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Tungsten–humic substances complexation

Zelin Xu[1,2], Xin Liu[1], Jincheng Peng[1], Chenchen Qu[3], Yifan Chen[2], Ming Zhang[3], Ding Liang[3], Ming Lei[1], Boqing Tie[1] and Huihui Du[1*]

Abstract

Tungsten (W) is an emerging contaminant whose environmental behaviors remain rather sketchy, narrow, and fragmentary. The mobility and fate of W in the aquatic environments may be influenced by naturally dissolved organic matter (DOM), nevertheless, no studies have addressed how W is bound to DOM. In this study, complexation behaviors and mechanisms of W(VI) with representative DOM, humic acid (HA) and fulvic acid (FA), were examined by batch adsorption, spectrometry, and isothermal titration calorimetry (ITC) under environmentally-relevant conditions. A higher W(VI) binding was observed at a lower pH. Compared to HA, FA showed a higher W(VI) complexing capability owing to the presence of more carboxylic groups. As shown in ITC, the carboxylic–W interaction was an endothermic process and driven by entropy, whereas the phenolic–W association was exothermic and driven by both entropy and enthalpy. The redox-active moieties within HA/FA molecules could reduce W(VI) to lower valence states species, predominantly W(V). The presence of Ca^{2+} not only promoted W–HA/FA complexation but also hindered W(VI) reduction. All in all, the role of dissolved organic matter in the complexation of W(VI) in the aquatic environments merits close attention.

Highlights

• W–humic substances complexation involved ligand exchange on carboxylic/phenolic sites.

• Humic/fulvic acid could reduce W(VI) to W(V), while Ca^{2+} hindered W(VI) reduction.

• W–humic substances interaction may greatly affect W's mobility in aquifers.

Keywords: Tungsten, Dissolved organic matter, Biogeochemical cycling, Complexation, Redox, Binding thermodynamics

*Correspondence: duhuihui@hunau.edu.cn

[1] College of Resources and Environment, Hunan Agricultural University, Changsha 410127, China
Full list of author information is available at the end of the article

Graphical Abstract
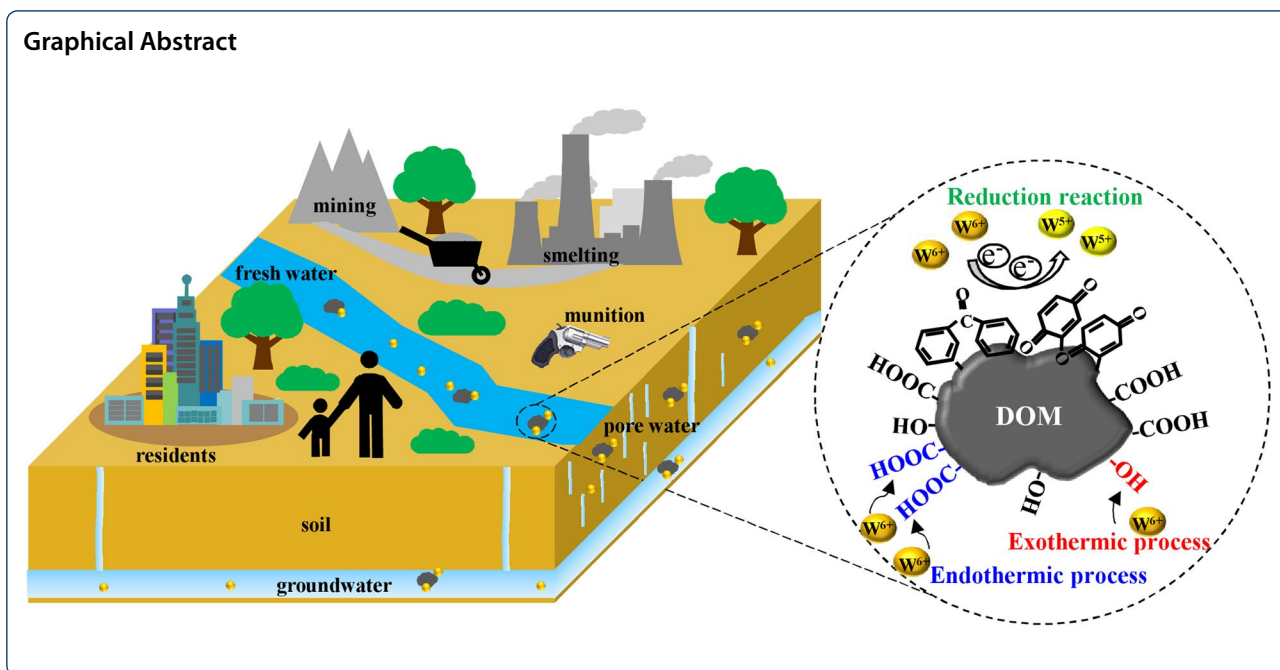
1 Introduction

Tungsten(W) is a transition element listed in the Group VI B of the periodic table, sharing the same subgroup as chromium (Cr) and molybdenum (Mo). As a strategic metal, W has been widely used in light sources, ammunitions, electronics, metallurgies, and chemical industries (Koutsospyros et al., 2006). Metallic W and its alloys can be quickly oxidized and dissolved into tungstate oxyanions at appropriate pH and redox potential in the environment (Hobson et al., 2020). To some extent, these soluble tungstate oxyanions are usually manifested as high mobility and can migrate with surface flows or be leached into groundwaters where they can negatively impact the biota and aquatic ecosystems (Lin et al., 2014; Guo et al., 2019; Cidu et al., 2021). In Falon, Nevada, USA, exposure to high levels of W in aquifers used as drinking water may be the leading cause of local childhood leukemia (Seiler et al., 2005). Natural surface water bodies normally contain < 2 µg/L W (Gaillardet et al., 2003; Steenstra et al., 2020), nevertheless, in mining/smelting-impacted regions, W concentration of the surface and pore waters can be as high as 7.1 mg/L (Petrunic and Al, 2005; Du et al., 2021).

Once present in solution, the concentration and mobility of W are greatly affected by adsorption on and desorption from the surface. In general, W might exhibit similar interfacial behaviors to other oxyanion-forming metals such as arsenic (As) that it is strongly sorbed to Fe/Mn (oxyhydr)oxides in oxic-to-anoxic waters (Johannesson

et al., 2013; Cao et al., 2019; Wasylenki et al., 2020; Cui and Gomes, 2021; Cui et al., 2021). In addition, aluminosilicates such as montmorillonite, kaolinite, and illite can also sequestrate tungstates at acid-to-neutral pH (Li et al., 2014; Iwai and Hashimoto, 2017; Du et al., 2022). In addition to minerals, the roles that organic surfaces, e.g., natural organic matter (NOM), play in determining W complexation and mobility in aquatic systems are still unknown.

Natural organic matter (NOM), particularly dissolved organic matter (DOM), is highly reactive and plays an essential role in the geochemical cycling of trace elements (Mostofa et al., 2013). Dissolved organic matter has a large number of functional groups on its surface, including phenolic hydroxyl (–OH), amino (–NH_2), and carboxyl (–COOH). In one aspect, these groups can complex metals via the formation of strong inner-sphere type complexes (Xiong et al., 2013; Shi et al., 2016), and the formed soluble DOM–metal complexes may increase their mobility and potential risks (Zhang et al., 2021). In another aspect, DOM may enhance metal cations or compete with oxyanions for binding onto surfaces such as ferrihydrite or alumina (Du et al., 2018a; Fariña et al., 2018; Xue et al., 2019), altering their distribution coefficients at the solid–liquid interface.

For the same subgroup elements Mo and Cr, the importance of carboxylic groups of NOM in metal–complexation reaction has been documented (Gustafsson et al., 2014; Gustafsson and Tiberg, 2015), and a Cr/Mo–O–C structure was observed in the second coordination shell.

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To the best of our knowledge, existing data regarding DOM–W interactions are scarce. In particular, the functional groups responsible for the complexation of W(VI) are still unclear. Moreover, NOM has unique redox properties and is therefore capable of reducing redox-sensitive metals such as Cr(V), Hg(II), and Cu(II) (Wittbrodt and Palmer, 1995; Gu et al., 2011; Pham et al., 2012). Whether and to what extent DOM can reduce hexavalent W(VI) to lower oxidation state species need to be illuminated. The above fundamental information is a prerequisite that enables us to evaluate the controls on W mobility in surface and groundwater flows in a more comprehensive way.

To fill this knowledge gap, this study aimed to examine W(VI) complexation behaviors by representative DOM, i.e., humic acid (HA) and fulvic acid (FA). We first determined the conditional distributions coefficients (D_{om}) for W(VI) on HA and FA by a batch equilibrium method at varied pHs and W concentrations. In addition, the influences of cations, Ca^{2+} as a representative, were explored. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), combined with isothermal titration calorimetry (ITC) were employed to figure out the complexation mechanisms. The information gleaned from this study has substantial implications for understanding the fate of tungsten in aquifers and evaluating its bioavailability and environmental risks.

2 Experimental section

2.1 Humic and fluvic acid preparation and characterization

HA and FA are both commercial products, provided by Sigma-Aldrich (product code, H16752) and Chengdu Euenreisi Chemical Reagent Co., LTD., China, respectively. HA was originally extracted from peat while FA was isolated from forest soil. Although the properties of humic substances vary differently with different sources, the major functional groups for metal(loid) complexation are always carboxylic and phenolic hydroxyls. Many studies have shown that FA has a higher acidity and more functional groups than HA in spite of environmental sources (Rashid and King, 1970; Weber and Wilson, 1975). Therefore, these two commercial and easily accessible humic substances were chosen as representatives. To prepare the dissolved humic substances, 500 mg of HA or FA was dissolved in 100 mL "Milli-Q" water, and 1 M NaOH or HCl was added if necessary to facilitate the dissolution. The solution was then filtered through a cellulose nitrate filter (specific diameter of 0.45 μm) and stocked in the refrigerator at 4°C before use. The carbon (C) concentration was determined by a Shimadzu TOC analyzer (Shimadzu, Japan). The carboxylic and phenolic hydroxyl groups were determined by potentiometric acid–base titrations using a Metrohm titrator 836. The titration data were processed in the FITEQL 4.0 software using a 2-sites non-electrostatic model (Fig. S1). FA and HA elemental compositions were determined using an elemental analyzer (Vario unicube, Elementar, Germany). The basic properties of HA and FA are listed in Table 1.

2.2 Batch equilibrium experiments

The W(VI) stock solution, ~1000 mg/L, was prepared by diluting of sodium tungstate (Aladdin) in "Milli-Q" water. Equilibrium complexation experiments were performed as a batch-type in 50 mL polypropylene centrifugate tubes. The reaction solutions (30 mL) contained 0.05 g C/L HA or FA and varied W(VI) concentrations (0 - 30 mg/L) in 0.01 M NaCl background electrolyte solutions. The suspension was adjusted to desired pH values (~5, 7, 9) using dilute NaOH and HCl, and shaken end-over-end for 48 h at 25 °C to an equilibrium. The suspension was centrifuged at 4500 g for 20 min and then filtrated through a 3 k Dalton ultrafilter (Millipore, Amicon) (Du et al., 2018b). Through this approach, the free and DOM bound W could be almost completely separated because 1) the Dalton of HA and FA is commonly larger than 8 k Dalton (Kim et al., 1990); 2) HA or FA might contain minimum smaller molecular entities that were smaller than 3 k Dalton, however, our preliminary experiment showed that the DOC in the 3 k Dalton filter was below the LOD (limit of detection, ~50 μg/L). Even if there were some DOM-bound W in the filtrate, they were negligible compared to the total DOM-bound W (dozens of mg/L, see the Results section). The filtrate was immediately analyzed for dissolved W(VI) concentration using ICP-OES (PerkinElmer Optima 8300). Quantification by ICP-OES was based on a comparison to a 5-point standard curve using the 207.9 nm emission line which had a detection limit of 10 μg/L. The DOM-bound W

Table 1 Chemical properties of humic acid (HA) and fulvic acid (FA)

| | Elemental composition (%) | | | Acidic sites | | | |
| | | | | Site 1 (carboxylic hydroxyl) | | Site 2 (phenolic hydroxyl) | |
	C	O	N	pK_a	Conc. (mol/kg)	pK_a	Conc. (mol/kg)
HA	53.4	37.2	1.2	5.6	0.33	8.0	0.32
FA	50.4	40.4	0.8	4.7	0.86	8.1	0.37

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was calculated by the difference between the total added and the dissolved concentrations. The effect of Ca^{2+} was investigated for an initial W concentration of 15 mg/L and varied Ca-to-W molar ratios (1:2, 1:1, and 5:1). Other treatments were the same as above. All batch experiments were performed in triplicates.

Conditional distribution coefficients (K_D) for W(VI) binding to DOM (K_D, L/kg) were calculated as follows (Buschmann et al., 2006):

$$K_D = \frac{[C_b]}{[C_f][\text{DOC}]}$$

where C_f and C_b are the free and DOM-bound W(VI) concentrations (mg/L), respectively; and [DOC] is the concentration of organic carbon in solution (kg/L).

2.3 Spectroscopic measurements

The complexation mechanisms including binding functional groups and possible reduction reactions were investigated by FTIR and XPS. XPS measurement was conducted on a KRATOS Axis Ultra X-ray photoelectron spectrometer (Thermo Fisher Scientific, US). Spectra of W 4f (5p) were collected with a step size of 0.05 eV. The C 1 s peak at ~ 284.8 eV was used to calibrate the binding energy, and the spectra were curve-fitted using XPSPEAK41 software. FTIR measurements were performed on a PerkinElmer infrared spectrometer. Each scanning spectrum was recorded from 4000 cm^{-1} to 650 cm^{-1} at a 4 cm^{-1} resolution. Before XPS and FTIR measurements, liquid solutions were freeze-dried into a fine powder.

2.4 Calorimetric titration

Isothermal titration calorimetry (ITC) was applied to directly measure the heat exchange during W(VI) complexation by DOM. Calorimetric titration was performed using a thermal activity monitor (TAM III, TA instruments) equipped with a 1-mL reaction vessel. Before measurements, 0.7-mL of HA or FA solution (0.05 g/L) was added to the reactor stirring at 120 rev/min. The reactor was loaded inside the instrument and left to stabilize to achieve a stable heat flow, i.e., a signal excursion < 250 nw/h. A W(VI) stock solution was subsequently titrated into the reactor using a fully automated micro-syringe. Each titration was 10 μL and the corresponding reaction heat flow was automatically recorded. In total, 250 μL of W(VI) stock solution was titrated. A blank experiment was performed in the same way but using the 0.01 M NaCl instead of the DOM solutions, to exclude the dilution heat that was not caused by W(VI) complexation. All measurements were conducted at pH ~ 7 and 25°C. Thermodynamic

parameters including enthalpy (ΔH), entropy (ΔS), Gibbs free energy (ΔG), and binding affinity (K_a) were determined using the software package TAM assistant (ver. 1.4) and NanoAnalyze (ver. 3.6) followed the methods described elsewhere (Du et al., 2020):

$$Q = V[M]\frac{n\Delta H K}{1 + K[L]}$$

where Q is the reaction heat, V is the reactor volume, [M] is the concentration of humic substances, ΔH represents the enthalpy (kJ/mol), K is the thermodynamic affinity, [L] is the total concentration of W(VI), and n represents the number of binding sites. The calculation of ΔG was: $\Delta G = -RT\ln K$ ($R = 8.314$ J/mol/K, $T = 298$ K). Entropy ΔS was determined by: $\Delta S = (\Delta H - \Delta G) / T$.
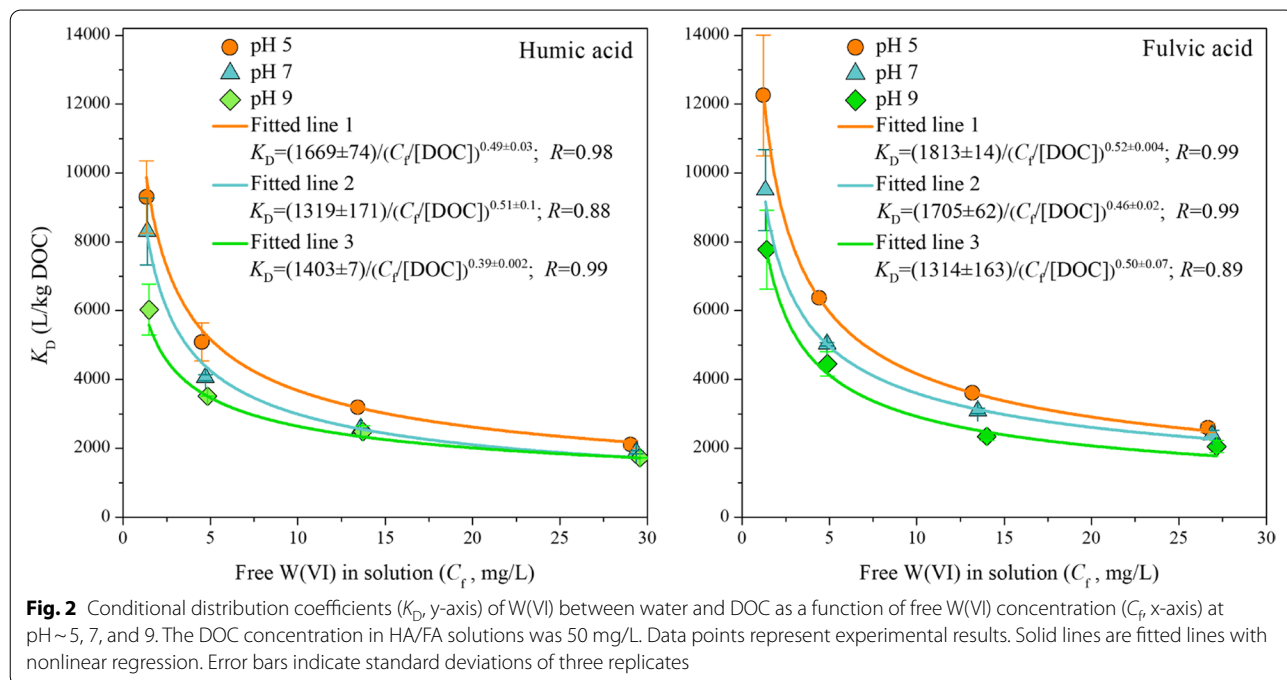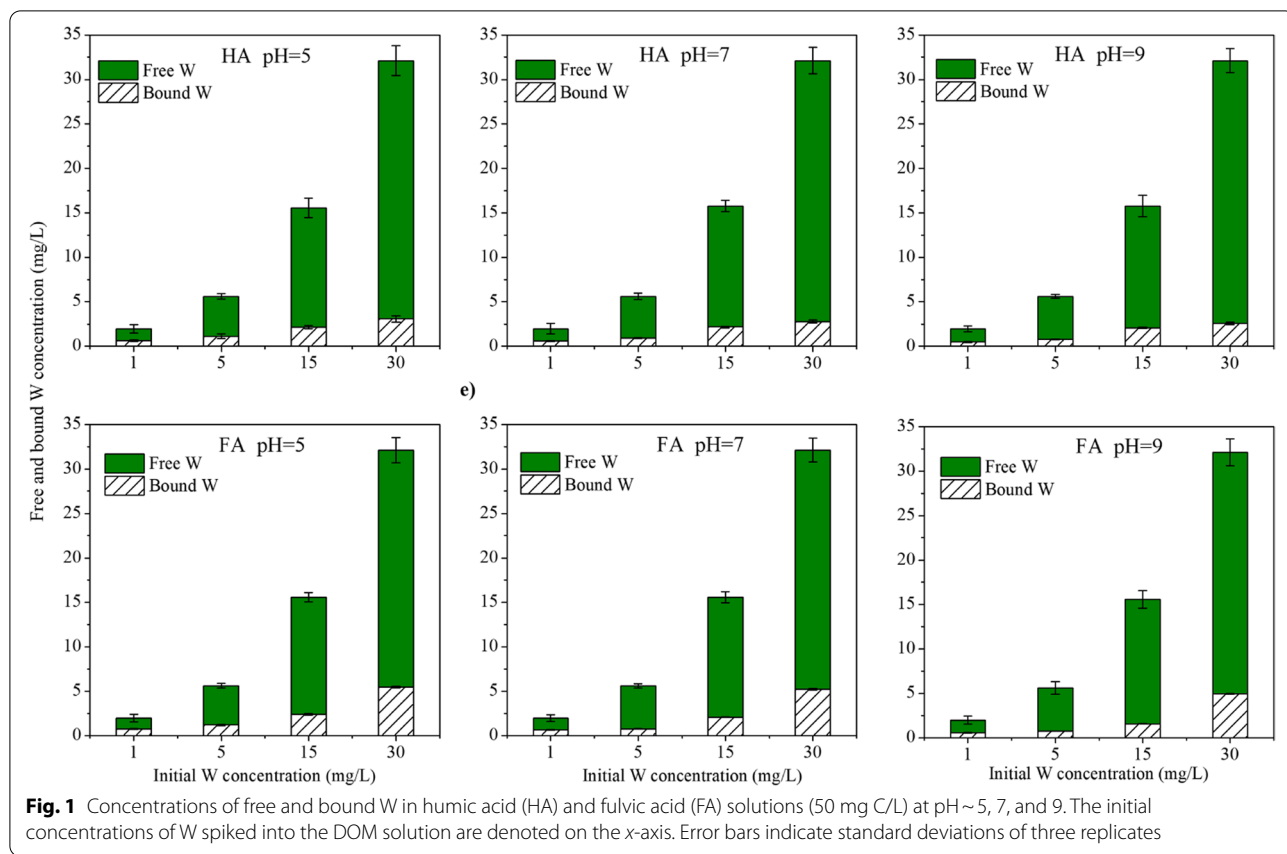
3 Results

3.1 DOM-bound W(VI) concentrations and conditional distribution coefficients

A noticeable fraction of W(VI) was bound to HA and FA at all studied pHs, with higher proportions at low initial W(VI) concentrations (Fig. 1). For HA, the bound W was from 0.47 mg/L (initial W = 1 mg/L) to 3.1 mg/L (initial W = 30 mg/L), corresponding to 47%–10% of the total W(VI) in solution. The bound W on FA ranged from 0.55 to 4.9 mg/L, equivalent to 55%–16% of total W(VI). Fulvic acid seemed stronger than HA to complex W(VI), which further can be inferred from its larger K_D values (Fig. 2). The values of K_D decreased with the increase of initial W(VI) concentrations and remained almost constant at higher W(VI) concentrations. Both HA and FA showed pH dependence of K_D values which increased with the decrease of pH, suggesting a pH-dependent W complexation behavior. Combined with the significance analyses (Fig. S2), lower pH favored W(VI) complexation by DOM, and FA showed a stronger complexation ability for W(VI) than HA.

When a specific complexation mechanism is assumed (see the Discussion section), the occupation of functional groups of DOM can be estimated (Buschmann et al., 2006). At the highest W concentration (30 mg/L), only ~ 2.5% and 2.2% of the total functional groups were occupied for HA and FA, respectively.

3.2 Influences of Ca^{2+} on W(VI) complexation

The presence of Ca^{2+} significantly promoted W(VI)–DOM complexation at almost all studied pHs, with greater W(VI) adsorptions at higher Ca:W ratios (Fig. 3). The highest W adsorption on FA, ~ 95 mg/g, occurred at a Ca:W ratio of 5 at pH 5, about 2 times larger than that without Ca^{2+}. Noticeably, the promotion effect of Ca^{2+}

Fig. 1 Concentrations of free and bound W in humic acid (HA) and fulvic acid (FA) solutions (50 mg C/L) at pH ~ 5, 7, and 9. The initial concentrations of W spiked into the DOM solution are denoted on the *x*-axis. Error bars indicate standard deviations of three replicates

Fig. 2 Conditional distribution coefficients (K_D, y-axis) of W(VI) between water and DOC as a function of free W(VI) concentration (C_f, x-axis) at pH ~ 5, 7, and 9. The DOC concentration in HA/FA solutions was 50 mg/L. Data points represent experimental results. Solid lines are fitted lines with nonlinear regression. Error bars indicate standard deviations of three replicates

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on W(VI)–DOM complexation was also dependent on pH. On HA, W(VI) adsorption increased by ∼ 43–61%, 28–55%, and 0–18%, respectively at pH ∼ 5, 7, and 9. On FA, W(VI) adsorption increased by ∼ 41–101%, 14–86%, and 13–68%, respectively at pH ∼ 5, 7, and 9. Overall, Ca^{2+} can promote W(VI) complexation by DOM, and lower pH favored the DOM–Ca–W(VI) ternary interactions.

3.3 Functional groups for W(VI) complexation

Two FTIR absorption bands have significantly changed after HA binding of W(VI): One was at ∼ 1613 cm^{-1}, corresponding to the antisymmetric vibration of COO^- (Niemeyer et al., 1992), and it shifted to higher frequencies; the other one was at ∼ 1403 cm^{-1}, which represented the symmetric vibration of COO^- and/or C–O stretching of phenols (Lumsdon and Fraser, 2005), showing reduced intensity and generating a new peak variation at ∼ 1457 cm^{-1} (Fig. 4a). These two spectral changes probably resulted from the ligand exchange of carboxyl and phenolic hydroxyl groups by W(VI) oxyanions. Similar changes in antisymmetric vibration of COO^- at ∼ 1607 cm^{-1} were observed when FA binding W(VI) (Fig. 4b). These observations suggested that carboxyls were the major functional groups for W(VI) complexation by DOM, and the phenolic group was likely to complex a portion of W(VI). In contrast to variations of carboxylic and phenolic groups, the absorption bands between 1000 and 1150 cm^{-1}, representative of C–O of ester and polysaccharide (Zhang et al., 2017), were almost unchanged, implying that the aliphatic structures were more resistant to W(VI) complexation.

3.4 Reduction of W(VI) to W(V) during complexation

In a typical W $4f_{7/2}$ XPS spectrum, the peak binding energies for W^{6+} and W^{5+} locate at ∼ 35.6 eV and 35.0 eV, respectively (Du et al., 2020) (Fig. 5). Approximately 46% of the total adsorbed W(VI) was reduced to W(V) on HA, compared to a mere 10% reduction of W(VI) on FA. Ca^{2+} inhibited W(VI) reduction on DOM, with almost no existence of pentavalent W(V) on HA. Collectively, HA exhibited a higher reducibility than FA, and Ca^{2+} played an inhibiting role in W redox reactions.
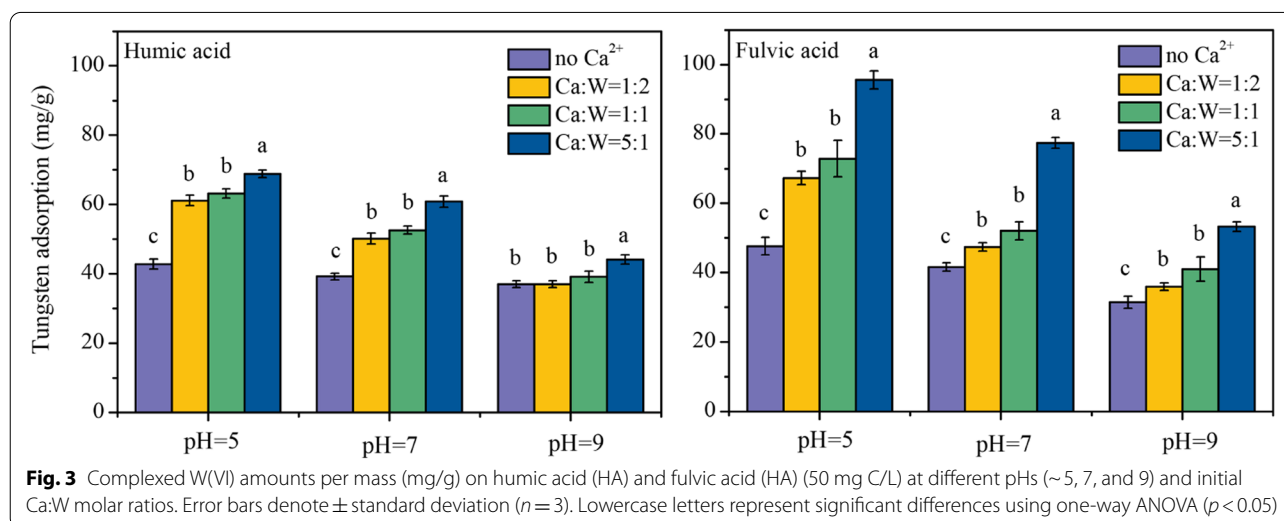
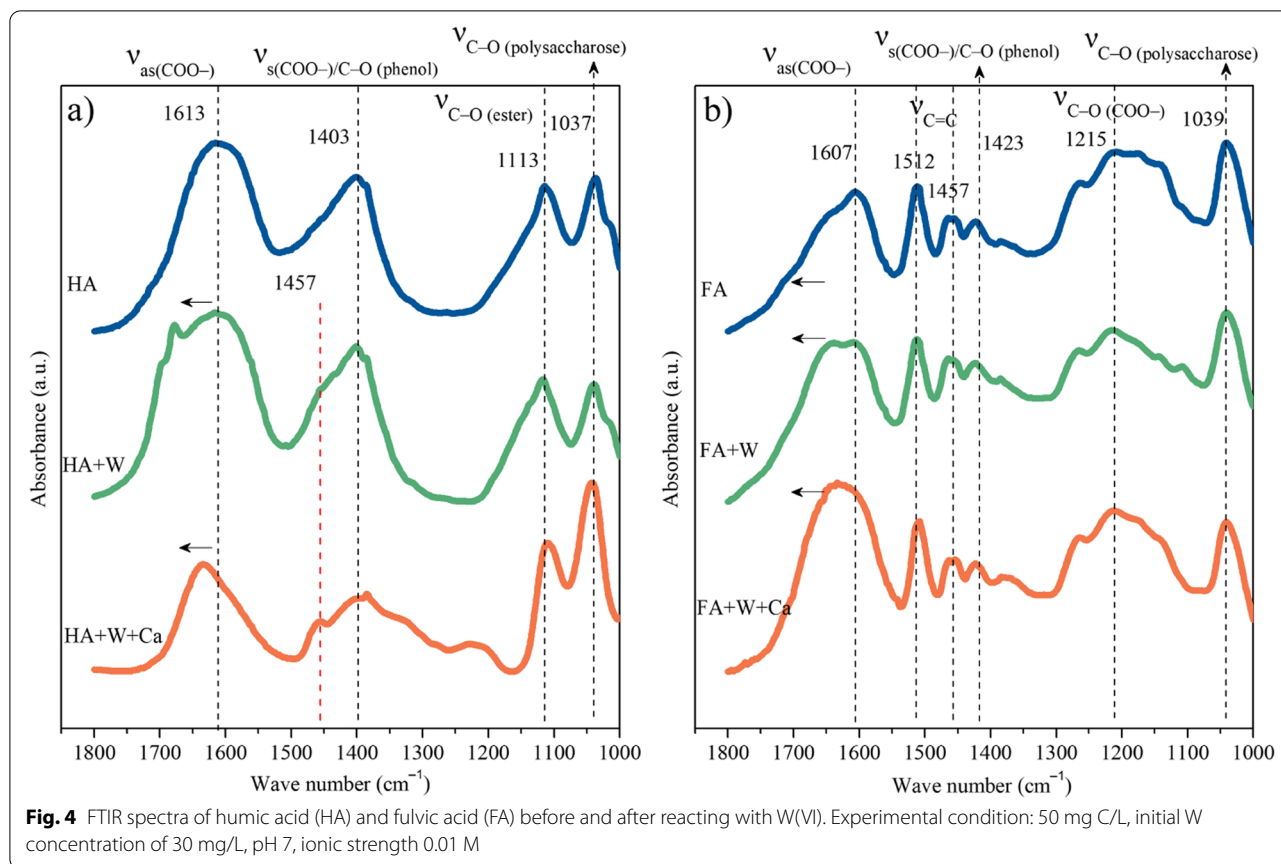### 3.5 W(VI) Complexation thermodynamics

For W(VI) complexation by HA and FA, the first 2 injections generated exothermic heat, followed by 8 releases of endothermic heat (Figs. S3 and 6). These observations suggested that two different complexation processes might occur, one was exothermic and the other one was endothermic. The peak amplitudes and areas decreased to almost zero after 10 injections, implying a complete consumption of available binding sites. For W–HA interaction, thermodynamic fitting results showed one process with negative ΔH (−5.2 kJ/mol) and positive ΔS (43.8 J/mol/K), and another with positive ΔH (30.8 kJ/mol) and ΔS (158.7 J/mol/K) (Table 2). The W–FA interaction generated a larger heat exchange of −17.8 kJ/mol and 158.6 kJ/mol. This result corroborated the batch adsorption results that more W(VI) was complexed by FA than by HA. The entropy changes for W–FA complexation were 6.7 and 597 J/mol/K. In conclusion, W(VI) complexation by HA and FA was a spontaneous process ($\Delta G < 0$) of entropy increase, and two different complexation mechanisms might occur with opposite thermal effects.

4 Discussion

4.1 W(VI) complexation mechanisms

Tungstate species are negatively charged, while HA and FA are overall negatively charged as well. Only

Fig. 3 Complexed W(VI) amounts per mass (mg/g) on humic acid (HA) and fulvic acid (HA) (50 mg C/L) at different pHs (∼ 5, 7, and 9) and initial Ca:W molar ratios. Error bars denote ± standard deviation (*n* = 3). Lowercase letters represent significant differences using one-way ANOVA (*p* < 0.05)

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Fig. 4 FTIR spectra of humic acid (HA) and fulvic acid (FA) before and after reacting with W(VI). Experimental condition: 50 mg C/L, initial W concentration of 30 mg/L, pH 7, ionic strength 0.01 M

weak W(VI) binding would be expected. However, we found quite a few W(VI) complexation by both HA and FA, suggesting a ligand exchange reaction might have occurred. For coordination numbers < 6, e.g., WO_4^{2-}, an associative ligand exchange mechanism at positively charged metal centers can take place (Huheey et al., 2014). As the tungstate center has a high formal charge + VI, an addition of hydroxyl entity (e.g., carboxylic or phenolic) at the electrophilic center followed by protonation and water molecule release might occur. Although the overall charge was negative for both reactants, this formed species can be stabilized through additional processes such as H−bridges (Buschmann et al., 2006). Such a process would consume H^+. That was why W(VI) complexation by HA/FA was stronger at acidic pH. Using FTIR, we only confirmed the participation of carboxylic groups in such ligand exchange reaction. ITC as a supplementary clearly showed two distinctly different complexation processes. Thus, carboxylic and phenolic hydroxyl groups both participated in the ligand exchange reaction (Fig. 7), consistent with previous observations for other metal(loid)s (Shi et al., 2016; Xu et al., 2016; Lu et al., 2017; Besold et al., 2019).

The p*K*a of carboxylic and phenolic groups were around 5 and 8, respectively (Table 1), so the carboxylic group seemed easier to protonate than the phenolic groups. However, previous studies have shown a higher affinity of proton binding to phenolic-type sites than to carboxylic-type sites (Xu et al., 2018), and phenolates are better Π-donors than carboxylates (Buschmann et al., 2006). That means when metal(loid)s, such as W(VI), are exposed to DOM, phenolic groups may first participate in the complexation reaction, followed by the carboxylic groups. Taken together with the ITC results that W(VI) complexation by DOM first generated an exothermic heat followed by an endothermic heat, we concluded that W(VI) complexation by phenolic-type sites of DOM was an exothermic process whereas the W−carboxylic complexion was an endothermic process. For either W−carboxylic or W−phenolic interaction, they both produced positive entropies (158.7 J/mol/K and 597 J/mol/K), likely due to the displacement of solvating water molecules from the coordination sites when ligand exchange was taken place (Chen et al., 2020; Du et al., 2020). The negative enthalpy and positive entropy of W−phenolic complexation suggested this process was driven by both
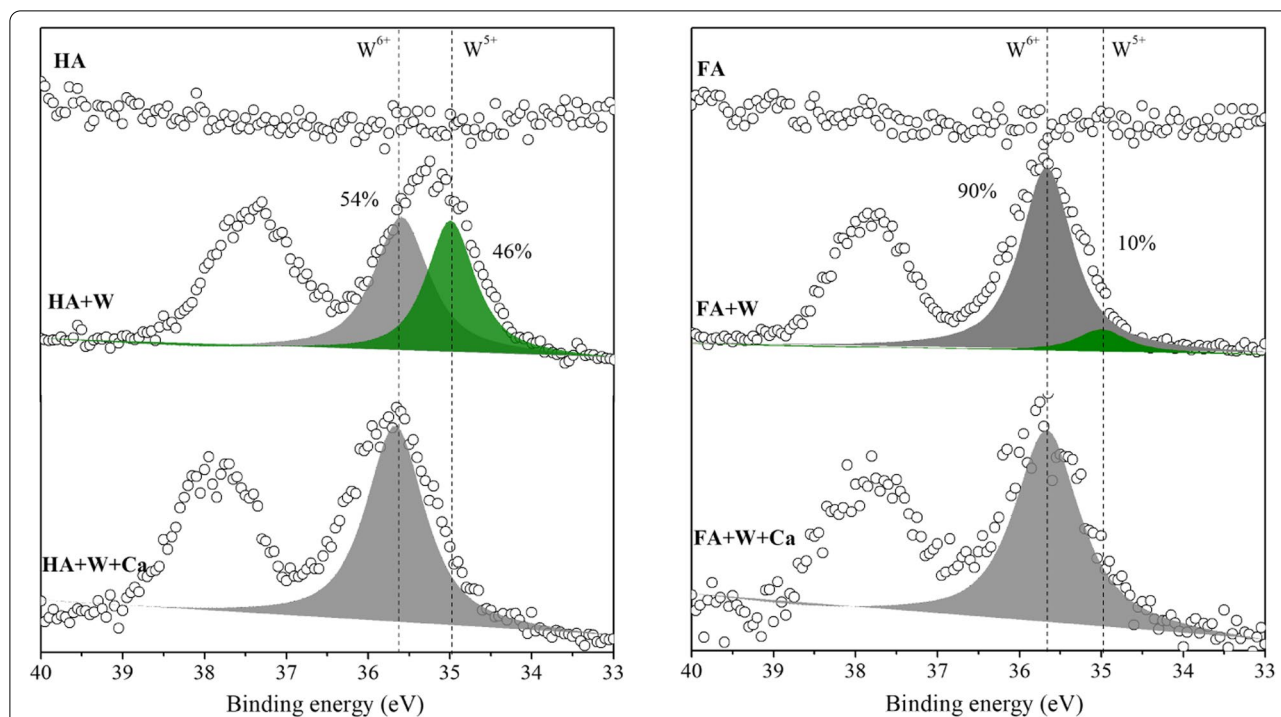
Fig. 5 Tungsten (4f, 5p) XPS spectra of W(VI)–DOM complexes under different conditions. Experimental condition: 50 mg C/L, initial W concentration of 30 mg/L, pH 7, ionic strength 0.01 M. The W $4f_{7/2}$ spectrum can be decomposed into W^{5+} $4f_{7/2}$ at $\sim$35.0 eV and W^{6+} $4f_{7/2}$ at $\sim$35.6 eV as appropriate, and the corresponding proportions(%) are given beside the peak
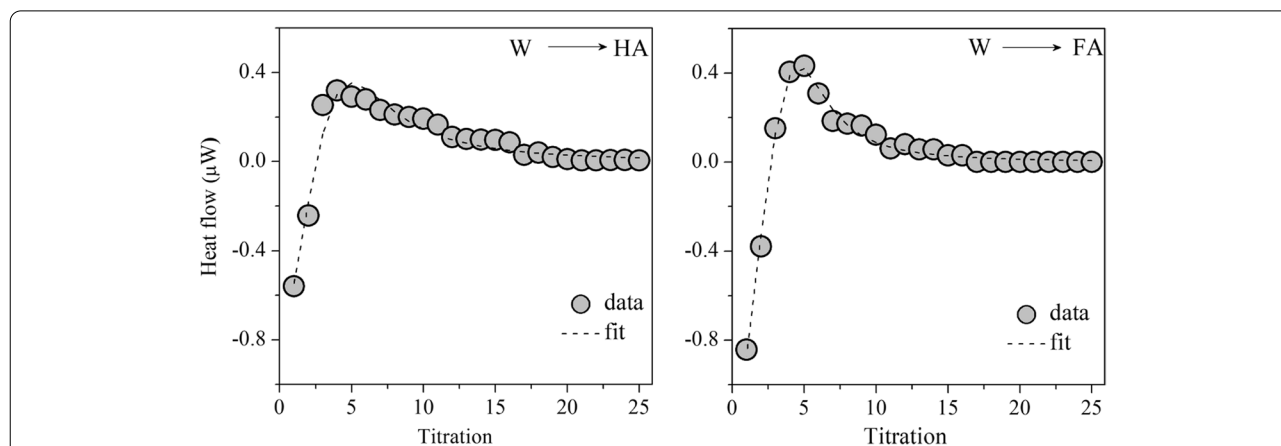
Fig. 6 Heat exchange (μJ) *versus* per titration for W(VI) complexation on humic acid (HA) and humic acid (FA) at pH $\sim$ 7.0. Lines are the two-sites model fits

Table 2 Complexation calorimetry parameters for W(VI) on humic acid and fulvic acid

	Reaction	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)	K_a (M^{-1})
HA	1	−18.2	−5.2	43.8	1574
	2	−16.5	30.8	158.7	769
FA	1	−19.7	−17.8	6.7	2870
	2	−19.2	158.6	597	2349

enthalpy and entropy, while the W–carboxylic association was driven only by entropy.

It should also be pointed out that, at pH 5, W(VI) formed polymeric species such as $H_2W_{12}O_{42}^{10-}$, $HW_7O_{24}^{5-}$ and $W_7O_{24}^{6-}$, based on our solution speciation analyses by Visual Minteq (Table S1). Therefore, multiply species, including poly-tungstate species, such as RC–O–W–O–W, might be present on DOM surfaces. Polymeric species are commonly metastable compared to the

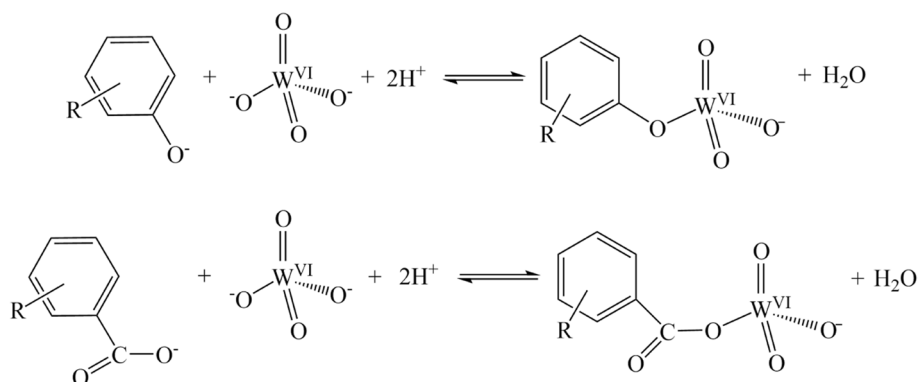Xu *et al. Carbon Research*   (2022) 1:11

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Fig. 7 Ligand exchange reaction of W(VI) by different functional groups of HA and FA

mono-tungstates (Sun and Bostick, 2015), further influencing W's solubility and mobility.

4.2 Complexation differences between HA and FA

Both batch adsorption and thermodynamic results showed a stronger complexation capacity of FA than HA, particularly at higher W(VI) concentrations. Although FA and HA had very close phenolic hydroxyl concentrations (0.32 and 0.37 mol/kg, Table 1), FA indeed possessed more carboxyls, which was 0.86 mol/kg for FA compared to 0.33 mol/kg for HA. At low W(VI) loading, phenolic hydroxyls preferentially participated in the complexation, hence the differences between HA and FA were not significant. We also observed that HA and FA could reduce W(VI) to W(V), indicative of the presence of redox-active functional moieties. To verify this assumption, we presented an electrochemical approach to study the redox properties of HA and FA (See supporting information). Direct electrochemical reduction of HA showed a decreased electron current from > 4 μA to ~ 1.8 μA when reached stable, while for FA, the decrease was only ~ 1.1 μA. Thus HA has a higher reductive potential than FA, leading to a greater reduction of W(VI) to W(V) as shown in XPS results. This reductive phenomenon is probably because DOM contains a variety of reductive moieties including quinones, substituted phenols, α-hydroxyl carboxylic acids, and α-carbonyls carboxylic acid (Wilson and Weber, 1979; Jiang et al., 2014), and humic substances are more redox-active than fulvic acid (Yang et al., 2016).

4.3 The role of Ca^{2+} on W(VI) complexation by HA/FA

We showed that Ca^{2+} promoted the W–HA/FA interactions at environmentally relevant concentrations (1.6 to 16.3 mg/L). Ca^{2+} is one of the most common

cations in natural aquifers, and usually affects the interaction of DOM with other metal pollutants such as arsenic (As). Ca^{2+} has a preference for binding to larger and more negatively charged molecules such as carboxylic groups, phenolic sites, and even amine moieties (Kinniburgh et al., 1999). Ca^{2+} can not only compete with other cations (i.e., Fe^{3+} and Cu^{2+}) for DOM's available sites (Adusei-Gyamfi et al., 2019), but also serve as bridges in oxyanions (i.e., As) binding to DOM (Ren et al., 2017; Zhang et al., 2021). Herein, the promoting role of Ca^{2+} in W(VI) complexation by DOM may be attributed to an indirect or a direct reason: 1) Binding of Ca^{2+} on DOM molecules reduced the negative charges and electric repulsion between DOM and W(VI) anions, hence allowing the two reactants to approach each other more readily; 2) By cationic bridging between carboxylic or phenolic groups and W(VI), a ternary DOM–Ca–W complex might be formed (Fig. 8, carboxylic groups as an example), and attracted additional W(VI) to be complexed by DOM. This bridging increased with increasing Ca^{2+} concentrations, which resulted in more bounded W(VI). Even though Ca^{2+} exhibits a relatively weak bonding with DOM, compared to trivalent cations such as Fe^{3+} and Al^{3+}, this bridging cannot be ignored considering the high concentration of Ca^{2+} in most aquifers; 3) At the experimental condition, scheelite ($CaWO_4$) was supersaturated according to our solution speciation analysis (Figs. S6–S7), approximately < 10% of total W(VI) can exist as precipitates which could also limit dissolved W concentrations. We also found that Ca^{2+} could almost completely inhibit W(VI) reduction by DOM. Because Ca^{2+} is not redox-active compared to, for example, Fe(III), thus Ca^{2+} was probably blocking the redox-active functional moieties of DOM to hinder the redox reaction.
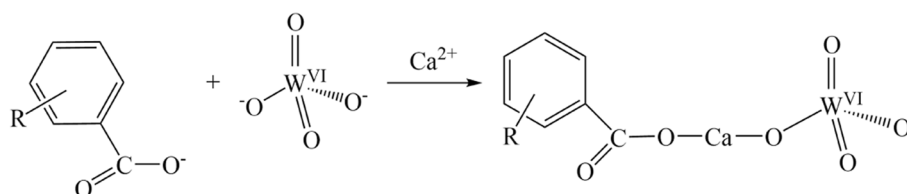
Fig. 8 Possible ternary DOM–Ca–W complex; carboxylic groups are taken as an example

4.4 Environmental considerations

When studying tungsten speciation and mobility in the aquifers, W complexation by dissolved organic substances including HA and FA should be taken into consideration. In aquatic systems that are impacted by W mining-smelting activities where W concentration can as high as several mg/L, ~ 20% of total W(V) can be bound to dissolved DOM. In natural aquifers with much lower W concentrations, this percentage is even higher. Coexisting cations in natural waters should also be taken into account because we observed that in the presence of Ca^{2+} more W(VI) was bound to HA and FA. Moreover, DOM is also capable of reducing W(VI) to a lower valence state of W(V) which may subsequently affect their biotoxicity and environmental risks.

5 Conclusions

Tungsten species were shown to react with DOM (HA and FA), and this association was highly dependent on pH, coexisting cations, and the concentration of W(VI). Tungsten–DOM interaction is proved to involve ligand exchange on the O-containing functional groups including carboxylic and phenolic sites. DOM could reduce hexavalent pentavalent W(VI) to W(V) via its redox-active moieties. The presence of Ca^{2+} promoted W–DOM complexation and inhibited W(VI) reduction on DOM. We conclude that DOM servers as an important pool of chelatable and redox-active for W in natural aquifers. Nevertheless, how this association would affect W's mobility, including the intensity of W adsorption onto the solid phases (i.e., iron (oxyhydr) oxides), needs further investigation. Overall, the study provides a basis for better evaluating the migration, bio-availability, and fate of tungsten in DOM-laden surface and ground waters and more appropriate designs of complexation-based treatment methods for tungsten in natural water.

Abbreviations

DOM: Dissolved organic matter; HA: Humic acid; FA: Fulvic acid; ITC: Isothermal titration calorimetry; NOM: Natural organic matter; FTIR: Fourier transform infrared spectroscopy; XPS: X-ray photoelectron spectroscopy; ΔH: Enthalpy; ΔS: Entropy; ΔG: Gibbs free energy; K_a: Binding affinity.

Supplementary Information

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Additional file 1.

Author's contributions

Zelin Xu: Methodology, Data analysis, Investigation, Visualization, Writing—Original Draft; Xin Liu: Investigation; Jincheng Peng: Investigation; Chenchen Qu: Data analysis, Investigation; Yifan Chen: Investigation; Ming Zhang: Investigation; Ding Liang: Investigation; Ming Lei: Supervision; Boqing Tie: Supervision; Huihui Du: Conceptualization, Data analysis, Visualization, Writing—Review & Editing, Funding acquisition. All authors read and approved the final manuscript.
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Availability of data and materials

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Author details

[1]College of Resources and Environment, Hunan Agricultural University, Changsha 410127, China. [2]College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China. [3]College of Resources of Environment, Huazhong Agricultural University, Wuhan 430070, China.

References

Adusei-Gyamfi J, Ouddane B, Rietveld L, Cornard J-P, Criquet J (2019) Natural organic matter-cations complexation and its impact on water treatment: a critical review. Water Res 160:130–147

Besold J, Kumar N, Scheinost AC, Lezama Pacheco J, Fendorf S, Planer-Friedrich B (2019) Antimonite complexation with thiol and carboxyl/phenol groups of peat organic matter. Environ Sci Technol 53:5005–5015. https://doi.org/10.1021/acs.est.9b00495

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Buschmann J, Kappeler A, Lindauer U, Kistler D, Berg M, Sigg L (2006) Arsenite and arsenate binding to dissolved humic acids: Influence of pH, type of humic acid, and aluminum. Environ Sci Technol 40:6015–6020

Cao Y, Guo Q, Shu Z, Jiao C, Luo L, Guo W, Zhao Q, Yin Z (2019) Tungstate removal from aqueous solution by nanocrystalline iowaite: an iron-bearing layered double hydroxide. Environ Pollut 247:118–127

Chen H, Tan W, Lv W, Xiong J, Wang X, Yin H, Fang L (2020) Molecular mechanisms of lead binding to ferrihydrite–bacteria composites: ITC, XAFS, and μ-XRF investigations. Environ Sci Technol 54:4016–4025

Cidu R, Biddau R, Frau F, Wanty RB, Naitza S (2021) Regional occurrence of aqueous tungsten and relations with antimony, arsenic and molybdenum concentrations (Sardinia, Italy). J Geochem Explor 229:106846

Cui M, Gomes M (2021) Impacts of manganese oxides on molybdenum and tungsten speciation and implications for their geochemistry in aquatic environments. Geochim Cosmochim Acta 312:217–234

Cui M, Luther GW, Gomes M (2021) Cycling of W and Mo species in natural sulfidic waters and their sorption mechanisms on MnO_2 and implications for paired W and Mo records as a redox proxy. Geochim Cosmochim Acta 295:24–48

Du H, Huang Q, Lei M, Tie B (2018a) Sorption of Pb(II) by nanosized ferrihydrite organo-mineral composites formed by adsorption versus coprecipitation. ACS Earth Space Chem 2:556–564

Du H, Peacock CL, Chen W, Huang Q (2018b) Binding of Cd by ferrihydrite organo-mineral composites: Implications for Cd mobility and fate in natural and contaminated environments. Chemosphere 207:404–412

Du H, Xu Z, Hu M, Zhang H, Peacock CL, Liu X, Nie N, Xue Q, Lei M, Tie B (2020) Natural organic matter decreases uptake of W(VI), and reduces W(VI) to W(V), during adsorption to ferrihydrite. Chem Geol 540:119567

Du H, Liu X, Li Y, luo Z, Lei M, Tie B (2021) A review on the environmental behavior and potential risk of tungsten in soils: progress and prospects. Acta Pedologica Sinica 59(3):654–665. https://doi.org/10.11766/trxb2 02011100503

Du H, Li Y, Wan D, Sun C, Sun J (2022) Tungsten distribution and vertical migration in soils near a typical abandoned tungsten smelter. J Hazard Mater 429:128292

Fariña AO, Peacock CL, Fiol S, Antelo J, Carvin B (2018) A universal adsorption behaviour for Cu uptake by iron (hydr)oxide organo-mineral composites. Chem Geol 479:22–35

Gaillardet J, Viers J, Dupré B (2003) Trace elements in river waters. Treatise on Geochemistry 5:605

Gu B, Bian Y, Miller CL, Dong W, Jiang X, Liang L (2011) Mercury reduction and complexation by natural organic matter in anoxic environments. PNAS 108:1479–1483

Guo Q, Li Y, Luo L (2019) Tungsten from typical magmatic hydrothermal systems in China and its environmental transport. Sci Total Environ 657:1523–1534

Gustafsson JP, Tiberg C (2015) Molybdenum binding to soil constituents in acid soils: An XAS and modelling study. Chem Geol 417:279–288

Gustafsson JP, Persson I, Oromieh AG, van Schaik JW, Sjöstedt C, Kleja DB (2014) Chromium(III) complexation to natural organic matter: Mechanisms and modeling. Environ Sci Technol 48:1753–1761

Hobson C, Kulkarni H, Johannesson K, Bednar A, Tappero R, Mohajerin TJ, Sheppard P, Witten M, Hettiarachchi G, Datta S (2020) Origin of tungsten and geochemical controls on its occurrence and mobilization in shallow sediments from Fallon, Nevada, USA. Chemosphere 260:127577

Iwai T, Hashimoto Y (2017) Adsorption of tungstate (WO_4) on birnessite, ferrihydrite, gibbsite, goethite and montmorillonite as affected by pH and competitive phosphate (PO_4) and molybdate (MoO_4) oxyanions. Appl Clay Sci 143:372–377

Jiang W, Cai Q, Xu W, Yang M, Cai Y, Dionysiou DD, O'Shea KE (2014) Cr(VI) adsorption and reduction by humic acid coated on magnetite. Environ Sci Technol 48:8078–8085

J Huheey E Keiter R Keiter 2014 Anorganischechemie: Prinzipien von Struktur und Reaktivität De Gruyter https://doi.org/10.1515/9783110307955

Johannesson KH, Dave HB, Mohajerin TJ, Datta S (2013) Controls on tungsten concentrations in groundwater flow systems: The role of adsorption, aquifer sediment Fe(III) oxide/oxyhydroxide content, and thiotungstate formation. Chem Geol 351:76–94

Kim JI, Buckau G, Li GH, Duschner H, Psarros N (1990) Characterization of humic and fulvic acids from Gorleben groundwater. Fresenius J Anal Chem 338:245–252

Kinniburgh DG, van Riemsdijk WH, Koopal LK, Borkovec M, Benedetti MF, Avena MJ (1999) Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. Colloids Surf A 151:147–166

Koutsospyros A, Braida W, Christodoulatos C, Dermatas D, Strigul N (2006) A review of tungsten: from environmental obscurity to scrutiny. J Hazard Mater 136:1–19

Li R, Luan R, Lin C, Jiao D, Guo B (2014) Tungstate adsorption onto oxisols in the vicinity of the world"s largest and longest-operating tungsten mine in China. Rsc Adv 4:63875–63881

Lin C, Li R, Cheng H, Wang J, Shao X (2014) Tungsten distribution in soil and rice in the vicinity of the world's largest and longest-operating tungsten mine in China. PLoS ONE 9:e91981

Lu Y, Yan M, Korshin GV (2017) Spectroscopic study of interactions of lead (II) ions with dissolved organic matter: Evidence of preferential engagement of carboxylic groups. Geochim Cosmochim Acta 213:308–316

Lumsdon DG, Fraser AR (2005) Infrared spectroscopic evidence supporting heterogeneous site binding models for humic substances. Environ Sci Technol 39:6624–6631

Mostofa KMG, Liu C-q, Feng X, Yoshioka T, Vione D, Pan X, Wu F (2013) Complexation of dissolved organic matter with trace metal ions in natural waters. In Photobiogeochemistry of Organic Matter: Principles and Practices in Water Environments: 769–849. https://doi.org/10.1007/978-3-642-32223-5_9

Niemeyer J, Chen Y, Bollag J-M (1992) Characterization of humic acids, composts, and peat by diffuse reflectance Fourier-Transform Infrared Spectroscopy. Soil Sci Soc Am J 56:135–140

Petrunic BM, Al TA (2005) Mineral/water interactions in tailings from a tungsten mine, Mount Pleasant, New Brunswick. Geochim Cosmochim Acta 69:2469–2483

Pham AN, Rose AL, Waite TD (2012) Kinetics of Cu(II) reduction by natural organic matter. J Phys Chem A 116:6590–6599

Rashid MA, King L (1970) Major oxygen-containing functional groups present in humic and fulvic acid fractions isolated from contrasting marine environments. Geochim Cosmochim Acta 34:193–201

Ren J, Fan W, Wang X, Ma Q, Li X, Xu Z, Wei C (2017) Influences of size-fractionated humic acids on arsenite and arsenate complexation and toxicity to Daphnia magna. Water Res 108:68–77

Seiler RL, Stollenwerk KG, Garbarino JR (2005) Factors controlling tungsten concentrations in ground water, Carson Desert, Nevada. Appl Geochem 20:423–441

Shi Z, Wang P, Peng L, Lin Z, Dang Z (2016) Kinetics of heavy metal dissociation from natural organic matter: Roles of the carboxylic and phenolic sites. Environ Sci Technol 50:10476–10484

Steenstra P, Strigul N, Harrison J (2020) Tungsten in washington state surface waters. Chemosphere 242:125151

Sun J, Bostick BC (2015) Effects of tungstate polymerization on tungsten(VI) adsorption on ferrihydrite. Chem Geol 417:21–31

Wasylenki LE, Schaefer AT, Chanda P, Farmer JC (2020) Differential behavior of tungsten stable isotopes during sorption to Fe versus Mn oxyhydroxides at low ionic strength. Chem Geol 558:119836

Weber JH, Wilson SA (1975) The isolation and characterization of fulvic acid and humic acid from river water. Water Res 9:1079–1084

Wilson SA, Weber JH (1979) An EPR study of the reduction of vanadium(V) to vanadium(IV) by fulvic acid. Chem Geol 26:345–354

Wittbrodt PR, Palmer CD (1995) Reduction of Cr(VI) in the presence of excess soil fulvic Acid. Environ Sci Technol 29:255–263

Xiong J, Koopal LK, Tan W, Fang L, Wang M, Zhao W, Liu F, Zhang J, Weng L (2013) Lead binding to soil fulvic and humic acids: NICA-Donnan modeling and XAFS spectroscopy. Environ Sci Technol 47:11634–11642

Xu J, Tan W, Xiong J, Wang M, Fang L, Koopal LK (2016) Copper binding to soil fulvic and humic acids: NICA-Donnan modeling and conditional affinity spectra. J Colloid Interface Sci 473:141–151

Xu J, Koopal LK, Fang L, Xiong J, Tan W (2018) Proton and copper binding to humic acids analyzed by XAFS spectroscopy and isothermal titration calorimetry. Environ Sci Technol 52:4099–4107

Xue Q, Ran Y, Tan Y, Peacock CL, Du H (2019) Arsenite and arsenate binding to ferrihydrite organo-mineral coprecipitate: Implications for arsenic mobility and fate in natural environments. Chemosphere 224:103–110

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Yang Z, Andreas K, Jiang J (2016) Reducing capacities and distribution of redox-active functional groups in low molecular weight fractions of humic acids. Environ Sci Technol 50:12105–12113

Zhang J, Chen L, Yin H, Jin S, Liu F, Chen H (2017) Mechanism study of humic acid functional groups for Cr(VI) retention: Two-dimensional FTIR and 13C CP/MAS NMR correlation spectroscopic analysis. Environ Pollut 225:86–92

Zhang F, Li X, Duan L, Zhang H, Gu W, Yang X, Li J, He S, Yu J, Ren M (2021) Effect of different DOM components on arsenate complexation in natural water. Environ Pollut 270:116221