HAL
archives-ouvertes.fr

Adsorption of copper, cadmium, lead and zinc onto a synthetic manganese oxide

Loïc Della Puppa, François Bordas, Michael Komárek, Jean-Claude Bollinger, Emmanuel Joussein

▶ To cite this version:

HAL Id: hal-00922675

https://hal-unilim.archives-ouvertes.fr/hal-00922675

Submitted on 29 Dec 2013

Adsorption of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} onto a synthetic Mn oxide

Loïc Della Puppa[a,b] , Michael Komárek[a,*] , François Bordas[b], Jean-Claude Bollinger[b] ,

Emmanuel Joussein[b]

[a] *Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, Prague 6 - Suchdol, 165 21, Czech Republic*

[b] *Groupement de Recherche Eau Sol Environnement, Université de Limoges, Faculté des Sciences, 123 Avenue Albert Thomas, 87060 Limoges, France*

* Corresponding author:

e-mail: komarek@fzp.czu.cz - Phone: +420 224 383 857 - Fax: +420 234 383 778

Abstract

Due to its simple and inexpensive synthesis, a new amorphous hydrous manganese oxide (AMO) has been studied as a possible chemical stabilizing agent for soils contaminated with metals. Preliminary experiments evaluating the stability of AMO in pure water have reported only minor dissolution (5.70 % and 0.24 % depending on the w/v ratio). Sorption kinetics have shown fast metal adsorption, especially for Pb. The sorption capacities of AMO for Cu, Cd, Pb and Zn have been described and compared with synthetic birnessite for pH 4 and 5.5. Both oxides show similar sorption capacities at pH 4 despite the fact that birnessite characteristics (pH of zero point charge, specific surface area and cation exchange capacity) are more favorable for metal sorption. Moreover, the pH adsorption-edges show that the AMO is more pH-dependent than birnessite.

Keywords

Manganese oxide, Sorption, Divalent metal cations, Birnessite

Highlights

►A new amorphous hydrous manganese oxide (AMO) has been studied ►Easy and cheap to synthesize ►Sorption capacities of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} equal to that of birnessite ►A possible chemical stabilizing agent for soils contaminated with metals.

1.   Introduction

The behavior and mobility of metals/metalloids in soils are significantly influenced by their sorption onto soil organic matter, clay minerals and secondary Fe and Mn (oxy)hydroxides (hereafter referred to as oxides). The main immobilization processes include adsorption and surface precipitation, and the parameters affecting these processes are mainly soil pH, soil composition and speciation of metals/metalloids [1].

Based on these assumptions, several methods for soil remediation (when contaminated with metals) have been studied, by the use of various amendments, e.g. zerovalent Fe, compost, phosphate, lime, clay minerals and a combined chemical method with phytoremediation [2]. These methods are all based on the reduction of metal/metalloid mobility through adsorption, complexation and (co)precipitation processes [3]. Chemical stabilization using oxides represents another important stabilization practice. The application of zerovalent iron as a precursor of Fe oxides has been successfully studied for metal immobilization [4-6]. Despite their high immobilization potential, Mn oxides have been examined to a much lesser extent for chemical stabilization than Fe oxides [3, 7].

Being ubiquitous soil components, Mn oxides could offer a major sink source for metal immobilization [7-9]; they typically occur as coatings and fine-grained aggregates and moreover can efficiently control the evolution and mobility of metals even at low concentrations in soils [10-12]. Except for As and Cr [3, 13-15], the use of synthetic Mn oxides has not been extensively assessed with regard to metal stabilization in contaminated soils despite such favorable and strong sorption characteristics [7]. Manganese oxides could therefore become a valuable alternative in chemical stabilization [15, 16]. The aim of the present study is to evaluate the sorption properties of a new synthetic amorphous hydrous

manganese oxide (AMO) prepared according to a protocol modified from that developed by

Ching *et al.* [17], which is commonly applied for the preparation of birnessite.

2.   Materials and methods

The solutions of metal elements introduced into sorption experiments were prepared using hydrated $CuNO_3$, $CdNO_3$, $ZnNO_3$ and $PbNO_3$ salts. A 0.01 M $NaNO_3$ solution served as the background electrolyte to set the ionic strength of the experimental solution. Deionized water from the Sci-aqua water system (with a conductivity of less than 0.14 µS/cm) was part of all solution preparations. All chemicals used were of analytical grade.

2.1   Synthesis of the manganese oxides

The amorphous manganese oxide (AMO) was prepared according to a modified sol-gel procedure [17] (advised for the preparation of birnessite), consisting of adding 0.5 L of a 1.4 M glucose solution to 0.5 L of a 0.4 M $KMnO_4$ solution. After gel formation, the solution was filtered and washed with 2 L of pure water in order to remove the excess of reactants. The gel was subsequently dried at room temperature. The protocol modification omitted the heating step (at 400°C) after gel drying. Pure birnessite was prepared according to the McKenzie [18] protocol, which consists of adding dropwise 1 L of a 1 M HCl solution to 1.25 L of a 0.5 M boiling $KMnO_4$ solution. The solution was then left to cool at room temperature, filtered and washed with pure water.

2.2   Characterization of the manganese oxides

X-ray diffraction (XRD) patterns were obtained using a Brucker-AXS D 5005 powder diffractometer featuring CuKα radiation (λKα = 0.154186 nm) and a graphite back monochromator. These patterns were derived under the following conditions: a dwell time of 2 s, and a 0.04° (2θ) step. FTIR spectra were generated from a ThermoFischer Scientific 380 infrared spectrometer (Nicolet) by implementing the attenuated total reflection (ATR) method. IR spectra were collected between 500 and 4,000 cm^{-1}, with a resolution of 4 cm^{-1}. The commercially available software OMNIC (Nicolet Instruments) was run for the data

acquisition and spectral analysis. Oxide morphology was investigated using scanning electron microscopy (SEM, Philips XL 30, 20 kV, SERMIEL - Université de Limoges, France) coupled with an EDS apparatus; over 50 SEM-EDS analyses were performed for each sample studied. The BET surface was determined at 105°C with the Quantachrome Instruments Nova® e-Series equipment.

The pH of the synthesized oxides was measured using either a 1/2.5 w/v ratio with deionized water or a 1 M KCl (ISO 10390) in conjunction with a Crimson micro pH 2000 pH-meter equipped with a combined electrode (reference Ag/AgCl) calibrated with two buffers (pH 4.01 and 7.00 at 25°C). The acidity constant and pH_{ZPC} (Zero Point Charge) were determined by acid-base titration according to Davranche *et al.* [19]. The zeta potential was calculated using Alphaphot-2 NIKON with the software ZetaPhoremeter II and a w/v ratio of 1/500. The cation exchange capacity (CEC) was measured by employing the cobalt hexammine trichloride method (NF EN ISO 23470). These samples were mixed for 3 hours with a 0.016 M cobalt hexammine trichloride solution at a w/v ratio of 1/5 and filtered on 0.2-μm cellulose nitrate filter (VWR). The excess $Co(NH_3)_6^{3+}$ was analyzed with a UV-visible spectrophotometer (Shimadzu UV-160) at 470 nm.

The average oxidation state of Mn was determined by applying the method described in Murray *et al.* [20]. 100 mg of solid was suspended in 50 mL of water; then, 10 mL of NaI solution (90 g in 150 mL) were added followed by 3 mL of 2 M H_2SO_4. The solution was stirred until achieving complete dissolution of the solid and titrated with a 0.18 M $Na_2S_2O_4$ solution. Each characterization was performed in triplicate.

2.3 AMO stability in pure water

The stability of this AMO was evaluated in a preliminary experiment that consisted of monitoring both the pH and amounts of Mn and K released into the solution during stirring in pure water at two different w/v ratios (1/500 and 1/10).

Oxygen consumption was measured for 11 days in the Oxytop® (WTW) system in order to observe the influence of AMO on microorganism respiration at a 1/500 w/v ratio and 22°C.

2.4 Kinetics of metal sorption onto AMO and birnessite

Kinetic batch experiments were performed at two different pH values (4.0 and 5.5) and at a 1/500 w/v ratio. The pH was manually set using 0.1 M HNO_3 and 0.1 M NaOH solutions. The initial metal concentration was fixed at 1 mM. After stirring (200 rpm on a KS501 digital, IKA Labortechnik), samples were filtered using a 0.2-μm cellulose acetate filter (VWR); moreover, the concentrations of studied metal elements (Cu, Cd, Zn, Pb) remaining in solution were analyzed by means of ICP-OES (Agilent Technologies 720 Series). The difference between initial and final values provided the metal element amounts adsorbed per gram of adsorbent. Each experiment was conducted in triplicate (the values shown represent the average and standard deviation).

Two distinct kinetic models were introduced for data interpretation: i) a pseudo-first order, and ii) a pseudo-second order [21]. Modeling results indicated that only the pseudo-second order kinetic model actually fit the data:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$$

where k_2 is the pseudo-second-order rate constant (g.mmol^{-1}.min^{-1}), q_e (mmol.g^{-1}) the amount adsorbed at equilibrium, and q_t (mmol.g^{-1}) the amount adsorbed at time t. When t = 0 and q_t = 0 (initial conditions), the equation becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

The adsorption rate constant k_2 can be obtained from the slope of the linear plot of t/q_t = f(t).

2.5   *Sorption isotherms and adsorption edges*

Sorption experiments (with Cu, Cd, Zn, Pb) were performed using 24 h as the equilibrium time (as determined from the kinetic study) at a w/v ratio of 1/500 in HD-PE bottles. For sorption isotherms, these experiments were conducted at two pH values (4.0 and 5.5). Each metal element was studied both individually and simultaneously in order to evaluate possible competition effects. The pH was manually set using 0.1 M HNO$_3$ and 0.1 M NaOH solutions. After stirring (200 rpm), samples were filtered (with a 0.2-µm cellulose acetate filter) and the concentrations of Cu, Cd, Zn, Pb and Mn remaining in solution were analyzed. The difference between initial and final values yielded the amount of metal elements adsorbed per gram of adsorbent. Each experiment was conducted in triplicate, with the values shown representing the average and standard deviation.

According to pH and metal concentration values, the potential risks of metal precipitation were predicted by speciation modeling using the MINEQL+4.6 software [22]. Sorption isotherms could therefore be constructed according to two distinct approaches: i) classical isotherms, where the total amount of metals was added at the start of the experiment; and ii) multiple addition sorption isotherms, where a solute concentration of 1 mM was

initially introduced and another 1 mM (1 mL of a 50 mM solution) was subsequently added every day in order to limit precipitation risks at higher metal concentrations. Each step lasted 24 h (i.e. the equilibrium time as determined from the kinetic study). The data were fitted to the Langmuir isotherm as follows:

$$S = \frac{S_{max} * K * [M^{2+}]}{1 + K * [M^{2+}]}$$

where S_{max} denotes the maximum sorption capacities (mmol.g^{-1}), K the Langmuir constant (L.mmol^{-1}), and $[M^{2+}]$ the concentration of metal elements in solution (mmol.L^{-1}). The Langmuir sorption isotherm parameters were obtained from the Bolster and Hornberger spreadsheets [23] using nonlinear fitting models based on the least sum of squared errors.

Adsorption edge studies were conducted with metal concentrations fixed at 1 mM, and the pH was manually set to vary from 4.0 to 7.5 in the presence of 0.1 M HNO$_3$ and 0.1 M NaOH solutions. The samples were then filtered (using 0.2-μm cellulose acetate) and the filtrate was analyzed to determine the remaining metal concentration in solution. Each experiment was conducted in triplicate; the given values represent the average and standard deviation.

## 3.	Results and discussion

*3.1	Characterization of the solids*

SEM images of the amorphous manganese oxide (AMO) are presented in Figure 1 at two different scales. Figure 1a shows that particles are agglomerates several micrometers in size and display conchoidal fractures. The presence of a film covering the surface is characteristic of a solid originating from a sol-gel procedure (Fig. 1b) and does not reflect any defined morphology that would indicate the amorphous nature of the solid. When using chloroethylene instead of glucose, the Mn oxide exhibits a cluster of small needle-shaped crystals [24], thus underscoring the impact of the organic compound type. The measured particle size distribution follows a Gaussian curve (600-1,200 nm), with a maximum at 1,000 nm.

Figure 2a shows the XRD spectra of both the AMO and birnessite. Despite a well-defined yet low-intensity peak, i.e. matching the pattern of birnessite, the XRD spectra reveal that the synthesized Mn oxide is amorphous. When chloroethylene is selected as the organic compound for manganese oxide synthesis, the characteristic peaks of crystallized manganese oxide are present [24]. This result highlights the critical role of the organic compound used for the synthesis. The prepared birnessite is a single-phase mineral, as indicated by three peaks at 3.68, 2.43 and 1.42 Å in its XRD pattern (XRD JCPDS file 23-1239), which prove to be characteristic for this mineral phase [17, 25].

The AMO IR spectra (Fig. 2b) displays bands at around 1,100 cm^{-1}, 2,900 and 3,000-3,600 cm^{-1}, which might possibly correspond to glucose bands (νC-O, νC-Hn and -O-H) originating from the glucose residue present even after washing (correlated with the organic carbon content, 17.0 mg of C/g). The band around 3,000-3,600 cm^{-1} might also correspond to the stretching vibrations of both the O-H group of water molecules and the lattice O-H groups

[26]. The band between 400 and 800 cm^{-1} can be attributed to the Mn-O lattice vibrations, while position and/or intensity changes can be associated with changes in the octahedral layered substructure [27-29]. The band around 1,600 cm^{-1} is typically attributed to O-H bending vibrations combined with Mn atoms [25]. When heating the AMO to 140°C, a peak appears around 600 cm^{-1}, corresponding to the birnessite structure [28-30]. After heating, the AMO structure changes and shows a better fit with the birnessite spectra, meaning that AMO becomes unstable as temperature increases. At 140°C, the band around 1,000 cm^{-1} disappears, which could be due to glucose degradation. The AMO can be considered as a protophase of birnessite during the sol-gel synthesis.

3.2   Chemical properties of the solids

Table 1 summarizes the main physicochemical characteristics of the AMO and birnessite. The difference between pH_{H2O} and pH_{KCl} values of birnessite indicates the presence of H^+ sorbed on the surface, which is not the case for AMO. Surface acidity constants pKa_1 and pKa_2 are acidic for birnessite, while those of the AMO are basic. At pH 4.0 and 5.5 (i.e. the conditions of the sorption experiments), the birnessite surface is therefore theoretically negatively charged, as opposed to the AMO surface, which is theoretically positively charged. The pH_{ZPC} value of the AMO is basic (8.3), in contrast with other Mn oxides prepared from the oxidation, for example, of trichloroethylene (pH 3.7) [24]. This value has been confirmed by a fast method that consists of measuring the pH value of oxide suspension (1/100 w/v ratio) in a 0.01 M $NaNO_3$ solution, which lies near the pH_{ZPC} value [31]. For AMO, the measured pH under this condition equals 8.20 (3.14 for birnessite). This value is similar to that obtained by following the Davranche *et al.* protocol [19]. The results derived with birnessite synthesized using concentrated HCl and hot $KMnO_4$ solutions are in good agreement with values found in the literature [32]; however, this value is protocol-dependent [33]. The pH_{ZPC} values found here suggest more favorable adsorption for cations

onto birnessite than onto AMO, due to the negative surface charge on birnessite at pH 4 and 5.5.

The CEC value of birnessite (247 meq/100 g) is greater than that of the AMO (34 meq/100 g) and in good agreement with the value observed by Golden *et al.* [34]. Moreover, the specific surface area of birnessite is greater than that of the AMO (Table 1); however, the various BET values listed in the literature (32.6 m²/g [35], 34.2 m²/g [26], 19.3 m²/g [36]) can be explained by the fact that BET analyses are strongly temperature-dependent. Using trichloroethylene instead of glucose, Li and Schwartz [24] found a specific surface area of 23.6 m²/g, which is closer to the AMO value (14.8).

All of the measured parameters seemed to be predicting better sorption properties for birnessite: higher CEC and BET, and a theoretically negatively charged surface due to its pH_{ZPC} value and the pH value set during the adsorption experiments. The average Mn oxidation state (AOS) in the AMO is about 2.52, which indicates that one Mn atom can be linked to 1.26 O atoms. Moreover, after 24 h of stirring in pure water at a w/v ratio of 1/500, this AOS value rises from 2.52 to 3.04, thus reflecting an increasing average Mn oxidation state. This outcome could be due to the release of weakly bound Mn from the AMO surface with an AOS greater than 3.04, originating from a residual fraction of the $KMnO_4$ reactant.

3.4   Stability of the AMO in pure water

The w/v ratio of 1/500 reveals, to some extent, the AMO behavior just before natural dispersion into the soil (migration, transport by pore water), whereas the 1/10 ratio simulates the behavior before dispersion, when the solid is locally located. For both ratios, the pH is close to 7 and remains stable over time (Fig. 3). The AMO appears to be stable for both the 1/500 and 1/10 w/v ratios after 200 h of stirring in pure water. Two dissolution steps (Fig. 3a) are observable for the 1/500 w/v ratio; the first step is reached after 20 h of stirring and might

correspond to the release of weakly adsorbed Mn. The second step is reached after 200 h and might correspond to dissolution of the AMO (with Mn released into the solution accounting for 5.7 % of total AMO content). For the 1/10 ratio, the AMO seems to be more stable, with less dissolution due to displacement of the dissolution balance within the solution. Another Mn dissolution step is observable (Fig. 3b) near 10 h, probably due to dissolution and/or release of the weakly bound Mn (an amount representing 0.24% of the solid). Regardless of the w/v ratio, the AMO seems to be stable in water. The potassium in solution was stable throughout the experiment and might have originated from the weakly bound fraction at the oxide surface and/or, to some extent, AMO dissolution. The fact that Ching *et al.* [17] found no potassium inside the birnessite structure synthesized by the sol-gel method however means that the potassium most likely originated from both the weakly bound fraction at the oxide surface and the residue of $KMnO_4$ used during the AMO synthesis.

The effect of the presence of AMO and birnessite on microbial respiration was monitored through O_2 consumption measurements. In the presence of birnessite, low O_2 consumption was observed (S. 1). On the other hand, the AMO increased the level of O_2 consumption, especially after 25 h, which corresponds to the activation of natural microbial flora. This result demonstrates that the AMO may exert no significant toxic effect on microbial flora. The time necessary to activate microbial flora corresponds to the start of the 2nd step observed during Mn solubilization, a determination that could be explained by the fact that the degradation of residual glucose (used in AMO synthesis) enhances microbial activity, thus improving either AMO dissolution or the release of Mn weakly bound to the solid. The organic carbon content in AMO lies near 17.0 mg of C/g, which confirms the presence of an organic glucose residue.

3.4   Sorption kinetics

The adsorption of metals on both solids occurs during the first few minutes (S. 2), with Pb being the most quickly adsorbed. During subsequent experiments, a time of 24 h was set as the optimal contact time on the basis of these results and for practical reasons. In the case of birnessite, the sorption of metal elements is not modified by the pH value over the studied range, which can be explained by: the high cationic exchange capacity, high specific surface area, and low pH_{ZPC} value (2.7) of birnessite. Sorption on the AMO is more acutely affected by pH value (i.e. better at pH 5.5 than at pH 4.0) due to its lower CEC, specific surface area and pH_{ZPC} (8.3). The adsorption of metal elements increases the pH_{ZPC} values (data not shown herein), thus indicating that specific adsorption occurs on both oxides [4]. Manganese oxides do in fact adsorb metals primarily in the form of specific adsorption [37, 38].

Pseudo-first and pseudo-second order kinetic models have been applied to the experimental data, whose fit shows that the pseudo-second order is more suitable. The parameters calculated using linear regression are listed in Table 2. The pseudo-second order rate constant (k_2) represents the affinity of the metal element for the solid. When comparing the affinity of these metal elements for AMO and birnessite, it appears that they present a greater affinity for birnessite regardless of pH (especially in the case of Pb). This greater affinity of metal elements for birnessite can be partially explained by the pH_{ZPC} and BET values, hence resulting in a higher specific surface area and a negatively charged surface under the given experimental conditions, which favor adsorption.

3.5   Adsorption isotherms

3.5.1   Standard isotherms

As expected, Figure 4 and Table 3 show that the sorption capacities of Cu, Cd, Zn and Pb increase with pH. For the metal elements studied herein, the sorption capacity (S_{max}) of

AMO at pH 4.0 respects the following order: Pb > Cu > Zn > Cd, and at pH 5.5: Pb > Cu > Cd > Zn. For birnessite, at pH 4: Pb > Cu > Zn > Cd, and at pH 5.5: Pb > Cu ≈ Cd > Zn. Similar results have been observed by other authors [39, 40]. Lead is strongly adsorbed on both oxides. It has been shown that Pb is capable of occupying both the interlayer and surface edge sites [10, 40]. When the metal elements are considered individually, birnessite is more effective in sorbing metal elements than the AMO, as justified by the respective K values (Table 3). Regarding maximum sorption capacities (S_{max}), the values are similar for the two sorbents despite the fact that birnessite has a greater CEC and specific surface area while a lower pH_{ZPC}. The accessibility of surface sites relative to both solids most certainly differs.

The results presented in Figure 5 were obtained by mixing multi-metal element solutions, containing all four elements, with the solids in order to highlight potential competition phenomena. Compared to the results found for each metal examined individually (Fig. 4), the amount of adsorbed Cd and Zn decreases as the amounts of Cu and Pb increase. Lead is the most strongly sorbed and the main competitor, displaying high affinity for both oxides. These results are in good agreement with the kinetic results (Table 2), as a consequence of the competition taking place between metal elements during their sorption; as previously shown, Cd and Zn have less affinity for the oxides than Cu and Pb.

Figure 6 shows the total amount of metals sorbed onto the solid vs. the total amount of metal in solution at equilibrium during the competition experiments (Fig. 5). It appears that despite the higher CEC and specific surface area of birnessite, the total sorbed amount is similar for both solids, except at pH 4.0. Therefore, the effective sorption of metal elements by AMO and birnessite is not directly correlated with their physicochemical properties (CEC, specific surface area, pH_{ZPC}). To explain these results, the surface charge of AMO was determined by zetametry (Fig. 7). With a freshly prepared AMO suspension, a pH_{ZPC} value of

9.0 was obtained, i.e. close to the value found by titration. Under these conditions, the variation in surface charge vs. pH is small and not correlated with either the protonation or deprotonation of the surface. However, when the AMO is in suspension for several days before the determination step, the pH_{ZPC} value output by zetametry equals 4.8. Under such conditions, the charge increases as pH values decrease, which is in good agreement with the protonation. These results have shown that AMO surface properties change with the contact time in aqueous solutions. This instability may be explained by the release of manganese weakly bound to the solid or by hydration of the newly-formed oxide or residual MnO_4^- ions, which are unstable in solution. Under the experimental conditions of sorption isotherms (pH 4 or 5.5), the surface charge of AMO is thus near zero or even negative, which could potentially explain the sorption properties of the AMO (Fig. 7).

Moreover, as revealed for example by Tunius and Sköld [41] with Al oxide, the entire specific surface of a solid is not necessarily available for sorption. The Mn sorbed on the oxide surface might also interfere with the specific surface area measurement, thereby clogging some of the smaller pores and reducing the available area for N_2 sorption during the BET measurement [26].

3.5.2 *Multi-adding isotherms*

The speciation of metal elements in the bulk solutions was determined using the speciation program MINEQL+4.6 [22]. The standard databases included with the software were applied. Each metal element has been considered separately, by taking into account the pH value, temperature, atmospheric CO_2, ionic strength, and Na and NO_3 concentrations (from the salt of metal elements as well as the background electrolyte).

The figure S. 3a and b present the speciation of Cu and Pb at pH 5.5. Results for pH 4.0 were not shown due to the fact that free Cu^{2+} and Pb^{2+} account for over 95% of the total

metal. Precipitation can occur whenever the concentration exceeds 1 mM for Cu and 3 mM for Pb. The thermodynamic calculations performed with MINEQL+4.6 indicate that Cu and Pb can precipitate at pH 5.5 (as CuO and $Pb(OH)_2$, respectively). In order to prevent any risk of precipitation, multi-adding batch experiments were conducted: 1 mM of metal elements was added on a daily basis until the desired cumulative amount was reached.

The results obtained for Pb and Cu at pH 5.5 by means of simple (classical) and multi-adding isotherms are similar (S. 3c, d), which confirms that Cu and Pb do not precipitate in the solution under our experimental conditions, despite speciation calculations predicting the formation of CuO and $Pb(OH)_2$. As previously shown, the AMO and birnessite adsorbed the metal elements very quickly and, consequently, limited the precipitation risk. The random nature of the first step of the precipitation phenomenon should also be mentioned and typically appears as a result of highly oversaturated solutions.

3.6   pH adsorption edges

The pH adsorption edges (Fig. 8) were determined from pH 4 to 8, since below pH 4 the AMO is altered while above pH 8 metal precipitation occurs. For birnessite, no significant pH effect on metal adsorption has been observed. The sorption rate normally decreases at lower pH values (as both the surface charge and competition between protons and metal elements increase), though the affinity of birnessite for metals is still sufficient to maintain the high adsorption rate, with sorption starting below pH 4 due to the pH_{ZPC} value. For the AMO, the strong sorption of Pb overshadows the pH effect; only a small increase in adsorption with increasing pH values is observable. For Cu, Cd and Zn, this adsorbed amount increases significantly as pH values rise. In comparison with birnessite, the sorption properties of the AMO are considerably affected by pH values due to the lower affinity of metal elements for AMO.

4. Conclusion

The AMO described in this work seems to be stable in pure water despite the appearance of some dissolution shortly after its contact with water (5.70% and 0.24% of the total amount at 1/500 and 1/10 w/v ratios, respectively). Birnessite and AMO display quite similar sorption capacities for the studied divalent metal cations (Cu, Cd, Pb, Zn); however, birnessite adsorbs faster than the AMO. Even though the CEC of AMO (34 meq/100 g) seems to predict a lower sorption capacity than for birnessite (247 meq/100 g), results indicate that the AMO acts as an efficient sorbent, especially for Cu and Pb (1.38 and 2.37 mmol/g for AMO, and 1.78 and 2.13 mmol/g for birnessite at pH 5.5). These findings may be due to the fact that not all of the specific surface is available for sorption as well as to the evolution in surface properties of the AMO in solution vs. time, as determined through the zetametry experiment. Adsorption edges show that the AMO is very sensitive to pH variations, in addition to being easy and inexpensive to synthesize and capable of providing a valuable amendment for use in stabilizing metals and metalloids in soils. Nevertheless, its stability in various soil types still needs to be evaluated further.

18

References

[1] H.B. Bradl, J. Colloid Interface Sci. 277 (2004) 1.

[2] M. Mench, N. Lepp, V. Bert, J.-P. Schwitzguébel, S.W. Gawronsku, P. Schröder, J. Vangronsveld, J. Soils Sediments 10 (2010) 1039.

[3] J.Kumpiene, A. Lagerkvist, C. Maurice, Waste Manage. 28 (2008) 215.

[4] W. Stumm, J.J. Morgan, Aquatic Chemistry, John Wiley and Sons, New-York, 1996.

[5] Y. Roh, S.Y. Lee, M.P. Elless, Environ. Geol. 40 (2000) 184.

[6] C. Bes, M. Mench, Environ. Pollut. 156 (2008) 1128.

[7] M. Komárek, A. Vaněk, V. Ettler, Environ. Pollut. 172 (2013) 9.

[8] J.E. Post, Proc. Natl. Acad. Sci. U. S. A. 86 (1999) 3447.

[9] M.L. Crimi, R.L. Siegrist, Water Res. 38 (2004) 887.

[10] S.E. O'Reilly, M.F. Hochella, Geochim. Cosmochim. Acta 67 (2003) 4471.

[11] S.B. Kanungo, S.S. Tripathy, S.K. Mishra, .B Sahoo, Rajeev, J. Colloid Interface Sci. 269 (2004) 11.

[12] Q. Su, B. Pan, S. Wan, W. Zhang, J. Colloid Interface Sci. 349 (2010) 607.

[13] M. Pantsar-Kallio, S.-P. Reinikainen, M. Oksanen, Anal. Chim. Acta 439 (2001) 9.

[14] A.L. Foster, G.E. Brown, G.A. Parks, Geochim. Cosmochim. Acta 34 (2003) 1937.

[15] M. Mench, J. Vangronsveld, V. Didier, H. Clijsters, Environ. Pollut. 86 (1994) 279.

[16] G.M. Hettiarachchi, G.M. Pierzynski, M.D. Ransom, Environ. Sci. Technol. 34 (2000) 4614.

[17] S. Ching, D.J. Petrovay, M.L. Jorgensen, S.L. Suib, Inorg. Chem. 36 (1997) 883.

[18] R.M. McKenzie, Mineral. Mag. 38 (1971) 493.

[19] M. Davranche, S. Lacour, F. Bordas, J.-C Bollinger, J. Chem. Educ. 80 (2003) 76.

[20] J.W. Murray, L.S. Balistrieri, B. Paul, Geochim. Cosmochim. Acta 48 (1984) 1237.

[21] G. Limousin, J.-P. Gaudet, L. Charlet, S. Szenknect, V. Barthès, M. Krimissa, Appl. Geochem. 22 (2007) 249.

[22] W.D. Schecher, D.C. McAvoy, MINEQL+: A chemical equilibrium modeling system, version 4.6 for Windows, user's manual, v2.00, Environmental Research Software: Hallowell, Maine, 2003.

[23] C.H. Bolster, G.M. Hornberger, Soil Sci. Soc. Am. J. 71 (2007) 1796.

[24] D.X. Li, F.W. Schwartz, J. Contam. Hydrol. 68 (2004) 39.

[25] P. Di Leo, M.D.R Pizzigallo, V. Ancona, F. Di Benedetto, E. Mesto, E. Schingaro, G. Ventruti, J. Hazard. Mater. 201-202 (2012) 418.

[26] E. Eren, H. Gumus, A. Sarihan, Desalination 279 (2011) 75.

[27] L. Kang, M. Zhang, Z.-H. Liu, K. Ooi, Spectrochim. Acta 67 (2007) 864.

[28] H. Cui, G. Qiu, X. Feng, W. Tan, F. Liu, Clays Clay Miner. 57 (2009) 715.

[29] F. Li, J. Wu, Q. Qin, Z. Li, X. Huang, J. Alloys Compd. 492 (2010) 339.

[30] Q. Feng, K. Yanagisawa, N. Yamasaki., J. Mater. Sci. Lett. 16 (1997) 110.

[31] E. Cristiano, Y.-J. Hu, M. Siegfried, D. Kaplan, H. Nitsche, Clays Clay Miner. 59 (2011) 107.

[32] J.W. Murray, J. Colloid Interface Sci. 46 (1973) 357.

[33] W.F. Tan, S.J. Lu, F. Liu, X.H. Feng, J.Z. He, L.K. Koopal, Soil Sci. 173 (2008) 277.

[34] D.C. Golden, J.B. Dixon, C.C. Chen, Clays Clay Miner. 34 (1986) 511.

[35] Y. Arai, Appl. Clay Sci. 53 (2011) 572.

[36] H. Yin, X. Feng, M. Liu, W. Tan, G. Qiu, J. Hazard. Mater. 196 (2011) 318.

[37] R.M. McKenzie, Aust. J. Soil Res. 19 (1980) 41.

[38] G. Pan, Y. Qin, X. Li, T. Hu, Z. Wu, Y. Xie, J. Colloid Interface Sci. 271 (2004) 28.

[39] E.F. Covelo, F.A. Vega, M.L. Andrade, J. Hazard. Mater. 140 (2007) 308.

[40] Y. Wang, X. Feng, M. Villalobos, W. Tan, F. Liu, Chem. Geol. 292-293 (2011) 25.

[41] M. Tunius, R. Sköld, Colloids Surf. 46 (1990) 297.

Figures and Tables captions

Fig. 1: SEM images of the AMO

Fig. 2: a) XRD spectra (A) of the AMO and birnessite and IR spectra (B) of AMO, b) AMO heated at 140°C for 10 min, c) heated for 12 h, and d) and birnessite

Fig. 3: Stability of AMO at a) 1/500 and b) w/v ratio in pure water

Fig. 4: Sorption isotherms of Cu, Cd, Zn and Pb onto AMO at a) pH 4 and b) pH 5.5, and birnessite at c) pH 4 and d) pH 5.5 using a 1/500 w/v ratio

Fig. 5: Simultaneous adsorption of Cu, Cd, Zn and Pb on AMO at a) pH 4 and b) pH 5.5, and birnessite at c) pH 4 and d) pH 5.5

Fig. 6: Total amount of Cu, Cd, Zn and Pb adsorbed onto AMO and birnessite as a function of total concentration in solution at pH 4 and 5.5

Fig. 7: Zeta potential of the AMO in pure water at two different contact times (0 days and 15 days) for a range of pH values

Fig. 8: pH adsorption edges of Cu, Cd, Zn and Pb onto a) AMO and b) birnessite

S. 1: Consumption of O_2 in the presence of AMO and birnessite in pure water at a 1/500 w/v ratio

S. 2: Kinetic sorption of Cu, Cd, Zn and Pb onto AMO at a) pH 4 and b) pH 5.5, and birnessite at c) and d) using a 1/500 w/v ratio and 1 mM metal element solutions in 0.01 M $NaNO_3$

S. 3: a) Cu and b) Pb speciation at pH 5.5 in a 0.01 M $NaNO_3$ solution, and adsorption isotherms of c) Cu and d) Pb at pH 5.5 onto AMO: comparison between simple and multi-adding isotherms

Table 1:
Characteristics of both birnessite and AMO

Table 2:
Pseudo-second order kinetic parameters of metal element adsorption onto AMO and birnessite at pH 4 and 5.5

Table 3:
Characteristics of the modeled Langmuir isotherm for both birnessite and the AMO

Graphical abstract : SEM image of the AMO