Research Article

Zhaojun Nie, Jinfeng Li, Haiyang Liu, Shiliang Liu, Daichang Wang, Peng Zhao, Hongen Liu*

Adsorption kinetic characteristics of molybdenum in yellow-brown soil in response to pH and phosphate

https://doi.org/10.1515/chem-2020-0501
received April 4, 2018; accepted February 21, 2020

Abstract: Molybdenum (Mo) adsorption by acidic yellow-brown soil was investigated as a function of a pH (1–13) and the equilibrium of P solution (0, 3.1, and 31 mg L\(^{-1}\)) concentration. Mo adsorption by acidic yellow-brown soil increased within the pH range from 1 to 4. Above pH 4, Mo adsorption decreases with an increase in pH. The maximum adsorption was found between pH 2 and 4. Competitive adsorption experiments showed that the equilibrium sorption data fitted into Langmuir and Freundlich isotherms. The sorption data of Mo on the acidic yellow-brown soil fitted well with the Langmuir isotherm model due to the higher \(R^2\) value. A reduction in Mo adsorption by the acidic yellow-brown soil was noticed at higher addition levels of P (3.1 and 31 mg L\(^{-1}\)). Therefore, P increasing the bioavailability of Mo and enhancing Mo uptake by plants might be related to the inhibition of Mo absorption by the acidic yellow-brown soil.

Keywords: molybdenum, adsorption, pH, phosphate, acidic yellow-brown soil

1 Introduction

Molybdenum (Mo) is a trace element found in soil and is essential for plant growth. As an important cofactor of more than 50 Mo enzymes found in all organisms, Mo participates in diverse metabolic processes, such as carbon metabolism, nitrate assimilation, ascorbate-glutathione cycle metabolism, and so on in plants [1,2]. Mo is present in soil at an average level of up to 2.3 mg kg\(^{-1}\), which is lower than the lithosphere levels of up to 2.5–15 mg kg\(^{-1}\) [3]. Mo in soil ranges from 0.11 to 6 mg kg\(^{-1}\) and at an average level of up to 1.7 mg kg\(^{-1}\), thus Mo deficiency in soil is very common. The critical value of 0.15 mg kg\(^{-1}\) is considered as Mo deficient; and according to that value, more than 446 million ha of arable lands were found to be Mo deficient [4]. Mo deficiency is notably serious especially in the acidic yellow-brown soil from the Middle–Low Reaches of the Yangtze River in Hubei, Anhui and Jiangsu Provinces [5,6].

Mo deficiency induces abnormal development, yellowing, and even death of the leaves, affecting the yield and quality of plants such as legumes, beet, tobacco, citrus, and so on. Availability of Mo to plants has a close relationship with the sorption and desorption of Mo by soils, which is affected by a number of factors, including the concentration of iron oxides, competing ions, and clay mineral; pH of the soil solution; temperature, etc. [7]. One of the most important factors is the pH of the soil solution [8,9]. The absorption of Mo by the soil colloid decreases the available Mo in soils with a pH of less than 5.5 [10]. As the soil solution becomes more alkaline, the Mo availability increases. On the other hand, the presence of other oxyanions that compete with Mo in the soil also...
influences the mobility of Mo in the soil solution [11]. Phosphate, with physicochemical properties similar to molybdate, has a competitive relationship with the adsorption of Mo by the soils. The competitive adsorption of phosphate noticeably reduced the adsorption of molybdate by the surfaces of clay mineral, especially at high P addition levels [12]. Molybdate transport in water is retarded by sorption, depending on the pH and the level of phosphate [13].

Previous work focused on the interaction effect of P and Mo supply on the yields, qualities, photosynthesis, uptake, and translocation of P and Mo in Brassica napus grown in acidic yellow-brown soil [14–16]. The results showed a synergetic effect on grain yield, qualities, and photosynthesis between Mo and P fertilizers. The coapplication of Mo and P could enhance Mo and P uptake and accumulation in B. napus. It has been speculated that Mo and P having a synergetic effect on Mo uptake was related to the increased bioavailability of Mo in soil. However, little is known about Mo absorption by acidic yellow-brown soil affected by pH and the addition levels of P. The objectives of this study were to investigate (i) the relationship between Mo adsorption amounts by acidic yellow-brown soil and Mo concentrations in a balanced solution and (ii) the effect of pH and competing phosphate ions on Mo adsorption by acidic yellow-brown soil at differential concentrations of P for soil systems. Such results are expected to give a new insight into the effects of pH and phosphate on Mo absorption kinetics of acidic yellow-brown soil to better understand a possible mechanism of the Mo uptake enhanced by the interaction of Mo and P in plants due to the change in Mo availability in soil.

2 Experimental section

2.1 Soil

In this study, acidic yellow-brown soil was used, which was collected from the surface layer (0–20 cm) of the cultivated soil in Xinzhou, Hubei Province, China. The basic physical and chemical properties of this soil are pH 4.6 (soil and water ratio of 1:5), organic matter 20.6 g kg\(^{-1}\), alkaline hydrolysis N 72.3 mg kg\(^{-1}\), Olsen-P 31.4 mg kg\(^{-1}\), available K 48.9 mg kg\(^{-1}\), and Tamm’s reagent (pH 3.3) extractable Mo 0.09 mg kg\(^{-1}\). The soil was air-dried, ground, passed through a 1 mm mesh sieve, and then thoroughly mixed.

2.2 Experimental procedure

Adsorption experiments were carried out to determine whether Mo adsorption was influenced by the pH. Samples of 1.0 g acidic yellow-brown soil containing Mo were added to 50 mL polypropylene centrifuge bottles and equilibrated with 20 mL of 0.1 mol L\(^{-1}\) NaCl solution by shaking for 20–24 h on a reciprocating shaker at 25°C. The equilibrating solutions contained 0.292 mmol L\(^{-1}\) Mo and had been adjusted to the desired pH values using 1.0 mmol L\(^{-1}\) HCl or 1.0 mmol L\(^{-1}\) NaOH that changed the total volume by 2% or less. After the samples were centrifuged at 4,000 rpm for 15 min, the supernatants were analyzed for pH and Mo concentrations using a graphite furnace with a ZEEnit-7000 series polarized Zeeman atomic absorption spectrometer (Analytik Jena, Germany), according to Zhao [17].

Competitive adsorption experiments were carried out with equilibrating solutions containing P concentration of 0, 3.1, or 31 mg L\(^{-1}\) and Mo concentration of 0, 1, 2, 4, 6, 8, 10, 12, 16, or 20 mg L\(^{-1}\). The anions were added simultaneously. The experimental procedure remained the same as the single-anion adsorption experiments previously described. The experiment was performed on three independent replications for each concentration. The Mo absorption amounts (mg kg\(^{-1}\)) were evaluated using the formula given by Vanderborght and Van Grieken [18]:

\[
Q = \frac{(C_i - C_e) V}{w},
\]

where \(Q\) is the amount of solute adsorbed from the solution, \(V\) is the volume of the adsorbate, \(C_i\) is the concentration before adsorption, \(C_e\) is the concentration after adsorption, and \(w\) is the weight in gram of the adsorbent. The absorption rate was determined by computing the percentage sorption using the formula in equation (2):

\[
\text{% Sorption} = \frac{C_i - C_e}{C_i} \times 100
\]

Langmuir represented the following equation:

\[
q_e = \frac{q_m K_a C_e}{1 + K_a C_e},
\]

The above equation can be rearranged in the following linear form:

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_a C_e},
\]

where \(C_e\) is the equilibrium concentration (mg L\(^{-1}\)), \(q_e\) is the amount of metal adsorbed (mg g\(^{-1}\)), \(q_m\) is the maximum monolayer coverage capacity (mg g\(^{-1}\)), and
$K_a$ is the Langmuir isotherm constant ($L \cdot mg^{-1}$). A plot of $C_e/q_e$ versus $C_e$ should indicate a straight line of slope $1/q_m$ and an intercept of $1/K_aq_m$.

Freundlich represented the following equation:

$$q_e = K_f C_e^n,$$  \hspace{1cm} (5)

where $K_f$ is the Freundlich isotherm constant ($mg \cdot g^{-1}$), $n$ is adsorption intensity, $C_e$ is the equilibrium concentration of adsorbate ($mg \cdot L^{-1}$), and $q_e$ is the amount of metal adsorbed ($mg \cdot g^{-1}$).

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e.$$  \hspace{1cm} (6)

### 2.3 Statistical analysis

The data of Mo absorption amount were fitted into the following isotherms: Langmuir and Freundlich isotherms using OriginLab Origin 8.0 software (Origin (Pro), Version “8.0”; OriginLab Corporation, Northampton, MA, USA). Data are presented as the average of three replicates. The results were statistically analyzed with least significant difference multiple comparison using SPSS 18 software. All statistically significant differences correspond to $P < 0.05$.

**Ethical approval:** The conducted research is not related to either human or animal use.

## 3 Results and discussion

### 3.1 Effect of pH on molybdate sorption by yellow-brown soil

The Mo adsorption influenced by pH was determined for the acidic yellow-brown soil. The Mo adsorption by acidic yellow-brown soil progressively increased as the pH increased from 1 to 4 but decreased as the pH increased further to 13 (Figure 1). Maximum adsorption was found at the pH range of 2–4, which is in agreement with the findings of Goldberg [19,20]. With pH > 4, the Mo adsorption by acidic yellow-brown soil rapidly decreased and reached the lowest value as the pH exceeded 8. These results suggested that soil pH will still be an agriculturally important factor affecting the extent of Mo adsorption. Gupta [21] and Liu [22] pointed out five chemical fractions of Mo in soil including water-soluble Mo, exchangeable (weak acid) Mo, iron (Fe)/manganese (Mn) oxide-bound Mo, organic-bound Mo, and residual Mo. The first four of these fractions (but not residual Mo) can transform into each other as the soil pH changes [21,23]. The charge of the iron oxides is positive at low and negative at high pH values, respectively [24]. Thus, iron oxides absorb and fix molybdate anion in acidic conditions but release molybdate through the exchange of OH$^-$ in solution with the molybdate anion of the iron oxides in the alkaline medium. This is one of possible reasons for the absorption of Mo by the soil; and even the bioavailability of Mo to plants is pH dependent. However, the relationship between Mo absorption by and chemical fractions in acidic yellow-brown soil, which are affected by pH, is worth further study.

### 3.2 Effect of phosphate on molybdate sorption by yellow-brown soil

To investigate whether the equilibrium relationship between molybdate and acidic yellow-brown soil is affected by the addition levels of P, two common equilibrium models were analyzed. These included the Langmuir and the Freundlich isotherms. The Langmuir sorption isotherm has been successfully applied to metal ion sorption processes and the most widely used for the sorption of a solute from a liquid solution [25]. The Freundlich adsorption isotherm is commonly used to
describe the adsorption characteristics of the heterogeneous surface.

Figure 2 shows the nonlinear plot of \( q_e \) versus \( C_e \). The \( R^2 \) value of the Langmuir isotherm was higher than that of the Freundlich isotherm at 0, 3.1, and 31 mg P L\(^{-1}\) (Table 1). These results proved that the sorption data of Mo by the acidic yellow-brown soil fitted well with the Langmuir isotherm model, which was in agreement with the findings of Harter and Baker [26]. They demonstrated that the characteristics of the adsorption reaction process were better reflected by the Langmuir isotherm than the Freundlich isotherm, because a practical parameter of adsorption characteristics of soil, maximum monolayer coverage capacity \( q_m \), could be obtained from the Langmuir isotherm.

Mo adsorption amount and adsorption rates in response to different P addition levels are shown in Figure 3. Mo adsorption by the acidic yellow-brown soil progressively increased with increased Mo concentration in the equilibrating solutions (Figure 3a). As the addition levels of P were increased, the Mo adsorption by the

Table 1: Coefficient \((R^2)\) value of the two nonlinear fit at three P addition levels

| P levels | Langmuir equation | Freundlich equation |
|----------|-------------------|---------------------|
| 0        | 0.9352**          | 0.9116**            |
| 3.1      | 0.9604**          | 0.9511**            |
| 31       | 0.9776**          | 0.9645**            |

Note: ** indicates significance at \( P < 0.01 \) for the coefficient.

Figure 2: Differences in Mo adsorption isothermal equation between two nonlinear fitting of three phosphate levels: (a) 0 mg P/L, (b) 3.1 mg P/L, and (c) 31 mg P/L.

Figure 3: (a) Mo adsorption amount and (b) adsorption rates in response to the different P addition levels.
acidic yellow-brown soil progressively decreased at each Mo concentration in the equilibrating solutions. It has been found that the differences in the Mo adsorption between the addition levels of P of 0 and 31 mg P L\(^{-1}\) are growing greater; while the Mo concentration in equilibrating solutions is higher, with the greatest value at an Mo concentration of 20 mg L\(^{-1}\). The Mo adsorption rates of the acidic yellow-brown soil increased first at low Mo concentration and then decreased at high Mo concentration in the equilibrating solutions (Figure 3b). Similarly, the highest P addition level (31 mg L\(^{-1}\)) significantly decreased the Mo adsorption rates at each Mo concentration, compared with the P addition level of 0 mg L\(^{-1}\). It revealed that the adsorption of molybdate by the acidic yellow-brown soil was greatly suppressed by the presence of P. This result is in agreement with the findings of Goldberg [12], i.e., the adsorption of molybdate by soils was unaffected by the presence of 3\( \times \) equimolar phosphate concentration but decreased by further progressive increases in the P concentration, i.e., to 30\( \times \) and 300\( \times \). The Langmuir and Freundlich isotherm constants predicted a decrease in Mo adsorption in the presence of phosphate (Table 2). The maximum monolayer coverage capacity, \( q_m \), for the three addition levels of P was 462.8, 378.9, and 341.7 mg kg\(^{-1}\) for 0, 3.1, and 31 mg P L\(^{-1}\), respectively. The values of the Langmuir constant \( K_a \) were 0.202, 0.191, and 0.087 L mg\(^{-1}\) at 0, 3.1, and 31 mg P L\(^{-1}\), respectively. The Langmuir constant \( K_a \) is an important factor for reflecting the absorbed ability of soil. The higher the \( K_a \), the quicker the absorption rate of ions in the soil [27]. Increased levels of P addition decreased the Langmuir constants \( q_m \) and \( K_a \), meaning that the presence of phosphate inhibited Mo exchange absorption by the acidic yellow-brown soil, so as to increase the bioavailability of Mo and even for Mo uptake by B. napus [14]. Freundlich isotherm constant \( K_f \) and adsorption intensity \( n \) also decreased with increase in P addition levels. Our results were consistent with the earlier studies of Stout et al. [28] and Karimian and Cox [29] who pointed out that phosphate anions could compete with the absorption sites of soil’s colloid surfaces having molybdate anion or form precipitates with Fe, aluminum (Al), and calcium (Ca) to release molybdate anions from the organic matter and mineral particles in soil, thereby finally enhancing the bioavailability of Mo to plants. Thus, high P addition level could increase Mo availability via decreasing Mo absorption by the acidic yellow-brown soil. The adsorption of Mo in the presence of different amounts of P at the optimal pH (such as over 8.0) of soil is also worth further study.

4 Conclusion

In this article, investigation of the Mo absorption by the acidic yellow-brown soil was carried out at a pH range from 1 to 13. The adsorption of Mo by the acidic yellow-brown soil was a strong function of pH and showed a maximum adsorption in the acidic pH range of 2–4. Thus, pH exceeding 8 could enhance Mo availability via inhibiting the Mo adsorption by the soil. Other Mo absorptions by the acidic yellow-brown soil at different P addition levels were studied. The sorption data fitted into the Langmuir and Freundlich isotherms, of which the Langmuir adsorption model was found to have the higher regression value and hence the well fit. Higher P addition level decreased the Mo absorption amount, the Mo absorption rate, and the values of Langmuir constants \( q_m \) and \( K_a \). It could be concluded that the presence of phosphate (especially 31 mg P L\(^{-1}\)) inhibited Mo absorption by the acidic yellow-brown soil so as to increase the bioavailability of Mo and therefore the uptake by plants. For the first time, these results will provide a new insight into soil Mo adsorption kinetic characteristics to better understand the possible mechanism of the Mo uptake by plants which in turn is enhanced by the interaction of P and Mo in the yellow-brown soil.

Acknowledgments: This work was supported by the National Natural Science Foundation of China (41201286, 41501311, and 41271471), the Basic Research Project of Henan Provincial Department of Education (19zx007), the Young Core Instructor Funding Scheme of Henan Province (2013-045), the Key Project of Science and Technology Research of Henan Province Education Department (12A210015), and Scientific and Technological Key Projects of Henan Province (17210210060).

Table 2: Langmuir and Freundlich isotherm constants for molybdate ion sorption by the acidic yellow-brown soil at three P addition levels

| P levels (mg/L) | Langmuir | Freundlich |
|-----------------|-----------|------------|
|                 | \( q_m \) (mg kg\(^{-1}\)) | \( K_a \) (L mg\(^{-1}\)) | \( K_f \) ((mg kg\(^{-1}\))·(L mg\(^{-1}\))\(^{1/n}\)) | \( n \) |
| 0               | 462.8     | 0.202      | 81.2       | 1.49 |
| 3.1             | 378.9     | 0.191      | 58.4       | 1.30 |
| 31              | 341.7     | 0.087      | 28.2       | 1.26 |
Conflict of interest: The authors declare no conflict of interest.

References

[1] Coughlan MP. Molybdenum and molybdenum-containing enzymes. Pergamon: Elsevier; 2014.
[2] Bittner F. Molybdenum metabolism in plants and crosstalk to iron. Front Plant Sci. 2014;5:28–33.
[3] Reddy KJS, Munn CL, Wang L. Chemistry and mineralogy of molybdenum in soils. In: Gupta UC, editor. Molybdenum in agriculture. New York: Cambridge University Press; 1997.
[4] Liu Z, Zhu QQ, Tang LH, Xu X, Yin CL. Geographical distribution of trace elements-deficient soils in China. Acta Pedologica Sin. 1982;19:209–223, (in Chinese with English abstract).
[5] Hong S, Chen JS, Zhou ZQ, Wang SP, Long Q, Zheng ZH. Environmental geochemical characteristics of some elements in the yellow brown soil of middle and lower reaches of Yangtze river. Sci Geogr Sin. 2000;20:320–325, (in Chinese with English abstract).
[6] Hong S, Zheng ZH, Chen JS. Environmental geochemical characteristics of some microelements in the yellow brown soil of Hubei Province. Acta Pedologica Sin. 2001;38:89–95, (in Chinese with English abstract).
[7] Siebert C, Pett-Ridge JC, Opfergelt S, Guicharnaud RA, Halliday AN, Burton KW. Molybdenum isotope fractionation in soils: influence of redox conditions, organic matter, and atmospheric inputs. Geochim Cosmochim Acta. 2015;162:1–24.
[8] Kaiser BN, Gridley KL, Brady JN, Phillips T, Tyerman SD. The role of molybdenum in agricultural plant production. Ann Bot. 2005;96:745–754.
[9] Savic IM, Savic IM, Stojiljkovic ST, Gajic DG. Modeling and optimization of energy-efficient procedures for removing lead (II) and zinc(II) ions from aqueous solutions using the central composite design. Energy. 2014;77:66–72.
[10] Duval BD, Natali SM, Hungate BA. What constitutes plant-available molybdenum in Sandy acidic soils? Commun Soil Sci Plan. 2015;46:318–326.
[11] Sun W, Selim HM. Molybdenum-phosphate retention and transport in soils. Geoderma. 2017;308:60–68.
[12] Goldberg S. Competitive adsorption of molybdenum in the presence of phosphorus or sulfur on gibbsite. Soil Sci. 2010;175:105–110.
[13] Davis JA. Field experiments. Proceedings Metal Speciation and Transport in Groundwaters. Chelsea, Michigan, Jekyll Island, Georgia: Lewis Publishers; 1989.
[14] Liu HE, Hu CX, Nie ZJ, Sun XC, Tan QL, Huang H. Interaction of molybdenum and phosphorus supply on uptake and translocation of phosphorus and molybdenum by Brassica napus. J Plant Nutr. 2010;33:1751–1760.
[15] Liu HE, Hu CX, Sun XC, Tan QL, Nie ZJ, Hu XM. Interactive effects of molybdenum and phosphorus fertilizers on photosynthetic characteristics of seedlings and grain yield of Brassica napus. Plant Soil. 2010;326:345–353.
[16] Liu HE, Hu CX, Sun XC, Tan QL, Nie ZJ, Su JJ, et al. Interactive effects of molybdenum and phosphorus fertilizers on grain yield and quality of Brassica napus. J Food Agric Environ. 2009;7:266–269.
[17] Zhao MY. Application of graphite furnace atomic absorption spectrometry to determine the molybdenum in solution. Innn Mongolia Sci Technol Econ. 2011;9:97–98, (in Chinese with English abstract).
[18] Vanderborgth BM, Van Grieken RE. Enrichment of trace metals in water by adsorption on activated carbon. Anal Chem. 1977;49:311–316.
[19] Goldberg S. Influence of soil solution salinity on molybdenum adsorption by soils. Soil Sci. 2009;174:9–13.
[20] Goldberg S, Scalera E, Adamo P. Molybdenum adsorption by volcanic Italian soils. Commun Soil Sci Plant. 2008;39:693–706.
[21] Gupta UC. Soil and plant factors affecting molybdenum uptake by plants. In: Gupta UC, editor. Molybdenum in Agriculture. New York: Cambridge University Press; 1997. p. 71–91.
[22] Liu Z. Soil trace element in China. Nanjing: Jiangsu Science and Technology Press; 1997.
[23] Das AK, Chakraborty R, Cervera ML, De la Guardia M. A review on molybdenum determination in solid geological samples. Talanta. 2007;71:987–1000.
[24] Sumner ME. Effect of iron oxides on positive and negative charges in clays and soils. Clay Minerals Bull: Citeseer; 1963. p. 218–226.
[25] Langmuir I. The constitution and fundamental properties of solids and liquids. I Am Chem Soc. 1916;38:2221–2295.
[26] Harter RD, Baker DE. Applications and misapplications of the Langmuir equation to soil adsorption phenomena. Soil Sci Soc Am J. 1977;41:1077–1080.
[27] Han W, Liang CH, Du LY, Liu L, Wu YM, An N. Phosphorus adsorption property onto synthetic iron oxides under different pH conditions. Acta Agri Zhejiangnsis. 2010;42:761–766.
[28] Stout PR, Meagher WR, Pearson GA, Johnson CM. Molybdenum nutrition of crop plants. I. Influence of phosphate and sulfate on absorption of molybdenum from soils and solution culture. Plant Soil. 1951;3:51–87.
[29] Karimian N, Cox F. Adsorption and extractability of molybdenum in relation to some chemical properties of soil. Soil Sci Soc Am J. 1978;42:757–761.