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1 **Tungstate adsorption onto the Oxisols in the vicinity of the world's largest and**
2 **longest-operating tungsten mine in China**

3 Ruiping Li, Rina Luan, Chunye Lin*, Deqi Jiao, Bobo Guo

4 **Abstract:**

5 Tungstate adsorption in soils is critical to understand tungstate mobility and bioavailability, but
6 the study on it is lacking. The objectives of this study are to investigate the kinetic and isotherm of
7 tungstate adsorption onto the Oxisols sample in the vicinity of the world's largest and
8 longest-operating tungsten mine in China. In addition, the effects of pH, ionic strength, and
9 phosphate anion on the tungstate adsorption onto the soil were studied. Results show that the
10 tungstate adsorption kinetics is fitted best by the pseudo-second order model. Micropore
11 (intraparticle) diffusion and ultramicropore (within clays) diffusion generally are the
12 adsorption-limiting mechanisms. Tungstate adsorption isotherms are fitted well by both Langmuir
13 model and Freundlich model. The maximal adsorption capacity of the Oxisols sample is 10.67
14 mmol kg⁻¹, while the distribution coefficient is 12.60 (mmol kg⁻¹)(mol L⁻¹)^{1/n}. Tungstate adsorption
15 decreased from 96.1% to 90.2% with the pH increase from 4.93 to 5.23, while it increased from
16 90.1% to 95.5% with the increase of ionic strength from 0.01 M to 0.1 M NaCl. With the increase of
17 phosphate from 0.008 mM to 0.215 mM, tungstate adsorption slightly decreased from 2.32 mmol
18 kg⁻¹ to 1.97 mmol kg⁻¹. These results demonstrate that tungstate might be adsorbed onto the
19 tungstate-specific adsorption sites of the soil minerals mainly via inner-sphere complexation..
20 Whereas the soil contains high tungsten (e.g. 21.9 mg kg⁻¹), it still has high tungstate adsorption
21 capacity.

22 **Keywords:** Soil, Tungstate, Adsorption

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23 1. Introduction:

24 Tungsten (W) is a transition metal and become a matter of increasing concern due to the
25 scrutiny of a children leukemia cluster in Nevada, its toxicity to organisms, and ubiquitous presence
26 of this element in the environment as a result of geogenic and anthropogenic processes.¹⁻⁶
27 Anthropogenic activities that may lead to W release include W mining and smelting, military
28 combat/training operations using W-containing hardware, agrochemical practices such as the
29 application of W-containing fertilizers, and non-sustainable disposals of W-containing substances
30 (e.g. disposal of light bulbs in landfills and land application of wastewater residuals)³. In general, W
31 exists as the tungstate anion and is thermodynamically stable in environments.^{3, 7, 8}

32 Whereas the geochemical behaviors of tungstate in environments are probably dependent, to a
33 large extent, on its adsorption/desorption to/from colloidal particle surfaces, only several studies
34 investigated the tungstate adsorption/desorption. In addition, these studies mainly focused on metal
35 oxides and silicate clay minerals.^{7, 9-14} Gustafsson investigated tungstate adsorption to ferrihydrite,
36 showing that tungstate adsorption was strongly pH dependent and could be described with use of
37 two monodentate complex. Tungstate adsorption on goethite has a broad adsorption envelop across
38 a wide pH range with maximal adsorption below pH 5.1, more than 50% of tungstate adsorption at
39 neutral pH, and only 10% above pH 10.¹² In addition, tungstate adsorption on goethite is
40 irreversible and the maximal adsorption capacity to goethite was estimated to be 225.7 $\mu\text{mol g}^{-1}$ by
41 Langmuir model.¹⁰ Vissenberg et al.¹¹ studied tungstate adsorption on $\gamma\text{-Al}_2\text{O}_3$, TiO_2 , and
42 amorphous silica alumina, demonstrating that most of the tungstate reacts irreversibly with acidic
43 and neutral OH groups and the other part adsorbs reversibly by electrostatic interactions with
44 protonated OH groups. Tungstate adsorption to peat and silicate clays were also investigated.^{9, 13,}
45 ¹⁵ The extent of the tungstate uptake is in the following order: peat > kaolinite > montmorillonite >

46 illite.⁹ The high uptake by peat may be related to the formation of complexes of tungstate with humic
47 substances. The maximal tungstate adsorption capacity of $8.28 \mu\text{mol g}^{-1}$ for kaolinite is much lower
48 than that for goethite ($225.7 \mu\text{mol g}^{-1}$).^{9, 10} One study investigated the retention of tungstate by
49 three Finnish soils, showing the highest retention from the most acidic samples.¹⁶ In addition,
50 retention of tungstate by these soils was strong and only small amount of the retained tungstate was
51 desorbed.

52 China is the world's largest W producer and consumer.¹⁷ Ganzhou in the south of Jiangxi
53 province, being the birth place of Chinese W industry, is extremely rich in W source. So Ganzhou is
54 called as "Tungsten capital of the world". There are three major tungsten mines: Xihuashan,
55 Dangping, and Piaotang, among which Xihuashan is the first tungsten mine operated in China. The
56 soil around tungsten mines has been contaminated by tungsten.¹⁷ The tungstate mining and smelting
57 there may still release tungstate to soils via atmospheric deposition, runoff, and irrigation with river
58 water in the future. Therefore, it is critical to understand tungstate adsorption/desorption to/from the
59 tungsten-contaminated soil in Ganzhou and quantify the maximal tungstate adsorption capacity. In
60 addition, the knowledge on tungstate adsorption/desorption to/from soils is lacking and thus would
61 be interesting to worldwide scientists.

62 The objectives of this study are: (1) to investigate the kinetic of tungstate adsorption to the soil
63 of Ganzhou; (2) to identify tungstate adsorption isotherms; and (3) to investigate the influences of
64 pH, ionic strength, and competitive anion (PO_4^{3-}) on the tungstate adsorption.

65 **2. Materials and Methods**

66 **2.1. Soil sampling and analysis**

67 Topsoil (about 0 to 20 cm depth) was sampled at 15 sites in the agricultural fields adjacent to
68 W mines in Ganzhou, the southern Jiangxi province of southern China. The soil samples were

69 air-dried in lab, crushed, passed through 2 mm. Afterwards, portions of these individual samples
70 were mixed together to composite one sample to represent the whole are soil. The climate of
71 Ganzhou is characterized by subtropical monsoon, with average annual precipitation and
72 temperature of 1591.5 mm and 18.5°C, respectively.

73 The pH value of each individual soil sample and the composite soil sample was analyzed in a
74 1:10 solid/liquid ratio suspension (left for ~0.5 h) using a combination pH electrode. The organic
75 matter (OM) concentration was measured and estimated by weight loss on ignition (LOI) to
76 400°C.¹⁸ The grain size was determined by a LS 230 laser diffraction particle analyser (Beckman
77 Coulter). Specific surface area was measured by the Model QS-7 Quantasorb surface area analyzer
78 (Quantachrom Co., Greenvale, NY).

79 Portions of each individual soil sample and the composite sample were digested with HNO₃–
80 HF–HClO₄.¹⁹ The Al and Fe in the extracts were measured using ICP-AES (IRIS Intrepid II,
81 Thermo Electron), while W was measured with ICP MS (X Series II, Thermo Electron). Together
82 with digestion and measurement of our soil samples, four reference soils (GSS13, GSS15, GSS17,
83 and GSS25), provided by Institute of Geophysical and Geochemical Exploration, Chinese Academy
84 of Geological Sciences, were digested and analyzed to check the analytical quality. Relative errors
85 were -0.4% to 3.4% for W, -6.3% to 4.2% for Al, and -1.5% to 1.5% for Fe.

86 **2.2. Adsorption experiments**

87 The sorption of tungstate by the composite soil sample was measured in an aqueous matrix
88 consisting of NaCl solution. Accurately weighed samples (~1 g soil each) were mixed with 25 mL
89 of matrix solution with varying tungstate concentrations (Na₂WO₄•2H₂O). The pH value of the
90 suspensions was adjusted by adding negligible volumes of 0.1 or 0.01 M HCl or NaOH.
91 Competitive anion was added as NaH₂PO₄•2H₂O. The suspensions were gently shaken for several

92 days at 25±2°C. Then the suspensions were centrifuged at 8000 rpm for 20 min using Xiang Yi
 93 centrifuge (H-1650, China). The supernatant was decanted and filtered through 0.45 µm filter.
 94 Tungsten in the solution was measured employing the ICP-AES (SPECTRO ARCOS EOP,
 95 SPECTRO Analytical Instruments GmbH) or ICP-MS (NexION300x, PerkinElmer Instruments Co.
 96 Ltd). Table 1 lists the detailed experimental parameters. Standard deviation of replica was generally
 97 less than 5%.

98 Table 1 Experimental parameters of tungstate adsorption onto the composite soil sample

Experiment	Initial pH	Ionic strength	Initial W concentration	Equilibrating time
Kinetic	5.0	0.1 N NaCl	0.04 mM	0.25 to 168 h
Isotherm	5.0	0.1 N NaCl	0.4 µM to 1.21 mM	168 h
pH influence	5.0, 7.0, 9.0	0.1 N NaCl	0.04 mM	168 h
Ionic strength influence	5.0	0.01, 0.05, 0.1 N NaCl	0.04 mM	168 h
Competitive anion influence	5.0	0.1 N NaCl	0.04 mM	168 h

99 Adsorption percentage (%) was derived from the difference of the initial concentration (C_0 ,
 100 mM) and the final one (C_e , mM):

$$101 \quad \text{Adsorption (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

102 Where C_0 (mM) is the initial tungstate concentration, C_e (mM) is the equilibrium tungstate
 103 concentration.

104 To further understand the tungstate adsorption characteristics, the first-order rate equation,²⁴
 105 the pseudo-second-order rate equation²⁵ and double-constant rate equation²⁶ were evaluated based
 106 on the experimental data as shown below by Eqs. (2) - (4):

$$107 \quad \ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

108 Where q_e is the adsorption amount at equilibrium (mmol kg⁻¹); q_t is the adsorption amount at time t
 109 (mmol kg⁻¹); k_1 (h⁻¹) is the rate constant of pseudo-first-order equation, and t is the equilibrium time
 110 (h).

$$111 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

112 Where k_2 ($\text{kg mmol}^{-1} \text{h}^{-1}$) is the rate constant of pseudo-second order equation.

$$113 \quad \ln q_t = a + b \ln t \quad (4)$$

114 Where a, b is the kinetic constant of double-constant rate equation.

115 The Langmuir model and Freundlich model have been widely used to model equilibrium
116 adsorption data.³³⁻³⁷ The Langmuir adsorption equation can be expressed as

$$117 \quad q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \quad (5)$$

118 Where C_e is the equilibrium concentration of tungstate in solution, q_e is the tungstate adsorption
119 amount, q_{\max} is maximal adsorption capacity, and K_L (L mmol^{-1}) is a constant related to the binding
120 energy.

121 The Freundlich equation is an empirical adsorption model.³⁸ It can be presented as

$$122 \quad q_e = K_F C_e^{1/n} \quad (6)$$

123 Where K_F ($(\text{mmol kg}^{-1})(\text{mmol L}^{-1})^{-1/n}$) is the distribution coefficient.

124 3. Results and discussion

125 3.1. General properties of soil

126 Table 2 summarizes general physiochemical properties of soil samples collected in the
127 agricultural fields near the W mines. Soil pH value ranged from 4.92 to 5.90, showing its acidic
128 property. The organic matter (OM) content varied between 1.19 and 7.58%. The soil in the area is
129 generally classified as ferrosols in Chinese taxonomy (Oxisols). The secondary minerals in the
130 Oxisols mainly included kaolinite, vermiculite, hydromica, and hematite.²⁰ The soil texture is
131 generally classified as clayey loam, with 10% to 35%, 10% to 45%, 30% to 80% of clay ($<1 \mu\text{m}$),
132 silt ($1 \mu\text{m}$ to $10 \mu\text{m}$), and sand ($>10 \mu\text{m}$), respectively.²⁰ The specific surface area ranged from 4.25
133 to $13.47 \text{ m}^2/\text{g}$. The mineral matrix element Al and Fe contents in the soil samples ranged from 4.15

134 to 8.02% and 1.51 to 3.54%, respectively. Tungsten content in the soil samples ranged from 3.18 to
 135 102.65 mg kg⁻¹, higher than its background contents in the soils of the Jiangxi province, China, and
 136 world.^{21, 22} The composite soil sample contained 21.92 mg kg⁻¹ W, 6.05% Al, 3.22% Fe, and 3.76%
 137 SOM, with 5.45 pH and 7.92 m²/g SSA.

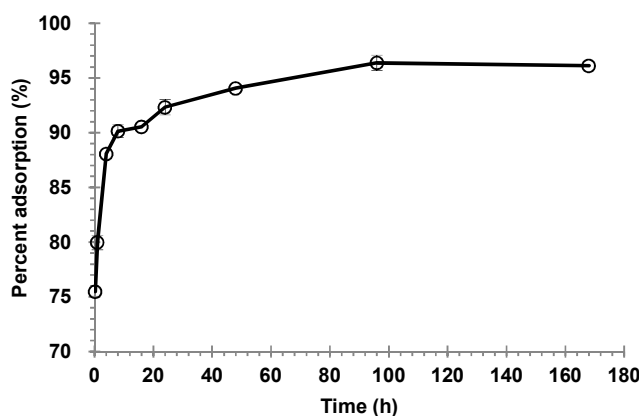
138 Table 2 General physiochemical properties and W contents of the soil samples

Sample no.	W µg/g	Al %	Fe %	OM %	pH	SSA m ² /g
1	4.39	6.16	2.19	5.18	5.53	7.56
2	3.18	4.98	1.74	5.77	4.92	6.66
3	5.29	8.02	2.56	6.46	5.16	9.10
4	4.61	5.13	3.12	6.19	5.04	12.71
5	5.64	6.78	2.14	7.58	4.98	6.23
6	16.28	7.37	3.48	7.06	5.90	13.47
7	4.41	6.20	3.54	4.35	5.58	10.22
8	102.65	7.77	2.24	6.19	5.38	9.82
9	88.06	5.55	1.90	4.54	5.22	6.87
10	72.83	6.09	1.79	4.66	5.13	5.68
11	4.75	6.64	1.84	1.19	5.44	5.59
12	12.39	7.50	2.65	6.98	5.11	10.01
13	3.98	6.29	1.85	5.00	5.34	7.40
14	5.37	4.15	1.79	3.16	5.17	9.59
15	22.37	4.66	1.51	2.87	5.45	4.25
Median	5.37	6.20	2.14	5.18	5.22	7.56
Maximal	102.65	8.02	3.54	7.58	5.90	13.47
Minimal	3.18	4.15	1.51	1.19	4.92	4.25
Composite	21.92	6.05	2.25	3.76	5.45	7.92
Jiangxi	5.28	8.60	2.88			
China	2.48	6.62	2.94			
World	1.50	7.10	4.00			

139 OM: soil organic matter; SSA: specific surface area.

140 3.2. Kinetics of tungstate adsorption

141 Adsorption kinetic is one of the most important characters which controls the solute uptake
 142 rate and represents the adsorption efficiency of the adsorbent. The adsorption kinetic of tungstate
 143 onto the composite soil sample at pH 5.0 is shown in Fig. 1.

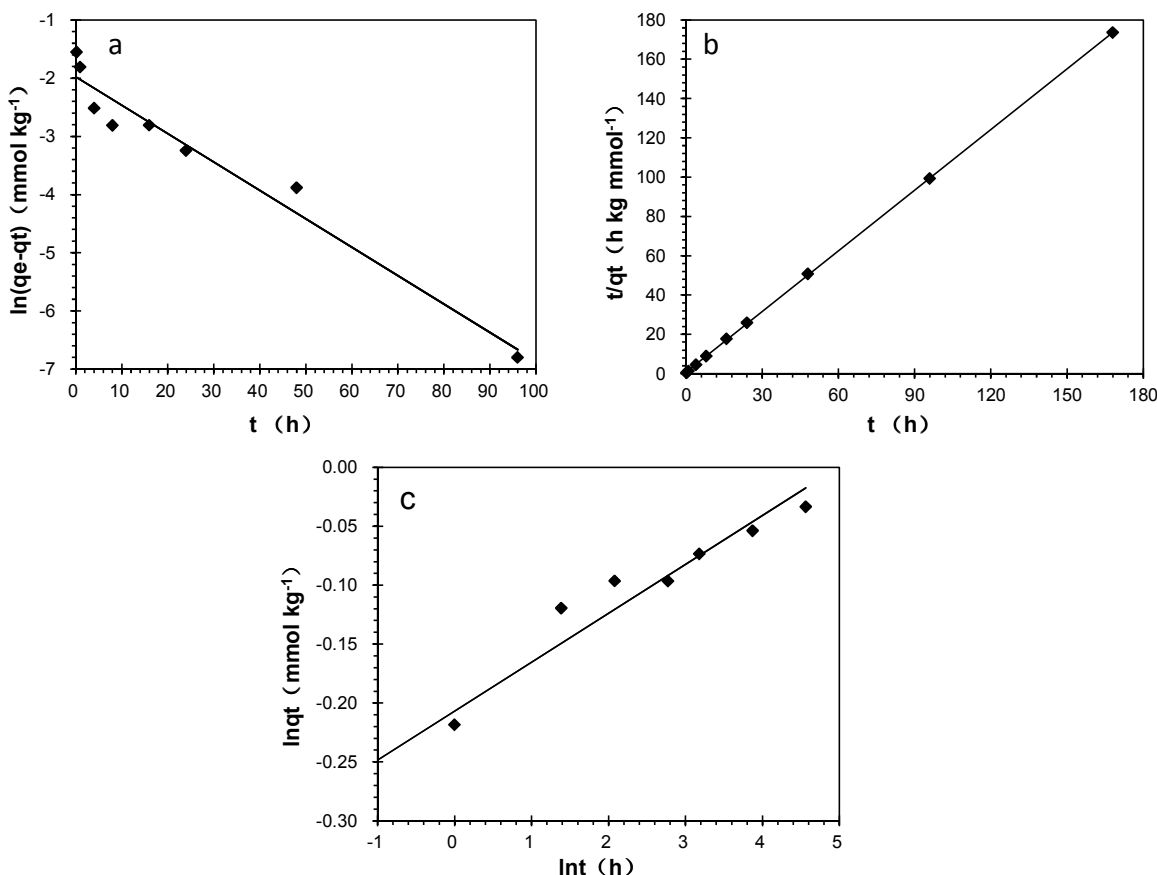


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145 Fig. 1 Adsorption kinetic of tungstate onto the composite sample. Experimental parameters are
146 listed in Table 1.

147 The results show that the tungstate adsorption was fast in the initial 24 h and afterwards
148 gradually reached apparent equilibrium within 168 h. The initial fast adsorption might be due to
149 tungstate adsorption on high affinity sites of adsorbents in the soil, while slow adsorption
150 afterwards might be due to tungstate adsorption on the low affinity sites.²³ According to the
151 adsorption kinetic in Fig. 1, equilibrium time for the following experiments was fixed at 168 h.

152 The linear regressions of adsorption kinetics are shown in Fig. 2a, 2b, 2c and fitted parameters are
153 listed in Table 3. The tungstate adsorption kinetics can be fitted with all three models, but the
154 pseudo-second-order was the best. The q_e value obtained from the pseudo-second-order equation is
155 more accurate ($SE < 1\%$) than that from the pseudo-first-order rate equation, and the calculated
156 correlation coefficient obtained from the pseudo-second-order equation is high ($R^2 = 0.99$).



157

158 Fig. 2 Kinetic simulation of tungstate adsorption onto the composite soil sample: (a) Pseudo-first
 159 order model, (b) Pseudo-second order model, and (c) Double-constant rate model. Experimental
 160 parameters are shown in Table 1.

161 Table 3 Parameters of adsorption kinetic models (tungstate concentration of 0.04 mM, pH= 5.0)

Model	$q_{e,exp}$ (mmol kg ⁻¹)	k	q_e (mmol kg ⁻¹)	a	b	R^2	SE%
Pseudo-first-order equation	0.97	1.98	0.13	---	---	0.96	646.15
Pseudo-second-order equation	0.97	1.05	0.96	---	---	0.99	1.04
Double-constant rate equation	0.97	---	---	0.04	0.21	0.94	---

162 $q_{e,exp}$: Measured adsorption capacity after contacting 168 h.

163 q_e : Estimated adsorption amount at equilibrium by the model.

164 $SE\% = (q_e - q_{e,exp}) / q_e \times 100$

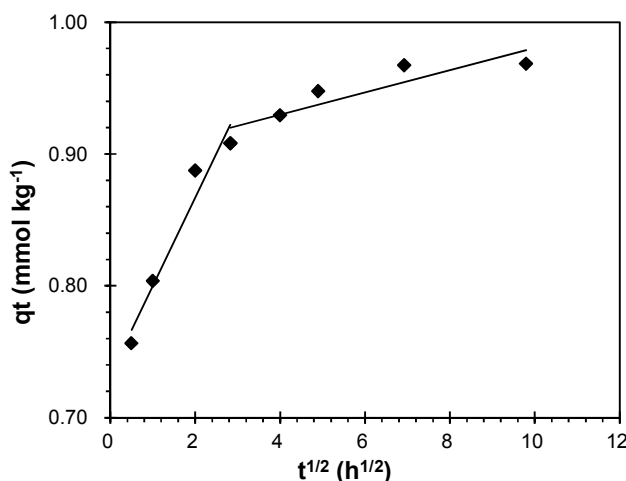
165 Generally, anions adsorption is often described as following mechanisms: external mass
 166 transfer (namely fluid film diffusion), intraparticle transport within the adsorbent, and
 167 chemiadsorption.²⁷⁻²⁹ The intraparticle diffusion mechanism is one of the most limiting factors
 168 which controls the adsorption kinetics.³⁰ Thus, the intraparticle diffusion model was utilized to

169 determine the rate limiting step of the adsorption process:^{31, 32}

$$170 \quad q_t = k_3 t^{1/2} \quad (7)$$

171 Where k_3 ($\text{mmol kg}^{-1} \text{h}^{-1/2}$) is the intraparticle diffusion rate constant.

172 According to this model, the relationship q_t versus $t^{1/2}$ is shown in Fig. 3. Two stages can be
173 identified: (a) the first part may be due to the micropore (within ped) diffusion or intraparticle
174 diffusion; (b) the second stage may be attributed to the ultramicropore (within clays) diffusion.



175

176 Fig. 3 Intraparticle diffusion model for the tungstate adsorption.

177 3.3. Tungstate adsorption isotherm

178 The tungstate isotherm data were fitted with the linearized Langmuir equation and Freundlich
179 equation (Fig. 4). The calculated isotherm parameters from the models are listed in Table 4.
180 Correlation coefficients (R^2) were 0.99 and 0.94 for the Langmuir model and Freundlich model,
181 respectively. The maximum adsorption capacity calculated from the Langmuir equation is 10.09
182 mmol kg^{-1} , while distribution coefficient is 12.6 (mmol kg^{-1}) (mmol L^{-1})^{-1/n} or 308.0 (mg kg^{-1}) (mg
183 L^{-1})^{-1/n}. Tuna et al.⁹ investigated the tungsten adsorption of from tungsten canister round munitions
184 onto montmorillonite, kaolinite, Pahokee peat, and illite. They found that tungsten adsorption onto
185 kaolinite was fitted best by the Langmuir model, while tungsten adsorption onto montmorillonite,
186 peat, and illite was fitted best by the Freundlich model. The maximal tungsten adsorption capacity

187 was $6.14 \text{ mmol kg}^{-1}$ for kaolinite, while distribution coefficients were 856, 27.4, and $22.9 \text{ (mg kg}^{-1})$
 188 $(\text{mg L}^{-1})^{-1/n}$ for peat, montmorillonite, and illite, respectively.³⁹ Tungstate adsorption onto goethite
 189 was fitted well by both the Langmuir model and the Freundlich model, with the maximal adsorption
 190 capacity of $225.7 \text{ mmol kg}^{-1}$ and the distribution coefficient of $159.1 \text{ (mmol kg}^{-1}) (\text{mmol L}^{-1})^{-1/n}$.
 191 Therefore, the maximal tungstate adsorption capacity onto the composite soil sample is similar to
 192 that for kaolinite, but much lower than that for pure goethite.

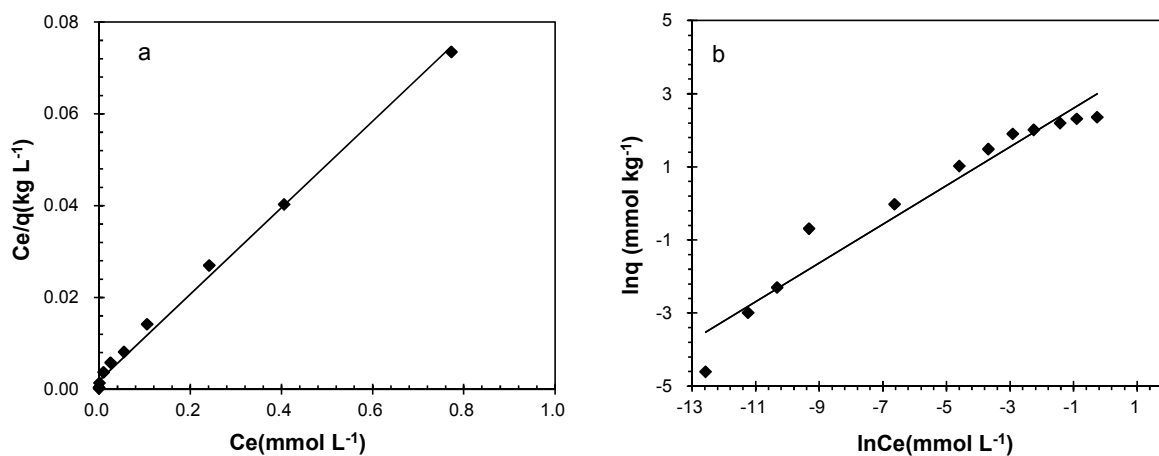
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194 Table 4 Parameters of Langmuir and Freundlich models

Model	K_L (L mmol^{-1})	Q_{\max} (mmol kg^{-1})	K_F $\text{mmol}^{1-1/n} \text{ kg}^{-1} \text{ L}^{1/n}$	$1/n$	R^2
Langmuir	0.035	10.67	---	---	0.99
Freundlich	---	---	12.60	0.28	0.94

195 K_L : Langmuir constant related to the binding energy; Q_{\max} : the maximal adsorption capacity of
 196 Langmuir model; K_F : Freundlich distribution coefficient; n : Freundlich correct factor.

197



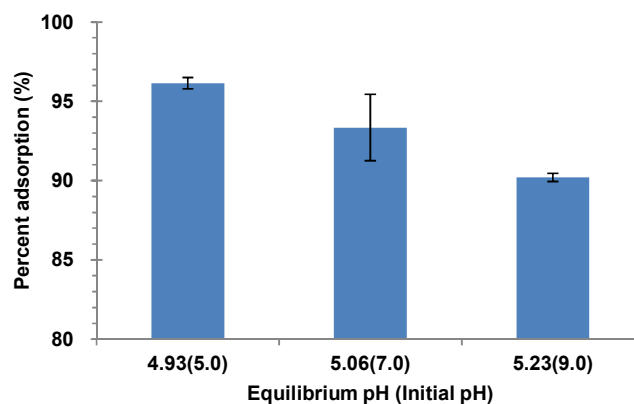
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199 Fig. 4 Langmuir (a) and Freundlich (b) isotherms of tungstate adsorption onto the composite soil
 200 sample.

201 3.4. Influence of pH on tungstate adsorption

202 Anion adsorption varies with pH, usually increasing with pH and reaching a maximum close to

203 the pKa for anions of monoprotic conjugate acids, and slope breaks have been observed at pKa
204 values for anions of polyprotic conjugate acids.^{40, 41} The initial pH values of the suspensions for
205 three treatments were adjusted to 5.0, 7.0, and 9.0. After equilibration of 7 days, the final pH
206 values for the three treatments decreased to 4.93, 5.06, and 5.23, respectively, due to the strong
207 buffering of the soil. Tungstate adsorption decreased from 96.1% to 90.2% with the pH increase
208 from 4.93 to 5.23 (Fig. 5). Xu et al.¹² observed that tungstate has a broad adsorption envelope
209 onto goethite across a wide pH range, with the maximum adsorption below pH 5.1, more than 50%
210 of WO_4^{2-} adsorption at neutral pH, and only 10% above pH 10 on the goethite surface. Tuna et
211 al.¹³ found that adsorption of tungstate on montmorillonite reaches a maximum at pH 3.5 and
212 become negligible (<5%) at pH 9.0. The effect of pH on the tungstate adsorption onto the
213 composite soil is consistent with the tungstate adsorption onto the soil minerals and three Finnish
214 mineral soils (e.g., goethite, ferrihydrite, $\gamma\text{-Al}_2\text{O}_3$, montmorillonite, kaolinite etc.).^{7, 12, 11, 14, 15} The
215 decline trend of adsorption of tungstate may be explained by the increase of negative surface
216 charge of the soil minerals with increasing pH.

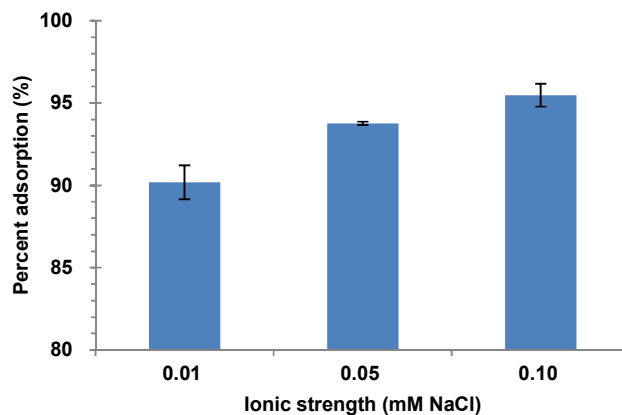


217
218 Fig. 5 The influence of solution pH on the tungstate adsorption onto the composite soil.

219 3.5. Influence of ionic strength on tungstate adsorption

220 Tungstate adsorption onto the composite soil increased from 90.1% to 95.5% with the increase
221 of ionic strength from 0.01 M to 0.1 M (Fig. 6). The effect of ionic strength on adsorption was used

222 to distinguish the inner-sphere surface complexation from the outer-sphere one in adsorption, and
223 hence, to give some useful information about the adsorption mechanism.⁴²⁻⁴⁵. In general, the
224 increase of ionic strength can decrease the outer-sphere complex due to ionic competition, but
225 might not have influence on the inner-sphere complex. Therefore, the increase of ionic strength
226 might usually decrease the overall adsorption. However, McBride⁴³ indicated that higher ionic
227 strength might lead to the transform of adsorbate from outer-sphere complex to inner-sphere
228 complex and hence might increase overall adsorption. The similar adsorption trend was reported for
229 borate and arsenate.⁴⁶⁻⁴⁹ Thus, the increase of ionic strength might the formation of the more
230 tungstate inner-sphere complex onto the soil colloids and thus increased the overall tungstate
231 adsorption onto them.



232

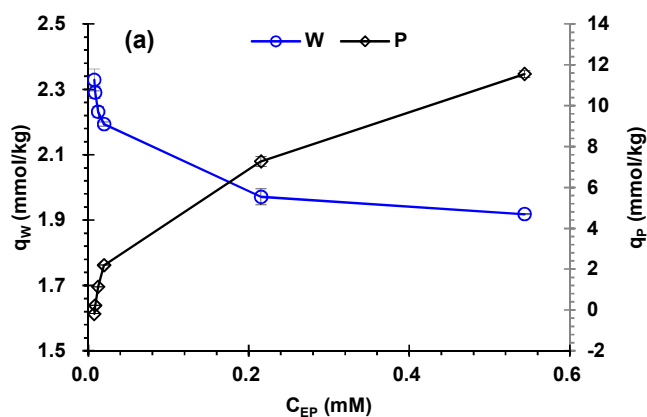
233 Fig. 6 The influence of solution ionic strength on the tungstate adsorption onto the composite soil.

234 3.6. Influence of competitive anions on tungstate adsorption

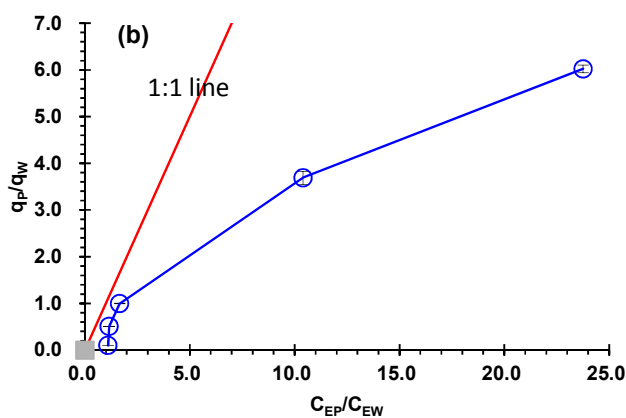
235 The mobility, bioavailability, and toxicity of tungstate in environments may also be greatly
236 affected by the presence of competitive anions. Anions such as PO_4^{3-} can compete with tungstate for
237 adsorption sites.^{3, 10, 50} In order to confirm competitive adsorption interactions between tungstate
238 (WO_4^{2-}) and phosphate (PO_4^{3-}), batch experiments were designed in which initial tungstate
239 concentration was 0.1 mM, while initial phosphate concentration ranged from 0.01 to 1.0 mM (Fig.
240 7). With the increase of equilibrium phosphate concentration (C_{EP}) from 0.008 mM to 0.215 mM,

241 tungstate adsorption decreased from $2.32 \text{ mmol kg}^{-1}$ to $1.97 \text{ mmol kg}^{-1}$, while phosphate adsorption
242 increased from $-0.19 \text{ mmol kg}^{-1}$ to $7.27 \text{ mmol kg}^{-1}$ (Fig. 7a). Afterwards, with the further increase of
243 C_{EP} to 0.544 mM , tungstate adsorption slightly decreased to $1.92 \text{ mmol kg}^{-1}$, but phosphate
244 adsorption continually increased to $11.55 \text{ mmol kg}^{-1}$. In addition, the molar ratio of equilibrium
245 phosphate concentration to tungstate concentration (C_{EP}/C_{EW}) was much higher than the molar ratio
246 of adsorbed phosphate to tungstate (q_P/q_W). Therefore, it can be concluded that the soil colloids
247 might have small adsorption sites common to tungstate and phosphate anions and large adsorption
248 sites specific to tungstate or phosphate anions.⁵¹ Mulcahy et al.⁵² concluded that tungstate adsorbs on
249 two types of surface sites of alumina, producing loosely and tightly bound surface species.

250



251



252

253 Fig. 7 The influence of phosphate on the tungstate adsorption onto the composite soil.

254 4. Conclusion

255 Tungstate adsorption onto the Oxisols soil generally reached equilibrium after 7 d equilibration.
256 The adsorption kinetics was fitted best with the pseudo-second-order reaction. Micropore
257 (intraparticle) diffusion and ultramicropore (within clays) diffusion might be the adsorption-limiting
258 mechanism. Tungstate adsorption isotherms are fitted well by both Langmuir model and Freundlich
259 model. The slight increase of pH from 4.93 to 5.23 slightly decreased the tungstate adsorption,
260 while the increase of ionic strength from 0.01 M to 0.1 M NaCl slightly increased the tungstate
261 adsorption. In addition, the increase of phosphate concentration from 0.008 mM to 0.215 mM
262 slightly decreased the tungstate adsorption. These results demonstrate that tungstate was adsorbed
263 onto the tungstate-specific adsorption sites of the soil minerals mainly via inner-sphere
264 complexation. Whereas the soil contains high tungsten (e.g. 21.9 mg kg⁻¹), it still has high tungstate
265 adsorption capacity.

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