Effects of Pristine and Palladium-doped γ-Al_2O_3 Nanoparticles in Urban Stream Environment: Interactions with Humic Acid, Clays, and Freshwater Aquatic Plants

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While α-Al_2O_3 is prevalent in nature, γ-Al_2O_3 is the most widely used form in nanomaterial application and fabrication. Due to excellent hydrothermal stability, small particle size, high surface area, and porosity, γ-Al_2O_3 nanoparticles (NPs) have been extensively used as a support material for the platinum group elements (PGEs) in catalytic reactions, and have shown to significantly enhance the effectiveness and selectivity of catalytic performance of PGEs. Therefore, the introduction of γ-Al_2O_3 and PGEs-doped γ-Al_2O_3 NPs to surficial environments is inevitable and is predicted to substantially grow; yet our understanding of their environmental behaviour and bioavailability, as opposed to natural α-Al_2O_3, is lacking.

In this study, we systematically examined the aggregation and colloidal stability of γ-Al_2O_3 and Palladium (Pd, 5 wt%)-doped γ-Al_2O_3 as a function of solution pH, ionic strength, and humic acid or clay mineral (e.g., montmorillonite) concentration, using dynamic light scattering and transmission electron microscopy techniques. In addition, we measured the bioavailability of the NPs, using two native macrophytes, *Lemna minor* (duckweed) and *Azolla filiculoides* (water fern) that are abundant in and vital to the urban watershed environment and ecosystem function.

In solutions where pH $\leq$ PZC (the point of zero charge) of the NPs, the presence of natural colloids seemed to increase the NPs colloidal stability through electrostatic interactions and steric hinderance. At those pHs, significant NP aggregation was only evident in high ionic strength solutions ($\geq$100 mM NaCl and 30 mM $CaCl_2$). However, when pH > PZC, very limited surface interaction between the NPs and natural colloids was observed. In regards to bioavailability, both NPs inhibited the macrophytes growth, more severely by Pd-γ-Al_2O_3, presumabily due to Pd release. A significant bioaccumuation of Pd and Al was noted in all macrophytes treated with NPs, but higher uptake occurred in *L. minor*. Thus, both environmental conditions and dopants appear to greatly modifiy surface conditions of the engineered NPs, and therefore, ultimately determine their environmental behavior and bioavialability.