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# Assessing the heteroaggregation of manufactured nanoparticles with naturally occurring colloids in a typical surface water

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## 1. Introduction

To assess the risk posed by nanotechnology-enabled products, it is necessary to consider the likelihood of engineered nanoparticle exposure through aqueous media, as it is a receptacle of these materials throughout their lifecycle. Many factors influence the balance between nanoparticle dispersion/transport and aggregation/deposition in aqueous systems, both environmental and intrinsic to the nanoparticles themselves. The predicted concentrations of engineered nanoparticles in surface water systems are expected in the  $\mu\text{g/L}$  level for nano- $\text{TiO}_2$ , and even lower for many other types such as nano-ZnO and nano-Ag. Consequently, in real aquatic systems, the probability that nanoparticles interact with each other may be lower relative to their collision frequency with naturally occurring colloids that are present at substantially higher concentrations. Suspended particulate matter (SPM) in surface water indeed ranges from a few mg/L in a river with low discharge to tens of g/L during flood conditions. Due to the high specific surface area and reactivity of colloids, they may act as a carrier phase in the water column and strongly affect the fate and transport of nanoparticles via the heteroaggregation process.

Thus, fate models aimed at predicting nanoparticle behaviour and concentration profiles at the river scale must account for heteroaggregation. A nanoparticle-colloid sticking efficiency, independent of nanoparticle or colloid concentrations and only dependent on the solution chemistry, here after called  $\alpha_{\text{hetero}}$ , is well suited as an input for such fate models. However,  $\alpha_{\text{hetero}}$  remains a challenge to determine experimentally.

Here, we present a novel method for determining  $\alpha_{\text{hetero}}$  values at environmentally relevant nanoparticle concentrations by using a combination of laser diffraction measurements and aggregation modeling based on the Smoluchowski equation. Interactions between titanium dioxide nanoparticles ( $\text{TiO}_2$  NPs, 15 nm) and different types of larger mineral colloids were used to demonstrate this new approach.

## 2. Materials and methods

In this work, we developed a mechanistic experimental approach based on laser diffraction that enabled the measurement of heteroaggregation kinetics for  $\text{TiO}_2$  nanoparticles and micrometric colloids. The objective was to elucidate the fundamental mechanisms and to identify the key variables governing the evolution of homo- and heteroaggregation kinetics for the colloids and nanoparticles. This was done at low nanoparticle concentrations (0.1 to 4 mg/L) with regard to the colloid occurrence (100 mg/L) to develop realistic fate scenarios for surface water systems. The impact of pH and natural organic matter on nanoparticle heteroaggregation was also explored.

Silica microspheres (dia. = 0.5  $\mu\text{m}$ ) were first used as a model analog of natural colloids. Heteroaggregation was evaluated as a function of water salinity ( $10^{-3}$  and  $10^{-1}$  M NaCl), pH (5 and 8), and nanoparticle concentration.

In a second step, because natural colloids are rarely monodisperse suspensions of homogenous composition and surface charge like the silica microspheres, smectite clay was used as a more relevant analog of natural colloids. Smectite exhibits a lamellar shape and a heterogeneous surface charge. The effect of the initial aggregation state of the clay was studied by adjusting the solution ionic strength. Preparation in  $10^{-3}$  M NaCl lead to dispersed colloids with lamellar shape and high specific surface area, whereas preparation in  $10^{-1}$  M NaCl lead to the clay being homoaggregated in large and rather spherical units with low surface area.

Finally, to validate this mechanistic approach, a holistic approach was also completed with natural surface water sampled on-field from the Rhone River (France). The suspended particulate and dissolved matter naturally occurring in this water were characterised, and the heteroaggregation of TiO<sub>2</sub> nanoparticles spiked into the system was measured and modeled at varied SPM and nanoparticle concentrations.

### 3. Results and discussion

#### 3.1. Heteroaggregation of nano-TiO<sub>2</sub> with silica colloids

We demonstrated that  $\alpha_{\text{hetero}}$  could be determined from the combination of laser diffraction experiments and an aggregation model, using the surface area ratio of nanoparticles attached to the colloids due to the fact that this ratio drives the probability that nanoparticles bridge the colliding colloids [1].

At pH 5, the TiO<sub>2</sub> NPs and the SiO<sub>2</sub> particles are of opposite charge, resulting in  $\alpha_{\text{hetero}}$  values close to 1. At pH 8, where all the particles are negatively charged,  $\alpha_{\text{hetero}}$  was strongly affected by the solution conditions, with  $\alpha_{\text{hetero}}$  ranging from <0.001 at low ionic strength to 1 at conditions with high NaCl or CaCl<sub>2</sub> concentrations. The presence of humic acid stabilised the system against heteroaggregation.

#### 3.2. Heteroaggregation of nano-TiO<sub>2</sub> with smectite

The TiO<sub>2</sub> nanoparticle affinity for clay is driven by electrostatic interactions. Opposite surface charges and/or high ionic strength favoured the formation of heteroaggregates via the attachment of nanoparticles to the clay. The initial shape and dispersion state of the clay as well as the nanoparticle/clay concentration ratio also affected the nature of the heteroaggregation mechanism. With dispersed clay platelets (10<sup>-3</sup> M NaCl), larger heteroaggregation, driven by bridging nanoparticles, occurred at a nanoparticle/clay number ratio > 0.5. In 10<sup>-1</sup> M NaCl, the clay was pre-aggregated into larger and more spherical units. This favoured larger heteroaggregation at lower nanoparticle concentrations that correlated to the nanoparticle/clay surface area ratio. In this latter case, a nanoparticle to clay sticking efficiency could be determined. Similar to the silica-TiO<sub>2</sub> system, the presence of humic acid also exhibited a stabilising effect on the clay-TiO<sub>2</sub> system.

#### 3.3. Heteroaggregation of nano-TiO<sub>2</sub> with natural river colloids

The TiO<sub>2</sub> nanoparticles demonstrated a significant affinity for the mineral SPM, with rapid heteroaggregation and subsequent sedimentation of the resulting aggregates. This mechanism was heavily dependent on the nanoparticle/SPM number ratio. The mineralogical characterisation of the SPM heteroaggregated with the nanoparticles suggested that the efficiency for SPM to bind with nanoparticles is driven more by the probability of collision than by the sticking efficiency.

### 4. Conclusions

Our data show that at relevant concentrations, nanoparticle behaviour is mainly driven by heteroaggregation with colloids, while homoaggregation remains negligible. The dimensionless  $\alpha_{\text{hetero}}$  value is a key parameter needed to feed environmental fate models and was calculated in this work with model and natural colloids under defined conditions. These considerations are of high importance in the field of risk assessment of engineered nanoparticles, as they contribute to better predict the exposure aspect in aqueous systems with continuously increasing relevance.

### 5. References

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