



Research paper

Molybdate adsorption by birnessite

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ABSTRACT

Molybdate (MoO_4^{2-}) adsorption by manganese (Mn) oxide was investigated using a synthetic birnessite. Experiments were carried out in a batch experiment as a function of time (1 min to 28 d), pH (2–10) and the competitive anions sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}). Furthermore, MoO_4^{2-} adsorption was described as a function of equilibrium concentration at pH 4–7 and the data were evaluated with the Freundlich and Langmuir equations. The amount of adsorbed MoO_4^{2-} was strongly dependent on time and reached roughly an equilibrium after three days. An increase in the pH by 1.15 units within 28 days indicates ligand exchange of surface hydroxyls with MoO_4^{2-} . Molybdate adsorption showed high sensitivity to pH and reached a maximum at pH 3, near the pK_{a1} and pK_{a2} for molybdic acid. The Freundlich equation adequately reconstructed the adsorption data. Molybdate adsorption also conformed to the Langmuir equation for the investigated pH values. The competition sequence of anions for MoO_4^{2-} adsorption by Mn oxide was $\text{SeO}_3^{2-} > \text{SeO}_4^{2-} > \text{PO}_4^{3-} > \text{SO}_4^{2-}$, assuming a strong adsorption mechanism of MoO_4^{2-} onto the surface of birnessite. These results indicate that Mn oxides have a strong effect on the adsorption of MoO_4^{2-} especially due to their higher specific surface area compared to aluminium or iron oxides. This is important regarding the availability of MoO_4^{2-} in soils under agricultural conditions (pH 4–7) as well as for the treatment of soils and groundwater affected by elevated intake from industries.

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1. Introduction

Molybdenum (Mo) is an essential trace element for plants, animals and humans (Gupta, 1997). Whereas most plants and humans are insensitive to high Mo concentrations, ruminants develop molybdenosis, which is a Mo-induced copper deficiency (Underwood, 1976). Kubota et al. (1967) suggested that the consumption of forage containing 10–20 mg kg^{-1} Mo by grazing animals leads to this disease. However, the National Research Council (1984) indicates a level of 6 mg kg^{-1} Mo for cows. Although toxic effects do not occur in humans, WHO (2011) determined a health-based reference value of 70 $\mu\text{g L}^{-1}$ Mo for drinking water.

Molybdenum in soil solution predominantly exists in the hexavalent oxidation state as molybdate (MoO_4^{2-}) over a broad pH region (Xu et al., 2013). Referring to speciation diagrams, HMoO_4^- and H_2MoO_4^0 can also occur in solution in the pH range of 3–5, but MoO_4^{2-} is the dominant Mo species in solution with pH > 4.24 (Lindsay, 1979). For simplicity, we summarize all aqueous Mo species as MoO_4^{2-} in the following.

The behaviour and mobility of MoO_4^{2-} in soils are influenced by sorption onto soil components such as clay minerals and organic matter as well as iron (Fe), aluminium (Al) and manganese (Mn) oxides. During the reductive dissolution of Mn oxides in a floodplain soil, there

was an increase in dissolved MoO_4^{2-} , which underlines the importance of these oxides for sequestering MoO_4^{2-} (Hindersmann and Mansfeldt, 2014). Molybdate adsorption on Fe and Al oxides has been sufficiently studied, but there are only a few studies of MoO_4^{2-} adsorption onto Mn oxides (Xu et al., 2013), since the amount of Mn oxides in soil is minor compared to other oxides. Zhao et al. (2010) investigated MoO_4^{2-} adsorption by hausmannite (Mn_3O_4) at different pH values. The data could be fitted with the Freundlich equation and the adsorption of MoO_4^{2-} on Mn_3O_4 was a multilayer adsorption. McKenzie (1983) investigated MoO_4^{2-} adsorption by birnessite in dependence on pH. In two further studies by Chan and Riley (1966) and Barling and Anbar (2004), MoO_4^{2-} adsorption by Mn oxides was also observed. Being a ubiquitous soil component, it is important to estimate the effect of Mn oxides on MoO_4^{2-} immobilization. Birnessite in particular plays an important role in geochemical cycles and is one of the most common Mn oxides in soils (Taylor et al., 1964). Manganese oxides are much more efficient in adsorbing some metals compared to Fe and Al oxides, especially due to their large specific surface area (SSA) and low point of zero charge (pH_{PZC}), which results in a high negative surface charge observed in the pH range of interest in soils (Komárek et al., 2013). Therefore, cation adsorption by Mn oxides has been extensively investigated (Feng et al., 2007). On the other hand, there are only a few studies of anion adsorption by Mn oxides, because adsorption is not expected due to the low pH_{PZC} . Balistrieri and Chao (1990) and Saeki et al. (1995) reported a high affinity of selenite (SeO_3^{2-}) for accumulation onto the surface of Mn oxides. Moreover, a study by Villalobos et al.

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(2014) showed arsenate (AsO_3^{3-}) adsorption on synthetic birnessite. Manganese oxides could therefore also be an important scavenger for MoO_4^{2-} and other trace metals in soils. Thus, the aim of the present study was to investigate the mechanism and characteristics of MoO_4^{2-} adsorption by birnessite. Therefore, (i) the time-dependent adsorption of MoO_4^{2-} by birnessite, (ii) the MoO_4^{2-} adsorption by birnessite as a function of pH and (iii) the influence of the competing anions sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), selenate (SeO_4^{2-}) and SeO_3^{2-} on MoO_4^{2-} adsorption by birnessite were investigated and (iv) the adsorption parameters derived from Freundlich and Langmuir isotherms were determined.

2. Materials and methods

2.1. Synthesis and characterization of birnessite

Birnessite was prepared according to Händel et al. (2013)'s method using 1 mL of sodium lactate ($\text{NaC}_3\text{H}_5\text{O}$, 50%) and 100 mL of a 63.3 mM potassium permanganate (KMnO_4) solution.

An X-ray powder diffraction pattern of birnessite was recorded using X-ray diffraction (XRD, X'Pert PRO MPD theta–theta, PANalytical) with cobalt $K\alpha$ radiation generated at 40 kV and 40 mA. The device was equipped with primary and secondary Soller slits, a secondary monochromator, a proportional counter and a sample changer (the sample diameter was 28 mm). The samples were investigated from 1 to $75^\circ 2\theta$ with a step size of 0.02° and a measuring time of 10 s per step. For sample preparation, the back-loading technique was used.

For measuring mid (MIR) and far (FIR) infrared spectra of birnessite, the potassium bromide (KBr) pellet technique (1 mg sample/200 mg KBr) was applied. Spectra were collected on a Thermo Nicolet Nexus FTIR spectrometer (MIR beam splitter: KBr, detector DTGS TEC; FIR beam splitter: solid substrate, detector DTGS PE). The resolution was adjusted to 2 cm^{-1} .

The pH of birnessite was measured potentiometrically using an ion-sensitive glass electrode (Aquatrode Plus, Metrohm) in 0.01 M CaCl_2 extract as well as in deionized water with 1/5 and 1/2500 w/v ratios. The pH_{PZC} was determined by the powder addition technique according to Mustafa et al. (2002). Therefore, 20 mL of 0.1 M sodium nitrate (NaNO_3) solution was added in different centrifuge tubes and the pH of the solutions was adjusted to 2–11 using nitric acid (HNO_3 , different concentrations) and sodium hydroxide solution (NaOH , different concentrations). After that, 0.1 g of the Mn oxide was added to each tube, the sample was shaken for 24 h, and the final pH of the solution was measured. The pH_{PZC} was detected at the point where the initial pH was equal to the final pH. The cation exchange capacity (CEC) was determined according to DIN EN ISO 23470 (2007). To determine the CEC value of birnessite 100 mg of birnessite was placed in a 50 mL polyethylene centrifuge tube and mixed for 1 h with 20 mL of a 0.0166 M cobalt hexamine trichloride $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ solution. After centrifugation and filtration through a $0.2\ \mu\text{m}$ cellulose acetate membrane filter, $\text{Co}(\text{NH}_3)_6^{3+}$ was measured spectrophotometrically at 470 nm using a UV/Vis spectrophotometer (Lambda 25, Perkin Elmer). The concentration of exchangeable Mn was analysed by flame atomic absorption spectrometry (AAS, iCE 3500, Thermo Scientific) with an air-acetylene flame at 279.5 nm. The SSA was calculated according to the Brunauer–Emmett–Teller (BET) method based on five-point nitrogen adsorption measurements using a Micromeritics VII 2390 surface analyser and a sample mass of 300 mg (DIN ISO 9277, 2010). Before measurement, the sample was preconditioned by heating at 105°C under vacuum for 12 h.

2.2. Adsorption experiments

2.2.1. Kinetics

The kinetics of MoO_4^{2-} adsorption was studied using the batch method. Samples of birnessite of 10 ± 0.05 mg were weighed out in

duplicate with a microbalance (XP6, Mettler Toledo) and placed into a 50 mL polyethylene centrifuge tube. This small mass was chosen to avoid complete adsorption, thus allowing improved interpretation of MoO_4^{2-} adsorption behaviour. Twenty-five millilitres of a solution containing 0.3 mM Mo ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) with a background electrolyte of 0.1 M sodium chloride (NaCl) was added and shaken at 20°C in a horizontal shaker (3005, GFL Gesellschaft für Labortechnik) at 200 oscillations per minute. This maximal Mo concentration was chosen to avoid the formation of Mo polymers (Carpéni, 1947). After 1, 5, 15, 60, 120, 180, 360, 720 and 1080 min and 1, 2, 3, 7, 14, 21 and 28 d, the samples were taken, subsequently centrifuged and filtered through a $0.2\ \mu\text{m}$ cellulose acetate membrane filter. The Mo concentration of the solution was determined by inductively coupled plasma mass spectrometry (ICP-MS, X-Series II, Thermo Scientific) and analysed for pH. Furthermore, the Mn concentration was measured by ICP-MS to monitor the amount of Mn released into the solution during shaking.

2.2.2. Effect of pH

Adsorption experiments at pH values of 2–10 were performed using 3 d as the equilibrium time (as determined from the kinetic study). Therefore, 20 mL of 0.1 M NaCl solution was added to 10 mg of the birnessite, whereupon HCl or NaOH was added (at different concentrations) to adjust the solution pH, which took several hours. After pH adjustment, 1 mL of a 7.5 mM Mo solution ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) was added and then a 0.1 M NaCl solution was added to make up a total volume of 25 mL (both solutions were also adjusted to the desired pH). The samples were analysed for Mo and Mn as described before.

2.2.3. Adsorption isotherms

For the adsorption experiments at pH 4–7, the same procedure as mentioned before was used, but the initial Mo concentrations ranged from 0.001 to 50 mmol L^{-1} for the Freundlich and the Langmuir isotherms. Altogether nine different initial Mo concentrations were investigated. We evaluated the adsorption experiments by fitting the Freundlich Eq. (1) and the Langmuir Eq. (2) according to Essington (2004) to the adsorption data using Origin 8.5 (OriginLab),

$$a_{eq} = K_F \cdot c_{eq}^n \quad (1)$$

$$a_{eq} = S_{max} \cdot K_L \cdot c_{eq} / (1 + K_L \cdot c_{eq}) \quad (2)$$

where a_{eq} is the adsorbed amount of MoO_4^{2-} (mmol kg^{-1}), K_F is the Freundlich constant ($\text{mmol}^{1-n} \text{kg}^{-1} \text{L}^n$), c_{eq} is the equilibrium concentration of Mo (mmol L^{-1}), n is the Freundlich exponent, S_{max} is a fitting parameter for the maximum amount of adsorbed MoO_4^{2-} (mmol kg^{-1}) and K_L the Langmuir constant (L kg^{-1}).

2.2.4. Competitive anions

The influence of competitive anions on MoO_4^{2-} adsorption by birnessite was investigated as described above, but an amount of 20 mg was chosen to consider the higher concentrations of adsorptives. The pH was adjusted to 6. The competing anions used were SO_4^{2-} , PO_4^{3-} , SeO_4^{2-} and SeO_3^{2-} . The molar ratios (anion/ MoO_4^{2-}) were 0.1, 1, 10, 100 and 1000 for all competing anions and furthermore 0.18 for SeO_3^{2-} and SeO_4^{2-} , 120 for SO_4^{2-} and 140 for PO_4^{3-} , considering the ratios of the anions in nature.

3. Results and discussion

3.1. Structural and chemical characterization of birnessite

The X-ray diffraction random powder pattern of birnessite (Fig. 1) showed typical broad basal plane diffraction peaks at around 7.4 and $3.6\ \text{Å}$ (Co radiation) as well as the non-basal plane diffraction peak at around $2.4\ \text{Å}$ indicating turbostratic disorder (Manceau et al., 2013).

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