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FACTORS AFFECTING MOLYBDENUM ADSORPTION BY SOILS AND MINERALS

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Molybdenum adsorption behavior was investigated on a variety of crystalline and X-ray amorphous aluminum and iron oxide minerals, clay minerals, and arid-zone soils as a function of solution pH, molybdenum concentration, ionic strength, particle concentration, competing anion concentrations, and temperature. All of these factors influenced the extent of the Mo adsorption reaction. Adsorption on all materials showed pronounced pH dependence in the pH range 3 to 10.5. Maximum adsorption occurred at low pH and then decreased rapidly with increasing pH until adsorption was virtually zero near pH 8. Adsorption as a function of pH was studied at two initial molybdenum concentrations. Adsorption on a percentage basis was greater for the smaller Mo concentration. Adsorption as a function of pH was studied at two particle concentrations. At the larger particle concentration, adsorption reached 100% over most of the pH range. At the smaller particle concentration, 100% adsorption did not occur, allowing better definition of the shape of the adsorption envelopes. The effect of ionic strength was studied in background electrolyte concentrations of 0.01, 0.1, and 1.0 *M* NaCl. On all materials, Mo adsorption was smallest for the largest solution ionic strength. The adsorbents exhibited diverse behavior in ionic strength dependence. Molybdenum adsorption was investigated as a function of temperature at 10, 25, and 40°C and was found to be endothermic, increasing with increasing temperature. In competitive systems containing arsenate or phosphate in concentrations equimolar or twice equimolar to molybdate, Mo adsorption was affected very little by the presence of the competing ion. Molybdenum adsorption on a variety of adsorbents showed dependence on solution Mo concentration and solution pH. Adsorption was affected little by other factors, including particle concentration, solution ionic strength, temperature, and competing ion concentration. These results will facilitate the incorporation of Mo adsorption reactions into chemical speciation and transport codes because only a few factors affecting Mo adsorption will have to be considered. (Soil Science 1997; 163, 109–114)

(Key words: Aluminum oxide, iron oxide, kaolinite, montmorillonite, illite, soils.

MOLYBDENUM is a trace element essential to both plants and animals. Molybdenum deficiencies are reported in many agronomic crops throughout the world (Murphy and Walsh 1972). Molybdate is taken up readily by forage plants and can accumulate to levels detrimental to grazing animals (Reisenauer et al. 1962). Knowledge of Mo adsorption chemistry is necessary to evaluate plant availability in soils.

Molybdenum adsorption reactions have been investigated as a function of various chemical factors, including equilibrium Mo concentration, solution pH, solution ionic strength, competing anion concentration, and temperature. Adsorption isotherms represent Mo adsorption as a function of equilibrium solution Mo concentration. Adsorption isotherms have been determined for

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aluminum and iron oxides (Jones 1957; Reisenauer et al. 1962; Reyes and Jurinak 1967; McKenzie 1983; Ferreiro et al. 1985; Spanos et al. 1990 a and b; Bibak and Borggaard 1994; Spanos and Lycourghiotis 1995), clay minerals (Jones 1957; Theng 1971; Phelan and Mattigod 1984; Motta and Miranda 1989), and soils (Jones 1957; Barrow 1970; Gonzalez et al. 1974; Roy et al. 1986, 1989; Xie and MacKenzie 1991). Adsorption isotherms conform to the Langmuir adsorption isotherm equation (Reyes and Jurinak 1967; Theng 1971; Gonzalez et al. 1974; Karimian and Cox 1978; Phelan and Mattigod 1984; Roy et al. 1986; Bibak and Borggaard 1994), the Freundlich adsorption isotherm equation (Reisenauer et al. 1962; Karimian and Cox 1978; Roy et al. 1986, 1989), and the Temkin adsorption isotherm equation (Xie and MacKenzie 1991).

Adsorption envelopes represent adsorption as a function of solution pH. Adsorption envelopes have been determined for aluminum and iron oxides (Jones 1957; Kyriacou 1967; McKenzie 1983; Ferreiro et al. 1985; Zhang and Sparks 1989; Spanos et al. 1990 a and b; Bibak and Borggaard 1994; Goldberg et al. 1996), clay minerals (Jones 1957; Goldberg et al. 1996), and soils (Jones 1957; Theng 1971; Gonzalez et al. 1974; Mikkonen and Tummavuori 1993; Goldberg et al. 1996). Molybdenum adsorption on all materials increased with increasing solution pH from 2 to 4, exhibited a maximum near pH 4, and decreased with increasing solution pH above 4.

Molybdenum adsorption as a function of solution ionic strength has been investigated on various soils and soil minerals (Zhang and Sparks 1989; Goldberg et al. 1997). The effect of ionic strength on Mo adsorption was slight with most materials, indicating strong, specific adsorption. Molybdenum adsorption has been studied as a function of competing arsenate and phosphate ion concentration (Roy et al. 1986; Xie and MacKenzie 1991) and was found to decrease with increasing competing ion concentration. Molybdenum adsorption has also been investigated as a function of temperature (Reyes and Jurinak 1967; Roy et al. 1989; Spanos et al. 1990b) and found to be endothermic, increasing with increasing temperature.

Particle concentration of the adsorbent is another factor that can influence the extent of metal ion adsorption (Di Toro et al. 1986). Particle concentration effects on Mo adsorption reactions have not yet been investigated.

The objectives of this study were to characterize Mo adsorption on a wide variety of adsorbents, aluminum and iron oxides, clay minerals, and soils, as a function of a variety of factors, including equilibrium solution Mo concentration, solution pH, ionic strength, competing anion concentration, temperature, and particle concentration. All of these factors may potentially affect Mo adsorption and may have to be considered when attempting to predict Mo adsorption reactions under natural conditions using speciation and transport models.

MATERIALS AND METHODS

Molybdenum adsorption behavior was studied on a variety of adsorbents. Aluminium Oxid C (δ-Al_2O_3) was obtained from Degussa and hematite from Fisher Scientific. Amorphous aluminum oxide, goethite, α-FeOOH, and poorly crystalline goethite were synthesized as described by McLaughlin et al. (1981). Amorphous iron oxide was synthesized as described by Sims and Bingham (1968) and gibbsite (γ-$Al(OH)_3$) according to the procedure of Kyle et al. (1975). Reference samples of kaolinite (KGa-1 and KGa-2), montmorillonite (SWy-1, SAz-1, and STx-1), and illite (IMt-1 and IMt-2) were obtained from the Clay Minerals Society's Source Clays Repository. The kaolinites and montmorillonites were used without pretreatment, and the illites were ground to pass a 50-μm sieve. Surface samples of three arid zone soil series, Hesperia (coarse-loamy, mixed, nonacid, thermic Xeric Torriorthent), Pachappa (coarse-loamy, mixed, thermic, Mollic Haploxeralf), and Porterville (fine, montmorillonitic, thermic, Typic Chromoxerert), consisted of the <2 mm fraction. Oxide mineralogy was verified using X-ray diffraction analysis. Trace impurities in the oxides and clay minerals were determined using X-ray diffraction powder mounts. To determine dominant clay mineralogy of the soils, X-ray diffraction peak areas obtained using oriented mounts were converted directly to clay mineral contents (Klages and Hopper 1982). Specific surface areas of the clay minerals and oxides were determined with a single-point BET N_2 adsorption isotherm. Specific surface areas of the soil samples were determined using ethylene glycol monoethylether adsorption (Cihacek and Bremner 1979). Chemical characterizations of the oxides, clay minerals, and soils used in this study were provided in Tables 1 and 2 of Goldberg et al. (1996).

Molybdenum adsorption experiments were carried out in batch systems to determine adsorption isotherms (amount of Mo adsorbed as a function of equilibrium solution Mo concentration) and adsorption envelopes (amount of Mo adsorbed as a function of solution pH per fixed total Mo concentration). Samples of adsorbent were

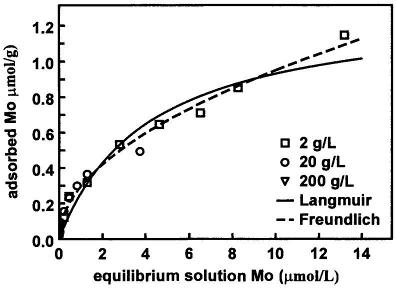

Fig. 1. Molybdenum adsorption on KGa-1 kaolinite as a function of equilibrium solution Mo concentration and particle concentration. Isotherm equation fits are indicated by lines.

mixed with equilibrating solutions for 20 h on a reciprocating shaker (160 strokes per min) for all experiments except the temperature-effect study, in which the samples were mixed for 2 h in a heating and cooling water bath. Reaction temperature was 23 ± 0.5°C for all experiments except the temperature-effect study, in which reaction temperatures were 10, 25, and 40 ± 0.1°C. The background electrolyte of the equilibrating solution was 0.1 *M* NaCl for all experiments except the ionic strength study, in which 0.01 *M*, 0.1 *M*, and 1.0 *M* NaCl solutions were used. For the adsorption isotherms, the equilibrating solutions contained 0.521, 1.04, 2.08, 4.17, 6.25, 8.34, 10.4, and 15.6 mol Mo m^{-3}. For the adsorption envelopes, the equilibrating solutions contained 0.67 mmol Mo m^{-3}, 0.292 mol Mo m^{-3}, or 1.04 mol Mo m^{-3} from $Na_2MoO_4 \cdot 2H_2O$ and were adjusted to the desired pH values using 1 *M* HCl or 1 *M* NaOH additions that changed the total volume by 2% or less. Experimental solution pH values ranged from 3 to 10.5. At least two particle concentrations were investigated for each adsorbent. In one competition experiment, an equimolar competing arsenate concentration was added at 0.67 mmol m^{-3}. Additional competition experiments were carried out in the presence of phosphate at 0.292 or 0.584 mol m^{-3}. After completion of the mixing time, the samples were centrifuged for 20 min at a relative centrifugal force of 7800 × *g* at 25°C. The decantates were analyzed for pH, filtered through 0.45-µm membrane filters, and analyzed for Mo concentration using inductively coupled plasma (ICP) emission spectrometry.

Initial Mo adsorption envelopes were carried out using equilibrating solutions containing 1.04 mol Mo m^{-3}. Subsequent adsorption envelopes were determined using equilibrating solutions containing 0.292 mol Mo m^{-3} to avoid the formation of Mo polymers (Carpéni 1947). For the aluminum and iron oxide minerals, initial adsorption experiments produced 100% adsorption over most of the pH range. Subsequent adsorption envelopes were determined at the smaller particle concentration to avoid 100% adsorption, thus allowing improved definition of Mo adsorption behavior.

RESULTS AND DISCUSSION

The effect of each of the various factors on Mo adsorption will be illustrated for a few representative solid surfaces. Molybdenum adsorption on kaolinite increased with increasing equilibrium solution Mo concentration (Fig. 1). The Mo adsorption data conformed to the Langmuir adsorption isotherm equation ($R^2 = 0.94^{**}$) and the Freundlich adsorption isotherm equation ($R^2 = 0.99^{**}$). The fit of the Freundlich equation was better than that of the Langmuir equation because the experimental isotherm does not indicate an adsorption maximum. Molybdenum adsorption on kaolinite and goethite is dependent on solution pH for the two initial Mo concentrations studies (Fig. 2). Molybdenum adsorption on a percentage basis was greater for the smaller initial Mo concentration. The adsorption envelopes were shifted to the smaller pH value with increasing initial Mo concentration. Thus, the shape of the adsorption envelope was dependent not only on the metal ion but also on the initial metal concentration. Overall similarity in the shape of the adsorption envelopes suggested little effect from the possible formation of Mo polymers in the larger initial starting solution.

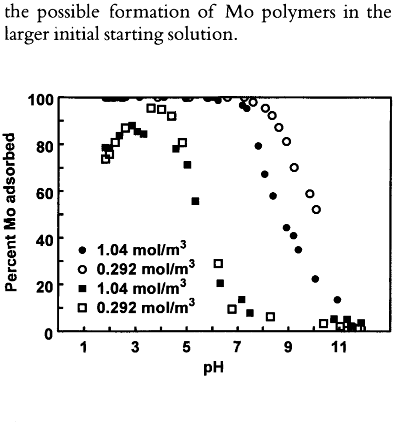

Fig. 2. Molybdenum adsorption on goethite (●, ○) and KGa-1 kaolinite (■, □) as a function of solution pH and initial Mo concentration.

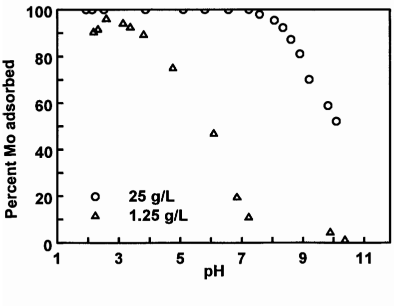

Fig. 3. Molybdenum adsorption on goethite as a function of solution pH and particle concentration.

Molybdenum adsorption as a function of solution pH on goethite is dependent on particle concentration (Fig. 3). Initial experiments carried out at the larger particle concentration produced 100% adsorption over a large portion of the pH range. Adsorption envelopes carried out at the smaller particle concentration did not reach 100% adsorption. Molybdenum adsorption showed pronounced pH dependence, exhibiting a maximum at low pH and decreasing sharply with increasing pH until adsorption was virtually zero above pH 8. It is clear from these results that adsorption envelopes resulting in 100% adsorption can mask large differences in the extent of metal adsorption that become evident at the smaller particle concentration. Historically, the majority of metal adsorption experiments have been carried out to attain 100% adsorption over at least a portion of the pH range (e.g., Hayes and Katz 1996). As evidenced by our data (Fig. 3), experiments leading to 100% adsorption should be avoided because they can confound the evaluation of adsorption affinity.

The effect of particle concentration on Mo adsorption is indicated in Fig. 3 for goethite and Fig. 4 for kaolinite. Figures 3 and 4 show vastly different adsorption envelopes at fixed initial Mo concentration and two different particle concentrations. Such behavior, referred to as the particle concentration effect, has been observed by Di Toro et al. (1986) for cobalt and nickel adsorption. However, because adsorption envelopes present adsorption data as a function of solution pH, the data have not been normalized for equilibrium solution Mo concentration. Molybdenum adsorption as a function of equilibrium solution Mo concentration is unaffected by particle concentration varying by two orders of magnitude (Fig. 1). These data do not show a particle concentration effect for Mo adsorption at constant equilibrium solution Mo concentration. As a result, the effect of particle concentration must be evaluated from adsorption isotherms at constant equilibrium solution metal concentration and cannot be determined from adsorption envelopes.

The effect of solution ionic strength on Mo adsorption as a function of solution pH varied with the adsorbent. For all adsorbents, Mo adsorption was smallest for the largest solution ionic strength. Gibbsite, δ-aluminum oxide, and kaolinite (results for kaolinite presented in Fig. 5a) exhibited ionic strength dependence. The soils showed ionic strength dependence only at the extreme pH values (results for the Porterville soil presented in Fig. 5b). Goethite and montmorillonite showed very little ionic strength dependence (data not shown). The lack of ionic strength dependence has been used as indirect evidence for

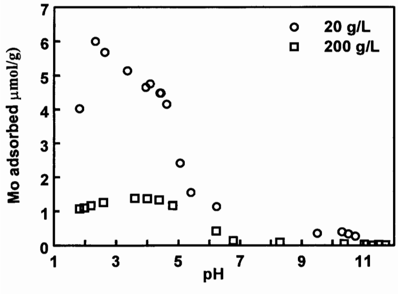

Fig. 4. Molybdenum adsorption on KGa-1 kaolinite as a function of solution pH and particle concentration.

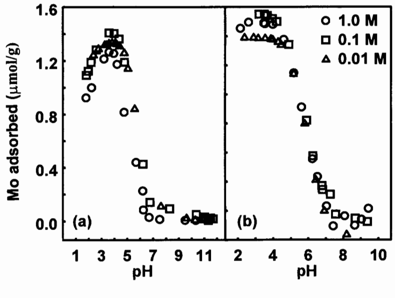

Fig. 5. Molybdenum adsorption as a function of solution pH and ionic strength: (a) KGa-1 kaolinite; (b) Porterville soil.

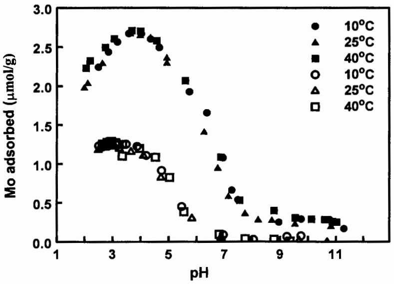

Fig. 6. Molybdenum adsorption on KGa-2 kaolinite (●, ▲, ■) and Pachappa soil (○, △, □) as a function of solution pH and temperature.

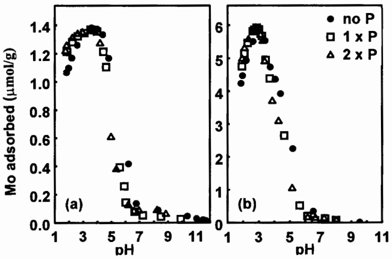

Fig. 8. Molybdenum adsorption as a function of solution pH and presence of equimolar (□) and twice equimolar (△) competing phosphate concentration: (a) KGa-1 kaolinite; (b) STx-1 montmorillonite.

strong, specific ion adsorption. Our results suggest that Mo is adsorbed specifically in arid zone soils.

Changes in temperature had little effect on the extent of Mo adsorption on kaolinite and the Pachappa soil (Fig. 6). Molybdenum adsorption on all materials increased slightly with increasing temperature, indicating an endothermic reaction. This trend has often been seen for specifically adsorbing anions, and it is in agreement with literature findings for Mo (Reyes and Jurinak 1967; Roy et al. 1989; Spanos et al. 1990b).

The effect of equimolar competing arsenate concentration on Mo adsorption by clay minerals was slight (Fig. 7). Molybdate and arsenate were added simultaneously at a concentration of 0.67 mmol m^{-3}. With the exception of kaolinite below pH 4, Mo adsorption was unaffected by an equimolar arsenate concentration. Because the adsorbing anion concentration was very small, there may have been sufficient sites available for both anions, and competition for sites did not occur.

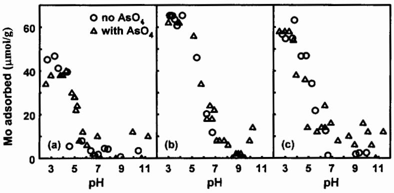

Fig. 7. Molybdenum adsorption as a function of solution pH and presence of equimolar competing arsenate concentration: (a) KGa-1 kaolinite; (b) SWy-1 montmorillonite; (c) IMt-2 illite. Data with arsenate from Fig. 11 in Manning and Goldberg (1996).

Even the competitive effect of the strongly adsorbing phosphate ion on Mo adsorption on clays was slight (Fig. 8). Phosphate and molybdate were added simultaneously at equimolar concentrations of 0.292 mol m^{-3}, a much larger concentration than in the previous experiment. Phosphate was also added at a concentration of 0.584 mol m^{-3}, twice equimolar to molybdate. Molybdenum adsorption was unaffected even in the presence of twice equimolar phosphate concentration. This lack of competition was surprising because molybdate is often adsorbed more weakly than phosphate (e.g., Ryden et al. 1987). These results suggested that adsorbing sites on the clay minerals are heterogenous, with some showing preference for Mo.

CONCLUSIONS

Molybdenum adsorption on a variety of soils and soil minerals showed dependence on solution Mo concentration and solution pH. Molybdenum adsorption on these materials was affected to a small degree by other factors, including particle concentration, solution ionic strength, temperature, and competing ion concentration. For the purpose of describing the reactions and transport of Mo under agricultural conditions, the advantage of our results is that they suggest that Mo adsorption can be described without consideration of changes in these variables. Thus, the incorporation of Mo adsorption reactions into chemical speciation and transport codes will be simplified and facilitated.

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