Oxyanion-calcium synergetic interactions on ferrihydrite nanoparticles

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The geochemical behaviour of phosphate and arsenate ions in soil and aquatic systems is determined by the presence of mineral surfaces and major ions. Information about the distribution of oxyanions over the solid and solution phases is essential for understanding the transport, bioavailability and toxicity of these compounds in the environment. Ferrihydrite is a reactive naturally occurring iron oxide. Its formation has been reported at near-neutral pH in a variety of redox-active environments, such as soils and sediments, or freshwater and marine settings. The oxidation and dissolution of Fe-bearing sulphide minerals associated with mine wastes and acid mine drainage also result in the formation of ferrihydrite, along with other secondary iron oxides [1]. Due to its abundance, large surface area and high reactivity it is considered a key mineral for metal sequestration and plays a crucial role in the cycling of iron and trace elements in natural systems.

In the present study, we have analysed the adsorption of arsenate and phosphate on ferrihydrite nanoparticles in the presence of calcium ions. The presence of calcium ions enhanced the retention of these oxyanions on ferrihydrite and *vice versa*. The arsenate-calcium and phosphate-calcium multi-component systems were described using a mechanistic surface complexation model. Use of this type of model enables prediction of the solution and surface speciation, along with analysis of oxyanion mobility in relation to environmental conditions. The mutual interactions between arsenate and calcium were successfully described with the model parameters, indicating that changes in the electrostatic forces at the solid/solution interface caused the observed enhancement. However, adsorption on the phosphate-calcium system was underestimated with the parameters of the single-component systems, indicating that additional mechanisms or processes should be considered, such as the formation of a phosphate-calcium ternary surface complex or surface precipitation.

[1] Jambor & Dutrizac (1998), *Chem. Rev.*, **98**, 2549–2585.