

Aggregation Behavior of Functionalized Engineered Nanoparticles in Aquatic Environments

Abstract

Many engineered nanoparticles (ENPs) are at present modified with surface coatings. These surface modifications extend the applications of ENPs to specific purposes and, as a result, the production of functionalized ENPs has increased dramatically over the last decade. These emerging applications will certainly lead to the release of functionalized ENPs into aquatic systems, resulting in unforeseen impacts on living organisms and on human health, due to the ecotoxicity of ENPs. Risk assessments concerning these ENPs (whether functionalized or not) in the environment are demanded by public concern. However, the shortage of available data on the behavior and eventual fate of ENPs presents a problem for such assessments.

This work reports on stepwise investigations into the influences that different types of functionalization have on the fate and behavior of ENPs in aquatic systems. Two different types of gold nanoparticles (GNPs), coated with either citrate or 11-mercaptoundecanoic acid (MUA), have been used as examples of functionalized ENPs. Time-resolved dynamic light scattering was employed to investigate the aggregation kinetics of these two types of GNPs under different water chemistry conditions.

Surface coatings were found to be a crucial factor in the stability of ENPs. Their physicochemical properties affect the stability of ENPs in different water chemistries. The results of these investigations show that citrate- and MUA-coated GNPs have different pH-related aggregation effects within a pH range between 12 and 2. In the absence of natural organic matter (NOM), MUA coatings on GNPs resulted in greater stability than citrate coatings, at naturally occurring pH values. In a fast aggregation regime, increasing the NOM concentration stabilized the citrate-coated GNPs in Na^+ and Mg^{2+} solutions but enhanced aggregation at high Ca^{2+} concentrations. In contrast, the addition of NOM did not result in any obvious change in the fast aggregation of MUA-

coated GNPs in Na^+ solutions, but enhanced their stability in both Ca^{2+} and Mg^{2+} solutions.

The value of combining spatial data on surface-water chemistries with results from in-vitro colloidal stability testing on nanoparticles has also been assessed in this study. Aggregation rates were used as indicators for the colloidal stability of particles. The regions where may or may not have occurrence of GNPs tested are found out according to the resulting contour maps of Europe. NOM was recognized as the most important parameter affecting the stability of the investigated GNPs in European streams. Climate and topography are also recognized as factors that have an indirect influence on ENP colloidal stability, since they affect the NOM content in streams. In addition, the interactions of GNPs with NOM, and also with different divalent cations (Ca^{2+} and Mg^{2+}), indicate that surface coatings need to be taken into account when predicting the aggregation behavior of ENPs.

These investigations are believed to be of crucial importance for understanding the aggregation, transport, and eventual fate of functionalized ENPs, and to provide a basis for extending the classical exposure models used in risk assessment.