

Synthetic and natural Zn-Al sulphate LDHs for removal of As(V) from NAMD

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Abstract In this study, we investigated the efficacy of natural and synthetic Zn-Al sulphate layered double hydroxides (LDHs) in removing As(V) from water solution in batch experiments. To better clarify LDHs properties, we experimented with different As dissolved concentrations and different element molar ratios in synthetic samples. Results showed that these phases are effective removers of As(V) from solutions through anionic exchange with sulphate in the interlayer. This result encourages further investigation of more complex aqueous systems and different inorganic pollutants.

Key Words Zn-Al-sulphate LDHs, arsenate-sulphate exchange, NAMD mine water treatment

Introduction

Layered double hydroxides (LDHs), a group of compounds with general formula $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot yH_2O$, have a high anionic exchange capacity (AEC), which can widely vary as a function of their composition. The general structure of LDHs (also called "anionic clays" or "hydrotalcites") is made up of brucite-type metal-hydroxide layers intercalated with anions and water molecules. A key feature of this mineral group is the substitution of M^{3+} cations for M^{2+} cations within the octahedral brucite-type layer. This makes the layer positively charged $[(M^{2+}_{1-x}M^{3+}_x)(OH)_2]^{x+}$, which is the reason for the presence of anionic groups in the interlayer $[(A^{n-})_{x/n}]^{x-}$. LDHs form spontaneously in a wide range of environments, including mine areas (Tumiati *et al.* 2008 and references therein; Cidu & Frau 2009; Ardaul *et al.* 2011).

In this study, we investigated the efficacy of Zn-Al sulphate LDHs in removing As(V) from water solution, evaluated through sorption of aqueous arsenate onto synthetic and natural samples in batch experiments. This choice ensued from field investigations, which pointed out the capacity of natural Zn-Al sulphate LDHs to attenuate dissolved As in NAMD (Net Alkaline Mine Drainage) from the old Baccu Locci mine (southeastern Sardinia, Italy) (Ardaul *et al.* 2011). The potential use of LDHs for As removal from contaminated mine water is based on the fact that the aqueous speciation of As under natural oxidizing conditions is dominated by oxyanions such as $H_2AsO_4^-$ and $HAsO_4^{2-}$.

Material and Methods

The natural Zn-(Cu)-Al sulphate LDH used for this study (from now on N_LDH) was a sample from the Baccu Locci mine (Sardinia). It is a fine-grained precipitate from NAMD waters, composed by a

mixture of micro-crystallites of glaucocerinite and zincowoodwardite (Raade *et al.* 1985; Witzke and Raade 2000). The average (Zn+Cu)/Al molar ratio is about 2 (Cu:Zn \approx 0.26); the material also contains some As (As:S molar ratio \approx 0.14) (see Ardaul *et al.* 2011, for further details and references on the occurrence of LDHs in this locality).

Synthetic LDH samples for this study were obtained by mixing an aqueous Al-Zn sulphate solution (with established Zn:Al ratios) with a NaOH solution, inducing precipitation at pH \approx 8.5. Syntheses were performed for Zn:Al molar ratios equal to 3, 2 and 1.6 (from now on 3HT, 2HT, 1.6HT). After aging (>7 days at 50 °C), the precipitates were filtered and washed with abundant deionised water.

Analogies between natural and synthetic samples were previously investigated through the combined use of several analytical techniques (i.e. ICP-OES, XRD, CHNS, SEM-EDX, IR) (Ardaul *et al.* 2011). Fig.1 (from those authors) shows IR spectra for three natural LDHs covering all ranges of structural order (from almost amorphous to well crystalline), compared with a synthetic sample of LDHs (zincowoodwardite). Spectra comparison confirms structural and chemical analogies of natural precipitates, despite their different degrees of structural order, and their correspondence with synthetic LDHs.

The experiments of sulphate-arsenate exchange were conducted by sorption of arsenate onto 1 g of Zn-Al sulphate LDH as sorbent. The material was left for \approx 48 hours under vigorous stirring in 100 mL of a solution obtained by dissolving $Na_2HAsO_4 \cdot 7H_2O$ in MilliQ water to achieve nominal As concentrations of 0.004, 0.008, 0.012, and 0.016 M. Aqueous solutions were analysed for Al, As, Na, S, and Zn at the start and at the end (assumed upon reaching of a stationary chemical composition of the aqueous so-

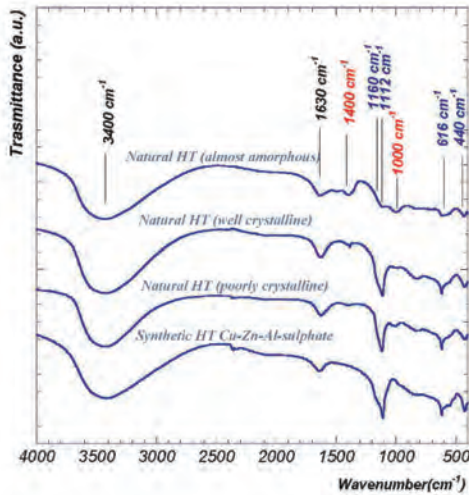


Figure 1. IR spectra from selected *Baccu Locci* LDH sulphates compared with a synthetic sample (from Ardau et al. 2011)

lution) of experiments. A portion of all solid materials (synthesis products and natural sample) was analysed by X-ray diffraction (XRD) and scanning electron microscope (SEM) before and after sorption experiments. Another portion was dissolved in 10% v/v HNO₃, and the solution analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine chemical composition. Finally, micro-Raman spectra were

collected for one synthetic sample (3HT) before and after the exchange experiment with a nominal As concentration of 0.016 M.

Results and Discussion

Chemical and mineralogical analysis of synthetic samples pointed out that 3HTs are composed by micro-crystallites of glaucocerinite and/or zincwoodwardite; small amounts of Na were detected for synthetic solutions with a Zn/Al molar ratio ≠ 3 (2HT and 1.6 HT samples). In these cases, the XRD patterns are close to that of motukoreaite, a LDH-like sulphate with the formula NaMg₆Al₃(SO₄)₂(OH)₁₈·12H₂O (Rius and Plana 1986). Empirical formulas for different Zn/Al molar ratio and N_LDH are reported in Table 1.

As shown in Figures 2 and 3, in all exchange experiments there is a dramatic decrease of As(V) concentration in solution, and a concomitant increase of S concentration. The composition of solids have a specular change, caused by a loss of S and gain of As in the course of the experiments (Table 2). Considering that, at the same time, concentrations of both Zn and Al in solution remain negligible (not shown), i.e. the sorbent phase does not dissolve to a significant extent, we can conclude that As(V) is mainly removed from solution as arsenate by an exchange process with sulphate.

When 3HT was used as the sorbent, we noticed that As removal was almost complete in experiments a and b. In experiments 1c and 1d, a certain amount of As remains in solution, since As in the starting solution exceeds the exchange capacity

Table 1 Empirical formulas of synthetic and natural phases used for exchange experiments

	Zn/Al	Zn/Al	Empirical formula
	starting solution	synthetic product	
	molar ratio	molar ratio	
3HT(1)	3.0	3.1	[Zn _{0.76} Al _{0.24} OH ₂](SO ₄) _{0.12} ·mH ₂ O
3HT(2)	3.0	2.9	[Zn _{0.74} Al _{0.26} OH ₂](SO ₄) _{0.14} ·mH ₂ O
3HT(3)	3.0	3.0	[Zn _{0.75} Al _{0.25} OH ₂](SO ₄) _{0.14} ·mH ₂ O
2HT(7)	2.0	1.9	Na _{0.05} [Zn _{0.65} Al _{0.35} OH ₂](SO ₄) _{0.20} ·mH ₂ O
1.6HT(16)	1.6	1.6	Na _{0.06} [Zn _{0.62} Al _{0.38} OH ₂](SO ₄) _{0.20} ·mH ₂ O
N_LDH	8.1*	2.0**	[Zn _{0.62} Cu _{0.14} Al _{0.38} OH ₂][(SO ₄) _{0.14} (AsO ₄) _{0.02}]·mH ₂ O

* For natural sample the value shown is for (Zn+Cu)/Al in the coexisting water (further parameters are reported in Ardau et al., 2011); ** the value shown is for (Zn+Cu)/Al.

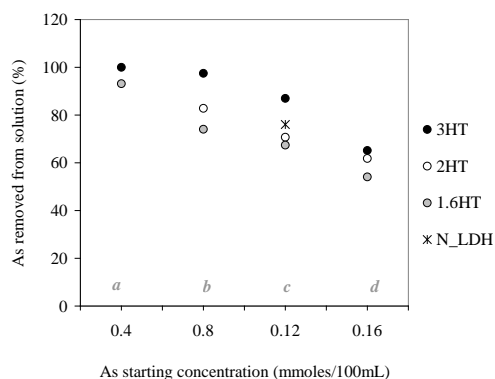


Figure 2 Variation of As concentration in aqueous solution during exchange experiments.

of the sorbent (i.e., one gram of sorbent does not contain enough sulphate to exchange for all of the arsenate in solution). For the 2HT and 1.6HT sorbents, we noticed the same trend. However, lesser As was removed, even if one gram of sorbent contained significantly higher levels of sulphate compared to 3HT (see table 1). The N_LDH have a Zn(Cu)/Al molar ratio similar to the 2HT sample,

Table 2 Composition of sorbent phases at the end of exchange experiments

experiment name	sample	S	As	As/S
		mmoles g ⁻¹ *	molar ratios	
experiments with 3HTs				
bulk	3HT	1.03**	none	
a	3HT(2)	0.68	0.37	0.5
b	3HT(1)	0.40	0.67	1.7
c	3HT(1)	0.19	0.90	4.7
d	3HT(3)	0.08	0.91	11
experiments with 2HTs				
bulk	2HT(7)	1.56	none	
b	2HT(7)	0.73	0.61	0.8
c	2HT(7)	0.56	0.75	1.3
d	2HT(7)	0.44	0.91	2.1
experiments with 1.6HTs				
bulk	1.6HT(16)	1.56	none	
a	1.6HT(16)	1.00	0.34	0.34
b	1.6HT(16)	0.75	0.59	0.79
c	1.6HT(16)	0.49	0.77	1.57
d	1.6HT(16)	0.42	0.87	2.07
experiments with N_LDH				
bulk	N_LDH	0.70	0.11	
c	N_LDH	0.08	0.87	11

* 1 g of sample referred to the starting composition weight

**average between 3HT(1), 3HT(2) and 3HT(3)

but less sulphate. Its behaviour is totally comparable with synthetic samples, even though it already contains some As (As:S molar ratio ≈ 0.14) at the start of the experiment.

Fig. 3 shows a good overlapping of S data for all three synthetic sorbents. More marked differences are evident for the As data, which could be attributed to some As removed by adsorption on the LDH surface. This aspect needs further investigation.

XRD patterns of the sorbent phases after the experiments (not shown) indicate that, in correspondence with the chemical changes, there was a certain degree of structural rearrangement. There was a generalized decrease of peak to background ratios, suggesting a certain loss of structural order. The LDH brucite-like layer may or may not be planar as a function of spatial distribution of anions present on each site of the layer (Tumiati *et al.* 2008). Such distortion can be further implemented by the presence of two different anions (sulphate and arsenate) in the interlayer.

From the Raman spectrum of the 3HT(2) sample (Fig. 4), six main bands, peaking at 452, 480, 540, 612, 980, and 1061 cm⁻¹, can be extracted in the 400–1100 cm⁻¹ region by using Lorentzian curves in the deconvolution process. The first three bands are due to the vibration of the cation-oxygen bonds of the A(OH)_x units (A= Zn, Al) (Wang *et al.*, 2003; Villegas *et al.*, 2003).

The peak centred at 612 and the very intense band at 980 cm⁻¹ can be respectively assigned to antisymmetric bending (ν_4) and to the symmetric stretching (ν_1) vibration of the sulphate tetrahedral oxyanion, and can be regarded as a clear fingerprint of the presence of sulphate in the host matrix (Frost *et al.* 2004).

The Raman spectrum of the 3HT(3) sample

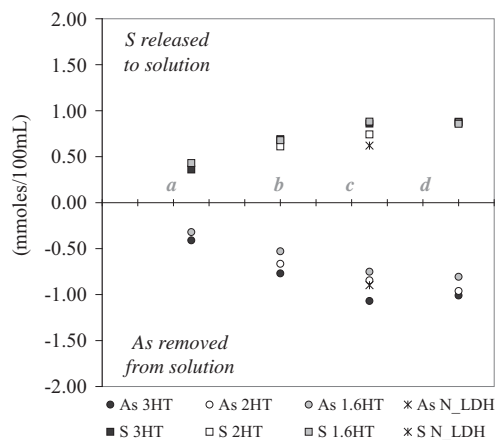


Figure 3 Comparison between S and As variation during exchange experiments.

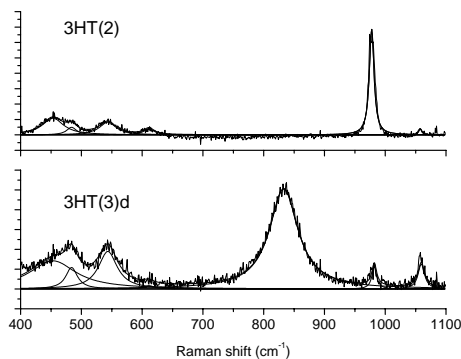


Figure 4 Raman spectra in the 400–1100 cm^{-1} spectral region of the samples 3HT(2) and 3HT(3)d with the calculated best fit curves.

after experiment 1d shows an additional band peaking at 830 cm^{-1} , which is attributed to the vibration of the (AsO_4) units. The abrupt decrease of the bands attributed to sulphate at 612 and 980 cm^{-1} , and the concurrent presence of the band at 830 cm^{-1} , suggests an almost complete substitution of AsO_4 tetrahedra in the crystalline structure of this sample. According to XRD data, a slight distortion of the crystalline structure can be deduced from an increase of about 10% of the full width at half maximum of the Lorentzian curves in the fitting process.

Conclusions

We investigated the efficacy of natural and synthetic Zn-Al sulphate layered double hydroxides (LDHs) in removing As(V) from water solution in batch experiments. Through combined use of chemical and mineralogical investigations, we also obtained useful information on the LDHs properties and processes involved during experiments.

Results showed that synthetic Zn-Al-sulphate LDHs are effective removers of arsenic from solutions through anionic exchange with sulphate in the interlayer. Minor amounts of As may be removed by surface adsorption. The efficiency of As removal increases with Zn/Al ratios, because of the reduced ionic charge of the brucite-like layer, facilitating release of sulphate, which is substituted by arsenate.

In the laboratory experiments, we used As concentrations several orders of magnitude higher than found in the field at Baccu Locci. However, experiments with natural LDHs showed a similar capacity in removing As(V) from water solution than synthetic samples, indicating that their potential exchange capacity is only partially exploited in the natural system, where LDHs may trap As at the moment of formation, and by subsequent interaction with As-rich waters.

The exchange reaction does not induce other major chemical changes. Specifically, at the pH values (≈ 9) of our experiments, there is no appreciable dissolution of the sorbent phase. The AEC shown by Zn-Al sulphate LDHs encourages further investigation of more complex aqueous systems and different inorganic pollutants.

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