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Sulphate-arsenate exchange properties of Zn-Al layered double hydroxides: preliminary data

Carla Ardaù^{1,*}, Franco Frau¹, Pier Carlo Ricci² and Pierfranco Lattanzi¹

¹Dipartimento di Scienze della Terra, Università di Cagliari, Via Trentino 51, 09127 Cagliari, Italy

²Dipartimento di Fisica, Università di Cagliari, Complesso Universitario di Monserrato, S.P. Monserrato-Sestu Km 0,700, I-09042 Monserrato (CA), Italy

*Corresponding author: carla.ardau@tiscali.it

Abstract

“Layered double hydroxides” (LDHs), a class 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, which can widely vary as a function of their composition. Such property is at the base of their use as catalysts and contaminant removers. In this study we investigated the capacity of Zn(Cu)-Al sulphate LDHs to remove As from solution. Previous field investigations coupled with preliminary laboratory experiments showed that natural LDHs of such composition (glaucozerinite and zincowoodwardite) are effective in the attenuation of As content in circum-neutral surface waters. Our laboratory studies confirm that these phases, both synthetic and natural, possess an excellent capacity to reduce As concentration in solution. The main mechanism suggested is a sulphate-arsenate exchange process in the interlayer, possibly with a contribution of surface adsorption. The efficiency of As removal increases with Zn/Al ratios, because the reduced ionic charge of the brucite-like layer facilitates release of sulphate. The removal potential shown by Zn(Cu)-Al sulphate LDHs encourage further investigation of more complex aqueous systems.

Key words: Zn-Al-sulphate LDHs; arsenate-sulphate exchange; mine water treatment.

Introduction

Layered double hydroxides (LDHs), also called “anionic clays”, or “hydrotalcite-like compounds” [from hydrotalcite, $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$, a typical LDH mineral], are a class of compounds of general formula $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^n)_{x/n} \cdot yH_2O$ (Gaines et al.,

1997). Their structure is characterized by brucite-type metal-hydroxide layers, intercalated with anions and water molecules. Since the anionic groups are linked to the octahedral layers by hydrogen bonding, LDHs exhibit high anionic exchange capacity (100-150 meq 100 g⁻¹. Álvarez-Ayuso and Nugteren, 2006, and references therein). Such property is at the base

of their use as catalysts or contaminant removers (Vaccari, 1998; Yang et al., 2005).

In a recent study, Ardaù et al. (2011) demonstrated, through field investigations and laboratory experiments, that glaucocerinite and zincowoodwardite, hydrated Zn-(Cu)-Al sulphates belonging to LDHs (Raade et al., 1985; Witzke and Raade, 2000), are effective in the attenuation of As content in NAMD (Net Alkaline Mine Drainage) of the Baccu Locci mine area (southeastern Sardinia, Italy), presumably by exchange of arsenate for sulphate in the anionic layer. However, because of the lacunose knowledge of the thermodynamic properties of these compounds, the exact mechanism remains speculative. To overcome this gap, a systematic study on the stability and exchange properties of Zn-Al LDHs was undertaken. In this paper, we report the data on the sulphate-arsenate exchange, evaluated through sorption of aqueous arsenate onto synthetic and natural Zn-Al-sulphate LDHs. The experiments are an extension of preliminary investigations of Ardaù et al. (2011). In the study by those authors the purpose was to simulate in laboratory possible processes occurring in the field (As coprecipitation/sorption with/on LDHs). Therefore, As concentrations and LDHs composition were selected according to that approach (i.e. in the coprecipitation experiment metals/As molar ratio was chosen to be roughly equal to natural samples). In this study we follow a more systematic approach, investigating variations of As removal as a function of LDHs composition and its concentration in solution.

Experimental

Synthetic 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 ~ 8.5. To avoid carbonate groups entering the interlayer, the experiments were conducted under controlled

Ar atmosphere. Syntheses were performed for Zn:Al molar ratios equal to 2 and 3 (from now on, respectively 2HT and 3HT). After aging (≤ 7 days at 50 °C), the precipitates were filtered and washed with abundant deionised water. The final product is a white powder with the consistency of talc.

The natural sample is a different aliquot of the same Zn-(Cu)-Al sulphate LDH from Baccu Locci, Sardinia, analyzed by Ardaù et al. (2011), to which the reader is referred for details and references on the occurrence of LDHs in this locality. The (Zn+Cu)/Al molar ratio is about 2 (Cu:Zn ~ 0.26); the material contains some As (As:S molar ratio ~ 0.14) (Table 1).

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 ~ 48 hours under vigorous stirring in 100 mL of a solution obtained dissolving Na₂HAsO₄·7H₂O in MilliQ water to achieve nominal As concentrations of 0.004, 0.008, 0.012, and 0.016 M. The pH of solutions was measured before adding the sorbent, and at the end of experiment. Aliquots of aqueous solutions were analysed for Al, As, Na, S and Zn at the beginning of experiment, and after a certain amount of time (3 to 48 hours), until reaching a stationary chemical composition of the aqueous solution. Table 2 summarizes the specific details of each exchange experiment.

A portion of all solid materials (synthetic products and natural sample) was analysed by powder 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 Elan 3500) to determine chemical composition. From replicate analyses of internal standards, we estimate that both accuracy and precision are 3-5% for most elements; accuracy is slightly worse for Na (7%). Finally, micro-Raman spectra were collected for

Table 1. Chemical analyses and empirical formulas of synthetic and natural phases used for exchange experiments.

	Zn/Al	Zn	Al	Cu	Na	S	As	Zn/Al	Empirical formula
	starting solution							solid product	
	molar ratio				%			molar ratio	
3HT(1)	3.0	41	5.4	np	<0.02	3.1	np	3.1	$[\text{Zn}_{0.76}\text{Al}_{0.24}\text{OH}_2](\text{SO}_4)_{0.12} \cdot \text{mH}_2\text{O}$
3HT(2)	3.0	38	5.5	np	<0.02	3.6	np	2.9	$[\text{Zn}_{0.74}\text{Al}_{0.26}\text{OH}_2](\text{SO}_4)_{0.14} \cdot \text{mH}_2\text{O}$
3HT(3)	3.0	36	4.9	np	<0.02	3.2	np	3.0	$[\text{Zn}_{0.75}\text{Al}_{0.25}\text{OH}_2](\text{SO}_4)_{0.14} \cdot \text{mH}_2\text{O}$
2HT(7)	2.0	33	7.3	np	0.95	5.0	np	1.9	$\text{Na}_{0.05}[\text{Zn}_{0.65}\text{Al}_{0.35}\text{OH}_2](\text{SO}_4)_{0.20} \cdot \text{mH}_2\text{O}$
N_LDH	8.1*	23	5.9	5.8	<0.02	2.5	0.86	2.0**	$[\text{Zn}_{0.62}\text{Cu}_{0.14}\text{Al}_{0.38}\text{OH}_2][(\text{SO}_4)_{0.14}(\text{AsO}_4)_{0.02}] \cdot \text{mH}_2\text{O}$

np = not present

* 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.

one synthetic sample (3HT) before and after the exchange experiment d (see Table 2).

XRD patterns were collected in the 5-70° 2θ angular range on an automated Panalytical X'pert Pro diffractometer with Ni-filter monochromatized Cu-K_{α1} radiation (λ = 1.54060 Å), operating at 40 kV and 40 mA, using the X'Celerator detector.

The SEM is a FEI Quanta 200 operated in "low-vacuum" conditions at 15 kV. Samples were generally analysed without any specific coating to avoid any possible interference during chemical characterisation by EDS. Gold coating was applied to few samples to obtain high quality morphological details.

Micro Raman spectra (RS) were collected in air at room temperature with a Raman spectrometer (Dilor XY800) operating with the 514.5 nm line of an argon ion laser (Coherent Innova 90C-4) in back scattering geometry. The signal, dispersed with a 1200 grooves/mm grating, was detected by

a 1024 × 256 liquid nitrogen cooled charge coupled detector (CCD), with a spectral resolution of < 0.7 cm⁻¹. Raman spectra were studied in two spectral regions, the first one between 400 and 1100 cm⁻¹, and the second between 2800 and 3700 cm⁻¹, where the main bands due to -OH vibrations can be observed.

Results

Phase properties

The products of syntheses were quite amorphous, but the crystallinity increased upon aging. Figure 1 shows the SEM (secondary electrons) image of a synthesized LDH (sample 2HT(7)). There is a close similarity with the crystal habitus of natural LDHs from Baccu Locci (see Figure 4 in Ardau et al., 2011). Replicate syntheses demonstrate a good reproducibility of the procedure, i.e. all products for a given Zn:Al ratio were quite similar in terms of both phase

Table 2. Variation of solution chemical parameters during exchange experiments.

experiment name	sample	solution As-molarity	pH	sampling time	Al	As	S	Zn
	(1 g)	M		(h)	mmoles/100 ml			
experiments with 3HTs								
a	3HT(2)	0.004	9.11	0	<0.13	0.41	<0.03	<0.023
				3	<0.13	<0.01	0.38	<0.023
				24	<0.13	<0.01	0.38	<0.023
			8.42	48	<0.001	<0.0001	0.36	0.002
b	3HT(1)	0.008	9.17	0	<0.02	0.79	0	<0.01
				3	<0.02	0.05	0.71	<0.01
				24	<0.02	<0.001	0.73	<0.01
			8.64	48	<0.002	0.02	0.69	<0.001
c	3HT(1)	0.012	9.23	0	<0.02	1.23	0	<0.01
				3	<0.02	0.25	0.92	<0.01
				24	<0.02	0.20	0.95	<0.01
			8.94	48	<0.002	0.16	0.86	<0.001
d	3HT(3)	0.016	9.34	0	<0.02	1.55	0	<0.01
				3	<0.02	0.67	0.46	<0.01
				24	<0.02	0.63	0.94	<0.01
			9.21	48	0.006	0.54	0.88	<0.001
experiments with 2HTs								
b	2HT(7)	0.008	9.34	0	np	0.80	np	np
				48	<0.002	0.14	0.61	<0.001
c	2HT(7)	0.012	9.40	0	np	1.19	np	np
				48	<0.002	0.35	0.74	<0.001
d	2HT(7)	0.016	9.43	0	np	1.55	np	np
				48	<0.002	0.59	0.87	<0.001
experiments with N_LDH								
c	N_LDH	0.012	9.40	0	np	1.18	np	np
				48	<0.002	0.28	0.62	<0.001

assemblage and chemical composition. The Zn:Al ratios were always within 10% of the nominal value (Table 2). Syntheses with Zn:Al = 3 produced mostly zincowoodwardite [Zn_{1-x}

Al_x(OH)₂][(SO₄)_{x/2}(H₂O)_n], with traces of glaucocerinite (Figure 2a and 2b). Glaucocerinite is the hydrated form of zincowoodwardite (Witzke and Raade, 2000).

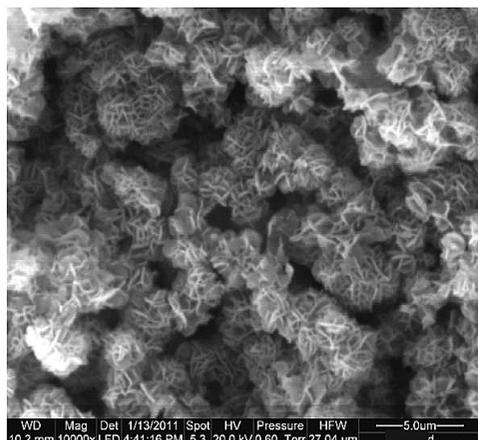


Figure 1. SEM (secondary electrons) image of synthesized LDH (sample 2HT(7), Zn/Al ratio 1.9).

Leaving the synthesis products in a water-saturated environment for few hours we observed the shift to prevalent glaucocerinite (Figure 2a). Conversely, leaving the sample in oven at 50 °C, we return to a predominance of zincowoodwardite (Figure 2b).

Two polytypes are known for zincowoodwardite (3R and 1T). According to d-spacing values the synthesised zincowoodwardite is closer to the 3R polytype. However, because peak position may vary as a function of different hydration degrees (Dinelli et al., 1998), this attribution should be taken cautiously.

Syntheses with Zn : Al = 2 (2HT) contain Na (see Table 1) and present an XRD pattern similar to that of motukoreaite, a LDH-like sulphate with formula $\text{NaMg}_6\text{Al}_3(\text{SO}_4)_2(\text{OH})_{18} \cdot 12\text{H}_2\text{O}$ (Figure 2c). This is a simplified formula as reported by Rius and Plana (1986); other, more complex, formulas are found in the literature (e.g., www.handbookofmineralogy.org). In LDHs, sodium and other large cations can enter as interlayer hydrated complexes.

Exchange experiments

The specific starting composition of materials

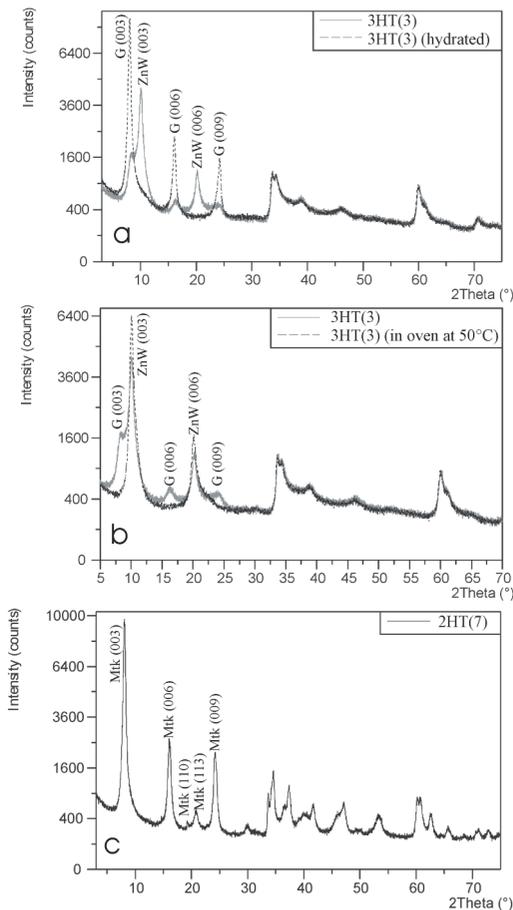


Figure 2. (a) XRD pattern ($\lambda = 1.5405 \text{ \AA}$) of synthetic LDH (sample 3HT(3), Zn/Al ratio ~ 3) compared with the XRD pattern of the same material after permanence in a water-saturated environment and (b) left in oven at 50 °C; (c) XRD pattern of synthetic LDH (sample 2HT(7), Zn/Al ratio ~ 2). ZnW = zincowoodwardite; G = glaucocerinite; Mtk = motukoreaite.

used as sorbents in the exchange experiments and their empirical formula are listed in Table 1, whereas the results of exchange experiments are reported in Tables 2 and 3, and graphically displayed in Figures 3 and 4. In all experiments, there is a dramatic decrease of As concentration

Table 3. Composition of sorbent phases at the end of exchange experiments.

experiment name	sample	Zn	Al	Na	S	As	As/S	Zn/Al	Δ Na
		mmoles g ⁻¹ *				molar ratios		Δ %	
experiments with 3HTs									
a	3HT(2)	5.69	1.97	<0.01	0.68	0.37	0.5	2.9	-
b	3HT(1)	5.67	2.02	<0.01	0.40	0.67	1.7	2.8	-
c	3HT(1)	5.51	1.95	<0.01	0.19	0.90	4.7	2.8	-
d	3HT(3)	5.61	2.00	<0.01	0.08	0.91	11	2.8	-
experiments with 2HTs									
b	2HT(7)	5.62	3.21	0.14	0.73	0.61	0.8	1.8	-67
c	2HT(7)	5.27	3.08	0.09	0.56	0.75	1.3	1.7	-78
d	2HT(7)	5.30	3.09	0.13	0.44	0.91	2.1	1.7	-68
experiments with a natural LDH									
c	N_LDH	3.45	2.24	<0.01	0.08	0.87	11	1.5	-

Δ Na: difference of the Na contents before and after the experiment

* 1 g of sample referred to the starting composition weight.

in solution in the first 3 hours, and a concomitant increase of S concentration. In experiments 1a and 1b, i.e. at comparatively low starting As concentrations, the removal is almost complete, whereas in the other experiments a certain amount of As remains in solution (i.e., the initial amount of As exceeds the sorbing capacity of the solid: see discussion). The composition of solids shows a specular change, that is, there is loss of S and gain of As in the course of the experiments. At the same time, concentrations of both Zn and Al in solution remain negligible, i.e. the sorbent phase does not dissolve to a significant extent. However, in experiments with 2HT as sorbent we observe a significant loss of Na from the solid (Table 3). The pH always starts

at values ≥ 9 , then slightly decreases. At these conditions, the dominant As species in solution is always HAsO_4^{2-} .

XRD patterns of the sorbent phases after the experiments (Figures 5a and 5b) indicate that, in correspondence of the above chemical changes, there is a certain degree of structural rearrangement. There is a generalized decrease of peak to background ratios, suggesting a certain loss of structural order. Moreover, we see the appearance of an additional peak at $2\theta \sim 12^\circ$ ($d \sim 7.4 \text{ \AA}$). The LDH brucite-like layer may or may not be planar as a function of spatial distribution of sulphate anions on each side of the layer (Tumiati et al., 2008). This factor may influence LDH degree of crystallinity. A fortiori,

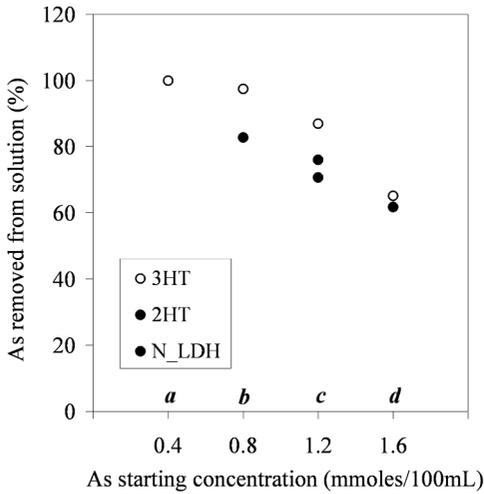


Figure 3. Variation of As concentration in aqueous solution during exchange experiments.

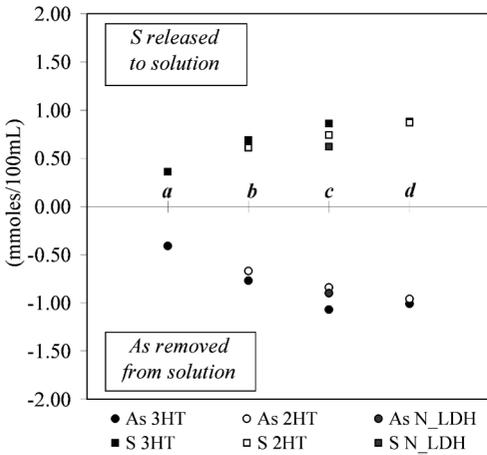


Figure 4. Comparison between S and As variation during exchange experiments.

we expect a further distortion when sulphate anions are partially replaced by arsenate anions.

From the RS of the 3HT(2) sample (Figure 6), six main bands, peaking at 452, 480, 540, 612,

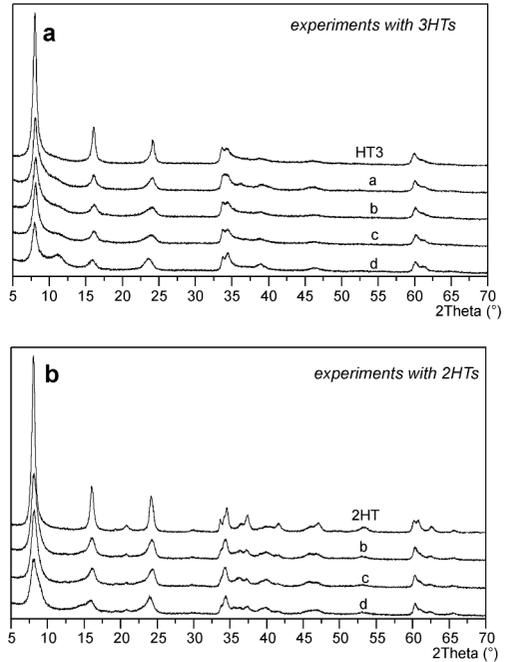


Figure 5. Comparison of XRD patterns ($\lambda = 1.5405 \text{ \AA}$) of synthetic 3HTs (a) and 2HTs (b) before and after the exchange experiment.

980 and 1061 cm^{-1} , can be extracted in the $400\text{--}1100 \text{ cm}^{-1}$ 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 $A(\text{OH})_x$ units ($A = \text{Zn, Al}$) (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). A quite weak band at 1061 cm^{-1} is typical of the symmetric stretching of carbonate molecules, either adsorbed at the sample surface or interlayered. The bands in the $2800\text{--}3700 \text{ cm}^{-1}$ spectral region belong to the vibration of the $-\text{OH}$ units (Figure 7). The experimental spectra

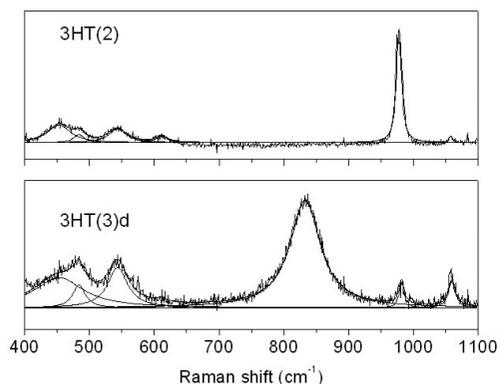


Figure 6. Raman spectra in the 400-1100 cm^{-1} spectral region of the samples 3HT(2) and 3HT(3)d with the calculated best fit curves.

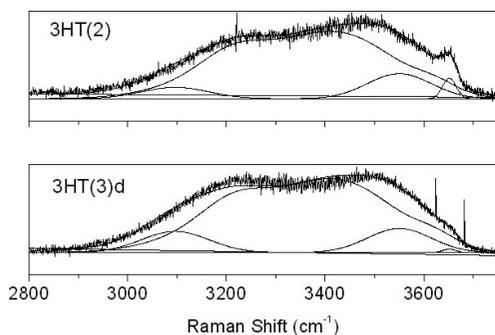


Figure 7. Raman spectra in the 2800-3750 cm^{-1} spectral region of the samples 3HT(2) and 3HT(3)d with the calculated best fit curves.

present a very large band due to different contributions, depending to the kind of linkage of the hydroxyl group to the crystalline structure and to the bond distances. This spectral region is not of specific interest for the following discussion, thus we will not present details of spectra interpretation.

The RS of the sample 3HT(3)d (Figure 6) presents 7 bands in the first spectral region considered (400-1100 cm^{-1}); six of them are

peaked at the same spectral positions, and, as in the sample before the experiment, can be assigned in the same way. 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. However, the fact that the central position does not change suggests that the main texture of the lattice is preserved. The additional band peaking at 830 cm^{-1} is attributed to the vibration of the (AsO_4) units (Myneni et al., 1998). 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. This trend is evidenced in Figure 8, that reports the percentage of the area of Raman bands with respect to the total fit of the experimental spectrum. On the other hand, the bands in the $-\text{OH}$ spectral region do not present significant variations in relative intensities (Figure 7), shapes and positions between the two spectra, except for a slight decrease in the relative intensity of the band at 3650 cm^{-1} in the spectrum after the experiment. Thus, lattice variations between the two samples do not involve these units.

Discussion

The use of LDHs for As removal from contaminated 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-} , that may be more or less readily taken up by LDHs as a function of intercalated anion(s) and surface charge. For instance, Gillman (2006) demonstrated that Mg/Al-Cl and Mg/Al- NO_3 LDHs are capable to reduce initial concentrations of 500-1000 $\mu\text{g/L}$ As to levels well below 10 $\mu\text{g/L}$ (recommended limit for As in drinking water by World Health Organization). As already mentioned in the

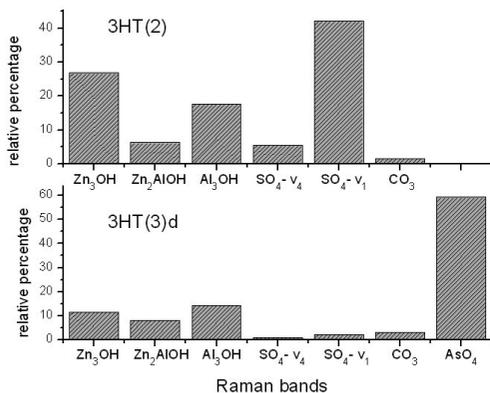


Figure 8. Relative percentage of the Raman bands area of the samples 3HT(2) and 3HT(3)d. The bands are identified with their attributions. See text for details.

Introduction, there were no previous detailed studies of the ability of Zn-Al-sulphate LDHs to remove As from waters, although the exchange properties of Zn-Al-chloride/carbonate LDHs with respect to other oxyanions such as phosphate, chromate, and selenate had been tested (Goh et al., 2008, and references therein). The results presented here document an excellent ability of Zn-Al-sulphate LDHs to remove As from waters. All experimental data are consistent with the interpretation that the main reaction occurring in the experiments is the exchange of arsenate for sulphate in the anionic LDH interlayer, although a certain amount of As could be adsorbed onto the surface rather than incorporated in the structure (see below). At the pH conditions of the experiments the dominant As species in solution is HAsO_4^{2-} . The substitution of this species for SO_4^{2-} would not require charge balance. However, at present we are not able to exactly define whether is that species or the fully deprotonated form AsO_4^{3-} that occurs in our samples. As previously reported, only in some experiments (1a and 1b) there is a total removal of As from solution. This fact is due to 1) in experiments 1c and 1d, As in

the starting solution exceeds the exchange capacity of the sorbent (i.e., one gram of sorbent does not contain enough sulphate to exchange for all arsenate in solution); 2) the exchange efficiency is lower for 2HT (experiments 2b, 2c, and 2d) than for 3HT. This result is consistent with the study by Wang et al. (2009), showing that the amount of As(V) adsorbed by Mg/Al- NO_3 LDHs decreases as the Mg/Al ratio increases from 2 : 1 to 4 : 1. Palmer et al. (2009) found that the mechanism involved in the inclusion of As(V) in Mg/Al LDHs is mainly adsorption on the external surface for Mg/Al = 2 : 1, and both adsorption and intercalation for Mg/Al = 3 : 1 and 4 : 1. Moreover, the 3 : 1 LDH shows the highest amount of As(V) in the structure, followed by the 4 : 1 and 2 : 1 phases.

In the experiment with the natural phase N_LDH (3c), we observe the concurrence of both the previously mentioned factors: the starting phase does not contain enough S to exchange for all As in solution, and its exchange efficiency is lower than that of synthetic 3HT, similar to synthetic 2HT. A noteworthy aspect concerning this natural phase is that it contained a certain amount of As at the beginning of the experiment. This fact did not decrease its ability to take up arsenic from solution to the same extent as the synthetic, As-free, equivalent (Figure 4). Thus, in natural systems Zn-Al-sulphate LDHs may trap As at the moment of formation, and by subsequent interaction with As-rich waters.

Our results clearly indicate a potential use of Zn-Al-sulphate LDHs in the treatment of arsenic-contaminated waters. Moreover, the natural counterparts may be effective traps for this element. Obviously, this potential was tested here in very simple systems, with high As concentrations and no other major anions in solution. In natural systems, even severely contaminated waters typically have As concentrations in the order of less than 1 mmole/L, i.e. orders of magnitude less than

major anionic species such as chloride, sulphate, or carbonate. The behaviour of these LDHs should thus be tested in more realistic systems. However, the results by Ardaù et al. (2011), showing the role of Zn-Al-sulphate LDHs in the attenuation of As contamination in the Baccu Locci stream (Sardinia, Italy), suggest that this potential is not just a mere speculation.

Conclusions

Preliminary experiments show that both synthetic and natural 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 the reduced ionic charge of the brucite-like layer facilitates release of sulphate, which is substituted by arsenate.

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, although there may be a partial release of loosely bound interlayer cations such as Na.

The adequacy of the tested phases as natural traps for As, or in remediation practices, should be confirmed in more complex systems representative of natural waters, where As species coexist with other, more abundant, anions.

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