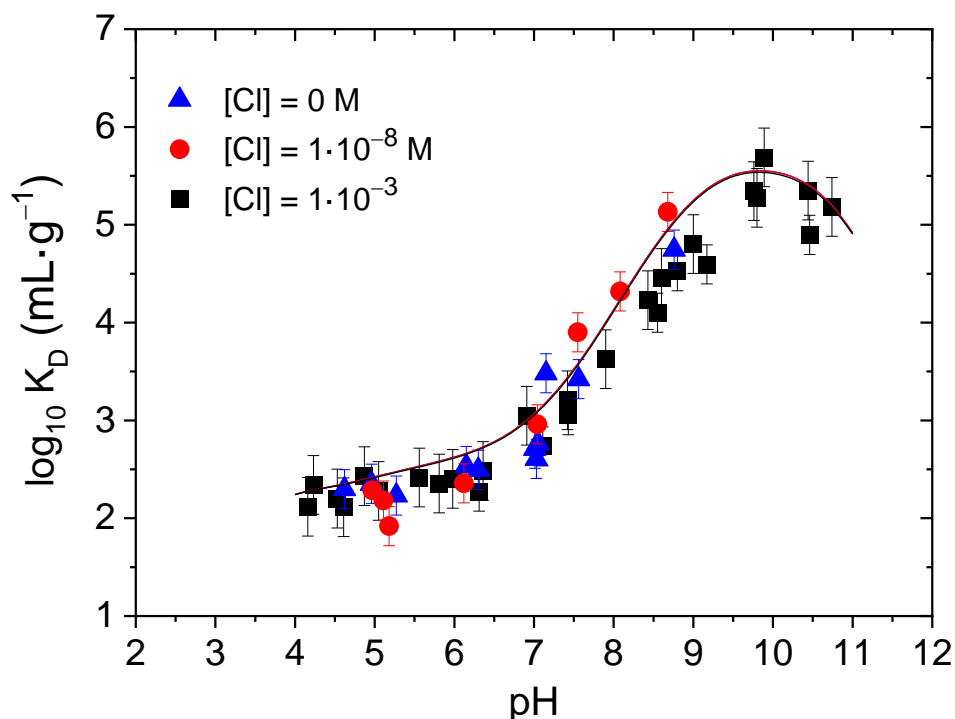


Figure S4. Cadmium sorption (as distribution coefficient K_D) on alumina nanoparticles (A) as a function of pH evaluated at different chloride concentrations according to the figure key. Colored solid lines represent the model of Cd sorption calculated using the parameters shown in Table 5 of the main text. $[A] = 0.5$ g/L, contact time = 7 days, $1 \cdot 10^{-1}$ M NaClO_4 , and $[\text{Cd}]_0 = 9.8 \cdot 10^{-8}$ M.

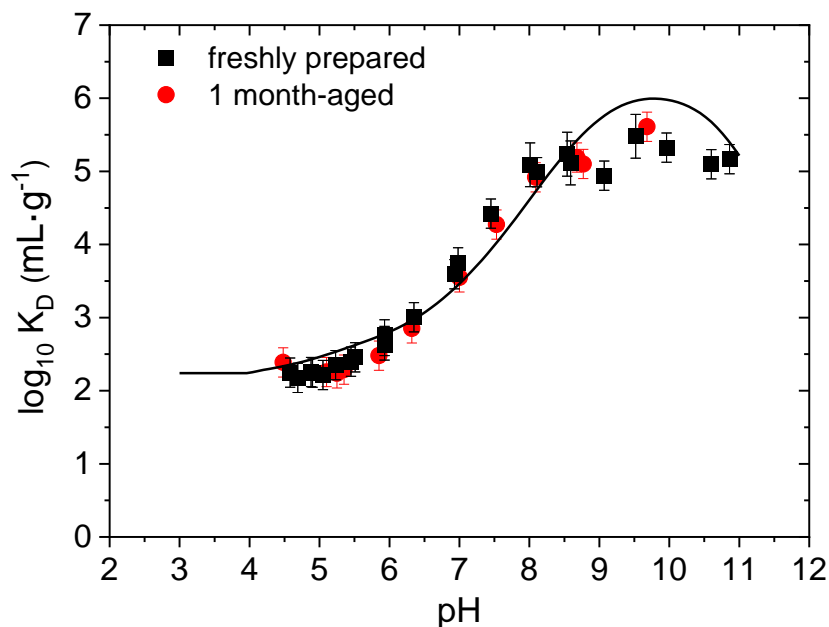


Figure S5. Cadmium sorption (as distribution coefficient K_D) on alumina nanoparticles (A) as a function of pH evaluated for two A suspensions: (black squares) freshly prepared and (red circles) aged for one month. Colored solid lines represent the model of Cd sorption calculated using the parameters shown in Table 5 of the main text. $[A] = 0.5$ g/L, contact time = 7 days, $1 \cdot 10^{-1}$ M NaClO_4 , and $[\text{Cd}]_0 = 4.6 \cdot 10^{-8}$ M.

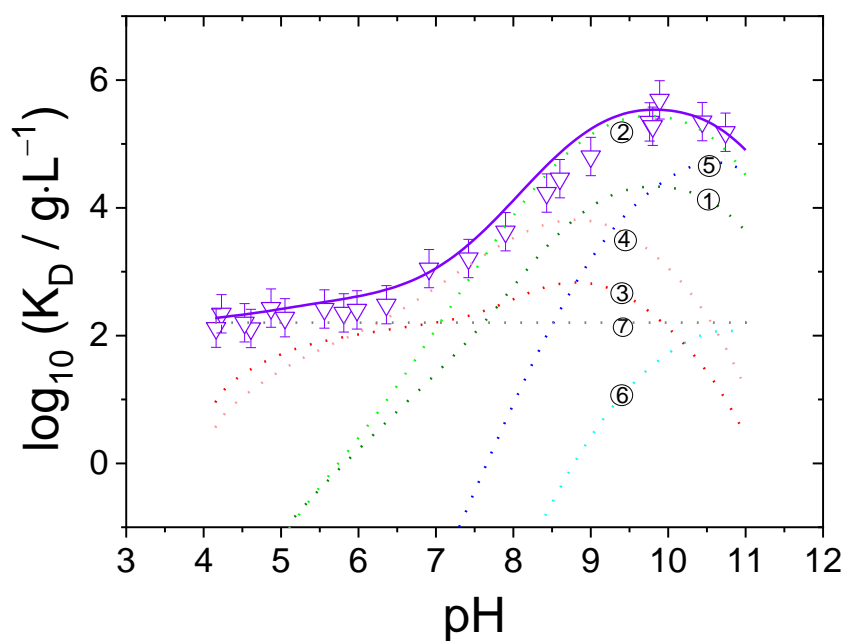
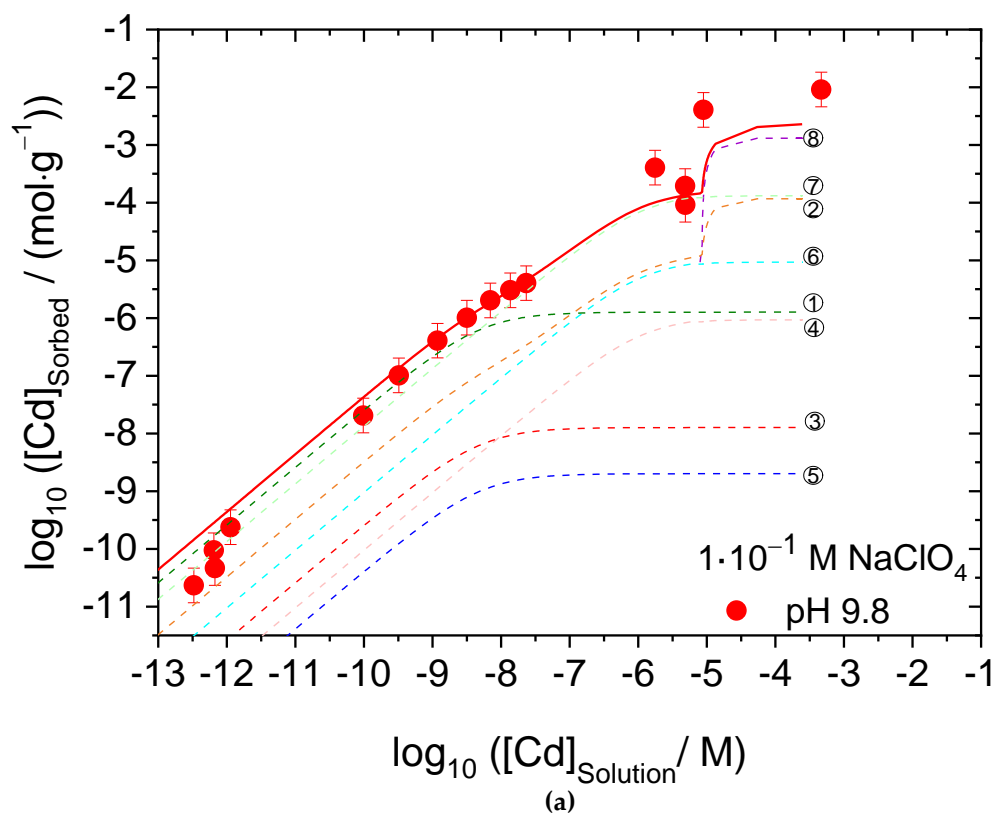
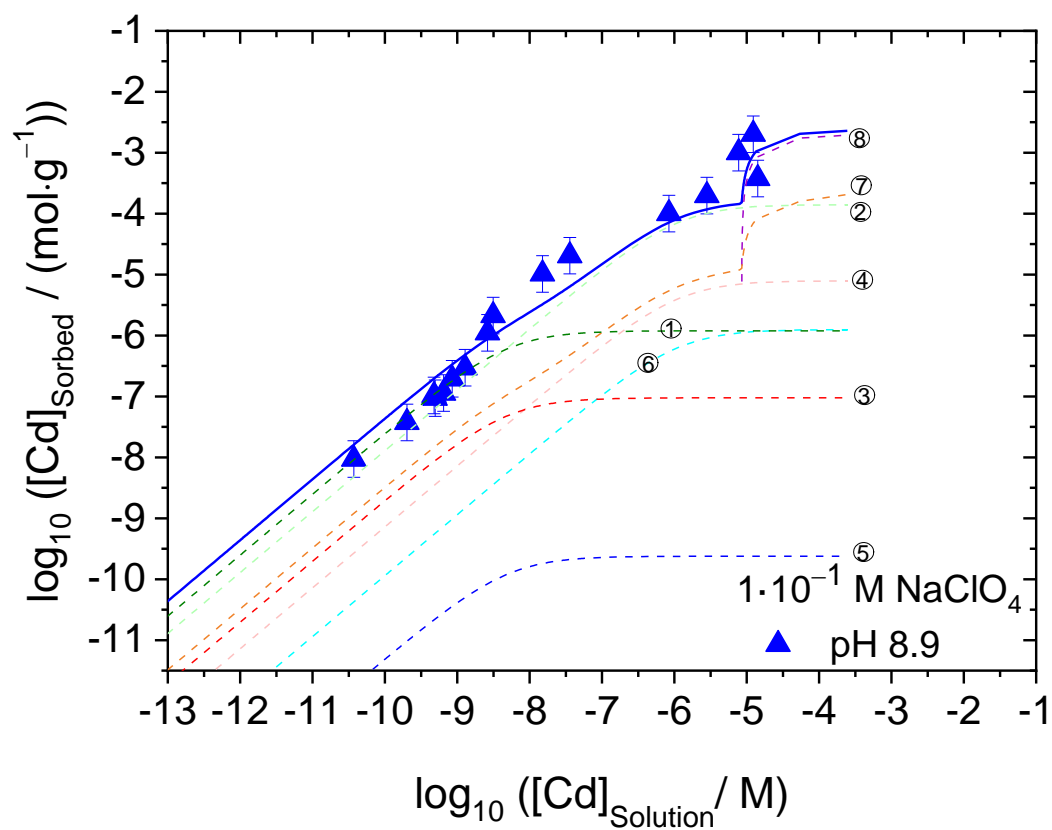
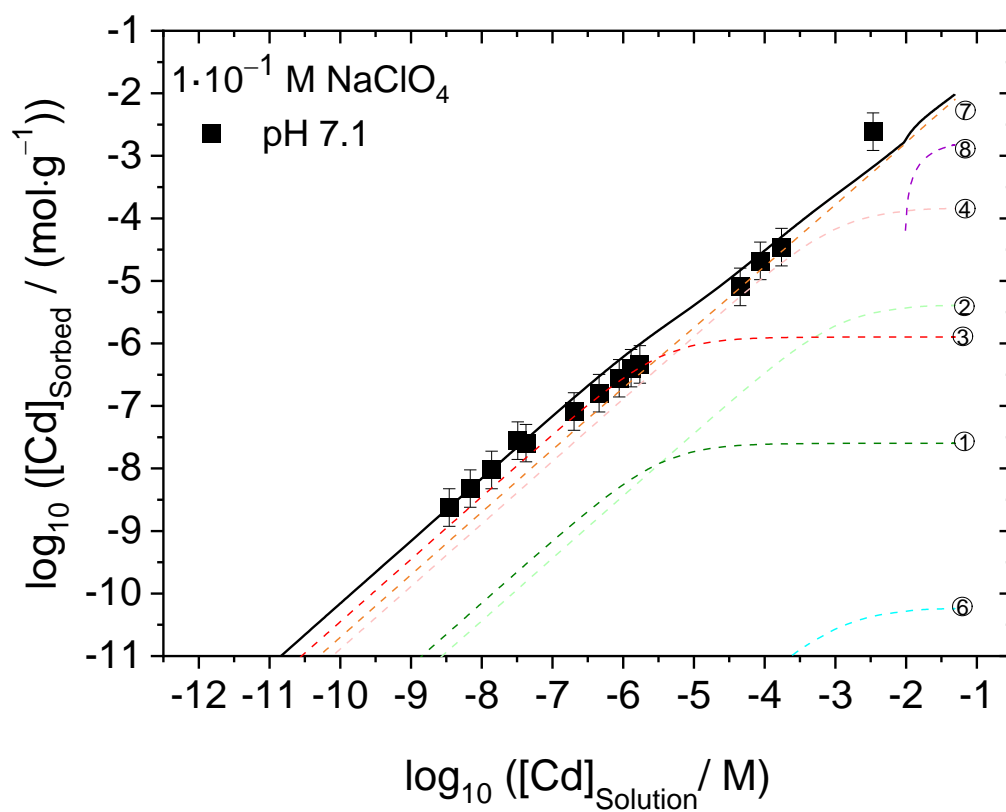


Figure S6. Cadmium sorption (as distribution coefficient K_D) on alumina nanoparticles (A) as a function of pH. Colored solid lines represent the model of Cd sorption calculated using the parameters shown in Table 5 of the main text. Dashed lines represent the individual contribution to Cd sorption: (1) $X^S\text{O}-\text{Cd}^+$, (2) $X^W\text{O}-\text{Cd}^+$, (3) $X^S\text{OH}-\text{Cd}^{2+}$, (4) $X^W\text{OH}-\text{Cd}^{2+}$, (5) $X^S\text{O}-\text{CdOH}$, (6) $X^W\text{O}-\text{CdOH}$, and (7) empirical Cd sorption. $[A] = 0.5 \text{ g/L}$, contact time = 7 days, $1 \cdot 10^{-1} \text{ M NaClO}_4$, and $[\text{Cd}]_0 = 1.0 \cdot 10^{-5} \text{ M}$.





(b)



(c)

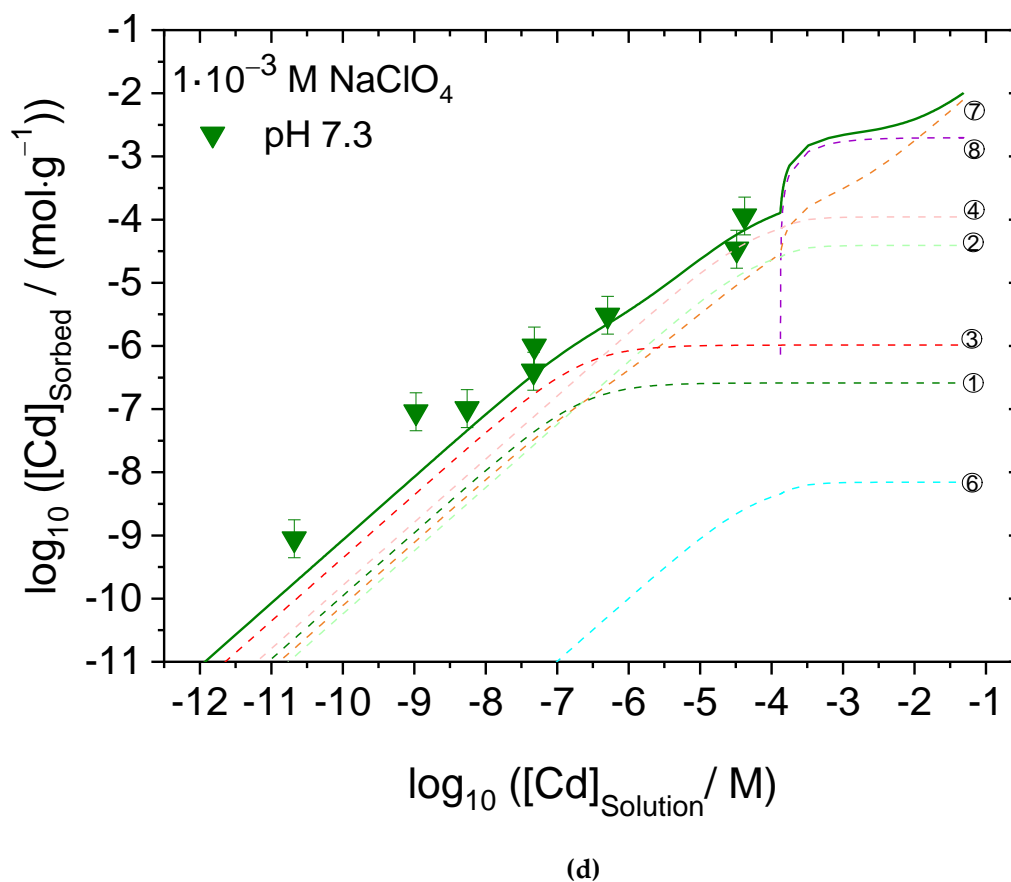


Figure S7. Cadmium sorption (as mol of Cd per gram of *A*) on alumina nanoparticles (*A*) as a function of Cd concentration in solution at different pH and ionic strengths. (a) pH 9.8 and $1 \cdot 10^{-1}$ M NaClO₄, (b) pH 8.9 and $1 \cdot 10^{-1}$ M NaClO₄, (c) pH 6.1 and $1 \cdot 10^{-1}$ M NaClO₄, and (d) pH 6.1 and $1 \cdot 10^{-3}$ M NaClO₄. Colored solid lines represent the model of Cd sorption calculated using the parameters shown in Table 5 of the main text. Dashed lines represent the individual contribution to Cd sorption: (1) $X^S O-Cd^+$, (2) $X^W O-Cd^+$, (3) $X^S OH-Cd^{2+}$, (4) $X^W OH-Cd^{2+}$, (5) $X^S O-CdOH$, (6) $X^W O-CdOH$, (7) empirical Cd sorption, and (8) precipitation of Cd species. $[A] = 0.5$ g/L, and contact time = 7 days.

3. S3 Cd sorption on mixtures of alumina nanoparticles and smectite.

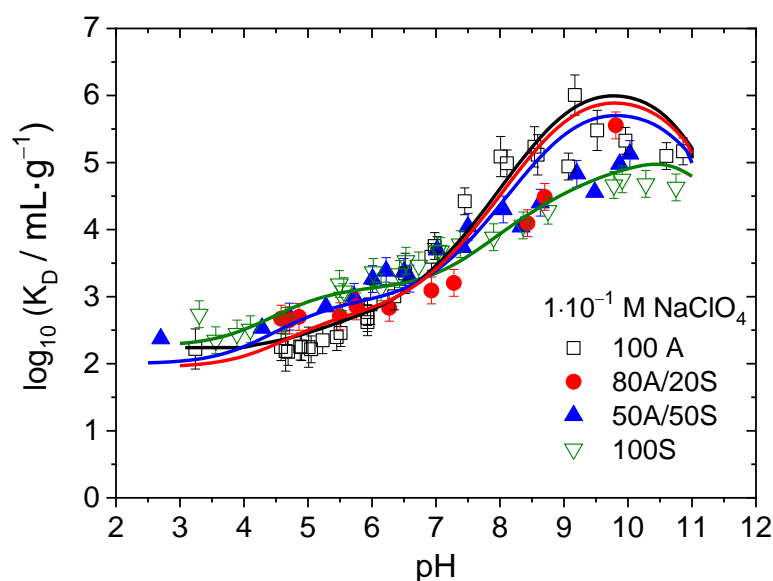


Figure S8. Cadmium sorption (as distribution coefficient K_D) on mixtures of alumina nanoparticles (A) and Na-homoionized smectite (S), A, and S as a function of pH (detailed in figure legend). Colored lines represent the Cd sorption on A, S, and A/S mixtures calculated using the data collected in Table 5. Solid lines represent the sorption of Cd including Al^{3+} competition. $[\text{A/S}]_{\text{total}} = 0.5 \text{ g/L}$, 50% A and 50% S, contact time = 7 days, $[\text{Cd}]_0 = 4.8 \cdot 10^{-8} \text{ M}$, and $[\text{Al}^{3+}] = 2 \text{ mg/L}$.

References

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