



# Analysis of anion adsorption effects on alumina nanoparticles stability



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## ABSTRACT

Nanoparticles and colloids can be relevant in contaminant migration if the contaminant is strongly adsorbed onto the particles and they are stable and mobile. The main conditions required for a colloidal system to be considered as “stable” are: (1) low ionic strength of the groundwater ( $\leq 1 \times 10^{-3}$  M) and (2) pH far from the point of zero charge ( $\text{pH}_{\text{PZC}}$ ). These conditions however, are too simplified to describe the colloidal behaviour in real cases; in fact, specific adsorption of different ions may also have an important impact on colloid stability.

In particular, in this study we analyse the effects of the adsorption of inorganic anions on  $\text{Al}_2\text{O}_3$  oxide nanoparticles (alumina NPs) stability, combining batch adsorption studies with electrophoretic and dynamic light scattering measurements. Selenite adsorption was studied in a wide range of pHs (3–11), ionic strengths ( $5 \times 10^{-4}$ – $1 \times 10^{-1}$  M) and selenite concentration. Different electrolytes were used to understand the competitive effects for selenite sorption of different anions in solution ( $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and especially their overall influence on alumina NPs stability.

The positive charge of alumina, under acid and neutral-alkaline pHs, favours anion adsorption which, in turn, may result in a decrease of the net surface charge, promoting particle aggregation and the destabilisation of the system. Results showed that, the higher the anion affinity for alumina surface and sites occupancy, the higher the destabilisation of particles. The sorption selectivity observed in our study was:  $\text{SeO}_3^{2-} > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{ClO}_4^-$ .

Upon anion adsorption, particles aggregation was evident, but a clear change in  $\zeta$ -potential, was only observed with very high surface occupancies. Surface complexation modelling has been shown to be useful supporting tool for stability studies.

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## 1. Introduction

Amongst the most interesting colloidal particles from an environmental point of view are: oxy-hydroxides and clay minerals that are ubiquitous in groundwater (Sen and Khilar, 2006). Furthermore, with a rising demand for their application, nano-oxides are candidates for multiple industrial uses and therefore their release to the environment, leading to possible harmful effects, is likely.

Under favourable chemical-physical conditions, colloids and nanoparticles (NPs) can travel large distances; thus their migration is of special interest when these particles may carry some type of contaminant. Many uncertainties still exist on colloid-driven contaminant transport and this is an issue of concern associated to hazardous waste repositories (Geckeis, 2004). NPs and colloids may enhance contaminant transport in groundwater, provided the contaminant is irreversibly adsorbed onto their surface and the particles are stable and mobile (McCarthy and Zachara, 1989; Miller et al., 1994; Sen and Khilar, 2006, and references therein).

The kinetics of processes and residence times play also a very important role in colloid transport thus, under certain conditions, NPs may enhance contaminant migration even its sorption onto the particle surfaces is (partially) reversible.

Surface properties mostly determine colloidal behaviour in terms of stability, mobility and ion adsorption, therefore their study is fundamental. Furthermore, changes in particle size upon aggregation alter colloid transport properties, their reactivity, toxicity and bioavailability. Furthermore, speciation of colloids through the whole transport system should be considered.

In general, oxide colloids are stable and more mobile, when the ionic strength of the groundwater is low ( $\leq 1 \times 10^{-3}$  M) and the pH is far from the point of zero charge ( $\text{pH}_{\text{PZC}}$ ). Some parameters like the critical coagulation concentration, CCC, the  $\text{pH}_{\text{PZC}}$  or the isoelectric point ( $\text{pH}_{\text{IEP}}$ ) are normally used to define the stability of colloidal systems. Nevertheless, these parameters are usually determined in simplified systems and using indifferent (non-sorbing) electrolytes; for this reason, sometimes, they are not totally representative of the real behaviour of colloids in nature.

In particular, it is well known that specific adsorption of different ions may have an important impact on colloid stability (Stumm

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et al., 1970). The CCC of a colloidal system is inversely proportional to the  $n^{\text{th}}$  power of the counterion (Schulze and Hardy rule) but it decreases if the ions in solution are sorbing (Stumm et al., 1970). This means that sorbable ions may destabilize colloid at much lower concentration than inert ions. This is a very important point because DLVO theory, which is widely used to assess the stability of colloidal particles, mostly neglects the dominating role that chemical forces may play in a system.

The description of the colloidal behaviour under real conditions deserves more in-depth analyses. Additionally, as the adsorption itself could modify surface colloid properties, the effects of ion adsorption on colloid stability are of special interest, for example, when colloid-driven contaminant migration is analysed (Benedicto et al., 2013). In this special case, it is necessary to understand under what conditions these surface modifications may occur, and if these modifications could enhance or inhibit contaminant transport.

In regard to colloid stability, the effects of organic anions or polyelectrolyte are largely documented. The stability of alumina NPs in the presence of natural organic matter was studied by Ghosh et al. (2008). In general, organic coatings are reported to increase substantially colloidal stability: these coatings impart negative charge masking the surface properties of the original particles and dominate interface reactions (Tiller and ÓMelia, 1993; Tipping and Higgins, 1982; O'Melia and Tiller, 1993; Illes and Tombacz, 2006). Tombacz et al. (1999) studied the influence of humate, gallate, salicylate onto clays and aluminium oxide at pH 7–8, in the presence of indifferent electrolytes. Under these conditions, they observed an increased stabilization of the oxide in the presence of relatively small quantities of organic ions. Other polyelectrolytes were also capable of modifying the surface properties of oxides and increase their stability (Singh et al., 2005; Puls et al., 1993; Liang and Morgan, 1990). In any case, the degree of stabilization (or destabilization) of the colloids depends on their point of zero charge and the specific interactions occurring.

On the other hand, the (potentially relevant) effects of inorganic anions present in solution on colloid stability are mostly neglected. Evaluating methods of preparation of aluminium oxide monodispersed suspensions, Brace and Matjevic (1973) already observed large effects of the presence of sulphate on the surface charge of the particles and their  $\text{pH}_{\text{PZC}}$ . But although many studies on adsorption on oxy-hydroxides of inorganic anions (carbonate, phosphate, sulphate, selenite/selenate arsenic) and competitive effects between them exist (Zhang and Sparks, 1990; Balistrieri and Chao, 1987; Peak, 2006; Missana et al., 2009; Wu et al., 2000, 2002; Yamani et al., 2014; Katai et al., 2012; Loffredo et al., 2011; Kim et al., 2004), the effects of inorganic anion adsorption on the stability of colloid has been scarcely reported. Chorover et al., 1997, reported the effects of phosphate adsorption on hematite coagulation; more recently, Benedicto et al. (2013) analysed the variations of  $\text{TiO}_2$  nanoparticle size distribution, caused by selenite adsorption, and suggested the importance of studying contaminant adsorption onto colloids and their aggregation behaviour in an integrated form, to assess the potential of colloid-facilitated migration.

The main aim of this study is to evaluate the effects of the adsorption of inorganic anions on  $\text{Al}_2\text{O}_3$  nanoparticle (alumina NPs) stability. This will show the importance of considering inorganic anions to assess the stability of a colloidal system in natural waters. The analysis will be done combining batch adsorption studies, electrophoretic and dynamic light scattering techniques being the combination of different techniques fundamental. Furthermore, as ion adsorption significantly affects nanoparticle stability, the use of (mechanistic) sorption models will be shown to be very useful tool for supporting stability studies.

Selenite is the main anion analyzed, and its adsorption is studied using different electrolytes, to verify the adsorption strength other

anions (through competitive effects with selenium) and their possible relevance on the oxide stability. Selenium is introduced in the environment from both natural and anthropogenic sources mainly combustion of fossil fuels, disposal of fly ash, mining activities and agriculture. It is an element of special concern also in the frame of nuclear waste repository for the long-life of the  $^{79}\text{Se}$  isotope and its high mobility. The effects of selenite adsorption, on alumina NPs stability, have been studied in a wide range of selenite concentrations as to cover different possible contamination scenarios.

The  $\text{pH}_{\text{PZC}}$  of alumina, as widely reported in the literature (Ghosh et al., 2008; Kosmulski, 2009a,b; Huang and Stumm, 1973; Sverjenski and Sahai, 1996; Schulthess and Sparks, 1986; Westall and Hohl, 1980) is in the alkaline range ( $\text{pH} = 8.0\text{--}9.5$ ); thus, the oxide presents positive charge in a wide range of pH and it is quite appropriated for studying anion adsorption. Additionally, alumina surface functional groups resemble those present at the edge of clay particles (aluminols), so this study can also help understanding the stability of natural clay colloids in natural systems, in the presence of inorganic anions.

## 2. Materials and methods

### 2.1. Nanoparticles

The nanoxide used in this work was alumina powder ( $\text{Al}_2\text{O}_3$ , CAS 1344-28-1) provided by Aldrich, with a particle nominal size  $<50$  nm. The  $\text{N}_2$ -BET specific surface area is  $136 \text{ m}^2/\text{g}$ . For stability and sorption experiments, the oxide was directly suspended in different electrolytes at the desired solid to liquid ratio and put in the ultrasound during 1 h, before the measurements.

The mean size of dried particles was analyzed by AFM. The AFM samples were prepared suspending the oxide (116 ppm) in deionized water at two different pH values (4.5 and 6.5). A drop of these suspensions was deposited onto a freshly cleaved mica substrate and dried in an oven at  $60^\circ\text{C}$ . Fig. 1 shows the AFM image obtained with the sample prepared at pH 6.5, which confirms that the primary particles have a mean size  $<50$  nm. Aggregates with a size around 100–200 nm are also visible. Both the size and the shape of the particles are not homogeneous. Similar images were obtained with the sample prepared at pH 4.5.

### 2.2. Selenium

The tracer used for sorption experiments was a carrier-free  $^{75}\text{Se}$  (as  $\text{H}_2\text{SeO}_3$  (selenite) in 0.1 HCl, Isotope Products). Most  $^{75}\text{Se}$

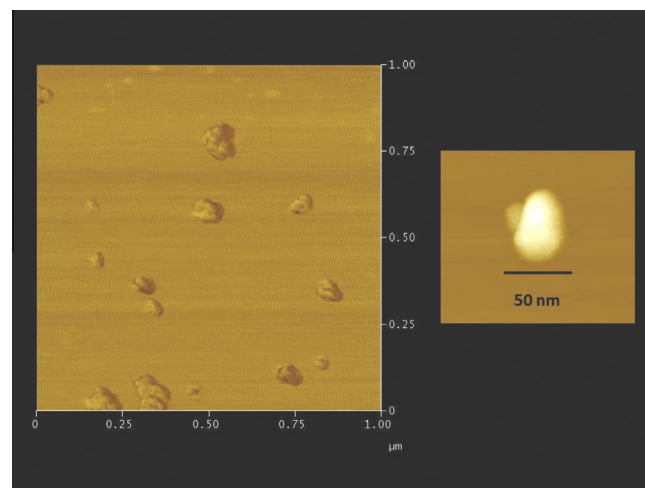


Fig. 1. AFM image (tapping mode) of the alumina nanoparticles, prepared at pH 6.5. In the right part of the figure a detail of a single particle is shown.

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