**Supplemental Material**

**Section S1. DLVO Prediction of AuNPs Deposition and AuNPs Aggregation**

The estimation of the classical DLVO interaction energies was used to assist in the understanding of the mechanisms that can control the AuNPs deposition and aggregation observed in the experimental results.

The DLVO theory states that the total interaction energy (*UDLVO*) is the sum of the van der Waals (vdW) attractions (*UvdW*) and the electrical double layer interaction energies (*UEDL*) [1, 2], and can be expressed by the following equation:

(S1)

where *UDLVO* is the total interaction energy between the PEG layers of the AuNPs and the sand surfaces in water as a media (DI water was considered with low ionic strength 0.001 M).

We considered that the interactions occurring between a single AuNP and a grain of silica sand in the column as interactions between a perfect sphere and an infinitely long plate respectively, reasonable due to their relative size differences, and were calculated using the following equation [1]:

(S2)

where *A* is the Hamaker constant for the interacting surfaces (PEG and silica interacting in water); *a*p is the AuNPs radius (*d*DLS), *h* is the separating distance, and λ is a characteristic wavelength of the dielectric, usually considered as 100 nm.

The calculation of the Hamaker constant between two materials and a medium *A*PEG/H2O/Si was based on the Hamaker constants for vdW interactions of the materials in vacuum (*A*PEG, *A*H2O and *A*Si) in a third media and was calculated with Equation (S3) [3]:

*A*PEG/H2O/Si = (*A*PEG1/2 - *A*H2O1/2) (*A*Si1/2 - *A*H2O1/2) (S3)

Based on reported Hamaker values in vacuo for *A*H2O, *A*PEG (approximate to the PEG used in this study) and *A*Si [3, 4], the Hamaker constant *A*PEG/H2O/Si was calculated to be 5.94×10-21 J.

Considering previously reported values of Hamaker constants in vacuo for *A*H2O, *A*PEG and *A*Si [3, 4], the Hamaker constant for the system *A*PEG/H2O/Si was previously calculated and found to be 5.94×10-21J.

For the *UEDL* calculations, the equation used (S4) assumes a constant potential interaction between a spherical particle and an infinitely flat plane [5], described by the following equation:

(S4)

where *UEDL* is the electrostatic interaction energy between the PEG surface of the AuNPs and silica sand surfaces dispersed in a water medium, *εr* is the relative permittivity of water (78.5), *ε*0 is the permittivity of a vacuum (8.854×10− 12), *ap* are the AuNPs radius (*d*DLS values were used), ζPEG are the surface potentials of the interacting surfaces (measured zeta potentials were used), the ζSand used was -32 ± 0 obtained following a similar method as [6], *h* is the separation distance and *κ* is the inverse Debye screening length, defined as:

(S5)

where *e* is the electron charge (1.60 × 10− 19C), *ni* and *zi* are the number concentration and valence of ion *i*.

The DLVO interaction energies were also estimated to evaluate the aggregation behavior of AuNPs with the following equations for the *UvdW* and *UEDL* interactions between two spherical AuNP of similar size and were calculated as follows:

(S6)

For the *UEDL* electrostatic interaction between two AuNPs acting as perfect spheres, a simplified equation can be used:

(S7)

The DLVO energy profiles for deposition on silica sand and aggregation are shown in Figures S1, S2 and S3 for AuNP10, AuNP50 and AuNP100 respectively after their normalization by *k*B*T*.

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Figure S1. DLVO plot describing AuNP10 deposition (solid line) and AuNP10 aggregation (dashed line).

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Figure S2. DLVO plot describing AuNP50 deposition (solid line) and AuNP50 aggregation (dashed line).

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Figure S3. DLVO plot describing AuNP100 deposition (solid line) and AuNP100 aggregation (dashed line).

The obtained DLVO energy profiles (Figures S1, S2 and S3) all show deep primary energy wells at smaller distances *h* (irreversible interaction) followed by the maximum energy barriers (values shown in Table S1) and very shallow secondary minimum (less than 1 *k*B*T*) appears several nanometers away from the surfaces.

The classical DLVO theoretical calculations estimate that colloidal interactions occur only via vdW and EDL interactions thus it does not consider other possible interactions such as steric effects (i.e., entropic and osmotic contributions), therefore, it cannot represent all the possible interactions involving the PEG-coated AuNPs.

However, qualitative explications regarding the role of the PEG-layers on the deposition and aggregation o the interacting surfaces can be obtained from the DLVO calculation results obtained.

When observing the calculated primary energy barriers for the different AuNPs, it can easily be observed that the energy barriers were much lower for aggregation than those for deposition onto silica sand (Table S1).

Table S1. Calculated maximum energy barriers (*UDLVO*) and distances for AuNPs interacting with sand and with another AuNPs.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Nanoparticle** | **Deposition Energy Barrier** | | **Aggregation Energy Barrier** | |
| *UDLVO*  (*k*B*T*) | Distance *h* (nm) | *UDLVO* (*k*B*T*) | Distance *h*  (nm) |
| AuNP10 | 6 | 5 | 1 | 4 |
| AuNP50 | 48 | 2 | 23 | 2 |
| AuNP100 | 57 | 2 | 22 | 2 |

The energy barriers for deposition onto silica sand were higher for the larger AuNPs, with values for AuNP50 of 48 *k*B*T* and for AuNP100 of 57 *k*B*T* while for AuNP10 it was near 6 *k*B*T* (where *k*B is Boltzmann constant and *T* is absolute temperature) as seen in Table S1.

For AuNPs aggregation, from Table S1 the energy barriers of the interaction energy were still higher for the larger AuNPs, with values of 23 *k*B*T* for AuNP50 and 22 for AuNP100 compared to the lower value for AuNP10 (1 *k*B*T*).

When comparing the maximum energy barriers for deposition with the energy barriers for aggregation (Table S1), the energy barriers for aggregation were significantly lower and such reductions indicate that aggregation is more likely to occur than deposition onto sand particles.

High energy barriers are indicators of high AuNPs stability, since vdW interactions are less probable to occur. In the calculations the larger AuNPs showed the higher energy barriers compared to the smaller AuNPs, but as the experiments showed, the stability was considered higher for the smaller AuNPs than for the larger AuNPs, since DLVO does not take into account the steric effects of the PEG coating on the AuNPs, and the degree of stability can also impact the interactions with silica sand.

**Section S2. Determination of the Single-Collector Contact Efficiency 𝜂0**

The single collector contact efficiency η0 is used to describe the probability of attachment of particles that come into contact with the silica sand that can occur mainly by the following mechanisms: Brownian diffusion, interception and gravitational sedimentation. In the case of individual suspended nanoparticles, Brownian diffusion (*η*D) is the dominant mechanism through which particles will come into contact with the surfaces of the collector (*η*0≈*η*D) [7, 8].

The attractive van der Waals (vdW) forces in the presence of coatings of PEG polymeric chains on the surfaces of the AuNPs may impact on the value of the Hamaker constant, thus it has to be taken into account. Therefore, it is reasonable to use the Hamaker constant between silica and PEG in water as medium (APEG/H2O/Si) for the theoretical calculations of *η*0 [8].

*η*0 was calculated [2] using the following correlation Equation (S8):

(S8)

where *AS* is the porosity parameter, *NR* is the aspect ratio between the collector porous media and the AuNPs, *NPe* is the Peclet number characterizing the ratio of convective to diffusive transport and *NvdW* is the van der Waals number characterizing the ratio of van der Waals interaction energy, and the parameters defined by the following equations:

where (S9)

(S10)

(S11)

(S12)

where *f* is the porosity of the medium, *d*p is the AuNPs diameter, *d*c is the silica sand grain diameter, *U* is the approach velocity of fluid, *D*∞ is the diffusion coefficient in an infinite medium (determined by the Stokes-Einstein equation), *A* is the Hamaker constant, *k*B is the Boltzmann constant and *T* is the absolute temperature.

The Hamaker constant between two materials and a medium *A*PEG/H2O/Si was calculated using the Hamaker constants for vdW interactions of the materials in vacuum (*A*PEG, *A*H2O and *A*Si) in a third media [3] and were calculated with Equation (S6) from Section S1.

The obtained η0 value was introduced in the Equation (S13) to obtain the attachment efficiencies (α) for each AuNPs [7, 8]:

(S13)

Table S2. Parameter Values Used for the *α* Numerical Calculations

|  |  |
| --- | --- |
| **Parameter** | **Value** |
| Boltzmann constant (*k*B)  Particle diameters (*dp*)  Collector diameter (*dc*)  Approach fluid velocity (*U*)  Hamaker constant (*A*)  Temperature (*T*)  Porosity (*f*) | 1.38x10-23 J/K  43, 82 and 127 nm  0.425 mm  7.96x10-5 m/s  5.94x10-21 J  298 K  0.41 |

**References**

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