Electronic Supporting Information

Adsorption and dissolution of silver nanoparticles by iron oxide colloids under environmentally relevant conditions

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**Text S1. Hydrodynamic diameters ($D_h$) and zeta ($\zeta$)-potentials of AgNPs and iron oxides.**

The hydrodynamic diameters ($D_h$) and $\zeta$-potentials of the AgNPs and iron oxides were monitored using dynamic light scattering (DLS; BI-200SM, Brookhaven, USA) and a zeta-potential analyzer (Zetasizer Nanosizer ZS, Malvern Instrument Co., UK), respectively.

For DLS analysis, the samples were mixed vigorously for 3 s using a vortex mixer (SCILOGEX MX-S, USA) and then quickly used in the measurements. Each autocorrelation function was accumulated over 30 s, and the intensity-weighted hydrodynamic diameter was derived using second-order cumulant analysis (Brookhaven software). For the $\zeta$-potential analysis, the solids were collected after completion of the batch experiments, centrifuged at 3000×$g$ for 10 min, rinsed with Milli-Q water twice, and freeze-dried. They were then re-suspended using the desired electrolytes and their $\zeta$-potentials were characterized. Triplicate experiments were performed for DLS and $\zeta$-potential measurements.

The initial aggregation rate was calculated using a linear least-squares analysis of the increase in $D_h$ with time. As shown in Figure 4 in the main text, the intensity of the scattered light from the binary AgNP-goethite suspension was significantly greater than that from the AgNPs but closer to that of goethite, indicating that goethite was the dominant light scatterer in the binary suspensions. Therefore, for the binary systems, the analysis was performed during the period of time that $D_h$ increased until it was 1.3-fold higher than the initial $D_h$ of the iron oxides. In the case of the slow
homoaggregation of goethite, in which $D_h$ failed to increase within the short time by 1.3-fold, a linear aggregation was performed over a longer time ($> 20$ min). This approach to determining the heteroaggregation rate was similar to that used by Huynh et al.. \(^1\)
Text S2. Derjaguin-Landau-Verwey-Overbeek (DLVO) interaction energy calculation.

In this study, classical DLVO theory, which takes into account both van der Waals (vdW) and electrostatic double-layer (EDL) interactions, was applied to quantitatively describe the stability of the AgNPs, goethite, and hematite under solution chemistries similar to those of the batch experiments. The vdW and EDL interaction energies were calculated for the AgNP-AgNP, goethite-goethite, and hematite-hematite systems, assuming a sphere-sphere configuration, and for the AgNP-goethite and AgNP-hematite systems, assuming a sphere-plate configuration. The expressions for calculating the vdW interaction energy (ΦvdW) for the sphere-sphere and sphere-plate configurations are presented in Eqs. (1) and (2), respectively:2,4

\[
\Phi_{vdW} = -\frac{A_{131}r_{h1}r_{h2}}{6h(r_{h1}+r_{h2})} \left[ 1 + \frac{14h}{\lambda} \right]^{-1} 
\]

\[
\Phi_{vdW} = -\frac{A_{132}r_{h}}{6h} \left[ 1 + \frac{14h}{\lambda} \right]^{-1} 
\]

where \( r_{h1} \) and \( r_{h2} \) in Eq. (1) refer to the average hydrodynamic radii of the two interacting particles (AgNPs, goethite, or hematite) determined by DLS measurements (see Table S1); \( r_{h} \) in Eq. (2) refers to the average hydrodynamic radius of AgNPs; \( h \) is the separation distance between two particles; \( \lambda \) is the characteristic wavelength of the interaction (usually 100 nm); and \( A_{131} \) and \( A_{132} \) are the Hamaker constants for AgNPs-water-AgNPs (or goethite-water-goethite, or hematite-water-hematite) and AgNPs-water-goethite (or AgNPs-water-hematite), respectively, obtained from the Hamaker constants of the individual materials using Eqs. (3) and (4):5

\[
A_{131} = (\sqrt{A_1} - \sqrt{A_{water}})(\sqrt{A_1} - \sqrt{A_{water}}) 
\]

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\[ A_{132} = (\sqrt{A_{\text{AgNPs}}} - \sqrt{A_{\text{water}}})(\sqrt{A_2} - \sqrt{A_{\text{water}}}) \]  

(4)

where \( A_1 \) is the Hamaker constant of the AgNPs \((A_{\text{AgNPs}} = 6.99 \times 10^{-20} \text{ J})\),\(^6\) of goethite \((A_{\text{goethite}} = 2.29 \times 10^{-20} \text{ J})\),\(^7\) or of hematite \((A_{\text{hematite}} = 4.30 \times 10^{-20} \text{ J})\); \( A_2 \) is \( A_{\text{goethite}} \) or \( A_{\text{hematite}} \); and \( A_{\text{water}} \) is the Hamaker constant of water \((3.7 \times 10^{-20} \text{ J})\).\(^9\)

The EDL interaction energy \((\Phi_{\text{EDL}})\) for the sphere-sphere and sphere-plate configurations can be calculated using Eqs. (5) (6), respectively.\(^3,4,10\)

\[ \Phi_{\text{EDL}} = 0.5 \pi \varepsilon_0 \varepsilon_r r_h \frac{r_{h1} r_{h2}}{r_{h1} + r_{h2}} \{ 2 \psi_1 \psi_2 \ln \left[ \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] + (\psi_1^2 + \psi_2^2) \ln [1 - \exp(-2\kappa h)] \} \]  

(5)

\[ \Phi_{\text{EDL}} = 0.5 \pi \varepsilon_0 \varepsilon_r r_h \{ 2 \psi_1 \psi_2 \ln \left[ \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] + (\psi_1^2 + \psi_2^2) \ln [1 - \exp(-2\kappa h)] \} \]  

(6)

\[ \kappa = \sqrt{\frac{1000 e^2 \sum n_0 z_j^2}{\varepsilon_0 \varepsilon_r k T}} \]  

(7)

where \( \varepsilon_0 \) and \( \varepsilon_r \) are the dielectric permittivity of the vacuum \((8.854 \times 10^{-12} \text{ C/Vm})\) and water \((78.5 \text{ at } 298 \text{ K})\), respectively; \( \psi_1 \) and \( \psi_2 \) are the \( \zeta \)-potentials of AgNPs, goethite, and hematite in Eq. (5); \( \psi_1 \) and \( \psi_2 \) are the \( \zeta \)-potentials of AgNPs and goethite/hematite, respectively, in Eq. (6) (see Table S1); \( \kappa \) is the Debye-Hückel parameter, which is determined using Eq. (7)\(^4\); \( e \) is the electron charge \((1.602 \times 10^{-19} \text{ C})\); \( n_0 \) is the number concentration of the ion in the bulk suspension \((6.022 \times 10^{23} \text{ mol}^{-1})\); \( z_j \) is the ion valence (note the valence for monovalent NaNO\(_3\)); \( k \) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ J/K})\); and \( T \) is the absolute temperature \((298 \text{ K})\).

DLVO theory as described above is based on a series of assumptions, including that the surfaces are molecularly smooth and spherically shaped for both the colloids and the collectors. In this study, however, neither goethite nor hematite was spherical.
(Figure S6). The particle size was obtained via DLS measurements, which was also calculated based on the assumption of spherically shaped goethite and hematite. Nonetheless, the above DLVO calculation provides a first approximation of the anticipated changes in the mean interaction energy in response to the variability in the electrolyte concentration and solution pH.
**Text S3. Langmuir modeling.**

The Langmuir model was used to describe the adsorption of AgNPs by goethite and hematite based on the hypothesis that only one type of surface site exists for AgNPs:

\[
\Gamma_e = \frac{\Gamma_{\text{max}} K_L C_e}{1 + K_L C_e}
\]

(8)

where \(\Gamma_e\) (mg m\(^{-2}\)) is the surface coverage of goethite and hematite by AgNPs; \(\Gamma_{\text{max}}\) (mg m\(^{-2}\)) is the maximum surface coverage of goethite and hematite by AgNPs; \(K_L\) (L mg\(^{-1}\)) is the constant related to the free energy of adsorption; and \(C_e\) (mg L\(^{-1}\)) represents the equilibrium concentrations of total Ag in the suspensions. The adsorption data were well fitted by the Langmuir model. The model-fitted parameters are listed in Table S2.
Table S1. Average hydrodynamic diameter ($D_h$) and zeta ($\zeta$)-potentials of the silver nanoparticles (AgNPs), goethite, and hematite used in the Derjaguin-Landau-Verwey-Overbeek (DLVO) calculations based on the different experimental conditions. The data are expressed as the mean ± SD ($n = 3$).

<table>
<thead>
<tr>
<th>pH</th>
<th>NaNO$_3$ (mM)</th>
<th>$D_h$ (nm)</th>
<th>$\zeta$-potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AgNPs</td>
<td>Goethite</td>
<td>Hematite</td>
</tr>
<tr>
<td>5.5</td>
<td>1</td>
<td>77.7±1.7</td>
<td>278±5</td>
</tr>
<tr>
<td>5.5</td>
<td>10</td>
<td>82.7±3.0</td>
<td>452±14</td>
</tr>
<tr>
<td>5.5</td>
<td>100</td>
<td>92.1±7.2</td>
<td>505±14</td>
</tr>
<tr>
<td>7.5</td>
<td>1</td>
<td>79.6±0.8</td>
<td>513±10</td>
</tr>
<tr>
<td>7.5</td>
<td>10</td>
<td>78.3±2.5</td>
<td>608±3</td>
</tr>
<tr>
<td>7.5</td>
<td>100</td>
<td>82.9±12.0</td>
<td>609±8</td>
</tr>
</tbody>
</table>
**Table S2.** Langmuir model-fitted parameters for AgNP adsorption by goethite and hematite.

<table>
<thead>
<tr>
<th>pH</th>
<th>NaNO₃ (mM)</th>
<th>Γₘₐₓᵃ (mg m⁻²)</th>
<th>R</th>
<th>Kₗᵇ (L mg⁻¹)</th>
<th>Γₘₐₓᵃ (mg m⁻²)</th>
<th>R</th>
<th>Kₗ (L mg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>1</td>
<td>0.095</td>
<td>0.97</td>
<td>6.62</td>
<td>0.016</td>
<td>0.87</td>
<td>0.28</td>
</tr>
<tr>
<td>5.5</td>
<td>10</td>
<td>0.187</td>
<td>0.99</td>
<td>2.41</td>
<td>0.017</td>
<td>0.98</td>
<td>0.66</td>
</tr>
<tr>
<td>5.5</td>
<td>100</td>
<td>0.326</td>
<td>0.97</td>
<td>2.52</td>
<td>0.020</td>
<td>0.98</td>
<td>0.76</td>
</tr>
<tr>
<td>7.5</td>
<td>1</td>
<td>0.072</td>
<td>0.98</td>
<td>6.15</td>
<td>0.014</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>7.5</td>
<td>10</td>
<td>0.114</td>
<td>0.99</td>
<td>2.34</td>
<td>0.014</td>
<td>0.96</td>
<td>1.59</td>
</tr>
<tr>
<td>7.5</td>
<td>100</td>
<td>0.215</td>
<td>0.98</td>
<td>0.60</td>
<td>0.022</td>
<td>0.97</td>
<td>0.27</td>
</tr>
</tbody>
</table>

ᵃ Γₘₐₓ is the maximum surface coverage of goethite and hematite by AgNPs (mg m⁻²).

ᵇ Kₗ is the constant related to the free energy of adsorption (L mg⁻¹).
<table>
<thead>
<tr>
<th>pH</th>
<th>NaNO₃ (mM)</th>
<th>AgNPs-AgNPs</th>
<th>Goethite-goethite</th>
<th>Hematite-hematite</th>
<th>AgNPs-goethite</th>
<th>AgNPs-hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Phi_{\text{max}}$</td>
<td>$\Phi_{\text{min2}}$</td>
<td>$h$ (nm)</td>
<td>$\Phi_{\text{max}}$</td>
<td>$\Phi_{\text{min2}}$</td>
</tr>
<tr>
<td>5.5</td>
<td>1</td>
<td>47.4</td>
<td>-0.004</td>
<td>112</td>
<td>355.6</td>
<td>-0.003</td>
</tr>
<tr>
<td>5.5</td>
<td>10</td>
<td>34.5</td>
<td>-0.057</td>
<td>26</td>
<td>338.2</td>
<td>-0.072</td>
</tr>
<tr>
<td>5.5</td>
<td>100</td>
<td>8.3</td>
<td>-0.847</td>
<td>5</td>
<td>176.1</td>
<td>-0.951</td>
</tr>
<tr>
<td>7.5</td>
<td>1</td>
<td>66.4</td>
<td>-0.004</td>
<td>116</td>
<td>183.2</td>
<td>-0.007</td>
</tr>
<tr>
<td>7.5</td>
<td>10</td>
<td>41.7</td>
<td>-0.051</td>
<td>27</td>
<td>56.1</td>
<td>-0.147</td>
</tr>
<tr>
<td>7.5</td>
<td>100</td>
<td>12.2</td>
<td>-0.698</td>
<td>5</td>
<td>16.8</td>
<td>-1.832</td>
</tr>
</tbody>
</table>

<sup>a</sup> $\Phi_{\text{max}}$ and $\Phi_{\text{min2}}$ are maximum repulsive energy barrier and attractive secondary minimum, respectively; $k$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J/K), and $T$ is the absolute temperature (298 K).

<sup>b</sup> $h$ is the separation distance from the AgNP (or goethite, or hematite) surface to the secondary minimum.

<sup>c</sup> NA denotes not applicable.
Table S4. EXAFS fitting parameters at the Ag K-edge for various samples ($S_0^2=0.854$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>$N^a$</th>
<th>$R$(Å)$^b$</th>
<th>$\sigma^2$(Å$^2$)$^c$</th>
<th>$\Delta E_0$(eV)$^d$</th>
<th>R factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag foil</td>
<td>Ag-Ag</td>
<td>12</td>
<td>2.86</td>
<td>0.0097</td>
<td>1.5</td>
<td>0.0013</td>
</tr>
<tr>
<td>pH 5.5</td>
<td>Ag-Ag</td>
<td>5.8</td>
<td>2.84</td>
<td>0.0029</td>
<td>-0.8</td>
<td>0.0024</td>
</tr>
<tr>
<td>pH 7.5</td>
<td>Ag-Ag</td>
<td>4.7</td>
<td>2.86</td>
<td>0.0028</td>
<td>-0.3</td>
<td>0.0144</td>
</tr>
</tbody>
</table>

$^aN$ is coordination number; $^bR$ is bond distance; $^c\sigma^2$ is Debye-Waller factor; $^d\Delta E_0$ is the inner potential correction. R-factor indicates the goodness of the fit. Amplitude reduction factor $S_0^2$ was set to 0.830, according to the Ag foil fit by fixing coordination number as the known crystallographic value.
Figure S1. Variation in the suspension pH used to measure silver nanoparticle (AgNP) adsorption by goethite (A) and hematite (B), respectively. The data are expressed as the mean ± SD (n = 3). The suspension pH was maintained at 5.5 and 7.5 using 10 mM 2-(N-morpholino)ethanesulfonic acid (MES, Biosharp Corp., China) and 3-morpholinopropanesulfonic acid (MOPS, Biosharp Corp.), respectively. The concentration of goethite and hematite in the respective suspensions was 2,500 mg L\(^{-1}\).
Figure S2. Average hydrodynamic diameter ($D_h$) of AgNPs at pH 5.5 and pH 7.5 with 10 mM MES (pH 5.5) or 10 mM MOPS (7.5) or without buffer.
Figure S3. Mass recoveries of Ag during the filtering process in 100 mM NaNO$_3$ at pH 7.5. The mass recoveries of 90.5–99.3% suggested negligible Ag loss due to blocking of goethite or hematite during filtering process. The data are expressed as the mean ± SD ($n = 3$).
Figure S4. Mass recoveries of Ag during the 24-h adsorption experiment in the absence of goethite and hematite. The mass recoveries of 90.2–106.3% suggested negligible Ag loss due to adsorption onto the vials and filtering membranes. The data are expressed as the mean ± SD (n = 3).
Figure S5 The volume-average hydrodynamic diameters (A and B) and number-average hydrodynamic diameters (C and D). Homoaggregation profiles of AgNPs at 10 mg L\(^{-1}\) and goethite at 100 mg L\(^{-1}\), as well as heteroaggregation profiles of AgNPs at 1 mg L\(^{-1}\) and goethite at 100 mg L\(^{-1}\). All experiments were conducted at 10 mM (A and C) and 100 mM (B and D) NaNO\(_3\) at pH 5.5.
Figure S6 Sedimentation history of AgNPs (A), goethite (B), hematite (C), AgNPs-goethite (D), and AgNPs-hematite (E) over the time frame of 0 – 30 min under different experimental conditions. Sedimentation was monitored by measuring optical density at 406 nm (AgNPs, AgNPs-goethite and AgNPs-hematite), at 425 nm (goethite and hematite) using UV–vis spectrophotometer.
Figure S7. Representative transmission electron microscopy (TEM) image (A), TEM-determined particle size distribution (B), TEM electron diffraction image (C), and dynamic light scattering (DLS) particle size distribution (D) of AgNPs in stock suspension. Scale bar = 50 nm in (A) and 5 nm in (C).
Figure S8. Zeta (ζ)-potentials of the AgNP, goethite, and hematite suspensions in 10 mM NaNO₃ as a function of pH. The pH was adjusted using 1 mM HNO₃ or NaOH. The AgNPs were negatively charged under the tested pH (4.0–11.0) conditions. Both goethite and hematite became more negatively charged at higher pH, due to the enhanced deprotonation effect. At a specified pH, goethite was more positively charged than hematite. The isoelectric point (IEP) was 8.2 for goethite and 7.4 for hematite. The data are expressed as the mean ± SD (n = 6).
**Figure S9.** Representative scanning microscopy images of goethite (A) and hematite (B). Scale bar = 1 μm.
Figure S10. Calculated DLVO interaction energy profiles between AgNPs and AgNPs (A–D), goethite and goethite (E–H), and hematite and hematite (I–L) based on NaNO₃ concentrations of 1, 10, and 100 mM, at pH 5.5 (A, B, E, F, I, and J) and pH 7.5 (C, D, G, H, K, and L), as a function of the separation distance using the Hamaker constant of A\textsubscript{AgNPs} (6.99×10⁻²⁰ J), A\textsubscript{goethite} (2.29×10⁻²⁰ J), and A\textsubscript{hematite} (4.30×10⁻²⁰ J). Panels A, C, E, J, I, and K shows the maximum repulsive energy barrier (\(\Phi\text{\textsubscript{max}}\)), and panels B, D, F, H, J, and L the secondary minimum (\(\Phi\text{\textsubscript{min2}}\)) of the interaction energy profile.
Figure S11. Hydrodynamic diameter ($D_h$) of AgNPs (10 mg L$^{-1}$) as a function of pH and ionic strength (IS).
Figure S12. Hydrodynamic diameter ($D_h$) of goethite (A) and hematite (100 mg L$^{-1}$) (B) as a function of pH and IS.
Figure S13. Hydrodynamic diameter ($D_h$) of AgNPs-goethite (A) and AgNPs-hematite (B) as a function of pH and IS. AgNPs: 1 mg L$^{-1}$; iron oxides: 100 mg L$^{-1}$. 
Figure S14. X-ray diffraction patterns of AgNPs-goethite (A) and AgNPs-hematite (B) at pH 5.5 and pH 7.5 in 100 mM NaNO₃. To better detect the silver signal, the initial concentration of AgNPs was 99.7 mg L⁻¹ and the concentration of iron oxides 2,500 mg L⁻¹.
Figure S15. Attenuated total reflectance-Fourier transform infrared spectroscopy spectra of the interaction of the AgNPs with goethite (A) and hematite (B). 1d–7d represent the 1–7 drops of AgNPs (99.7 mg L$^{-1}$, approximately 10 μL per drop) added to the goethite or hematite.
**Figure S16.** Ag k-space EXAFS spectra (A) and the Fourier transforms (B) for Ag foil and goethite after batch experiments.
Figure S17 Cumulative pore volume calculated from BET-N₂ method.
Figure S18. Adsorption isotherm of Ag$^+$ ion on goethite and hematite in 10 mM NaNO$_3$ at pH 5.5 and pH 7.5. The data are expressed as the mean ± SD (n = 3).
References:


