Adsorption of Molybdate onto Hematite: Kinetics and Equilibrium

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Abstract: - In the present study, the effects of pH, adsorbate/adsorbent ratio, and ionic strength on the adsorption of molybdate [Mo(VI)] onto hematite were investigated. Results showed that the adsorption of Mo(VI) on hematite strongly depended on all the parameters: higher adsorption at lower pH, lower adsorbate/adsorbent ratio, and/or higher ionic strength. It was observed that pH was a very strong factor in immobilization of molybdate onto hematite by adsorption. The adsorption process followed a parabolic diffusion kinetics. The experimental data of isotherms at various pHs on hematite showed a very close match to Freundlich equation.

Key-Words: - Molybdenum, Molybdate, Adsorption, Hematite, Kinetics, Equilibrium, pH, Ionic Strength

1 Introduction
Molybdenum is an essential trace element for plants, animals and microorganisms because of the role in enzymatic redox reactions and its specific geochemical behavior [1]. However, high concentrations of Mo cause adverse effects. Most of Mo consumption is in the production of stainless steel and catalysts.

One of the main factors controlling the distribution of molybdenum in natural environment is sorption on soil and sediment [2-6]. The adsorption of molybdenum on the mineral surface affects its mobility, reactivity, bioavailability and toxicity in soil and water. Investigation of molybdenum adsorption under various conditions is necessary to find the effective treatment of the contaminant in environment.

Adsorption of molybdenum onto soils and minerals has been studied well [2-4]. Goldberg and Forster [5] have reported that the effect of ionic strength on Mo adsorption onto goethite was minor. Also it has been reported that the amount of adsorbed Mo onto soil increased slightly with temperature [4]. Metal oxides including iron and aluminum could be important minerals for Mo adsorption, especially at low pH [6].

In the present study, the adsorption of molybdate onto hematite was investigated in terms of kinetics and equilibrium. The effects of initial concentration of Mo, pH, and ionic strength on the adsorption were characterized.

2 Materials and Methods
Hematite was synthesized using the method of Sugimoto et al. [7]. The stock solution of molybdate [Mo(VI)] (2000 µmol/L as Mo) was prepared by dissolving 0.484g of Na$_2$MoO$_4$·2H$_2$O in deionized water and adjusting the final volume to 1L. Molybdenum solutions for this experiment were prepared by diluting the stock solution.

2.1 Adsorption kinetics
The experiments of adsorption kinetics were conducted for two molybdenum solutions, which have different initial concentrations (0.20 and 0.40 mmol/L as Mo; corresponding to 0.20 and 0.40 mmol/Mo/kghematite$^{-1}$, respectively). Synthesized hematite (0.05g) and each molybdenum solution (50 mL) were placed in thirteen 125 mL Erlenmeyer flasks. Then, total 26 flasks were shaken using a platform shaker (225 rpm, 25±1 °C). One flask of each solution was removed from the shaker after each of the time intervals (5min, 10min, 15min, 20min, 30min, 1h, 1.5h, 2h, 3h, 5h, 10h, 15h and 24h). Then, the pHs of suspended mixture were measured. The final pH was considered as the experimental pH value. After filtering the suspended mixture using a 0.45 µm membrane filter, the molybdenum concentration in the filtrate was determined by an atomic absorption spectrophotometer.
2.2 Adsorption isotherms
Adsorption isotherms on hematite were obtained at different pHs, 2.4, 5.9 and 6.8. At each of the pH conditions, a total of 11 initial molybdate solution concentrations were prepared to obtain the adsorption equilibrium: 0.05, 0.10, 0.20, 0.30, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75 and 2.00 mmol/L. The pH of the suspension was adjusted to attain the desired pH, using HCl or NaOH, before each experiment. The temperature was 25±1°C. Synthesized hematite (0.05g) and each molybdenum solution (50 mL) were placed in a 125 mL Erlenmeyer flask, and the suspension was shaken for 24 hours. The rest of the experiments were conducted using the same experimental method as mentioned previously.

2.3 Effects of pH and ionic strength on the adsorption of molybdenum
The effect of pH on the molybdate adsorption was investigated over a pH range from 1.8 to 11.1 at various ionic strengths. Each set of adsorption suspensions contained constant initial molybdate concentration (0.20 mmol/L as Mo; corresponding to 0.20 mmol$_{Mo}$/kg$_{hematite}$). The ionic strength was adjusted using background electrolyte concentrations of 0.001, 0.01 and 0.1M NaCl. The pH of the molybdenum solution was adjusted using HCl or NaOH. For all experiments, suspensions were shaken on a platform shaker for 24 hours at 25±1°C. The rest of the experiments were conducted using the same experimental method as mentioned previously.

3 Results and Discussion

3.1 Adsorption kinetics
During the kinetic experiments, the pH value of the solution is maintained relatively constant (pH=1.8-2.6). The results of adsorption kinetics are shown in Figure 1. The adsorption of molybdenum on hematite was relatively fast at low pH. For the two initial molybdenum concentrations (0.20 and 0.40 mmol/L as Mo; corresponding to 0.20 and 0.40 mmol$_{Mo}$/kg$_{hematite}$, respectively), the molybdenum adsorption, after 1 hour of reaction, was 90.9 and 65.1% of that after 24 hours, respectively. The adsorption equilibrium was achieved after 10 hours of reaction for all the experimental sets. The rate of adsorption increased sharply for first 1 hour, then reached semi-equilibrium after about 3 hours, and finally reached equilibrium after about 10 hours.

Therefore, all further adsorption procedures were performed for 24 hours, long enough to reach equilibrium. At equilibrium, 29-42% of molybdenum from the initial molybdenum solution was adsorbed on hematite surface: 42 and 29% for initial concentrations of 0.20 and 0.40 mmol$_{Mo}$/kg$_{hematite}$, respectively.

The fitness of the kinetic data obtained in this study to existing kinetic models was graphically examined. The models include first order, second order, simple Elovich, power function, and parabolic diffusion equations. The correlation coefficients (R$^2$) were calculated using a least-square method. The kinetic data of adsorption were very well described by parabolic diffusion equation for all two molybdenum concentrations (R$^2$>0.98).

3.2 Adsorption isotherms
Based on preliminary results of kinetic study, the reaction time of 24 hours was selected to allow adequate equilibration. The results of adsorption isotherms are shown in Figure 2. Isotherms, plotted at constant pH, show that the amount of adsorbed molybdenum increased with the molybdenum concentration of equilibrium solution under all the experimental conditions. The molybdenum adsorption was the highest at the condition of pH 2.4 (low pH).

The experimental data of isotherms under various pHs were graphically examined for the fitness to existing isotherm models, Freundlich and Langmuir equations.
The effect of pH on the adsorption of Mo(VI) was evaluated in the pH range of 1.6-11 at various ionic strengths. The wide pH range was selected to obtain equilibrium solutions with various molybdenum species (H₂MoO₄, HMoO₄⁻ and MoO₄²⁻). The charge of hematite surface would be changed depending on the pH of suspension.

The adsorption of Mo(VI) obtained in the examined pH range is shown in Figure 3. The present results were similar to those observed in previous studies: high (low) adsorption at low (high) pH [2, 8]. For all the experiments, the maximum adsorption occurred at pH<4, and the adsorption decreased with increasing pH. The amounts of molybdate adsorbed on hematite decreased approximately linearly from 187, 102 and 90 mmol Mo₉kg⁻¹ at pH 3.3, to 127, 61 and 8.5 mmol Mo₉kg⁻¹ at pH10-11, for experiments with background electrolyte concentrations of 0.001, 0.01 and 0.1M NaCl, respectively in 0.20 mmol/L (corresponding to 0.20 mol Mo₉kg⁻¹) initial molybdate solution. The lower adsorption of Mo(VI) at higher pH value is attributable to an increased repulsion between the more negatively charged molybdate species and negatively charged surface sites.

Mo(VI) is present in negatively ionic form under most pH conditions of natural water. MoO₄²⁻ is the predominant dissolved species under natural pH condition since molybdic acid (H₂MoO₄) has pKₐ values of 3.61 and 3.89 [9]. The monoprotonated species, HMoO₄⁻ remained minority species [10]. As shown in Figure 3, the broad maximum adsorption appeared in the wide range of pH, i.e. pH 2-4. It is a well-known phenomenon that the maximum in the adsorption of anions occurs at pH values close to their dissociation constants (pKₐ) [11].
of hematite (7.5) [12], at low pH the surface of hematite has a net positive charge that would attract HMoO$_4^-$ and MoO$_4^{2-}$ ions and molybdate is present in anionic form, causing adsorption by electrostatic attraction. As pH increases, however, the portion of positively charged surface sites on hematite decreases, increasing repulsion of anionic molybdenum species, and reducing adsorption. Under the condition, the molybdate adsorption does not occur by electrostatic interaction, but by specific chemical interaction between the negatively charged hematite surface and molybdenum ion [2, 4].

There was difference among the adsorption edges of molybdate measured at different background electrolyte concentrations (Figure 3). Adsorption behavior that is dependent on the variation in ionic strength is a macroscopic evidence for an outer-sphere adsorption mechanism [13].

4 Conclusion
In assessing the mobility of molybdenum in natural environment, not only the form of molybdenum but also its partitioning between the dissolved and solid phases has to be considered. The major conclusion of the study is that molybdate can be adsorbed in much larger amount at low pH, at low adsorbate/adsorbent ratio, and/or at high ionic strength.

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References: