

Size-dependent surface charging of TiO₂ nanoparticles

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Metal oxide nanoparticles show variations in their structure relative to corresponding larger microparticles of the same material, often with new unexpected features occurring in the nanoscale size range. Generally, nanoparticles have increased roughness and curvature of the surface, large specific surface area and high abundance of active binding sites; thus are very reactive. The surface charge is highly affected by the surrounding media, which in turn affects the colloidal stability of nanoparticles.

This study focuses on the size-dependent surface charging of TiO₂ (anatase) nanoparticles. TiO₂ nanoparticles with well-defined particle sizes (<30 nm) and without any coatings or surfactants were synthesized using low-temperature hydrolysis of TiCl₄. Temperature during synthesis reaction, dialysis and storage was found to strongly influence the particle size and crystal structure, according to [1]. The nanoparticles were extensively characterized using several techniques and were found to have a sphere-like shape. In order to study the size-dependence on the pHPZC (point of zero charge), potentiometric titrations were used to determine the surface charge of the TiO₂ nanoparticles at 25 °C, and at varying ionic strengths obtained with NaCl as background electrolyte. Further, zeta potential measurements were performed under similar conditions.

The experimentally determined size-dependent surface charging behavior of TiO₂ nanoparticles are compared with the corresponding surface charge densities calculated by classical surface complexation models, as well as by the Corrected Debye-Hückel (CDH) theory [2].

[1] Abbas *et al.* (2011) *Colloids Surf. A: Physicochem. Eng. Aspects* **384**, 254-261. [2] Abbas *et al.* (2008) *J. Phys. Chem. C*, **112**, 5715-5723.

Biom mineralization and fate of the Fe^{II}-Fe^{III} hydroxy salt green rust vs. magnetite

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It is well known that iron oxide reduction by *Shewanella* spp. bacteria promotes the formation of Fe^{II} bearing minerals, such as the mixed Fe^{II}-Fe^{III} hydroxysalt green rusts (GRs), in anaerobic conditions. Although the microbial-promoted generation of GRs is widely demonstrated, the mechanisms and factors governing the GR formation as the main secondary iron mineral at the expense of other products in lab-scale investigations or environmental systems are largely unknown. As GR is an effective reductant for several contaminants the mechanism controlling the formation routes of GR merit investigation, from both the environmental and engineering points of view.

Some factors such as cellular material (i.e. autoclaved cells and/or bacterial polymers), synthetic anionic polymers or oxyanions have been identified to control the route of the GR mineralization as secondary mineral at the expense of other products such as magnetite.

The arrangement mode of the heterogeneous aggregates resulting from the interactions between bacterial cells, iron oxide particles and polymers was suggested to influence the routes of formation of secondary iron minerals by limiting the diffusion of reactive species and thus creating favorable microenvironment for GR formation. In these aggregates, the electron transfer from cells to iron oxides is supported by organic electron shuttles.

On the other hand, anionic polymers, colloidal and aqueous silicates were found to also influence the nature of the secondary iron minerals through the stabilization of the GR crystals.

These results indicate clearly that the bacterial cells drive indirectly the nature of the secondary Fe^{II}-bearing mineral. Moreover, they give new insights into the understanding of the mechanisms of « biogenic » mineral formation based on the electron transfers from bacteria towards iron oxides. Finally, this work contributes to our understanding of the processes leading to green rust formation in environmental systems, such as soils or aquatic systems biofilms, in which a very high cell density can be found at a micro-scale level, associated to exocellular polymers and natural silica mineral composites.