



Article

# A Comparison among Synthetic Layered Double Hydroxides (LDHs) as Effective Adsorbents of Inorganic Arsenic from Contaminated Soil–Water Systems

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**Abstract:** The need for cost-effective adsorbents of inorganic arsenic (As(III) and As(V)) stimulates the academia to synthesize and test novel materials that can be profitably applied at large-scale in most affected areas worldwide. In this study, four different layered double hydroxides (Cu-Al-, Mg-Al-, Mg-Fe- and Zn-Al-LDH), previously synthesized and studied for As(III) removal capacity, were evaluated as potential adsorbents of As(V) from contaminated systems, in absence or presence of common inorganic anions ( $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{H}_2\text{PO}_4^-$ ). The As(V) desorption by  $\text{H}_2\text{PO}_4^-$  was also assessed. Lastly, the As(V) adsorption capacities of the four layered double hydroxides (LDHs) were compared with those observed with As(III) in a complementary paper. All the LDHs adsorbed higher amounts of As(V) than As(III). Fe-Mg-LDH and Cu-Al-LDH showed higher adsorption capacities in comparison to Mg-Al-LDH and Zn-Al-LDH. The presence of competing anions inhibited the adsorption of two toxic anions according to the sequence:  $\text{Cl}^- < \text{F}^- < \text{SO}_4^{2-} < \text{HCO}_3^- < \text{H}_2\text{PO}_4^-$ , in particular on Mg-Al-LDH and Zn-Al-LDH. The kinetics of As(V) desorption by  $\text{H}_2\text{PO}_4^-$  indicated a higher occurrence of more easily desorbable As(V) on Zn-Al-LDH vs. Cu-Al-LDH. In conclusion, synthetic Cu- and Fe-based LDHs can be good candidates for an efficient removal of inorganic As, however, further studies are necessary to prove their real feasibility and safety.

**Keywords:** inorganic arsenic contamination; layered double hydroxides; arsenate; arsenite; adsorption; Langmuir isotherm; competing anions; adsorption inhibition; kinetics of desorption; phosphate

## 1. Introduction

Arsenic (As) contamination of soil and groundwater is one of the most serious problems for human health worldwide [1,2]. Ingestion of inorganic-As is a main pathway leading to chronic human exposure, strong cytotoxic effects to both macrophages and lymphocytes, high cancer risks and other negative health effects, such as dermal and cardiovascular diseases, hypertension and diabetes mellitus [3–7]. Due to the high toxicity, the World Health Organization (WHO) recommends a maximum contamination limit of  $10 \mu\text{g As L}^{-1}$  in drinking water [8], the principal route of As intake by humans. Arsenite (As(III)) and arsenate (As(V)) are the two inorganic forms of As generally present in the environment [9,10]. Arsenic occurs in more than 200 different mineral forms, of which about 60% are arsenates, sulfides and sulfosalts make 20% and arsenides, arsenites, oxides, silicates and elemental arsenic make the remaining 20% [11]. In soil environments, inorganic As is often associated with Fe (hydr)oxides and multiple processes/reactions govern its release into groundwater, including abiotic or biotically mediated oxidation-reduction and ligand exchange reactions [12]. The pH and redox

potential (Eh) are two important parameters regulating the dynamics and speciation of As. At a pH lower than 6.9 under oxidizing conditions, the  $\text{H}_2\text{AsO}_4^-$  negatively-charged As(V) species is the major anion, while at higher pH values,  $\text{HAsO}_4^{2-}$  is the predominant species. For As(III), the uncharged  $\text{H}_3\text{AsO}_3$  species is predominant at a pH lower than 9.0 under reducing conditions [8].

It is therefore crucial to mitigate the occurrence, mobility and bioavailability of As in the soil–water systems. One of the most feasible and effective techniques for the remediation of contaminated environments is the adsorption on highly-affine adsorbents [13,14]. In the last decades, the scientific community was thus prone to synthesize novel adsorbing materials that could be profitably applied, at low cost, in the most affected areas worldwide, which often tackle As contamination issues with scarce financial resources [15].

Recently, a class of anionic clays known as layered double hydroxides (LDHs) was found to be particularly effective in the removal of inorganic As from contaminated solutions [16,17]. LDHs are easy-to-synthesize minerals, very similar to the green rusts naturally occurring in hydromorphic soils under reducing conditions, due to the slow oxidation of Fe [18,19]. In this type of soil, widely exploited for agricultural purposes to produce rice (a staple food worldwide), where the reducing conditions of aquifers promote the dissolution of large amounts of As in the groundwater [3], the presence of effective adsorbents such as LDH-based green rusts may strongly mitigate the mobility of inorganic As at the soil–water interface.

The term “layered double hydroxides” refers to structural characteristics, due to the presence of two metallic cations in the lamella of these compounds [17]. LDHs can be represented by the general formula  $(\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_6)^{x+} ((\text{A}^{n-})_{x/n} m \text{H}_2\text{O})^{x-}$ , where  $x$  is the molar ratio  $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ , taking values between 0.20 and 0.33, while  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are divalent (Ca, Mg, Co, Fe, Cu, Ni, Mn) and trivalent metal cations (Al, Fe, Cr), respectively, and A is an interlayer anion (e.g.,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ) of valence  $n$ . These adsorbents are composed of positively-charged brucite-like sheets and the positive charges are balanced by intercalation of anions in the hydrated interlayer regions [20,21]. The LDHs have relatively weak interlayer bonding and, as a consequence, the original anions adsorbed in the interlayers are easily exchanged with many inorganic and organic anions by simple ion exchange methods [22]. The point of zero charge (PZC) of these materials was reported to be in the range 7–9 [23].

In a complementary study, we assessed the ability of four different LDHs (Cu-Al-, Mg-Al-, Mg-Fe- and Zn-Al-LDH) in removing As(III) from aqueous systems in the absence or presence of inorganic anions [24]. In this experimental work, we aimed to study the adsorption capacity of the four previously-synthesized LDHs for As(V) in the presence of some of the most abundant inorganic anions of soil–water systems (i.e., bicarbonate ( $\text{HCO}_3^-$ ), chloride ( $\text{Cl}^-$ ), fluoride ( $\text{F}^-$ ), phosphate ( $\text{H}_2\text{PO}_4^-$ ), sulfate ( $\text{SO}_4^{2-}$ )). Specifically, we studied: (i) the adsorption isotherms of As(V) onto Cu-Al-, Mg-Al-, Mg-Fe- and Zn-Al-LDH, at pH = 7 and 20 °C; (ii) the effect of common competing anions ( $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{H}_2\text{PO}_4^-$ ) on the As(V) adsorption on LDH surfaces at different molar ratios: anion/As(V) = 1, 2 and 3, at 50% of surface coverage; and (iii) the kinetics of As(V) desorption by  $\text{H}_2\text{PO}_4^-$  at pH = 7 on Cu-Al- and Zn-Al-LDH, with a  $\text{H}_2\text{PO}_4^-/\text{AsO}_4$  molar ratio of 3. Lastly, the performance of the four synthetic LDHs in the adsorption of As(V) was compared with the findings obtained with As(III), discussed in a complementary study [24].

## 2. Materials and Methods

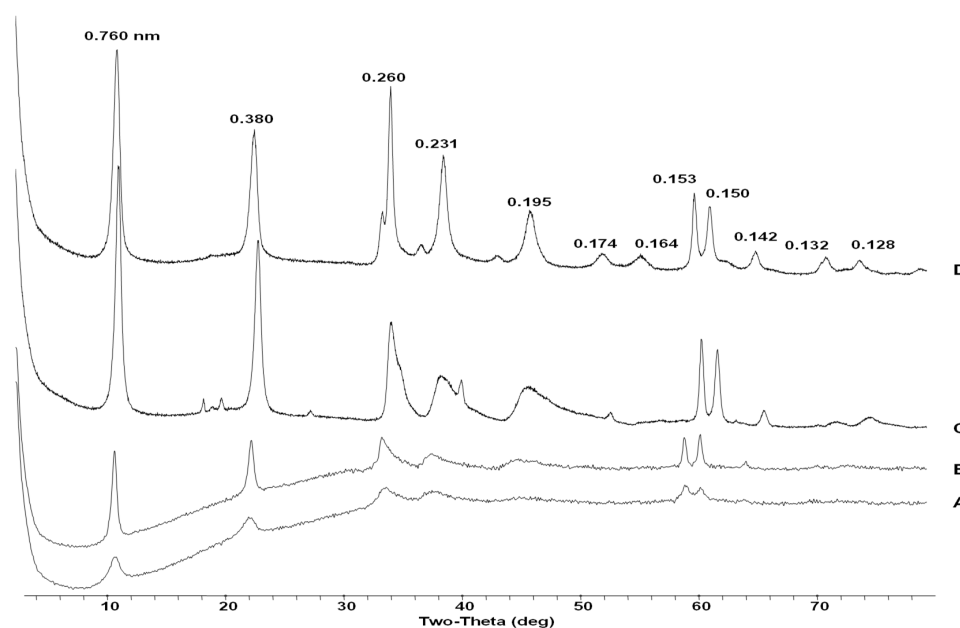
### 2.1. Synthesis of the Four Different Layered Double Hydroxides

The four LDHs were synthesized according to the coprecipitation method of Costantino and Pinnavaia [21]. A comprehensive and detailed description of the synthesis procedure is reported in Pigna et al. [24]. Briefly, proper amounts of solutions containing salts of either Mg, Cu or Zn and either Al or Fe (initial divalent/trivalent anion molar ratio of 2) were mixed under stirring at room

temperature to NaOH solutions at pH = 10. The pH was kept constant for 24 h, then the suspensions were washed, centrifuged, dialyzed for 15 days, freeze-dried and gently pulverized.

## 2.2. LDHs Characterization

The LDHs were characterized by X-ray diffraction (XRD). The patterns of randomly oriented samples were the results of eight summed signals. The equipment (Rigaku diffractometer, Tokyo, Japan equipped with a Cu X-ray source) and its setting up (Cu K $\alpha$  radiation generated at 40 kV and 30 mA and a scan speed of 2° 2 $\theta$  min<sup>-1</sup>) are also described elsewhere [24]. Specific surface area of different LDH complexes was determined by assessing H<sub>2</sub>O adsorption by each sample at 20% of relative humidity, according to the Quirk method [25]. The outcomes of these characterizations are widely described in a complementary study [24]. Briefly, the authors stated that the four synthetic LDHs showed all the characteristic sharp (at 0.760, 0.380, 0.260, 0.153 and 0.150 nm) and asymmetric (at 0.231 and 0.195 nm) peaks of hydrotalcite. X-ray diffractograms (Figure 1) of Mg-Al-LDH (C) and Zn-Al-LDH (D) showed narrow and sharp peaks indicating a well-crystalline structure, while the peaks of Mg-Fe-LDH (A) and Cu-Al-LDH (B) were broader and weaker, thus evidencing a lower degree of crystallinity and particle size [24]. As a consequence, the two poorly-crystalline LDHs showed a surface area 30% higher than that of the two more crystalline LDHs (Table 1).



**Figure 1.** Powder X-ray diffraction patterns of Mg-Fe (A), Cu-Al (B), Mg-Al (C) and Zn-Al (D) layered double hydroxides (modified from Pigna et al. [24]).

**Table 1.** Surface area, Langmuir maximum adsorption capacity ( $S_m$ ), K value (K) and coefficient of determination ( $R^2$ ), as obtained from As(V) adsorption isotherms onto the four layered double hydroxides (LDHs).

LDH Sample	Surface Area	$S_m$	K	$R^2$
	$m^2 g^{-1}$	$mmol kg^{-1}$		
Zn-Al-LDH	200 ± 10	1384 (569) *	10.4 (2.3) *	0.85
Mg-Al-LDH	210 ± 10	1431 (562)	13.4 (2.7)	0.86
Cu-Al-LDH	305 ± 14	1723 (760)	18.8 (9.8)	0.88
Mg-Fe-LDH	280 ± 12	1916 (1312)	15.0 (4.0)	0.90

\* Values in parentheses indicate the  $S_m$  and K values of As(III) adsorption isotherms on the LDHs (from Pigna et al. [24]).

### 2.3. Arsenate Adsorption Isotherms

Each LDH sample (100 mg, in triplicate) was suspended in 0.005 mol L<sup>-1</sup> KCl at pH = 7 and 20 °C in 25 mL Erlenmeyer flasks. Varying volumes of 0.1 mol L<sup>-1</sup> Na<sub>2</sub>HAsO<sub>4</sub> · 7H<sub>2</sub>O solution were added to attain an initial As(V) concentration ranging from 5 · 10<sup>-4</sup> to 1 · 10<sup>-2</sup> mol L<sup>-1</sup>. By a stirred pH-stat apparatus, 0.1 or 0.01 mol L<sup>-1</sup> HCl or KOH solutions were added to each suspension to keep the pH constant at pH = 7. The final volume was adjusted to 20 mL with 0.01 mol L<sup>-1</sup> KCl in all the flasks. The suspensions were shaken (24 h at 20 °C) by magnetic stirrer, centrifuged (10,000 rpm for 20 min) and filtered by 0.22 µm membrane filters.

### 2.4. Arsenate Adsorption in the Presence of Competing Anions

In 25 mL Erlenmeyer flasks, each LDH (100 mg, in triplicate) was suspended in solutions containing 0.005 mol L<sup>-1</sup> KCl and proper volumes of 0.1 mol L<sup>-1</sup> Na<sub>2</sub>HAsO<sub>4</sub> · 7H<sub>2</sub>O (to have 50% of surface coverage according to adsorption isotherms) at pH = 7 and 20 °C. Simultaneously, suitable volumes of solution containing either Cl<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> or H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, were added to have initial anion/As(V) molar ratios (R) equal to 1, 2, and 3. The final volume was adjusted to 20 mL with 0.01 mol L<sup>-1</sup> KCl in all the flasks. The suspensions were stirred for 24 h at 20 °C, at a pH of 7 kept constant by the addition of 0.1 or 0.01 mol L<sup>-1</sup> HCl or KOH by a pH-stat apparatus. The suspensions were then centrifuged (10,000 rpm for 20 min) and filtered by 0.22 µm membrane filters.

### 2.5. Kinetics of Desorption of As(V) by H<sub>2</sub>PO<sub>4</sub><sup>-</sup>

Cu-Al-LDH and Zn-Al-LDH (100 mg each, in triplicate) were suspended in solutions containing 0.005 mol L<sup>-1</sup> of KCl and proper volumes of 0.1 mol L<sup>-1</sup> Na<sub>2</sub>HAsO<sub>4</sub> · 7H<sub>2</sub>O (to have 50% of surface coverage according to adsorption isotherms) at pH = 7 and 20 °C in 25 mL Erlenmeyer flasks and kept to react under stirring for 24 h at constant pH (7). Preliminary kinetics of adsorption (not shown) demonstrated that after 24 h all the As(V) added (800 mmol kg<sup>-1</sup>) was completely adsorbed by LDHs. Then, proper volumes of solution containing H<sub>2</sub>PO<sub>4</sub><sup>-</sup> were added under stirring to the suspensions (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/As(V) molar ratio 3) to induce As(V) desorption. The kinetics of As(V) desorption by H<sub>2</sub>PO<sub>4</sub><sup>-</sup> was monitored over time (from 0.16 to 48 h).

### 2.6. Arsenate Determination

A Dionex DX-300 Ion Chromatograph (Dionex Co Sunnyvale, CA, USA), equipped with Ion Pac As11 column (4.0 mm) and autosuppressed by CD20 Conductivity Detector (eluent: 0.05 mol L<sup>-1</sup> NaOH, flow rate: 1 mL min<sup>-1</sup>), was used to measure As(V) concentration in all the filtrates. Standard concentrations ranged from 0.2 to 2 mmol L<sup>-1</sup>. The amount of As(V) adsorbed was determined by subtracting the final from initial concentrations. The efficiency (%) of each anion in the inhibition of As(V) adsorption on LDHs was calculated by subtracting the As(V) adsorbed in the presence of the anion from As(V) adsorbed in the absence of the anion, divided by the As(V) adsorbed in the absence of the anion. A quality check of the analytical measurements (repeatability and precision) was carefully carried out.

### 2.7. Statistical Analysis

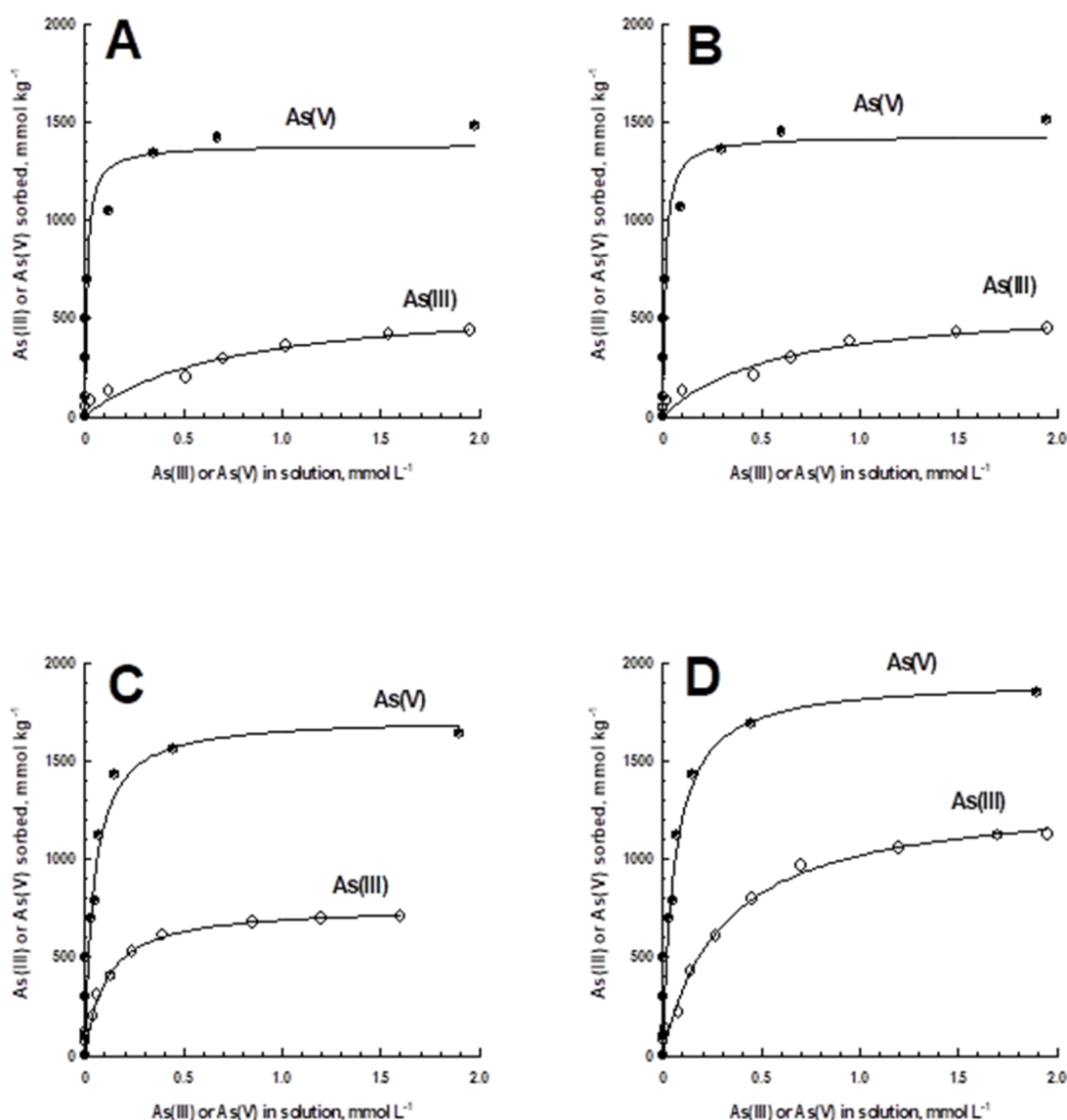
One-way (post hoc test: HSD Tukey test) analysis of variance (ANOVA) was performed by the software IBM SPSS Statistics v23 (Armonk, NY, USA). Statistical differences were assumed at  $p < 0.05$ .

## 3. Results and Discussion

### 3.1. Arsenate Adsorption Isotherms

The adsorption isotherms of As(V) onto LDHs at pH = 7 are shown in Figure 2. The adsorption isotherms of As(III) on the four LDHs, described in Pigna et al. [24], are also included in Figure 2 for

comparison purposes with As(V) data. The As(V) adsorbed onto the LDHs conformed to the Langmuir equation [26], reported and well-explained elsewhere [23,24].



**Figure 2.** Adsorption isotherms of As(III) and As(V) onto Zn-Al (A), Mg-Al (B), Cu-Al (C) and Mg-Fe (D) layered double hydroxides, at pH = 7 and 20 °C, after 24 h of reaction time (As(III) data from Pigna et al. [24]).

The shape of the As(V) adsorption isotherms at pH = 7 on the four LDH samples can be classified as an H-type curve (Figure 2). The H-type is a high affinity isotherm, characteristic of a strong adsorbate–adsorptive interaction, where even low As(V) concentrations added to the system are rapidly and almost completely adsorbed on the LDH adsorption sites. H-shaped isotherms of As(V) on other well-known adsorbents, such as ferrihydrite, goethite, hematite, Al(OH)<sub>x</sub> and Mn oxides, were also highlighted in recent literature [13,27,28]. According to Pigna et al. [24], the shape of As(III) adsorption isotherms on Cu-Al-LDH and Mg-Fe-LDH can be described by an H-type curve as well, while the shape of As(III) adsorption isotherms on Mg-Al-LDH and Zn-Al-LDH can be classified as a typical L-type curve.

According to the isotherm K value (i.e., a constant related to the binding energy), As(V) showed the highest affinity for Cu-Al-LDH binding sites (K = 18.8), then for the adsorbing surfaces of Mg-Fe-LDH

( $K = 15.0$ ), Mg-Al-LDH ( $K = 13.4$ ) and Zn-Al-LDH ( $K = 10.4$ ) (Table 1). This trend may indicate that the electrostatic interactions, basically occurring in the interlayer region between the positive LDH charges and the toxic anion, might also be integrated by stronger bonds directly involving surface Cu or Fe ions and As(V) to form stable inner-sphere complexes. A similar tendency of  $K$  values was also observed with As(III), although at lower binding energies (Table 1 and Pigna et al. [24]). Recently, Kang et al. [29], studying the adsorption of As(V) and  $F^-$  on calcinated Mg-Fe-LDH by XRD, Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS), demonstrated that the adsorption mechanism involved surface adsorption, ion exchange interaction and original LDH structure reconstruction by rehydration of mixed metal oxides and concomitant intercalation of  $F^-$  and As(V) ions into the interlayer region. Moreover, by an XRD study, Bagherifam et al. [1] found that the main underlying adsorption mechanism of As(III) and As(V) on Zn-Al- $SO_4$  LDHs might be the exchange on the external surfaces and edges, but possibly some topotactic exchange may occur through the substitution of As ions with  $SO_4^{2-}$  in the interlayer region. Similarly, Guo et al. [30], studying the adsorption of As(V) onto Cu-Mg-Fe-La-LDHs by XRD, FT-IR and SEM, postulated that As(V) adsorption by LDHs is regulated by the ion exchange and the ligand exchange process with the layer  $OH^-$  group which caused inner-sphere As(V) complexes.

The maximum As(V) adsorption capacity ( $S_m$ ) of the Cu-Al and Mg-Fe-based LDHs was found to be much higher than that of the Mg-Al- and Zn-Al-based LDHs (Table 1). In particular the Mg-Fe-LDH showed the highest value of  $S_m$  ( $1916 \text{ mmol kg}^{-1}$ ) and the best fit with Langmuir isotherm model (highest coefficient of determination:  $R^2$ ), probably for the presence of Fe in the mineral layered structure, an element which was proven to be highly affine for As(V) ions [28,31]. On the other hand, the high  $S_m$  value of the Cu-Al-LDH complex ( $1723 \text{ mmol kg}^{-1}$ ) is basically attributable to the high surface area of this sample ( $305 \text{ m}^2 \text{ g}^{-1}$ , Table 1) and likely to the presence of Cu, which may have favored the formation of a poorly-crystallized precipitate particularly affine for As(V) ions [32]. This behavior was also previously observed with As(III) [24].

The comparison between the As(V) adsorption isotherms on the four LDHs with those discussed by Pigna et al. [24] (Figure 2), revealed that the Mg-Fe-LDH is the complex that adsorbed the greatest amounts of both anions ( $S_m$  of  $1916$  and  $1312 \text{ mmol kg}^{-1}$  for As(V) and As(III), respectively), while the other samples, in particular Mg-Al-LDH and Zn-Al-LDH, adsorbed the two anions at a lower extent. According to the isotherm  $K$  values, the Cu-Al-LDH was the complex which adsorbed the two toxic anions with the highest binding energy (Table 1 and Pigna et al. [24]). Thus, although the Cu-Al-based LDH did not show the maximum As(III) or As(V) adsorption capacities ( $S_m$ ) of the Mg-Fe-based LDH, it can be considered a feasible and reliable adsorbent for inorganic-As contaminated soil–water systems. As stated by Guo et al. [30], transition metal oxides, especially those containing Cu, show good potential catalytic properties. Recently, Lu et al. [33] studied the adsorption of As(V) onto Zn-Fe-LDH and demonstrated that this adsorbent removed very high amounts of As(V), greater than those observed in our study using Zn-Al-LDH or Mg-Fe-LDH. Thus, the presence of Cu and Fe in LDH samples evidently promotes the removal of As(V) from contaminated solutions. Conceivably, the possible use of a novel synthetic Cu-Fe-LDH could be very promising. To the best of our knowledge, only Guo et al. [30] synthesized a Cu-Fe-based LDH and studied its adsorption performance for As(V) in aqueous solutions. Thus, the adsorption behavior of novel LDH samples towards inorganic As is worth to be investigated further.

### 3.2. Arsenate Adsorption in the Presence of Competing Inorganic Anions

The adsorption of As(V) on Cu-Al-, Mg-Al-, Mg-Fe- and Zn-Al-LDH at  $pH = 7$  and at 50% of surface coverage, in the presence of increasing amounts of inorganic ligands (either  $Cl^-$ ,  $F^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$  or  $H_2PO_4^-$ ), with initial anion/As(V) molar ratios = 1, 2 and 3, after 24 h of reaction, are shown in Tables 2–4. The efficiency (%) of the competing anions in the inhibition of As(V) adsorption on LDHs is reported in Figure 3, in comparison with the inhibition of As(III) observed by Pigna et al. [24].

**Table 2.** Arsenate adsorption ( $\text{mmol kg}^{-1}$ ) in the presence of competing inorganic anions on the four LDHs, after 24 h of reaction at  $\text{pH} = 7$  and  $20^\circ\text{C}$ . Initial anion/As(V) ratio equals to 1, with 50% of surface coverage.

Sample	As(V) Added	As(V) Adsorbed Alone	As(V) + $\text{Cl}^-$	As(V) + $\text{F}^-$	As(V) + $\text{SO}_4^{2-}$	As(V) + $\text{HCO}_3^-$	As(V) + $\text{H}_2\text{PO}_4^-$
	$\text{mmol kg}^{-1}$						
Zn-Al-LDH	700	680 a <sup>°</sup>	635 ab (6.6) *	610 bc (10.3) *	605 bc (11.0) *	580 c (17.2) *	510 d (25.0) *
Mg-Al-LDH	700	690 a	650 ab (5.8)	645 ab (6.5)	630 bc (8.7)	590 c (14.5)	520 d (24.6)
Cu-Al-LDH	800	780 a	760 a (2.5)	745 a (4.5)	730 a (6.4)	720 ab (7.7)	660 b (15.4)
Mg-Fe-LDH	900	850 a	830 a (2.3)	820 a (3.5)	805 a (5.3)	785 a (7.6)	700 b (17.6)

<sup>°</sup> Different letters in the same row indicate significant differences according to one-way ANOVA, HSD Tukey test ( $p < 0.05$ ). \* Values in parentheses refer to the percentage of inhibition of As(V) adsorption on LDHs due to the presence of the competing anion.

**Table 3.** Arsenate adsorption ( $\text{mmol kg}^{-1}$ ) in the presence of competing inorganic anions on the four LDHs, after 24 h of reaction at  $\text{pH} = 7$  and  $20^\circ\text{C}$ . Initial anion/As(V) ratio equals to 2, with 50% of surface coverage.

Sample	As(V) Added	As(V) Adsorbed Alone	As(V) + $\text{Cl}^-$	As(V) + $\text{F}^-$	As(V) + $\text{SO}_4^{2-}$	As(V) + $\text{HCO}_3^-$	As(V) + $\text{H}_2\text{PO}_4^-$
	$\text{mmol kg}^{-1}$						
Zn-Al-LDH	700	680 a <sup>°</sup>	615 b (9.6) *	580 bc (14.7) *	575 bc (15.4) *	545 c (19.8) *	400 d (41.2) *
Mg-Al-LDH	700	690 a	635 b (8.0)	600 bc (13.2)	610 bc (11.2)	565 c (18.1)	415 d (39.9)
Cu-Al-LDH	800	780 a	750 ab (4.0)	730 ab (6.4)	725 ab (7.0)	700 b (10.2)	560 c (28.2)
Mg-Fe-LDH	900	850 a	810 ab (4.7)	805 ab (5.3)	790 ab (7.6)	750 b (11.8)	590 c (30.6)

<sup>°</sup> Different letters in the same row indicate significant differences according to one-way ANOVA, HSD Tukey test ( $p < 0.05$ ). \* Values in parentheses refer to the percentage of inhibition of As(V) adsorption on LDHs due to the presence of the competing anion.

**Table 4.** Arsenate adsorption ( $\text{mmol kg}^{-1}$ ) in the presence of competing inorganic anions on the four LDHs, after 24 h of reaction at  $\text{pH} = 7$  and  $20^\circ\text{C}$ . Initial anion/As(V) ratio equals to 3, with 50% of surface coverage.

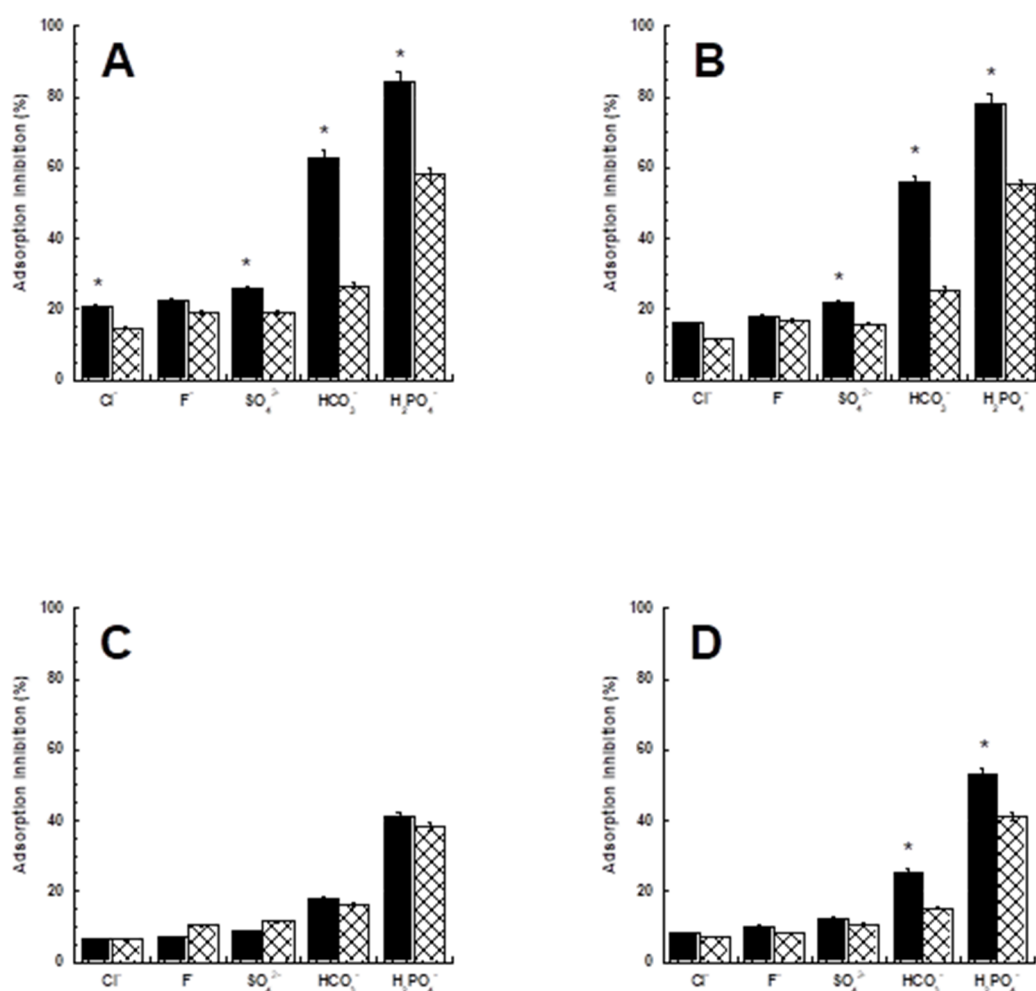
Sample	As(V) Added	As(V) Adsorbed Alone	As(V) + $\text{Cl}^-$	As(V) + $\text{F}^-$	As(V) + $\text{SO}_4^{2-}$	As(V) + $\text{HCO}_3^-$	As(V) + $\text{H}_2\text{PO}_4^-$
	$\text{mmol kg}^{-1}$						
Zn-Al-LDH	700	680 a <sup>°</sup>	580 b (14.7) *	550 b (19.1) *	550 b (19.1) *	500 c (26.5) *	280 d (58.3) *
Mg-Al-LDH	700	690 a	610 b (11.6)	575 b (16.7)	580 b (15.9)	515 c (25.4)	310 d (55.1)
Cu-Al-LDH	800	780 a	730 ab (6.4)	700 bc (10.3)	690 bc (11.5)	670 c (16.2)	480 d (38.5)
Mg-Fe-LDH	900	850 a	790 ab (7.1)	780 bc (8.2)	760 bc (10.6)	720 c (15.3)	500 d (41.2)

<sup>°</sup> Different letters in the same row indicate significant differences according to one-way ANOVA, HSD Tukey test ( $p < 0.05$ ). \* Values in parentheses refer to the percentage of inhibition of As(V) adsorption on LDHs due to the presence of the competing anion.

The inorganic anions showed different competitive abilities in the binary systems, inhibiting the As(V) on LDH adsorption sites in the following increasing order:  $\text{Cl}^- < \text{F}^- \leq \text{SO}_4^{2-} < \text{HCO}_3^- < \text{H}_2\text{PO}_4^-$ , regardless of the initial anion/As(V) molar ratio (Tables 2–4). This order is consistent with that observed by Guo et al. [30], who studied the adsorption of As(V) onto Cu-Mg-Fe-La-LDHs in the presence of either  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , carbonate ( $\text{CO}_3^{2-}$ ) or  $\text{H}_2\text{PO}_4^-$  for 24 h at  $\text{pH} = 6$  and Yang et al. [34] in a competitive adsorption between As(V) and these anions on uncalcined and calcined LDH- $\text{CO}_3$ . Our sequence was also ascertained by Wang et al. [35], in a study assessing the As(V) removal by Mg-Al-LDH in the presence of either  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  or  $\text{H}_2\text{PO}_4^-$  for 2 h at  $\text{pH} = 5$ .

Since LDHs show a greater affinity toward anions with a high ionic charge density [36], the competing anions with a higher ionic charge density had a greater negative impact on the As(V) adsorption. According to the principle of ion exchange, if a competing anion is better suited stereochemically for inclusion into the interlayer of LDHs, it has a greater ability to cause the release of the anion of interest from LDH interlayers [37]. Indeed, many factors may affect the adsorption of

inorganic anions onto LDHs, as the valence, the size and the capacity of each single competitive anion to form outer- or inner-sphere complexes on the surfaces of the minerals [23].



**Figure 3.** Inhibition (%) of As(III) (black bars) and As(V) (checked bars) adsorption by competing inorganic anions from Zn-Al (A), Mg-Al (B), Cu-Al (C) and Mg-Fe (D) layered double hydroxides, after 24 h of reaction at pH = 7 and 20 °C. Initial anion/As(V) ratio equals to 3, with 50% of surface coverage. Asterisks indicate significant differences according to one-way ANOVA, HSD Tukey test (*p* < 0.05).

As regards the behavior of the individual anions, no significant differences between Cl<sup>-</sup> and F<sup>-</sup> in terms of competitive capacity were found, since they are both monovalent and nonspecific anions in solid–liquid interfacial reaction [24]. The competition between anions and As(V) was more prominent in the case of SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>. These anions can be basically bound by outer-sphere complexes by LDH binding sites, but HCO<sub>3</sub><sup>-</sup> anions may form as well more stable inner-sphere complexes [28]. On the other hand, SO<sub>4</sub><sup>2-</sup> ions are able to form bonds of inner-sphere type only at acidic pH values (3.5–4.5), not at sub-neutral pHs [28]. Ardaud et al. [38] studied the influence of selected competing anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, molybdate (MoO<sub>4</sub><sup>2-</sup>), HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) on the removal of As by Zn-Al-LDH from contaminated solutions; these authors demonstrated that only carbonates in the fully deprotonated form (pH > 10) affected the As adsorption significantly. In our study, the most efficient anion in the competitive adsorption with the As(V) was the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> because it essentially forms inner-sphere complexes at pH = 7. It is well-known that As(V) and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> have a similar chemical behavior. Both the oxyanions are specifically adsorbed on soil minerals, mainly on variable charge minerals (Al, Fe and Mn oxides), but also on LDH-based green rusts, forming stable inner-sphere complexes. Actually, these anions may form three different surface complexes onto inorganic soil components:



a monodentate complex, a bidentate-binuclear complex and a bidentate-mononuclear complex, in different proportions depending on surface coverage, pH and nature of the soil adsorbents [14,39–41].

Apart from the chemical properties and behavior of each anion, the efficiency of the competing anions in the inhibition of As(V) adsorption on the four LDH samples was affected by their own adsorption capacities, binding energies towards As(V) ions (Tables 2–4) and thus by the adsorption mechanisms. Accordingly, As(V) adsorption was greatly inhibited on the Mg-Al- and Zn-Al-based LDHs than on the Cu-Al- and Mg-Fe-based LDHs, evidently because of the greater affinity of As(V) for the adsorption sites of the latter complexes. As proved by Wang et al. [35], Mg-Al-LDH basically adsorbs As(V) by Coulombic attraction between the toxic anion and the positively-charged sites of LDH, since the authors did not find any evidence of specific adsorption between the As(V) and Mg-Al-LDH surface by extended X-ray absorption fine structure spectroscopy (EXAFS).

The comparison in the inhibition (%) of As(III) and As(V) adsorption on the four LDHs showed in Figure 3 basically highlighted a higher (significantly higher in the most of the cases) inhibition of As(III) than As(V) by the competing anions, at an initial anion/As(III) or As(V) molar ratio of 3. An opposite trend (with  $F^-$  and  $SO_4^{2-}$ ) or more slight differences between As(III) and As(V) were recognized only on the complex Cu-Al-LDH (Figure 3C). The greater stability of the As(V) on the LDH binding sites, even in the presence of competing anions commonly present at high concentrations in the soil–water systems, can be attributed to the different nature of the bindings with sorbent surfaces. As demonstrated by Goldberg and Johnston [42], As(V) forms inner-sphere surface complexes on both Fe- and Al-based minerals, while As(III) tends to form inner- and outer-sphere surface complexes on Fe-based hydroxides and outer-sphere surface complexes Al-based hydroxides.

### 3.3. Kinetics of Desorption of As(V) by $H_2PO_4^-$

The As(V) desorbed from the Cu-Al- and Zn-Al-LDH by  $H_2PO_4^-$  (initial  $H_2PO_4^-$ /As(V) molar ratio of 3, pH = 7), as a function of time, is shown in Table 5. The amount of As(V) desorbed from the two LDHs increased with time, being characterized by an initial very fast desorption reaction (0.16–10 h), followed by a much slower desorption reaction until a plateau was reached (Table 5). The As(V) desorbed after 10 h by  $H_2PO_4^-$  from Cu-Al-LDH and Zn-Al-LDH surfaces was 31% and 39%, respectively, suggesting that the more easily desorbable As(V), bound by weaker bindings, was more unstably retained by Zn-Al-LDH than Cu-Al-LDH. A similar study performed at pH = 6 by Caporale et al. [23] evidenced that  $H_2PO_4^-$  desorbed greater amounts of easily desorbable As(V) from Mg-Al-LDH in comparison to Mg-Fe-LDH; after 5 min from  $H_2PO_4^-$  addition, these authors found that Mg-Fe-LDH and Mg-Al-LDH released the 42% and 53% of the As(V) bound on their surfaces, respectively. On the other hand, Pigna et al. [27] assessing the kinetics of As(V) desorption by  $H_2PO_4^-$  (initial  $H_2PO_4^-$ /As(V) = 4) at pH = 6 from Al (gibbsite and noncrystalline Al hydroxide) and Fe (ferrihydrite and goethite) (oxy)hydroxides, found that only ~25% and ~15% of the As(V) were desorbed from the Al- and Fe-based minerals, respectively. The higher desorption of the As(V) by  $H_2PO_4^-$  from LDH adsorbing sites in comparison to Al and Fe (oxy)hydroxides is mainly due to different adsorption mechanisms (Coulombic attraction vs. specific adsorption) between adsorbent and adsorbate and thus to the binding energy and bond's strength. Therefore, although synthetic LDHs show higher As(V) adsorption capacity (Table 1) in comparison to Al and Fe (oxy)hydroxides [27], they can more easily release the toxic anion in solution in the presence of a strong competitor for adsorbing sites such as  $H_2PO_4^-$ . However, it was demonstrated by Sommella et al. [14] that when As(V) is co-precipitated with Mg and Al to form LDHs and thus it lays into the lattice of these minerals, it is more stably retained by LDHs and hence is released less in the environment in the presence of external perturbations.

**Table 5.** Kinetics of desorption of As(V) by  $\text{H}_2\text{PO}_4^-$  on Zn-Al-LDH and Cu-Al-LDH, at pH = 7. Surface coverage about 50% ( $800 \text{ mmol kg}^{-1}$ );  $\text{H}_2\text{PO}_4^-/\text{As(V)}$  molar ratio = 3; residence time of As(V) = 24 h.

Sample	Time with $\text{H}_2\text{PO}_4^-$	As(V) Added	As(V) Desorbed	As(V) Desorption Rate	As(V) Adsorbed	As(V) Adsorption Rate
	h	$\text{mmol kg}^{-1}$	$\text{mmol kg}^{-1}$	%	$\text{mmol kg}^{-1}$	%
Zn-Al-LDH	0.16	800	249 e	31.1 e	551 a	68.9 a
	1.0	800	269 de	33.6 de	531 ab	66.4 ab
	2.5	800	285 cd	35.6 cd	515 abc	64.4 abc
	5.0	800	302 bc	37.8 bc	498 bcd	62.3 bcd
	10	800	311 ab	38.9 abc	489 bcd	61.1 bcd
	24	800	325 ab	40.6 ab	475 cd	59.4 cd
	48	800	332 a	41.5 a	468 d	58.5 d
	Cu-Al-LDH	0.16	800	205 d	25.6 d	595 a
1.0		800	226 c	28.3 cd	574 a	71.8 a
2.5		800	238 bc	29.8 bc	562 ab	70.3 ab
5.0		800	243 bc	30.4 bc	557 ab	69.6 ab
10		800	251 b	31.4 b	549 ab	68.6 ab
24		800	274 a	34.3 a	526 b	65.8 b
48		800	281 a	35.1 a	519 b	64.9 b

Different letters in the same column indicate significant differences according to one-way ANOVA, HSD Tukey test ( $p < 0.05$ ).

#### 4. Conclusions

The adsorption efficiency of cost-effective and easy-to-synthesize adsorbents such as LDHs towards As(V) was tested by different batch experiments aiming at evaluating the adsorption capacity not only in a single system, but also in binary systems, i.e., in the presence of some of the most abundant inorganic anions of soil–water systems, usually occurring at higher concentrations if compared to inorganic-As. Indeed, the aqueous systems adopted in this study can also simulate the soil–water interface in paddy soils, where the mobility and transfer of inorganic As from soil to water may occur to a worrying extent. Moreover, the assessment of adsorption performance of novel synthetic LDHs (Cu-Al- and Zn-Al-LDH, in particular) towards water-soluble inorganic As is one of the most innovative aspects of the current study. The results indicate that the nature, the degree of crystallinity and the chemical composition of the different LDHs strongly affected their adsorption capacities and binding energies towards As(V) ions, and consequently, their ability to stably retain the As(V) on the adsorbing sites, even in the presence of competing anions. Overall, analyzing the data of this study and matching these findings with those found previously with As(III), it clearly emerges that the two most effective LDH complexes in the adsorption of inorganic As (both As(III) and As(V)) are the Fe-Mg-LDH, showing the greatest adsorption capacities ( $S_m$ ), and the Cu-Al-LDH, able to retain more stably and tightly the two toxic anions (even in the presence of competing anions), thanks to very high binding energies ( $K$ ). These findings thus encourage more deeper studies on the two novel adsorbents aiming to better understand the adsorption mechanisms and properties, in order to prove their actual feasibility and safety for human health (e.g., no release of potentially toxic elements such as Al, Cu and Zn in solution arising from the mineral layers) in a potential use at large-scale in the remediation of As-contaminated soil–water systems.

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