Exploring the first steps of iron(III) oxyhydroxide nucleation using a competitive ligand kinetic approach

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Under favourable conditions, nucleation of iron (III) oxyhydroxides (FeOx) is typically rapid compared to subsequent processes. To date, little work has been done to examine the first steps of FeOx nucleation, namely the initial polymerisation of dissolved monomeric iron (III) complexes, which may be rate-limiting in the nucleation process.

I have investigated the kinetics of iron (III) polymerisation over a wide range of pH values using a competitive ligand approach in which the complexation of monomeric iron (III) by desferrioxamine B (DFB) competes with iron (III) polymerisation when conditions conducive to nucleation are induced. Polymerisation was induced by the rapid (< 5 ms) mixing of acidified solutions of dissolved iron (III) with a pH-buffered DFB solution using a micromixer chip. Formation of the orange coloured iron (III)-DFB complex was quantified over time from 100 ms after mixing onwards at concentrations down to ~10 nM with a stopped-flow long (1 m) optical pathlength spectrophotometry system (Figure 1).

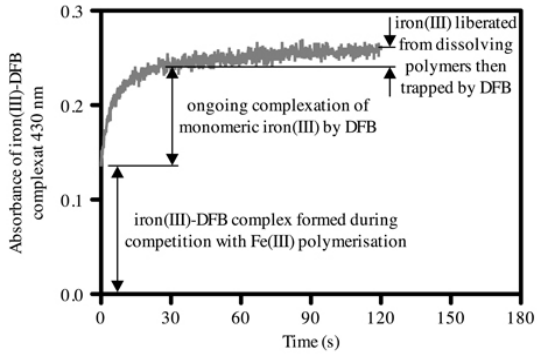

Figure 1: Kinetic traces reveal initial rapid partitioning of iron(III) between the iron(III)-DFB complex and iron(III) polymers, followed by the slow redissolution of polymers.

Kinetic parameters for FeOx polymerisation (obtained by simultaneously fitting data from multiple iron (III) and DFB concentrations at each pH) varied with pH in a manner consistent with control of the initial polymerisation step by the exchange of water bound to monomeric iron (III). The initial steps in FeOx nucleation can thus be interpreted in a similar context to other aquatic chemical processes.

Environmental impact of engineered nanoparticles and nanomaterials through their life cycle

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Even though preliminary risk assessments of manufactured nanoparticles (NPs) are emerging, information on NPs bioavailability to aquatic biota and trophic transfer are largely lacking, and early studies have yielded incomplete and contradictory results. Moreover, a considerable confusion exists concerning the distinction between 'nanotechnology' and 'nanomaterial' which are most often considered to be synonymous of nanoparticles. But for most applications nanoparticles can be surface modified and generally are embedded in the final product and therefore do not come into direct contact with consumers or the environment. So what about their toxic effects when surface modified?

The aim of our stufy is to better constrain the transfer, transformation and ecotoxicity of by-products released from nanomaterials during their life cycle. Two examples will be detailed 1) nano-TiO_2 incorporated as UV filter in sunscreens ii) nano-SiO_2 based composite (polymeric matrixes including polyamides, polypropylenes and polyurethanes as bulk materials) to compare impact between by-products and bare nanoparticles. Methodology and experimental issues concerning durability characterisation using accelerated aging protocols, characterisation will be adressed.

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