Zn-Al sulphate layered double hydroxide for Mo uptake

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Abstract

The efficacy of synthetic Zn-Al-SO_4 LDH (layered double hydroxide) in removing aqueous molybdate was tested through batch sorption experiments. Up to 54% Mo was removed; the most efficient mechanism was sulphate-molybdate exchange within the LDH interlayer. The Mo uptake was influenced by the Zn/Al molar ratio: higher ratios (Zn/Al = 3) facilitated the release of sulphate from the interlayer and the entrance of molybdate, while for lower ratios (Zn/Al = 2 and 1.7) surface adsorption of molybdate became an important uptake mechanism. The Mo removing potential shown by Zn-Al-SO_4 LDH may prove useful for the treatment of moderately contaminated waters from metallurgical and mining activities.

Keywords: layered double hydroxide, molybdate-sulphate exchange, molybdate surface adsorption, polluted water treatment

Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays (general formula $M^{2+}_{1-x}M^{3+}_{x}(OH)_2(A^{n-})_{x/n} \cdot yH_2O$), are a group of compounds with a structure consisting of brucite-type metal-hydroxide layers, where bivalent cations are partially replaced by trivalent cations; these positively charged layers are balanced by interlayered inorganic or organic anions. This structure allows exchange with anions in solution, making LDHs potentially suitable for the production of advanced catalytic materials, or for the removal of contaminants from waste waters (Vaccari 1998, Smith et al. 2005, Yang et al. 2005).

Among the many possible LDHs compositions, we focused our interest on Zn-Al sulphate LDHs (Rojas Delgado et al. 2008). They are much less studied and widespread in nature than the most common Mg-Al LDHs. However, Zn-Al-SO_4 LDHs have been reported as secondary minerals in several mine areas, where they can exert a specific influence on the local geochemical cycle of As (Ardau et al. 2011a). Indeed, laboratory studies (Ardau et al. 2011b) documented an excellent capacity of Zn-Al-SO_4 LDHs in removing arsenate from waters.

The aim of this study was to investigate the capacity of Zn-Al-SO_4 LDHs in removing molybdenum from aqueous solutions. Molybdenum is an essential micronutrient required for growth of most organisms. However, it has a narrow range between deficiency and toxicity (McGrath et al. 2010). Molybdenite (MoS_2) is the most abundant Mo mineral, while in soils and natural waters the metal occurs predominantly in its anionic form MoO_4^{2-}. The WHO (World Health Organization) recommends a maximum level of 0.07 mg/L Mo in drinking water (WHO 2006). High concentrations of Mo may occur in association with metallurgical and mining activities (Leybourne and Cameron 2008). There are only a few previous studies on the intercalation of molybdate in LDH structures, mostly related to technological applications (Mitchell and Wass 2002, Smith et al. 2005, Yu et al. 2009, Zhang and Reardon 2003).

Methods

Synthetic samples for this study were prepared by a coprecipitation method. An aqueous Zn-Al sulphate solution (0.2 mol/L), with established Zn^{2+}/Al^{3+} ratios, was added dropwise by a peristaltic pump into a reactor containing 200 ml of Milli-Q water (Millipore), under vigorous stirring (500 rpm). The precipitation was induced at pH ~8.5, by dropping a NaOH solution (0.5 mol/L) into the reactor. To avoid carbonate groups entering the interlayer, the experiments were conducted under controlled argon atmosphere (Ardau et al. 2011b). Syntheses were performed for Zn^{2+}/Al^{3+} ratios equal to 5/3, 2/1 and 3/1 (from now on 1.7LDH, 2LDH, 3LDH). Precipitation started instantly, and resulted in the formation of a white gel. After aging (>7 days at 50 °C), the precipitates were filtered and washed with abundant deionised water.

The initial composition of LDHs used as sorbents in the sorption experiments and their empirical formulas are listed in Table 1. The Zn^{2+}/Al^{3+} ratio of synthetic phases corresponded approximately to that in the starting solutions.

Table 1 *Chemical analyses and empirical formulas of synthetic LDHs used for sorption experiments.*

	Zn/Al starting solution	**Zn**	**Al**	**Na**	**S**	**Zn/Al synthetic product**	**Empirical formula**	***Δ**
	(molar ratio)	(weight %)				(molar ratio)		(%)
3LDH	3.0	37	5.4	<0.033	3.7	2.9	$Zn_{0.74}Al_{0.26}(OH)_2(SO_4)_{0.15}\ yH_2O$	-1.75
2LDH	2.0	37	7.1	0.3	4.0	1.9	$Na_{0.01}Zn_{0.65}Al_{0.35}(OH)_2(SO_4)_{0.16}\ yH_2O$	+1.71
1.7LDH	1.7	30	7.8	<0.033	4.4	1.6	$Zn_{0.61}Al_{0.39}(OH)_2(SO_4)_{0.18}\ yH_2O$	-1.26

*Charge balance calculated as: [(Σ positive charges - Σ negative charges)/0.5·(Σ positive charges + Σ negative charges)]·100

For batch sorption experiments, 1 g of LDH was suspended in a series of beakers, each containing 100 ml of aqueous molybdate solution, obtained dissolving Na_2MoO_4 in Milli-Q water to achieve nominal Mo concentrations of 4, 8, 12, and 16 mmol/L (from now on (a), (b), (c), (d)). The suspension was left for 72 h under vigorous stirring, and the pH was monitored, but not fixed; throughout all experiments, it varied slightly in the range of 7-8. At these pHs, the dominant form of Mo in solution is the molybdate anion MoO_4^{2-}. Small volumes of solution were sampled at different time intervals, filtered at 0.4 µm, and acidified with HNO_3 for the analyses of Mo, S, Zn, and Al by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The analysis of dissolved Zn and Al allowed determination whether a partial dissolution of LDH occurred during the sorption experiment, while the dissolved concentration of sulphate (adjusted for the possible contribution from dissolution) provided information on exchange process with molybdate. At the end of each experiment, the sorbent was washed with abundant deionised water and filtered. A portion of all solid materials was analysed by XRD before and after sorption experiments. XRD patterns were collected in the 5-70° 2θ angular range on an automated Panalytical X'pert Pro diffractometer with Ni-filter monochromatized Cu-Kα_1 radiation (λ = 1.54060 Å), operating at 40 kV and 40 mA, using the X'Celerator detector. Because these phases are hydrophilic (Ardau et al. 2011b), all XRD patterns were collected after leaving samples in oven at 50 °C for 24 h. Another portion of the solids was dissolved in 10 % v/v HNO_3 (15 mol/L), and the solution analysed by ICP-AES to determine chemical composition.

Results

Chemistry of batch solutions

Sorption of Mo by Zn-Al-SO_4 LDH was quite fast, mostly occurring within the first 3 h. As a general rule, for a given Zn^{2+}/Al^{3+} ratio the uptake of Mo increased from (a) to (d), that is for increasing values of the starting aqueous Mo concentration (Figure 1a), while the percentage of removed Mo decreased from (a) to (d) (Figure 1b). The efficiency of removal was clearly influenced by Zn^{2+}/Al^{3+} ratios: higher ratios favoured molybdate uptake, according to the sequence 3LDH >> 2LDH ≥ 1.7LDH, but the decrease of percentage removed from (a) to (d) was more pronounced for 3LDH (Figure 1b).

Molybdenum uptake was accompanied by a concomitant release of sulphur to solution, increasing from (a) to (d) according to the sequence 3LDH >> 1.7LDH > 2LDH (Figure 1a). Sulphate released from the 3LDH sample was about twice the amount released from the 1.7LDH sample. This difference increased if the percentage of S released is considered, since the 3LDH sample contained less S than the 1.7LDH sample (Table 1). As expected the difference between 2LDH and 1.7LDH was less pronounced.

The molar amount of Mo removed almost always exceeded that of S released; the difference was very low for 3LDH but significant for 2LDH and 1.7LDH. Moreover, as observed for Mo, S released from 3LDH was more influenced by the starting aqueous Mo concentration.

Very low amounts of Zn were released to solution during the experiments, decreasing from (a) to (d), and according to the sequence 3LDH >> 2LDH > 1.7LDH, while Al was always below the detection limit. This release indicates that at pH values in the range of 7–8 the LDHs were slightly soluble. Equilibrium calculations, carried out with the geochemical code PHREEQC (ver. 2.18.5570) coupled with the minteq.v4.dat database (Parkhurst and Appelo 1999), which includes Mo species, indicate oversaturation conditions with respect to $ZnMoO_4$ in all solutions. Thus, it is possible that some Mo was subtracted from solution by $ZnMoO_4$ precipitation, but this possible amount would be minor with respect to Mo sorbed by LDH and/or remaining in solution.

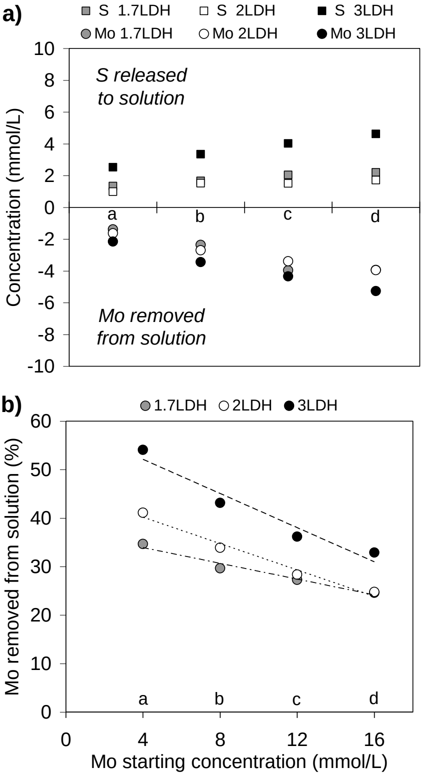

Figure 1 *Chemical changes in solutions of sorption batch experiments after 72 h. a) variations of S and Mo contents; b) percentage of Mo removed from solutions.*

Sorbents

In correspondence of the above chemical changes, there was a certain degree of structural rearrangement of the samples, more evident for increasing Zn^{2+}/Al^{3+} ratios (Figure 2). For the 3LDH samples, the analysis of the portion in the 5-30° 2θ angular range, where basal reflections fall, indicated a shift of basal reflections toward higher 2θ values (which implies a shortening of d-spacings), and the splitting of the (006) reflection (2θ ~20°) into two broad reflections (2θ = 21.5° and 23°), suggesting a loss of structural order, probably due to inhomogeneities of interlayers (e.g. systematic variations of anion distribution). For 1.7LDH and 2LDH samples, the shift of the basal X-ray reflections was not evident, while in 2LDH samples the (006) reflections (2θ ~20°) presented a gradual broadening from (a) to (d) suggesting a loss of structural order, and an asymmetry, which could be a hint of a reflection splitting.

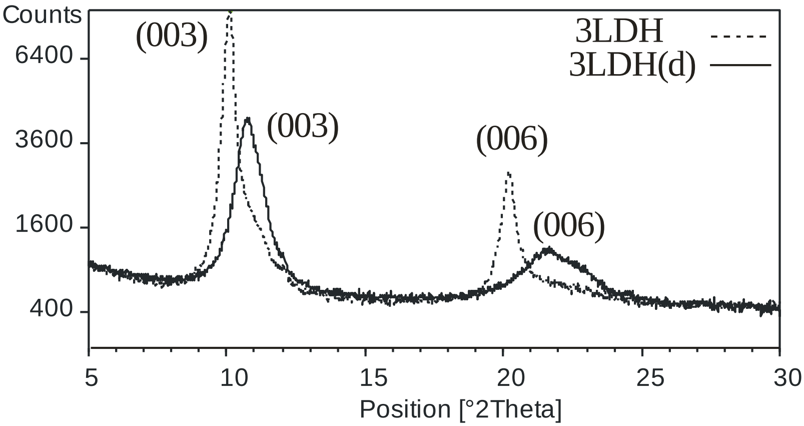

Figure 2 *A detail of the XRD patterns of 3LDH (portion in the 5-30° 2θ angular range) before and after the (d) experiment.*

Discussion

The results of batch experiments documented a moderate ability of Zn-Al-SO_4 LDHs to remove molybdate from solution through sorption processes. In the conditions of our experiments, removal of Mo ranged between 24 % and 54 % of the total in solution, i.e. much less than reported for arsenate in similar experiments (Ardau et al. 2011b). In agreement with other studies on LDH (e.g. Goh et al. 2008) the efficiency of removal was influenced by Me^{2+}/Me^{3+} ratios, with the maximum removal obtained for the highest Zn^{2+}/Al^{3+} ratio. For a given Zn^{2+}/Al^{3+} ratio, the absolute amount of removed Mo increased with increasing starting Mo concentration, but at the same time the process became less efficient (i.e. the percentage of total removed Mo decreased).

Two different mechanisms control the removal of anions by LDHs from aqueous media: interlayer anionic exchange and surface adsorption (Mohan and Pittman 2007). The former is favoured by high Me^{2+}/Me^{3+} ratios, due to a reduced positive charge of brucite-like layers, which facilitates release of interlayer anions (in this case, sulphate) from the solid to the aqueous medium. Ionic radii of MoO_4^{2-} and SO_4^{2-} are fairly close, respectively 0.246 and 0.230 nm; considering also the same charge, MoO_4^{2-} and SO_4^{2-} should have a similar affinity for the LDH interlayer. On the other hand, for an exchange process involving exclusively anions in the interlayer of the LDH structure, the amount of MoO_4^{2-} removed should be equal to SO_4^{2-} released. On the contrary, in all experiments MoO_4^{2-} removed exceeded SO_4^{2-} released; the difference increased toward lower Zn^{2+}/Al^{3+} ratios of the sorbent, when sulphate in the interlayer is more strongly bound to the structure due to a higher positive charge of brucite-like layers. Accordingly, we suggest that Mo uptake partially took place through adsorption onto the external surface of the LDH phase, which did not involve the release of sulphate. The contribution from adsorption was higher for low Zn^{2+}/Al^{3+} ratios. An effective visualisation of the two processes is shown in Figure 3, where S and Mo in the sorbent after each experiment were calculated from aqueous concentrations. As a first approximation, we assumed that the Mo sorption by Zn-Al-SO_4 LDHs was explained by the quantification of the anions removed from/released to solution. Under this assumption, Mo concentration under the dashed line in Figure 3 (marking out the starting S concentration in the solid) represents the exchanged molybdate, while Mo concentration above the dashed line represents molybdate adsorbed onto the surface. When $Zn^{2+}/Al^{3+} = 3$, the adsorbed fraction was negligible or within the analytical error, while for 2 and 1.7 ratios the estimated amount of Mo adsorbed increased significantly up to 56 % of total Mo sorbed (Figure 4). This double mechanism of Mo removal, although is a simplification of the exchange process, can explain the more pronounced decrease of Mo percentage removed from (a) toward (d), observed for increasing Zn^{2+}/Al^{3+} molar ratios (Figure 1b). As said above, molybdate uptake in the interlayer implies an expulsion of sulphate from the structure. This expulsion slows down approaching the maximum exchange capability of the phase from (a) to (d). On the contrary, when Mo uptake takes place on the external surface of the phase, the number of available adsorption sites is independent on the release of sulphate from solid to solution.

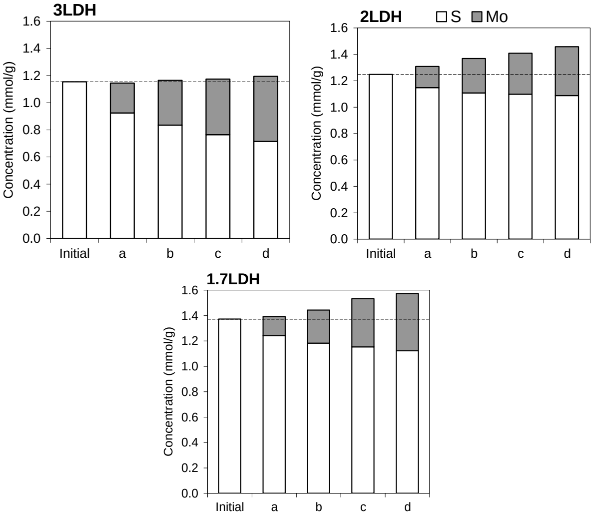

Figure 3 *Calculated variations of sorbent chemistry (Mo and S contents) before and after sorption experiments at 48 h. Dashed line marks the amount of Mo entered the interlayer needed to balance the S released; the excess of Mo above the dashed line is assumed to be adsorbed at the external surface.*

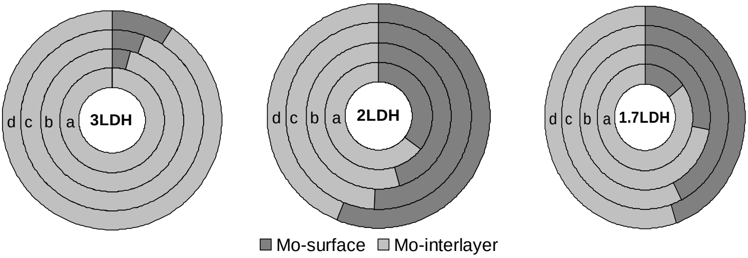

Figure 4 *Estimated distribution of sorbed Mo in Zn-Al-SO_4 LDHs.*

The loss of crystallinity after MoO_4^{2-} sorption suggested by XRD patterns could reflect a distortion of the brucite-like layer from planarity, as a consequence of a disordered spatial distribution of anions on each side of the layer (Tumiati et al. 2008). The maximum distortion was observed in the 3LDH samples, where the molybdate loading was highest. In this case a shift of the X-ray reflections toward higher angles (lower d-spacing values) was also observed, giving indirect evidence, in agreement with solution data, of the sulphate-molybdate exchange in the interlayer of the structure. Splitting of basal reflections were also observed, suggesting inhomogeneous characteristics of interlayers (i.e. preferential distribution of sulphate-molybdate in specific interlayers).

Conclusions

According to sorption experiments performed in this study, Zn-Al-SO_4 LDHs can act as removers of molybdate from water, although less efficient than for arsenate. The value of Zn^{2+}/Al^{3+} ratio in LDH was critical for the efficacy of the process. In fact, it determined the extent of the two main mechanisms of MoO_4^{2-} removal: interlayer anionic exchange and surface adsorption. The former clearly prevailed for $Zn^{2+}/Al^{3+} = 3$, while the latter played an important role for $Zn^{2+}/Al^{3+} \leq 2$. The sulphate-molybdate exchange in the LDH interlayer was the most efficient mechanism, although the most affected by the starting aqueous Mo concentration. The layered structure was preserved during the sorption process, though with a partial loss of the structural order. In conclusion, Zn-Al-SO_4 LDHs can be effective in the treatment of waters moderately contaminated by molybdate with pH in the range of 7–8.

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