

Size-dependent sorption of *myo*-inositol hexakisphosphate and orthophosphate on nano- γ - Al_2O_3



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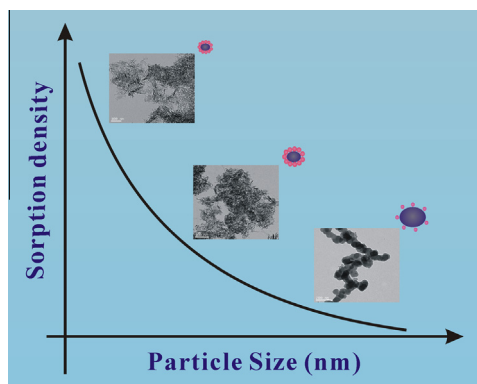
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GRAPHICAL ABSTRACT



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ABSTRACT

The effects of particle size (5, 35 and 70 nm) on the sorption of *myo*-inositol hexakisphosphate (IHP) and inorganic phosphate (KH_2PO_4 , Pi) on γ - Al_2O_3 nanoparticles were investigated using batch sorption experiments, zeta potential measurements and solid-state nuclear magnetic resonance spectroscopy (NMR). The results show that the maximum sorption densities ($\mu\text{mol m}^{-2}$) for IHP and Pi increase with decreasing γ - Al_2O_3 particle size. The sorption affinity of γ - Al_2O_3 for IHP and Pi generally increases with decreasing particle size, and the sorption affinity for IHP is approximately one order of magnitude greater than that for Pi. In our experimental time scale, surface complexation is the main mechanism for IHP and Pi sorption on large size γ - Al_2O_3 . While an additional surface precipitation mechanism, indicated by solid-state ^{31}P and ^{27}Al NMR data, is partly responsible for the greater sorption density on very small size γ - Al_2O_3 . Compared with Pi, the effect of particle size on the sorption of IHP is more pronounced. The results suggest a size-dependent surface reactivity of Al_2O_3 nanoparticles with Pi/IHP. The underlying mechanism will also be relevant for other small nanosize (hydroxide) particles and is important for our understanding of the role of small nanoparticles in controlling the mobility and fate of organic and inorganic phosphates in the environment.

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1. Introduction

Aluminum (Al) (oxyhydr)oxide minerals are ubiquitous in natural environments and they are widely investigated in fields of catalysis and interfacial chemistry of nutrient elements and environmental pollutants [1–5]. The sorption of phosphorus (P) compounds on Al (oxyhydr)oxides is as strong as that on iron (oxyhydr)oxides and is of practical importance for soil fertility and eutrophication [6–8]. The sorption characteristics and mechanisms of inorganic phosphate (Pi) on Al (oxyhydr)oxides have been widely studied [1,9–15] and the general conclusion is that inner-sphere surface complexes and surface precipitates are formed on Al (oxyhydr)oxides. Aluminum phosphate surface precipitates (AlPO₄) have been observed on γ -Al₂O₃ at pH 3 [10], high phosphate concentrations [1,10], and long (12 d) equilibration times [1].

In addition, organic phosphates (e.g., *myo*-inositol hexakisphosphate, IHP) occur widely in the environment [16,17], but their sorption on Al (oxyhydr)oxides nanoparticles has received less attention. IHP strongly sorbs on Al (oxyhydr)oxides via the surface complexation mechanism. Guan et al. [18] used *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and molecular orbital calculations to study the adsorption of IHP to amorphous aluminum hydroxide (AAH) and concluded that IHP formed inner-sphere complexes with three of the six phosphate groups bound to the surface while the other three remained in contact with the solution. Ruyter-Hooley et al. [19] investigated the sorption of IHP on gibbsite by ³¹P solid-state nuclear magnetic resonance (NMR) spectroscopy; the observed chemical shifts suggested that the binding process involved a combination of both outer- and inner-sphere complexation and surface precipitation. Our previous studies showed (i) that the sorption of organic phosphates on Al (oxyhydr)oxides depended on the mineral crystallinity [20] and (ii) that on AAH IHP was initially adsorbed through inner-sphere complexation via ligand exchange, followed by AAH dissolution and ternary complex formation and that lastly the ternary complexes were rapidly transformed to surface precipitates and bulk aluminum phytate [21].

In addition to crystallinity, the crystallite size of Al (oxyhydr)oxides is also a key factor affecting the sorption of P compounds. When the particle size of a mineral has physical dimensions of approximately 1–30 nm, the physical and chemical properties of the mineral may be different from those of samples of the same mineral with large particle sizes [22–26]. For small nanoparticles the surface and near-surface atomic structure, stability, and reactivity will change with the particle size and these characteristics have been found to affect biogeochemical reactions in the Earth's surface environments and the mobility and bioavailability of nutrients and contaminants in soil environments [26–29]. Several recent studies have investigated the influence of crystallite size on the surface reactivity (e.g., dissolution and sorption) of metal oxides. For instance, the size of nanoparticles has been shown to affect the dissolution rate of goethite [30–32] and hematite [33,34] and the sorption of Cu(II) [35] and Pb(II) [36] on hematite, and of Pi on ferrihydrite [37] were all size-dependent.

To the best of our knowledge, there are no studies assessing the effect of particle size on the sorption of organic and inorganic phosphates on Al (oxyhydr)oxides. Therefore, in the present study, the effect of particle size (5, 35, and 70 nm) on IHP and Pi sorption on γ -Al₂O₃ nanoparticles was investigated with emphasis to IHP. Information has been attained by combining batch sorption experiments, electrokinetic measurements and solid-state NMR spectroscopy. The sorption experiments give direct information on Pi and IHP sorption under different conditions; the electrokinetic measurements reveal the iso-electric points (IEP) of the particles

and provide a first impression on the changes of the electrostatic potential in the vicinity of the particle surface upon Pi or IHP sorption and the NMR spectroscopy gives information on the binding mechanisms and possible surface precipitation. To further assess the possibility of Al–IHP surface precipitates also some dissolution experiments of the samples have been carried out.

2. Materials and methods

2.1. Materials and reagents

Analytical reagent grade chemicals and ultra-pure water (resistivity >18.3 M Ω cm) were used to prepare all the solutions and suspensions. Dipotassium *myo*-inositol hexaphosphate (IHP) was obtained from Sigma–Aldrich (product number-P5681-5G, purity greater than 95%). IHP is a compound in which all six hydroxyl groups of *myo*-inositol are esterified as phosphates [17] (Fig. S1). As inorganic phosphate (Pi) KH₂PO₄ (Reagent grade) was obtained from Sinopharm Chemical Reagent Co., Ltd was used. Stock solutions of IHP and Pi were prepared in ultra-pure water and refrigerated. The hydrolysis of IHP in the stock solution was monitored before each use by measuring the orthophosphate level in the stock solution.

Three γ -Al₂O₃ samples with different average particle diameters were obtained from different companies: the 70 nm sample was acquired from Alfa Aesar (product number-43266), the 35 nm sample from Sigma–Aldrich (product number-544833) and the 5 nm sample from Sky Spring Nanomaterials Inc (product number-1328QI). The CAS number of γ -Al₂O₃ is 1344-28-1. The samples were further characterized by Transmission Electron Microscopy (TEM), powder X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany), and N₂ gas adsorption–desorption (total 86 dots) measurements at 77 K. For the latter experiments the dry samples were outgassed under vacuum at 110 °C.

2.2. Sorption isotherm and sorption pH edge experiments

Before sorption, the γ -Al₂O₃ particles were dispersed for 24 h in 0.1 M KCl solution acidified with HCl to pH 5.0 to equilibrate the suspensions. The relatively high KCl concentration assures that the ionic strength of the solutions is hardly or not affected by the P concentration. During the 24 h the pH was re-adjusted regularly and the final suspension was purged overnight with N₂ gas to remove CO₂. The solid concentration of the stock suspensions varied with particle size: 2.0 g L⁻¹, 1.5 g L⁻¹ and 0.75 g L⁻¹ for, respectively, the 70, 35 and 5 nm particles to account for the differences in specific surface area. To a series of 10.0 mL of P-containing solutions (58–580 μ M IHP; 69.6–1392 μ M Pi) at pH 5.0 in 0.1 M KCl, 10.0 mL of γ -Al₂O₃ stock suspensions were added. The suspensions were shaken in the dark at 25 °C. After shaking for 6 h, 24 h, and nearly 30 h, the pH of each batch sample was measured and re-adjusted to pH 5.0 if necessary. After 30 h the samples were centrifuged (16000g for 15 min), and filtered through 0.22- μ m membrane filters and the P concentrations were measured. These batch IHP/Pi sorption isotherm experiments were performed in triplicate.

Sorption-pH edge experiments of IHP and Pi on γ -Al₂O₃ were carried out at pH 4–10 following a similar procedure as described for the sorption isotherm. The total solution volume was 20 mL, the solid amounts were 20, 15 and 7.5 mg γ -Al₂O₃, for, respectively, the 70, 35 and 5 nm particles and the initial concentrations of IHP and Pi were 203 μ M and 522 μ M, respectively. Also these experiments were also performed in triplicate.

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