



# Tungstate sorption mechanisms on boehmite: Systematic uptake studies and X-ray absorption spectroscopy analysis

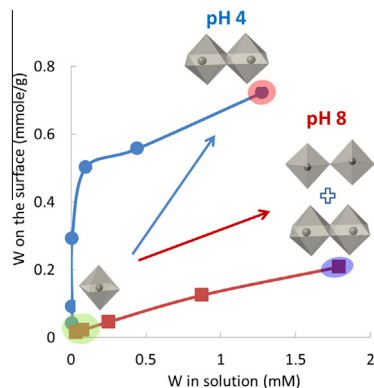


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## GRAPHICAL ABSTRACT



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## ABSTRACT

Mechanisms of tungstate sorption on the mineral boehmite ( $\gamma$ -AlOOH) were studied using batch uptake experiments and X-ray absorption spectroscopy. Batch uptake experiments over the pH range 4–8 and  $[W] = 50$ – $2000 \mu\text{M}$  show typical oxyanion behavior, and isotherm experiments reveal continued uptake with increasing tungstate concentration without any clear uptake maximum. Desorption experiments showed that sorption is irreversible at pH 4 and partly reversible at pH 8. Tungsten  $L_{1-}$  and  $L_{3-}$  edge XANES spectroscopy indicates that all sorbed tungstates are octahedrally coordinated, even though the dominant solution species at pH 8 is a tetrahedral monotungstate. Tungsten  $L_{3-}$  edge EXAFS analysis shows that sorbed tungstate occurs as polymeric form(s), as indicated by the presence of corner- and edge-sharing of distorted tungstate octahedra. The occurrence of polymeric tungstate on the surface at pH 8 indicates that sorption is accompanied by polymerization and a coordination change from tetrahedral (in solution) to distorted octahedral (on the surface). The strong tendency for tungstate polymerization on boehmite can explain the continued uptake without an apparent maximum in sorption, and the limited desorption behavior. Our results provide the basis for a predictive model of tungstate uptake by boehmite, which can be important for understanding tungstate mobility, toxicity, and bioavailability.

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## 1. Introduction

Until recently, little consideration has been given to the environmental impact of tungsten. This industrially important metal has been widely thought to be nontoxic in its pure or alloyed forms

[1,2]. Oxidation of metallic forms of tungsten results in dissolution and formation of soluble anions that are mobile in aquatic and soil systems under appropriate conditions of pH and redox potential [3]. The most stable oxidation state in surface environments is W (VI), tungstate, which forms many different oxyanions, including monooxycation and polyoxycation forms [4–6]. The study of tungstate behavior in the environment is complex due to the occurrence of multiple species associated with polymerization and their interactions with environmental materials. It is now recognized that the presence of dissolved tungstate may lead to adverse environmental effects, including soil acidification as well as toxic effects on plants, soil microorganisms and invertebrates [7–9]. Recent studies have shown that the toxicity of tungstate is related to its speciation. Strigul et al. studied toxicities of tungstate species in fish, and reported that polymeric tungstates were more toxic than monotungstate [10]. Investigation of tungstate behavior in aqueous systems, including its toxicity, has become increasingly important as industrial applications and releases to the environment have escalated.

Tungstate oxyanion speciation in solution depends on pH as well as total W concentration, showing some similarities with molybdenum oxyanion behavior [11,12]. Like molybdate, the dominant oxyanion species of tungstate at basic pH is monomeric  $\text{WO}_4^{2-}$  with tetrahedral coordination. As pH is decreased, tungstate forms polymeric species having mainly octahedral coordination as shown for selected species in Fig. 1 and described further in Supporting Information. Polymerization is favored with increasing tungstate concentration. In the VIB group, the tendency for polymerization increases with increasing atomic number, so that occurrence of polymeric forms of tungstate may be more common than molybdate for equivalent conditions [11]. Tungstate speciation has been studied by several researchers with  $^{187}\text{W}$  nuclear magnetic resonance (NMR) spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and Raman spectroscopy [4,5,13,14]. These studies have shown that general trends of tungsten polymerization are known under acidic conditions, yet the mechanisms are still not completely understood. Furthermore, the kinetics of formation of some polymeric species is sluggish, so that equilibrium speciation is not necessarily obtained over the time scale of laboratory experiments [4,5,11].

Sorption processes on mineral surfaces play an important role in regulating the distribution and mobility of trace metals in natural aquatic and soil systems. Tungstate has been shown to adsorb strongly on iron oxyhydroxide mineral surfaces at low pH conditions [15–17]. Hernandez performed sorption experiments and IR spectroscopy to characterize  $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$  sorption on iron and aluminum (hydr)oxide surfaces [15]. Gustafsson used a 2-pK Diffuse Layer Model and a 1-pK CD-MUSIC model to describe tungstate (and molybdate) sorption on ferrihydrite, accounting for monomeric and polymeric tungstates to fit the experimental data for both models [17]. The competitive sorption of tungstate and other oxyanions on goethite was studied by Xu et al. [16]. Tungstate sorption was found to be strongly competitive with molybdate and phosphate at the surface, whereas silicate and sulfate sorption were affected minimally by tungstate. Tungstate speciation in natural soils was studied by Clausen and Korte [2] and Bednar et al. [3], who found tungstate forming polymeric species with phosphate and silicate, and proposed a general transformation pathway for tungstates in nature. However, little is known of the influence that tungstate speciation plays in sorption behavior over a broader pH range and on other mineral sorbents. This fundamental information is important inasmuch as it may control tungstate mobility, toxicity, and bioavailability in natural systems.

In the present study, we investigate tungstate sorption behavior on the aluminum oxyhydroxide mineral boehmite,  $\gamma\text{-AlOOH}$ , over the tungsten concentration range 5–2000  $\mu\text{M}$ . Although the lower

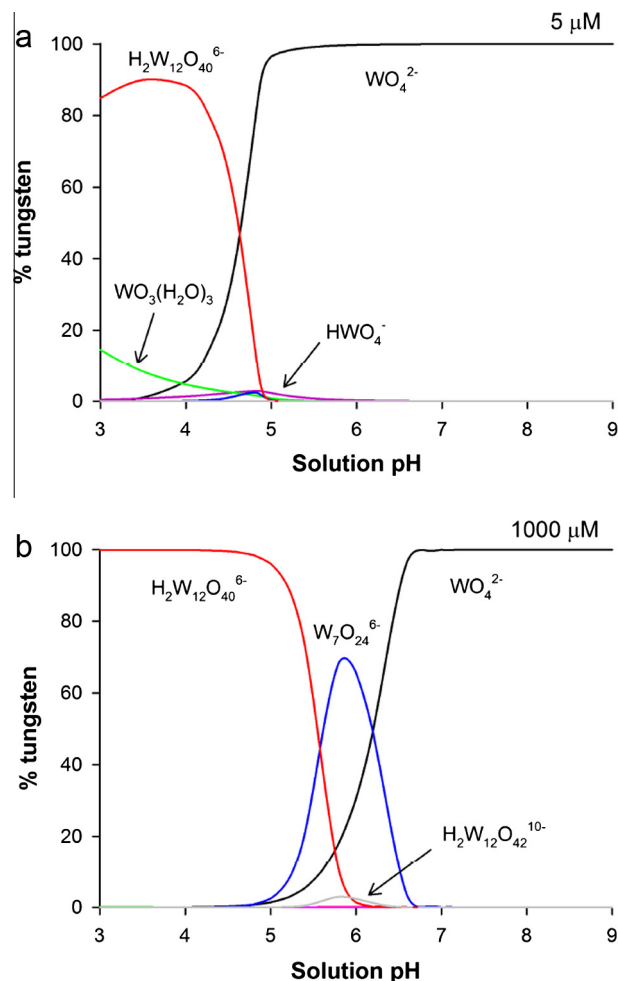


Fig. 1. Aqueous tungstate speciation at total tungstate concentrations of 5 and 1000  $\mu\text{M}$ , calculated using the program PHREEQC with stability constants reported in Table S1 (Supporting Information) at ionic strength 0.01 M. Polymerization is favored with increasing tungstate concentration. Species present at low concentrations are not labeled.

end of this concentration range is more relevant environmentally, dissolved tungsten concentrations as high as 400 mg/L (2175  $\mu\text{M}$ ) have been reported at highly contaminated sites [2]. Boehmite occurs naturally as a common weathering product and is an effective sorbent for both cations and anions [18–21]. Tungsten  $L_{1-}$  and  $L_{3-}$  edge XANES spectroscopy was used to distinguish coordination environments around W atoms. The local structure and coordination of tungsten at the surface were determined using tungsten  $L_{3-}$  edge EXAFS, which allowed us to further characterize the binding mechanism as well as the dependence of tungstate sorption on environmental parameters such as pH, metal concentration, and ionic strength. This initial work provides a foundation for subsequent studies of tungstate sorption on other solids. The findings also have possible implications for tungsten toxicity in natural environments.

## 2. Materials and methods

### 2.1. Sorbent

Boehmite from CONDEA Chemie GmbH was used in this study. Powder XRD was used to confirm the structure, and no other phases were detected. The specific surface area of the boehmite was found to be 136  $\text{m}^2/\text{g}$  by five-point  $\text{N}_2$  Brunauer–Emmett–Teller (BET) analysis. The point of zero charge (PZC) determined

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