Supplementary Information (SI) for Environmental Science: Nano.

SUPPORTING INFORMATION (SI A)

When does the aggregation matter? The CLUMP scheme for classifying nanoparticles based on the influence of aggregation on environmental fate

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1. Characteristics of the tested nanomaterials.

Table 1. List of tested nanomaterials with the values of Hamaker constants in vacuum and density.

ENP	Hamaker's constant [10^{-20} J]	Density [kg/m^3]	References
Ag	29.0	10500	1
Al	25.6	2700	1
Al_2O_3	15.2	3950	2
Au	34.9	19300	1
$BaTiO_3$	18.0	6000	2
Be	34.8	1850	3
BeO	14.5	3000	3
CaF_2	7.0	3180	2
CdS	11.4	4800	2
CeO_2	8.5	7100	4
Cr	36.5	7200	3
Cu	32.2	8960	3
CuO	6.2	6500	5
Fe_3O_4	4.3	5200	6
LiF	6.3	2540	2
MgF_2	5.9	3150	2
MgO	12.1	3600	2
Mo	46.8	10200	3
MoS_2	54.0	5000	7
PbS	8.2	7200	2
Pt	24.0	21450	8
Si_3N_4	16.7	3200	2
SiC	24.6	3210	2
SiO_2	7.6	2200	2
$SrTiO_3$	14.8	5000	2
TiO_2	15.3	4230	2
V	36.6	6100	3
W	49.8	19300	3
WS_2	58.0	7300	7
Y_2O_3	13.3	5000	2
ZnO	9.2	5600	2
ZnS (cubic)	15.2	4000	2
ZnS (hexagonal)	17.2	4050	2
ZrO_2	20.3	5600	2
α-Fe_2O_3	9.2	5200	6
γ-Fe_2O_3	6.8	5000	6

Table 2. Nanomaterials with assigned solubility rate constant.

ENP	Dissolution rate [s^{-1}]	References
Ag	2.7×10^{-7} - 4.8×10^{-5}	9–11
Al_2O_3	3.7×10^{-7} - 1.7×10^{-6}	12
CdS	2.5×10^{-7} - 1.7×10^{-5}	13
Cu	3.0×10^{-8} - 8.0×10^{-6}	14,15
CuO	1.2×10^{-7} - 5.4×10^{-4}	16–20
ZnO	8.4×10^{-7} - 2.7×10^{-3}	21–25

For nanomaterials not listed explicitly, assumed dissolution rate = 0.

2. Environmental conditions and parameters of DLVO and EFM simulations.

Parameter	Distribution	Range	Unit	Used in modeling	Reference
Diameter of natural colloids	Pareto	50-2000	nm	DLVO, EFM	[26]
Zeta potential of natural colloids	Triangular	-9.5; -8.8; -7.9	mV	DLVO	[27]
Density of natural colloids	Triangular	1.1×10^3; 1.3×10^3; 2.5×10^3	kg/m^3	EFM	[28]
Number concentration of natural colloids	Triangular	4.8×10^{13}; 1.7×10^{14}; 4.0×10^{14}	$\#/m^3$	EFM	[29]
Diameter of suspended particles	Lognormal	5; 0.6	µm	DLVO, EFM	[30]
Zeta potential of suspended particles	Triangular	-16; -14; -12	mV	DLVO	[27]
Density of suspended particles	Uniform	1.1×10^3 - 2.5×10^3	kg/m^3	EFM	[30]
Number concentration of suspended particles	Uniform	9.2×10^9 - 6.3×10^{10}	$\#/m^3$	EFM	[30]
Inverse of Deby's length	Lognormal	19.14; 0.81	m^{-1}	DLVO	[31]
Ion valance	Triangular	1.0; 1.2; 2.0	-	DLVO	[32]
Water depth	Weibull	3; 15	m	EFM	[33]
Temperature	Lognormal	2.49; 0.28	K	DLVO, EFM	[34]
Shear rate	Uniform	0 -10	s^{-1}	EFM	[30]
Water flow	Lognormal	2.3×10^3; 8.9×10^2	m^3/s^{-1}	EFM	[33]

3. Attachment efficiency calculations based on DLVO theory.

The symbols used in the equations below are defined as follows:

h - separation distance [m]

A_H - Hamaker constant [J]

r_{ENP}, r_{other} - radii of ENP and natural particle [m]

ε_0 - vacuum permittivity (8.85×10^{-12}) [F/m]

ε_{water} - water dielectric constant

k_b - Boltzmann constant (1.38×10^{-23}) [J/K]

T - temperature [K]

z - ion valence

e - elementary charge (1.60×10^{-19}) [C]

$\zeta_{ENP}, \zeta_{other}$ - zeta potentials [V]

k_{Debye} - inverse Debye length [m^{-1}]

$$\alpha = \frac{\int_0^\infty \left[\frac{\exp\left(\frac{V_{VDW}}{k_bT}\right)}{\left(\frac{r_{ENP}\times r_{other}}{r_{ENP}+r_{other}}+h\right)^2}\right]dh}{\int_0^\infty \left[\frac{\exp\left(\frac{V_T}{k_bT}\right)}{\left(\frac{r_{ENP}\times r_{other}}{r_{ENP}+r_{other}}+h\right)^2}\right]dh}$$

Equation. 1 Calculation of binding efficiency (α) by applying DLVO theory[35,36].

$$V_{VDW} = -\frac{A_{H(ENP/water/other)}\times r_{ENP}\times r_{other}}{6h(r_{ENP}+r_{NCP})}$$

Equation. 2 Expression for Van der Waals attraction between ENP and natural particle[36].

$$V_{EDL} = 64\pi\varepsilon_0\varepsilon_{water}\left(\frac{r_{ENP}\times r_{other}}{r_{ENP}+r_{other}}\right)\left(\frac{k_bT}{ze}\right)^2 \tanh\left(\frac{ze\zeta_{ENP}}{4k_bT}\right)\tanh\left(\frac{ze\zeta_{other}}{4k_bT}\right)e^{(-k_{Debye}h)}$$

Equation. 3. Expression for Electric Double Layer repulsion between ENP and natural particle[36].

$$V_T = V_{VDW} + V_{EDL}$$

Equation. 4. Expression for total interaction

Conversion of the Hamaker constant of a nanoparticle in vacuum to the Hamaker constant in interaction with a natural particle in water[37]:

$$A_{ENP/water/other} = \left(\sqrt{A_{ENP}}-\sqrt{A_{water}}\right)\left(\sqrt{A_{NCP}}-\sqrt{A_{water}}\right)$$

Equation. 5. Hamaker constant for ENP in interaction with natural particle in water.

The Hamaker constant of natural particles is represents by SiO_2 and:

$A_{SiO_2} = 7.59\times10^{-20}$ J [2] $A_{water} = 3.70\times10^{-20}$ J [38].

4. Calculation aggregation rate constant

The heteroaggregation process is described as first-order kinetics with an effective rate constant:

$$k_{agg} = \alpha \times f$$

The frequency of all collisions between ENP nanoparticles (radius R_S) and other particles (radius r) consists of three mechanisms:

$$f = f_I + f_B + f_G$$

a. Collisions related to macromixing (fluid shear):

$$f_I = \frac{4}{3}\dot{\gamma}(R_S + r)^3$$

where $\dot{\gamma}$ is the shear rate (1/s).

b. Brownian collisions (thermal diffusion):

$$f_B = \frac{2k_B T}{3\mu}\frac{(R_S + r)^2}{R_S r}$$

where k_B is the Boltzmann constant, T temperature, μ dynamic viscosity.

c. Gravitational collisions (sedimentation velocity difference):

$$f_G = \pi(R_S + r)^2 |V_{set}(R_S) - V_{set}(r)|$$

where

$$V_{set}(x) = \frac{2(\rho_x - \rho_w)gx^2}{9\mu}$$

is the sedimentation velocity of a particle with radius x and density ρ_x, in a medium with densityρ_w and gravitational acceleration g.

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