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Research paper

The adsorption of *myo*-inositol hexaphosphate onto kaolinite and its effect on cadmium retention

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ABSTRACT

Anions are known to affect the adsorption of metal ions to soil minerals, with the change in adsorption depending on the nature of the anion. Organic phosphates, like inositol hexaphosphate (IP₆), are present in significant amounts in most soil systems but little is known about their effect on metal ion adsorption. Since strong complexes are formed between organic phosphates and metal ions, their presence in soils should significantly affect metal ion adsorption. Adsorption edge and isotherm experiments were performed for binary IP₆–kaolinite, Cd(II)–kaolinite and IP₆–Cd(II) systems, and the ternary IP₆–Cd(II)–kaolinite system. All results were modeled with Extended Constant Capacitance surface complexation models. The presence of IP₆ significantly increased the adsorption of Cd(II) to kaolinite in the pH range from 4 to 8.5 with a small decrease in adsorption at higher pH values. There was evidence of Cd(II)–IP₆ precipitate formation at higher concentrations. Modeling indicated that IP₆ was bound to the surface as both inner- and outer-sphere complexes while two extra ternary complexes were required to fit the IP₆–Cd(II)–kaolinite data. Suppression of Cd(II) adsorption at higher pH most probably resulted from the formation of soluble Cd(II)–IP₆ complexes.

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1. Introduction

Adsorption to mineral surfaces influences the availability and mobility of organic compounds in soil environments. For example, the accumulation of organic phosphorus in soils is thought to occur through adsorption to mineral surfaces (Celi and Barberis, 2007). Organic phosphorus compounds can account for up to 80% of total phosphorus in soils and, of these organic compounds, the inositol phosphates are dominant with *myo*-inositol hexaphosphate (IP₆) often the most important source of organic phosphorus in soils (Harrison, 1987; Giles et al., 2011).

A number of studies have investigated the adsorption of IP₆ to iron and aluminium oxide surfaces (Anderson et al., 1974; Celi et al., 2001; Guan et al., 2006; Johnson et al., 2012; Yan et al., 2014; Ruyter-Hooley et al., 2015). For example, Celi et al. (2001) studied the effect of different background electrolytes on IP₆ adsorption to goethite. In the presence of KCl adsorption was shown to decrease with increasing pH. However, when CaCl₂ was present IP₆ adsorption increased with increasing pH. Johnson et al. (2012) also studied the adsorption of IP₆ to goethite using Attenuated Total Reflection Fourier Transform Spectroscopy (ATR-FTIR), and concluded that adsorption occurred largely by outer-sphere complexation, with hydrogen bonding playing a crucial role in the adsorption process. Similarly using ATR-FTIR, Guan et al. (2006) investigated the adsorption of IP₆ to amorphous aluminium hydroxide.

Their results suggested that adsorption occurred through the formation of inner-sphere surface complexes. More recently, Yan et al. (2014) studied IP₆ adsorption to amorphous aluminium hydroxide using X-Ray Diffraction (XRD), ATR-FTIR, Nuclear Magnetic Resonance spectroscopy (NMR), zeta potential and hydroxyl release measurements and proposed that IP₆ adsorbed initially as an inner-sphere complex which was then transformed rapidly into precipitate species.

While several studies have explored the adsorption of IP₆ to iron and aluminium oxide surfaces very few studies have investigated the adsorption of IP₆ to clay minerals. Celi et al. (1999) studied the adsorption of IP₆ to goethite, illite and kaolinite and found that much less adsorbed to either illite or kaolinite than to goethite. These authors suggested that the organic moiety may hinder adsorption to illite and kaolinite by blocking surface sites. From a comparison of the amounts of IP₆ and phosphate adsorbed, they suggested that two phosphate groups interacted with illite and kaolinite surfaces. Ruyter-Hooley et al. (2016a, 2016b) also investigated the adsorption of IP₆ onto kaolinite with particular reference to the effect of humic acid on adsorption. They found that less IP₆ adsorbed to kaolinite than to the same surface concentration of gibbsite, and that the order of addition of IP₆ and humic acid had a marked effect on the amount of IP₆ adsorbed, with substantial suppression of IP₆ adsorption at lower pH values when humic acid was already present on the kaolinite surface.

In soil environments, the presence of complexing ligands can affect the adsorption of metal ions. Previous work on metal-ligand-mineral systems has indicated that ligands can enhance or suppress the

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adsorption of metal ions (Davis and Leckie, 1978; Kuo and McNeal, 1984; Harter and Naidu, 1995; Angove et al., 1999a; Boily et al., 2005). The effect of a ligand on metal adsorption can depend on the strength of the interactions between ligand, metal ion and mineral surface, the concentration of each species and the pH of the system (Angove et al., 1999a; Lackovic et al., 2004a).

Enhancement or suppression of metal adsorption can occur in a number of ways. For example metal ion adsorption may be suppressed if ligands and metal ions compete for the same set of surface sites. The formation of soluble metal–ligand complexes can also suppress adsorption to mineral surfaces if the complex does not sorb to the surface, leaving the metal ion in solution. Metal ion adsorption may be enhanced through the formation of ligand bridges where metal ions are complexed by mineral-bound ligands. The adsorption of ligands to mineral surfaces can also increase the negative charge at the surface which will result in an increase in the electrostatic attraction between the surface and metal ions thus increasing the amount adsorbed. Similarly, the formation of negatively charged metal–ligand complexes in solution may lead to an increase in metal ion adsorption to positively charged surface sites. Finally, formation of insoluble metal–ligand precipitates may contribute to an apparent increase in metal ion adsorption.

Cadmium (Cd(II)) is a highly carcinogenic and moderately toxic heavy metal that is able to accumulate through the food chain (Webb, 1979). The adsorption of Cd(II) to mineral surfaces has been well studied, with findings suggesting that adsorption is influenced by pH, ionic strength and the type of substrate (Johnson, 1990; Spark et al., 1995a; Spark et al., 1995b). Previous studies have been conducted on Cd(II)–ligand–mineral systems with ligands as diverse as oxalate and humate (Lamy et al., 1991; Davis and Bhatnagar, 1995; Boily and Fein, 1996; Angove et al., 1999a; Collins et al., 1999; Elzinga and Kretzschmar, 2013; Ruyter-Hooley et al., 2016a, 2016b). Using Extended X-ray Absorption Fine Structure spectroscopy (EXAFS), Collins et al. (1999) studied the influence of phosphate, sulfate, humic acid, citrate and oxalate on Cd(II) adsorption to goethite. The results indicated that the observed increase in Cd(II) adsorption in the presence of oxalate and citrate, most probably resulted from precipitate formation. While phosphate and sulfate also enhanced Cd(II) adsorption, no ternary complexes were found which suggested that the increase in adsorption resulted from electrostatic changes to the surface caused by adsorbed phosphate or sulfate. In contrast, while (Stietiya et al., 2011) also found that phosphate enhanced the adsorption of Zn to kaolinite throughout the pH range, their EXAFS data suggested that the increase resulted from the formation of a Zn–PO₄ precipitate at both pH 5.5 and 7.5. (Ruyter-Hooley et al., 2016a, 2016b) found that IP₆ increased the adsorption of Cd to gibbsite below pH 9. By use of ³¹P MAS NMR spectroscopy and surface complexation modeling they proposed that two ternary outer-sphere complexes accounted for the enhanced Cd adsorption when IP₆ was present.

Angove et al. (1999a) investigated Cd(II) adsorption to goethite and kaolinite in the presence of various benzene carboxylic acids. Mellitic acid had the greatest influence on Cd(II) adsorption to both goethite and kaolinite. While mellitic acid increased Cd(II) adsorption to goethite at all concentrations studied, on kaolinite, low concentrations of mellitate enhanced adsorption while higher concentrations suppressed adsorption. This suppression was suggested to occur because of the formation of soluble mellitic acid–Cd(II) complexes that did not sorb to kaolinite.

Surface complexation modeling of adsorption results can provide valuable insights into the adsorption process. Ruyter-Hooley et al. (2015) used an Extended Constant Capacitance Model (ECCM) guided by adsorption and ³¹P solid-state NMR results to investigate the adsorption of IP₆ on gibbsite. The surface complexation model indicated that IP₆ adsorption involved a combination of inner- and outer-sphere complexation together with surface precipitation.

Ternary systems have also been investigated by surface complexation modeling. The ECCM was used to investigate the effect of citric

acid on Cd(II) adsorption to goethite (Lackovic et al., 2004a), and kaolinite and illite (Lackovic et al., 2004b). For adsorption on goethite they proposed that two outer-sphere ternary complexes dominated adsorption while for kaolinite adsorption was suppressed because the Cd(II)–citrate complexes formed in solution appeared not to sorb. Ruyter-Hooley et al. (2016a, 2016b) also needed two outer-sphere ternary complexes to fit ternary Cd(II)–IP₆–gibbsite adsorption data.

This study sought to understand the adsorption reactions controlling the interaction of IP₆ with kaolinite, an important mineral in weathered soils. Then the effect of IP₆ on the adsorption of Cd(II) was investigated in order to determine the impact of organic phosphorus on metal ion adsorption to kaolinite. Adsorption isotherm and edge data for both the binary and ternary systems were used to develop Extended Constant Capacitance surface complexation models of each adsorption system, which provide valuable insights into the adsorption reactions.

2. Materials and methods

2.1. Reagents

All solutions used in these experiments were prepared using Milli-Q water (Millipore, Bedford, MA USA). IP₆ was in the form of phytic acid sodium salt, from corn (Sigma, Sydney Australia) which, from previous work by Johnson et al. (2012), has a formula weight of $880 \pm 10 \text{ g mol}^{-1}$ and molecular formula Na₆C₆H₆(HPO₄)₆·5H₂O. Fresh IP₆ solutions were made before each experiment to reduce the effect of hydrolysis, with the same IP₆ sample used for all experiments. Cd(II) solutions used in these experiments were prepared from 1000 ppm Cd(NO₃)₂ solution (Merck). All other chemicals used were of analytical reagent grade.

2.2. Adsorbent

Kaolinite (KGa-2) obtained from the Clay Minerals Society (2016) (specific surface area $23.5 \text{ m}^2 \text{ g}^{-1}$) was used in these experiments without further treatment. KGa-2 has a Cation Exchange Capacity (CEC) of 0.033 meq/g.

2.3. Equipment

All experiments were conducted in glass water-jacketed reaction vessels. Water, maintained at 25 °C, was circulated through the water jacket of the reaction vessel by use of a Haake K15 circulator (Thermo Fisher Scientific, Australia) to maintain a constant temperature during experiments. pH measurements used an Ross Orion Sureflow pH electrode (Waltham, MA, USA) coupled to a Metrohm model 691 pH meter (Herisau, Switzerland). pH adjustments were made with either HNO₃ or NaOH solution while the pH electrode was calibrated at the reaction temperature before each experiment using 0.05 M potassium hydrogen phthalate, 0.025 M phosphate and 0.01 M borax buffers.

2.4. Adsorption experiments

Adsorption experiments were carried out in duplicate with all experimental data shown in the accompanying figures. All adsorption experiments were performed under an atmosphere of N₂ to reduce the possibility of CO₂ contamination and at 25 °C. Preliminary kinetic experiments indicated that the adsorption process was complete within 15 min; hence the system was left for 30 min to equilibrate before each sample was taken.

For adsorption experiments, a sufficient amount of kaolinite to provide a surface area of $100 \text{ m}^2 \text{ L}^{-1}$ was added to a glass reaction vessel containing 0.10 M NaNO₃, and stirred for at least 12 h to equilibrate. For ternary systems, before the commencement of adsorption edge and isotherm experiments, the required amount of IP₆ (0.075 mM) was added to the kaolinite dispersion and left to equilibrate for 30 min.

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