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Influence of phosphate on tungstate sorption on hematite: A macroscopic and spectroscopic evaluation of the mechanism

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HIGHLIGHTS

- Tungstate (VI) sorption was affected by P.
- Tungstate (VI) surface complexation mode differed when P was present.
- Both W (VI) and P sorption decreased with increasing pH.
- The presence of P changed the W—O antisymmetric stretching band.

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ABSTRACT

The environmental fate of the tungstate (VI) oxyanion [e.g. mono tungstate and several polytungstate, generally expressed by W (VI)] is largely controlled by sorption on soil minerals, especially on iron oxide minerals. Molecular scale evaluation of W (VI) retention on iron oxides in the presence of competing oxyanions is scarce in literature. Here we report surface interaction mechanisms of W (VI) on hematite in the presence of phosphate (P) using macroscopic and *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic experiments. Batch sorption experiments were conducted using 2 g L^{-1} hematite and 100 μM W (VI) and P, in single ion system and in binary mixtures as a function of pH (4–11). *In situ* ATR-FTIR spectroscopic evaluation of P and W (VI) sorption on hematite was also carried out. The results from macroscopic experiments indicated that W (VI) sorption on hematite was not affected by P when W (VI) was added first. The influence of P on W (VI) sorption was noticed when W (VI) & P were added simultaneously or P was added first. The *in situ* ATR-FTIR spectroscopic data corroborated these findings. In addition, the spectroscopic data revealed that in the presence of P, the surface complexation mode of W (VI) differed as noted from either the absence of W—O antisymmetric infrared (IR) band or the W—O—W stretching band. This study provides useful information on molecular level understanding of W (VI) surface complexation on hematite in the presence of competing ions such as P.

1. Introduction

The link between elevated tungstate (W (VI)) concentrations in the tap water, ground water, and tree ring samples to a childhood leukemia cluster in NV highlighted the importance of considering tungsten (W) as an ‘emerging contaminant’ (EPA, 2017). Even though no conclusive results could be obtained by an investigation led by The Center for Disease Control (CDC) to strengthen this link, the circumstantial evidence encouraged many researchers to perform a thorough investigation on W (VI) toxicity (Sheppard et al., 2006; Steinberg et al., 2007). Experiments on mice suggested that 16 weeks of chronic W (VI) exposure (conc. 15–200 mg L^{-1}) can cause DNA damage and promote tumor development (Kelly et al., 2013). Strigul et al. (2005) found that soil incubated with W powder for 3 months led to the death of 95% of the soil bacteria.

Tungsten (W) is heavily used for domestic and industrial purposes (Koutsospyros et al., 2006). Approx. 86,400 metric tons of W were mined worldwide in 2016 (USGS, 2017) for applications such as tungsten-cemented carbide, military and hunting ammunition, medical equipment, and light bulb filaments (Koutsospyros et al., 2006). Due to lead (Pb) toxicity, W had replaced Pb in many small caliber military and hunting ammunition rounds by the late 1990s

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(Fisher et al., 2006; Thomas et al., 2009). In addition to industrial and domestic uses, dissolution of W-bearing minerals was found to be another major source for W (VI) occurrence in the environment (Seiler et al., 2005).

The high provenance of W and its compounds in the environment, as well as suspected toxicity to human and ecological health, prompted many fate studies (Koutsospyros et al., 2006). Soil minerals can control the fate of W(VI) by sorption, and consequently, many studies have evaluated the sorption mechanisms of W (VI) on various soil minerals (Gustaffsson, 2003; Xu et al., 2006, 2009; Lorenz, 2009; Lorenz et al., 2011; Kashiwabara et al., 2013; Davantes and Lefevre, 2015; Sun and Bostick, 2015; Hur and Reeder, 2016; Rakshit et al., 2017). In general, W (VI) displays a high affinity for iron-and aluminum hydr (oxide) minerals (Gustaffson, 2003; Xu et al., 2009; Davantes et al., 2015; Hur and Reeder, 2016). To support the findings in macroscopic sorption isotherm and envelope, researchers determined molecular level information on the surface retention mechanism using EXAFS and *in situ* ATR-FTIR spectroscopic tools. (Davantes and Lefevre, 2015; Hur and Reeder, 2016; Davantes et al., 2017; Rakshit et al., 2017). These spectroscopic measurements are very sensitive and resulted in detailed information about surface complexes at an environmental W (VI) conc. range (Hur and Reeder, 2016; Davantes et al., 2017; Rakshit et al., 2017).

A challenge of studying the molecular mechanism of W (VI) interaction with mineral surfaces is that the currently available W (VI) solution speciation cannot always be linked to the probable surface complexation at a given solution property. This is because thermodynamic data were unavailable in an environmental W (VI) conc. range (Rakshit et al., 2017). For example, the seminal papers which determined W solution speciation listed conc. range of W (VI) as 0.5–123 mM (Cruywagen and van der Merwe, 1987), 0.5 M (Shijun et al., 1998), 3 M (Smith and Patrick, 2000), and 2 mM (Hur and Reeder, 2016). Interestingly, W (VI) is known to polymerize at higher concentration even at unfavorable pH values (Hur and Reeder, 2016). Thus, extrapolating the solution speciation conducted at mM and M levels to μM should be interpreted carefully.

Although important molecular level information about W (VI) –Fe/Al(hydr)oxide surface complexes at an environmental conc. range is currently available in literature, no studies to the best of the authors' knowledge determined the nature of surface complexes in the presence of a competing anion such as phosphate (P) using surface sensitive spectroscopic probes. The likelihood of the coexistence of P and W (VI) in the environment is high. Thus, some macroscopic competitive sorption studies with W (VI) and P on Fe/Al(hydr)oxide clay minerals are already available in literature (Gustaffsson, 2003; Xu et al., 2009; Iwai and Hashimoto, 2017). These studies indicated that P has influence in reducing W (VI) sorption on Fe/Al-(hydr)oxide minerals. However, due to the lack of molecular level information about probable surface complexes of W (VI) in the presence of P, the fit of surface complexation model (SCM) in the competitive system was not successful in some cases (Gustaffson, 2003). Thus, molecular level spectroscopic studies on P and W (VI) competitive sorption on common iron oxides, such as hematite, are unavailable in literature. Hence, the main objective of this study is to probe the surface interaction mechanism of W (VI) on hematite in the presence of P using macroscopic and *in situ* ATR-FTIR spectroscopic investigations under various solution properties.

2. Materials & methods

2.1. Reagent and materials

Hematite was synthesized following a procedure described in our earlier study (Rakshit et al., 2017), which was mainly derived from the hematite synthesis procedures published by Sugimoto et al. (1993) and Elzinga and Kretzchmar (2013). In short, 500 mL of 2 M $FeCl_3$ solution was mixed dropwise to a continuously stirred 500 mL 5.4 M NaOH solution within a period of 5 min. The gel-like precipitate was collected in a pyrex glass bottle, sealed, and heated in a drying oven at 101 °C for 8 days. The solid was then cooled to room temperature, washed with Milli-Q water (18.2 MΩ cm) until the EC value was $<5\ \mu S\ cm^{-1}$. The suspension was then freeze-dried and stored in a dry place at room temperature. The mineral identity was confirmed using X-ray diffraction (Rigaku, Woodlands, TX). The surface area of hematite produced by this procedure is in the range of $24\ m^2\ g^{-1}$ (Elzinga and Kretzchmar 2013). Sodium dihydrogen phosphate (NaH_2PO_4) and sodium tungstate (Na_2WO_4, $2H_2O$) were purchased from Sigma Aldrich (St. Louis, MO). This hematite preparation method may be subjected to minor silica contamination.

2.2. Macroscopic sorption experiments

Three types of macroscopic batch sorption experiments were conducted to determine the competitive effect of P on W (VI) surface interaction on hematite. These experiments are termed 'W 1st, P 2nd'; 'W, P simultaneous'; and 'P 1st, W 2nd' experiments. These batch sorption experiments were performed in triplicate in 10 mL volumes in an anaerobic chamber (Coy Laboratory Products, Grass Lake, MI) to avoid interference from carbonate during pH control (Leuz et al., 2006). For 'W 1st, P 2nd'', W (VI) stock was added to the hematite suspension ($2\ g\ L^{-1}$) to make 100 μM concentration at I = 0.01 M NaCl, and at a pH range of 4–11. The suspension was then equilibrated for 24 h at a fixed temperature (298 K). The pH was controlled using small additions of 0.1 M NaOH and HCl and the final pH value was recorded. The suspension was then centrifuged and decanted carefully to keep the solid in the centrifuge tube. The filtrate was collected to analyze the W (VI) in ICP-OES (iCAP 7400, Thermo Electron, West Palm Beach, FL). The remaining solid was washed with electrolyte solution (i.e. 0.01 M NaCl), centrifuged, and decanted to remove the interstitial sorbate. This wash solution was analyzed by ICP-OES to ensure that the sorbed fraction was not removed. 10 mL of a 100 μM P solution was then added to each solid at respective pH values and equilibrated for 24 h at 298 K. The filtrate was then collected for analysis in ICP-OES for total W (VI) and P. Appropriate standards and quality control samples were run in ICP-OES to satisfy the standard quality control/quality assurance protocol.

For 'W, P simultaneous' experiments, 100 μM of both W (VI) and P were added simultaneously (10 mL total volume), equilibrated for 24 h at 298 K, I = 0.01 M NaCl, and with a pH range of 4–11. The suspension was then centrifuged, decanted, and the filtrate was analyzed for total W and P by ICP-OES. For 'P 1st, W 2nd' experiments, the hematite suspension was equilibrated with 100 μM P at pH range of 4–11. After 24h of equilibration at 298 K, the content was centrifuged, decanted carefully to save the solid, and filtered. The filtrate was collected to analyze total P by ICP-OES. The solid was washed with 0.01 M NaCl solution to remove any interstitial P in the reaction mixture. The wash solution was collected and measured in ICP-OES to verify if any P was removed from the sorbed phase. 10 mL of W (VI) stock solution was then added in the suspension of P sorbed hematite to attain an initial W (VI) concentration of 100 μM at ionic strength of 0.01 M NaCl, and a pH range of 4–11, equilibrated at 298 K for 24h, centrifuged, decanted, and filtered. The filtrate was analyzed for total W and P in ICP-OES. These three types of competitive sorption experiments portray a comprehensive view of the influence of P on sorption of W (VI) on hematite. All wet chemical experiments were performed in triplicates with a mean value and standard deviation plotted. Control experiments without the hematite in the reaction mixture were