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Formation of CoAl layered double hydroxide on the boehmite surface and its role in tungstate sorption

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ABSTRACT

Sorption of tungstate on boehmite (γ-AlOOH) is increased by co-sorption with Co^{2+} over the near-neutral pH range. Batch uptake experiments show up to a 3-fold increase in tungstate uptake over the range $[WO_4^{2-}]$ = 50–1000 μmol/L compared to boehmite not treated with Co^{2+}. Desorption experiments reveal a corresponding decrease in sorption reversibility for tungstate co-sorbed with Co^{2+}. Reaction of boehmite with Co^{2+} results in the formation of CoAl layered double hydroxide (LDH), as confirmed by X-ray diffraction and X-ray absorption spectroscopy. Tungsten L_3-edge X-ray absorption near edge structure (XANES) reveals that W(VI) is octahedrally coordinated in all sorption samples, with polymeric tungstate species forming at higher tungstate concentrations. X-ray diffraction and X-ray absorption spectroscopy indicate that the mechanism for enhancement of tungstate uptake is the formation of surface complexes on boehmite at low tungstate concentrations, while exchange into the CoAl LDH becomes important at higher tungstate concentrations. The results provide a basis for developing strategies to enhance tungstate sorption and to limit its environmental mobility at near-neutral pH conditions.

Introduction

Recently, tungsten has received attention because of increasing awareness of its presence in soil and aquatic systems. Although it had long been considered as environmentally benign, recent findings suggest that oxidized species are both mobile and potentially toxic (Strigul, 2010). Tungsten metal and alloys undergo oxidative dissolution under suitable conditions, forming tungstate, W(VI). The formation of tungstate may lead to adverse environmental effects, including soil acidification and toxicity effects in plants, soil microorganisms and invertebrates (Dermatas et al., 2004; Ringelberg et al., 2009; Strigul et al., 2005). Recent studies have suggested that the toxicity of tungstates is strongly linked to their speciation (Strigul, 2010). Under acidic soil and aquatic conditions, orthotungstate, WO_4^{2-}, the dominant species at near-neutral and basic pH, polymerizes to form a range of polymeric species (Strigul, 2010). The polymerization reactions are complex and strongly related to W concentration, solution pH, and reaction time (Strigul, 2010; Strigul et al., 2009). Recent studies have suggested that polytungstates may be more toxic than orthotungstate (Strigul, 2010), underscoring the importance of determining environmental factors that limit the mobility and reactivity of tungstates in natural and engineered systems.

The fate of contaminants in aquatic and soil systems is commonly controlled by sorption reactions at mineral surfaces. Tungstate has been shown to adsorb on mineral surfaces depending on pH and other factors (Gustafsson, 2003;

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Kashiwabara et al., 2013; Xu et al., 2006). Tungstate uptake onto ferrihydrite has been studied experimentally and modeled using a 2-p*K* diffuse layer model and the 1-p*K* CD-MUSIC model, accounting for sorption of monomeric and polymeric tungstate (Gustafsson, 2003). Tungstate shows sorption behavior on mineral surfaces that is typical for anions, consistent with their dominant speciation in solution over a wide pH range (Gustafsson, 2003; Xu et al., 2006). Maximum sorption occurs at acidic pH, and uptake decreases with increasing pH, so that sorption becomes significantly less effective at near-neutral pH and higher. In a previous study, we examined the character of surface complexes resulting from tungstate uptake onto boehmite over the pH range 4–8 (Hur and Reeder, 2016). A striking finding was the dominance of polymeric surface complexes, thought to be more toxic, over the entire pH range, even though the dominant solution species at pH > 6 is orthotungstate. The decreased effectiveness of sorption in limiting the mobility of dissolved tungstate at near-neutral and basic pH makes it important to identify other factors that might enhance uptake on common mineral surfaces in order to develop effective methods for tungstate remediation in the environment.

Other studies have demonstrated that the presence of anions and cations together in aqueous solution may have a profound effect on their mutual sorption behaviors (Grafe and Sparks, 2005; Li et al., 2012b, 2007; Mustafa et al., 2008; Sahai et al., 2007; Tang and Reeder, 2009; Taylor et al., 2009). Often, these mutual effects result not only in the formation of more stable surface complexes but also enhanced uptake on the surface (Tang and Reeder, 2009; Taylor et al., 2009; Yoon et al., 2002). Previous studies have demonstrated co-precipitation reactions of cations and anions on mineral surfaces (Grafe and Sparks, 2005; Li et al., 2012b; Sahai et al., 2007; Taylor et al., 2009). Other studies reported enhanced uptake as a result of a change of zero point of charge and surface area (Li et al., 2007; Mustafa et al., 2008; Wang and Xing, 2002, 2004). The effects of cation presence on anion speciation have also been reported (Elzinga and Kretzschmar, 2013). Tungstate sorption on γ-alumina has been observed to increase with the addition of cations (Spanos, 1999a, 1999b). In these studies, tungstates were more effectively sorbed on the surface at and above neutral pH in the presence of Co^{2+} or Ni^{2+}. The authors suggested that the increased tungstate uptake was a result of ternary complex formation on the surface with the cation, although no direct evidence was provided to support this.

It is well known that interactions of some divalent cations, including Mg^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, and Zn^{2+}, with aluminum (oxyhydr)oxide surfaces may result in the formation of layered double hydroxides (LDHs) containing Al^{3+} (Boyle-Wight et al., 2002b; Li et al., 2012a; Scheidegger et al., 1997; Towle et al., 1997). Co^{2+} sorption has been extensively investigated on a variety of mineral surfaces (Chisholm-Brause et al., 1990; Katz and Hayes, 1995a, 1995b; O'Day et al., 1994; Papelis and Hayes, 1996; Schenck et al., 1983; Towle et al., 1997). In previous studies of alumina, Co^{2+} sorption mechanisms were found to depend on surface loading (Boyle-Wight et al., 2002a). At low surface coverage (below 0.25 μmol/m^2), Co^{2+} was observed to form mononuclear, inner-sphere complexes, whereas Co^{2+} formed a CoAl LDH as surface loading increased above 0.5 μmol/m^2 (Boyle-Wight et al., 2002a). Distinctive features in extended X-ray absorption fine structure (EXAFS) spectra have confirmed the formation of LDH on the surface, although some of the observed features share similarities to those of $Co(OH)_2$ precipitates (Boyle-Wight et al., 2002b). The CoAl LDH phase, based on the hydrotalcite structure, has been identified in previous spectroscopic studies (Boyle-Wight et al., 2002b; Chisholm-Brause et al., 1990; d'Espinose de la Caillerie et al., 1995; Scheidegger et al., 1997; Towle et al., 1997). The formation of a Co^{2+}-containing hydrotalcite-like structure, with a high capacity for anion sorption, could be an important mechanism for enhanced tungstate uptake on Al^{3+}-containing solids.

In the present study we examine the effect of Co^{2+} on tungstate sorption on the boehmite surface at near-neutral pH (7.5), where tungstate uptake in the absence of Co^{2+} is near minimal values (Hur and Reeder, 2016). Boehmite (γ-AlOOH), an alteration product present in many soils, has aluminum in octahedral coordination, forming layers connected by hydrogen bonding (Li et al., 2010; Nordin et al., 1999). Initial experiments revealed that tungstate uptake on boehmite was enhanced in the presence of Co^{2+} at near-neutral pH conditions over a range of Co^{2+} and tungstate concentrations. Here, we focus on the formation of CoAl LDH on the boehmite surface and its role in enhanced tungstate uptake. X-ray absorption spectroscopy (XAS) is utilized to investigate the local structural environment of the tungstate and cobalt. The findings provide a basis for developing strategies for enhancing tungstate remediation in contaminated systems. Our choice of Co^{2+} for this study is not aimed toward environmental applications, but instead reflects that this element is better suited for XAS study than more environmentally acceptable divalent cations, such as Mg^{2+} and Ca^{2+}. Hence, by using Co^{2+}, which is similar in size to Mg^{2+}, we are better able to examine local structure and coordination which provide a basis for understanding possible mechanisms for enhanced uptake.

1. Materials and methods

1.1. Chemicals

Boehmite from CONDEA Chemi GmbH was used in this study without further treatment. Powder XRD confirmed the absence of second phases. The surface area as measured by BET analysis is 136 m^2/g, and a point of zero charge (PZC) was previously reported in the range 8.6–9.1 (Li et al., 2010; Nordin et al., 1999; Strathmann and Myneni, 2005). Boehmite was equilibrated at pH 7.5 in deionized water at least one day prior to further experiments. NaCl was added as a background electrolyte to achieve an ionic strength of 0.01 mol/L.

A reference sample of CoAl layered double hydroxide (LDH) was synthesized using a method previously described to yield a ratio 2 Co:1 Al (Perez-Ramirez et al., 2001). $CoCl_2$ (Acros) solution was added drop-wise into an $AlCl_3$ (Fisher Scientific) solution at pH 8, controlled using an auto-titrator and a 0.1 mol/L NaOH solution. A pink-colored, milky suspension formed upon addition of the $CoCl_2$ solution. After reaction, the suspension was filtered, rinsed and dried in an oven at 60°C. A powder XRD pattern was collected for the dry solid to confirm

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