



Influences of co-existing species on the sorption of toxic oxyanions from aqueous solution by nanocrystalline Mg/Al layered double hydroxide

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ABSTRACT

The influences of common oxyanions (i.e. nitrate, silica, sulfate, carbonate, and phosphate) and natural organic matter (NOM) on the sorption of arsenate, chromate, bromate and vanadate (toxic oxyanions) by nanocrystalline Mg/Al layered double hydroxide (LDH) were investigated. Besides the type and concentration of the co-existing species, sorption competition was greatly dependent on the solution pH. In general, based on their sorption competitiveness with the toxic oxyanions, the co-existing common oxyanions were ranked in the order of nitrate < silica ≤ sulfate < carbonate < phosphate, while the toxic oxyanions could be ranked in the order of bromate < arsenate ≈ chromate ≤ vanadate, indicating the oxyanions with lower ionic potentials were less preferably sorbed by the LDH. Based on the comprehensive study on sorption of arsenate by the LDH, the decrease in sorption of toxic oxyanions could be attributed to the competition of common oxyanions for common sorption sites on the LDH which predominantly occurred via ion exchange mechanism. NOM inhibited toxic oxyanion sorption through shielding LDH surface sites, directly competing for sorption sites of LDH, and co-precipitating the LDH. The presence of common oxyanions and NOM generally did not affect the mineral stability of the nanocrystalline LDH.

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1. Introduction

Layered double hydroxides (LDHs), whose main layers are positively charged, have recently gained considerable interest for use as effective adsorbents for sequestering toxic oxyanions such as arsenate, chromate, vanadate, etc. [1–5]. They possess high anion exchange capacity, and can be economically synthesized, engineered for specific applications, and also regenerated for reuse. For practical application in removing the toxic oxyanions in aqueous system, the influences of various matrix species in water on the affinity of LDHs for the target oxyanions should be evaluated. Several types of omnipresent oxyanions in the surface waters and wastewaters potentially exert direct competition with the toxic oxyanions for the available sorption sites or alter the surface electronic charge of the LDHs. The prerequisite to successful application of LDHs for removing toxic oxyanions in water treatment is an in-depth understanding of the potential interferences induced by the aqueous matrix species on the sorption reaction.

To date, only a limited number of studies report the effects of common oxyanions such as chloride, nitrate, sulfate, carbonate, and phosphate on the sorption of arsenate by LDHs [6,7]. To the best of

our knowledge, there has been no comprehensive and systematic investigation of the selectivity of LDH for other toxic oxyanions in the presence of various co-existing common oxyanions. The influence of pH which regulates protonation/deprotonation of oxyanions and their speciation should be also evaluated, because the speciation of the oxyanions can affect their ionic potentials and intrinsic binding affinities for sorption sites.

Besides chloride, nitrate, sulfate, carbonate, and phosphate, the dissolved silica is a ubiquitous anion constituent of surface waters, groundwaters, and wastewaters. It is naturally occurring due to weathering of minerals and is constantly dissolving and precipitating over a large part of the earth's surface [8]. The silica concentration in water ranges from a few ppm in surface water to over 100 ppm in water of some wells. Though ubiquitous, there is no information available in the literature on the influence of silica on toxic oxyanion sorption by LDHs.

Besides ionic species, NOM is also commonly present in natural waters and wastewaters, and it has a high tendency to be adsorbed onto sorbent surfaces [9] which could subsequently modify their properties [10]. It has been reported that NOM inhibited arsenic adsorption onto iron oxide surfaces because of the competition between NOM and arsenic for available adsorption sites [11–13]. However, there has no study on how NOM may affect toxic oxyanion sorption by LDHs.

This study investigated the effects of various co-existing species including NOM and common oxyanions such as nitrate, silica, sul-

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fate, carbonate, and phosphate on the sorption of several toxic oxyanions (arsenate, chromate, vanadate and bromate) by a LDH over a wide pH range. The oxyanions investigated have varying molecular properties and ionic potentials (μ), as shown in Table 1. The ionic potential is defined as z/r , where z is the ionic charge and r is the molecular radius [14]. It can greatly influence the degree to which water dipoles are attracted to an anion, and thus the fate or mobility of the anion in the aqueous solution. The LDH investigated was the hydrothermally treated nanocrystalline Mg/Al LDH which possessed high surface area and anion exchange capacity. The effect of co-existing species on the time-dependent sorption of toxic oxyanions and the mineral stability of nanocrystalline LDH were also examined. Chloride, another common anion in waters, was not specifically investigated in this study, but our preliminary study showed that it has a comparable degree of competitiveness with that of nitrate.

2. Materials and methods

2.1. Chemicals

All chemicals used in the experiments were of analytical grade. All solutions were prepared with Milli-Q ultrapure water (18.2 M Ω cm) and the water was adequately purged with N₂ before use. The solutions of toxic oxyanions, i.e. arsenate, bromate, chromate, and vanadate were prepared by dissolving Na₂HAsO₄·7H₂O (Sigma, Assay 99.4%), NaBrO₃ (Merck, Assay 98%), K₂CrO₄ (Merck, Assay 99.5%), and Na₃VO₄ (Aldrich, Assay 99.9%), respectively, in ultrapure water.

Purified magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, Assay 99%) was obtained from HiMedia Laboratories Pvt. Ltd., aluminum nitrate nonohydrate (Al(NO₃)₃·9H₂O, Assay 98%) from Fluka Chemika, and sodium hydroxide (NaOH, Assay 97%) from Scientific Resources. Five types of commonly found oxyanions were used as received: sodium nitrate (NaNO₃, Merck, Assay 99.5%), sodium metasilicate enneahydrate (Na₂SiO₃·9H₂O, Hayashi Pure Chemical, Assay 99%), sodium sulfate anhydrous (Na₂SO₄, BDH, Assay 99%), sodium carbonate anhydrous (Na₂CO₃, Merck, Assay 99.5%), and sodium dihydrogen phosphate (NaH₂PO₄·2H₂O, Merck, Assay 99%). NOM (represented by humic acid) was obtained from Aldrich. Humic acid stock solution was prepared by dissolving a predetermined amount of humic acid sodium salt into ultrapure water followed by filtering through a 0.45- μ m membrane filter (cellulose acetate). Humic acid concentration was expressed as dissolved organic carbon (DOC).

2.2. Synthesis and characterization of nanocrystalline Mg/Al LDH

The nanocrystalline Mg/Al LDH with a Mg:Al ratio of 2:1 used in this study was prepared by fast coprecipitation with subsequent hydrothermal treatment method. The detailed synthesis procedure has been described elsewhere [15]. QuantaChrome Autosorb-1 Analyzer was used to determine the BET surface area and porosity characteristics. Scanning electron microscope (SEM) image was obtained using a JEOL JSM-6340F microscope. Powder X-ray diffraction patterns for the fresh and reacted LDH samples were obtained using Bruker AXS (D8 Advance) XRD ($\lambda = 1.54 \text{ \AA}$). FTIR spectra of the LDH samples as KBr pellets were recorded with a PerkinElmer 2000 FTIR spectrometer. The spectra were collected in transmission mode at a resolution of 4 cm⁻¹, and 100 scans were recorded in the 4000–370 cm⁻¹ to ensure good signal to noise ratio.

2.3. Batch sorption experiment

All the experiments were performed in the air-tight batch sorption system at a sorbent dose of 0.4 g/L and at 25 °C. A toxic oxyanion

Table 1
Molecular properties of various oxyanions investigated in this study.

Oxyanion	Acid dissociation constant (pK _a)	Molecular properties at the investigated pH range of ~8–11.5			Ionic potential, μ (nm ⁻¹)	Reference for molecular radius
		Predominant species	Ionic charge	Molecular radius (nm)		
Toxic oxyanion						
Arsenate	H ₃ AsO ₄ $\xrightarrow{pK_{a1}=2.2}$ H ₂ AsO ₄ ⁻ $\xrightarrow{pK_{a2}=7.0}$ HAsO ₄ ²⁻ $\xrightarrow{pK_{a3}=11.5}$ AsO ₄ ³⁻	HAsO ₄ ²⁻	2	0.248	8.06	Wilkinson et al. [35]
Chromate	H ₂ CrO ₄ $\xrightarrow{pK_{a1}=1.0}$ HCrO ₄ ⁻ $\xrightarrow{pK_{a2}=6.5}$ CrO ₄ ²⁻	CrO ₄ ²⁻	2	0.240	8.33	Wilkinson et al. [35]
Vanadate	H ₃ VO ₄ $\xrightarrow{pK_{a1}=3.5}$ H ₂ VO ₄ ⁻ $\xrightarrow{pK_{a2}=7.8}$ HVO ₄ ²⁻ $\xrightarrow{pK_{a3}=12.5}$ VO ₄ ³⁻	HVO ₄ ²⁻	2	0.260	7.69	Jenkins and Thakur [36]
Bromate	HBrO ₃ $\xrightarrow{pK_{a1}=1.9}$ BrO ₃ ⁻	BrO ₃ ⁻	1	0.214	4.67	David [37]
Common oxyanion						
Nitrate	HNO ₃ $\xrightarrow{pK_{a1}=1.4}$ NO ₃ ⁻	NO ₃ ⁻	1	0.200	5.00	David [37]
Silica	H ₂ SiO ₃ $\xrightarrow{pK_{a1}=6.9}$ HSiO ₃ ⁻ $\xrightarrow{pK_{a2}=9.5}$ SiO ₃ ²⁻	HSiO ₃ ⁻	1	0.204	4.90	David [37]
Sulfate	H ₂ SO ₄ $\xrightarrow{pK_{a1}=3.0}$ HSO ₄ ⁻ $\xrightarrow{pK_{a2}=1.9}$ SO ₄ ²⁻	SO ₄ ²⁻	2	0.230	8.70	Gmelin [38]; Wilkinson et al. [35]
Carbonate	H ₂ CO ₃ $\xrightarrow{pK_{a1}=6.3}$ HCO ₃ ⁻ $\xrightarrow{pK_{a2}=10.3}$ CO ₃ ²⁻	HCO ₃ ⁻ and CO ₃ ²⁻	1 (HCO ₃ ⁻) 2 (CO ₃ ²⁻)	0.163 (HCO ₃ ⁻) 0.185 (CO ₃ ²⁻)	6.13 (HCO ₃ ⁻) 10.81 (CO ₃ ²⁻)	Waddington [39]
Phosphate	H ₃ PO ₄ $\xrightarrow{pK_{a1}=1.7}$ H ₂ PO ₄ ⁻ $\xrightarrow{pK_{a2}=6.5}$ HPO ₄ ²⁻ $\xrightarrow{pK_{a3}=12.1}$ PO ₄ ³⁻	HPO ₄ ²⁻	2	0.238	8.40	Gmelin [38]; Wilkinson et al. [35]

concentration of 0.4 mM was used in this study in order to obtain the approximate maximum sorption capacity of the nanocrystalline LDH. Batch experiments were carried out with each solution containing a target oxyanion with one of the co-existing species investigated. Triplicate measurements were performed for most of the experiments.

Two series of experiments were conducted. For the first series, the effects of co-existing common oxyanions on the sorption of toxic oxyanions having different molecular properties by LDH were investigated. Arsenate, bromate, chromate, or vanadate solutions containing different common oxyanions (i.e. nitrate, silica, sulfate, carbonate, or phosphate) were prepared by dissolving various amounts of their sodium salts in 0.4 mM arsenate, bromate, chromate, or vanadate solutions, and the resultant molar ratios of common oxyanion/toxic oxyanion were 0, 10, and 100. LDH was then added to each of the solutions in 50-mL centrifuge tubes and the suspensions were reacted for 24 h. After centrifugation and filtration, the concentrations of arsenate, chromate, and vanadate were determined by inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer Optima 2000) while the concentration of bromate was determined by ion chromatograph (IC, Dionex ICS-1000).

For the second series of experiment, arsenate was used as a model toxic oxyanion. Kinetic experiments were conducted by adding LDH into solutions containing 0.4 mM arsenate and one of the common oxyanions or NOM at a range of concentrations. The suspensions were then stirred for 6 h, and at selected time intervals, 4 mL samples were extracted, filtered, and the arsenate concentrations were determined. Sufficient agitation (250 rpm) was provided in order to overcome the mass transfer limitation in the batch system. The initial and final pH values as well as the amount of precursor metals (Mg and Al) released were monitored. For pH-dependent sorption experiments, hydrated LDH suspensions and arsenate solutions containing nitrate, silica, sulfate, carbonate, phosphate, or NOM, both with pre-adjusted pH ranging from 4 to 10, were mixed and stirred for 4 h. Intermittent pH adjustment was carried out using HNO_3 and NaOH , and such adjustment resulted in less than 1% increment in the total volume. The use of buffer was intentionally avoided in this study in order to prevent the addition of another foreign species to the solution matrix that might complicate the analysis of sorption results. The amount of Mg and Al released from LDH at different pH in the presence of common oxyanions and NOM was also assessed.

3. Results and discussion

3.1. Properties of nanocrystalline Mg/Al LDH

The LDH synthesized in this study has a specific surface area of $127 \text{ m}^2/\text{g}$, a pore volume of $0.31 \text{ cm}^3/\text{g}$, and a pore size of 8 nm. The LDH was observed as well-formed and overlapping plate-like particles with a uniform size ranging from 40 to 100 nm (Fig. 1). Its positive charge engineered during synthesis was primarily balanced by nitrate intercalated between its main layers. The XRD patterns of the freshly synthesized LDH and LDH reacted with different matrix solutions are depicted in Fig. 2. Three major peaks at lower 2θ values, i.e. 11.5° , 22.9° , and 34.7° , that are associated with the respective (003), (006), and (009) planes of characteristic LDH compounds were observed for all the LDH samples. After reaction in all but the carbonate solution, the intensities of LDH reflections decreased. After reaction in the carbonate solution, the carbonate intercalated into the interlayer region of LDH and subsequently formed prismatic interlayer sites that strongly accommodated carbonate ions with their planes parallel to the layers, resulting in the strong LDH peaks comparable to the fresh LDH.

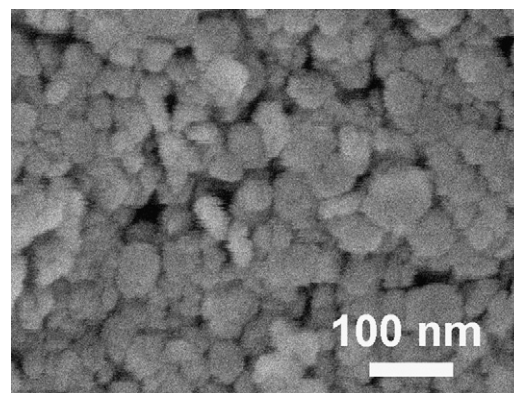


Fig. 1. SEM image of freshly synthesized LDH particles.

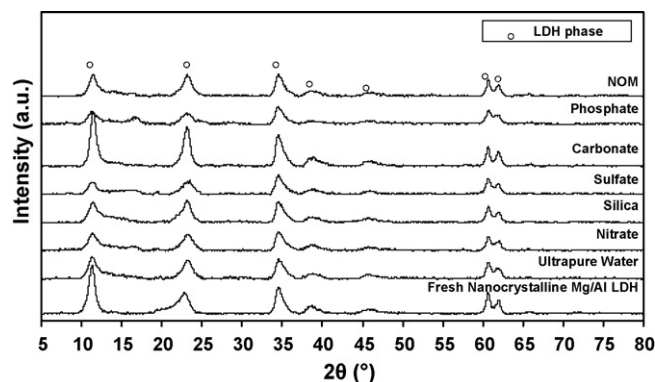


Fig. 2. XRD patterns of freshly synthesized LDH and LDH after reaction in ultrapure water, common oxyanion, and NOM solutions.

The FTIR spectra of the fresh and reacted LDHs (Fig. 3) show that the spectrum is broadly divided into three main adsorption regions: (1) $4000\text{--}2000 \text{ cm}^{-1}$, (2) $2000\text{--}1200 \text{ cm}^{-1}$, and (3) $1200\text{--}400 \text{ cm}^{-1}$. The fairly broad band between 3400 and 3500 cm^{-1} in each spectrum corresponds to OH stretching vibration of hydrogen-bonded groups in the brucite-like sheets. In the second region, the peak at 1636 cm^{-1} in each of the spectra refers to the water bending vibration of the interlayer water whereas the strong peak at 1384 cm^{-1} is due to the nitrate intercalated in the interlayer space. The peaks at 1390 and 1559 cm^{-1} in the spectrum of the reacted sample in the presence of NOM could be due to the symmetric and asymmetric vibrations of carboxylate in humic acid [10] and the diminution of the nitrate peak could be ascribed to the coverage of NOM on LDH due to adsorption. The band observed at 1363 cm^{-1} in the spec-

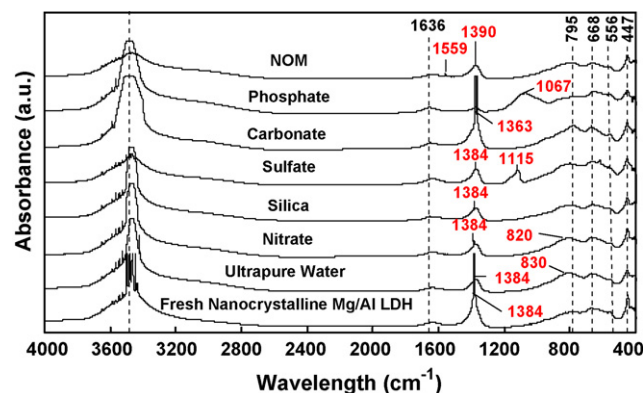


Fig. 3. FTIR spectra of freshly synthesized LDH and LDH samples reacted with arsenic in ultrapure water and in solutions containing a common oxyanion or NOM.

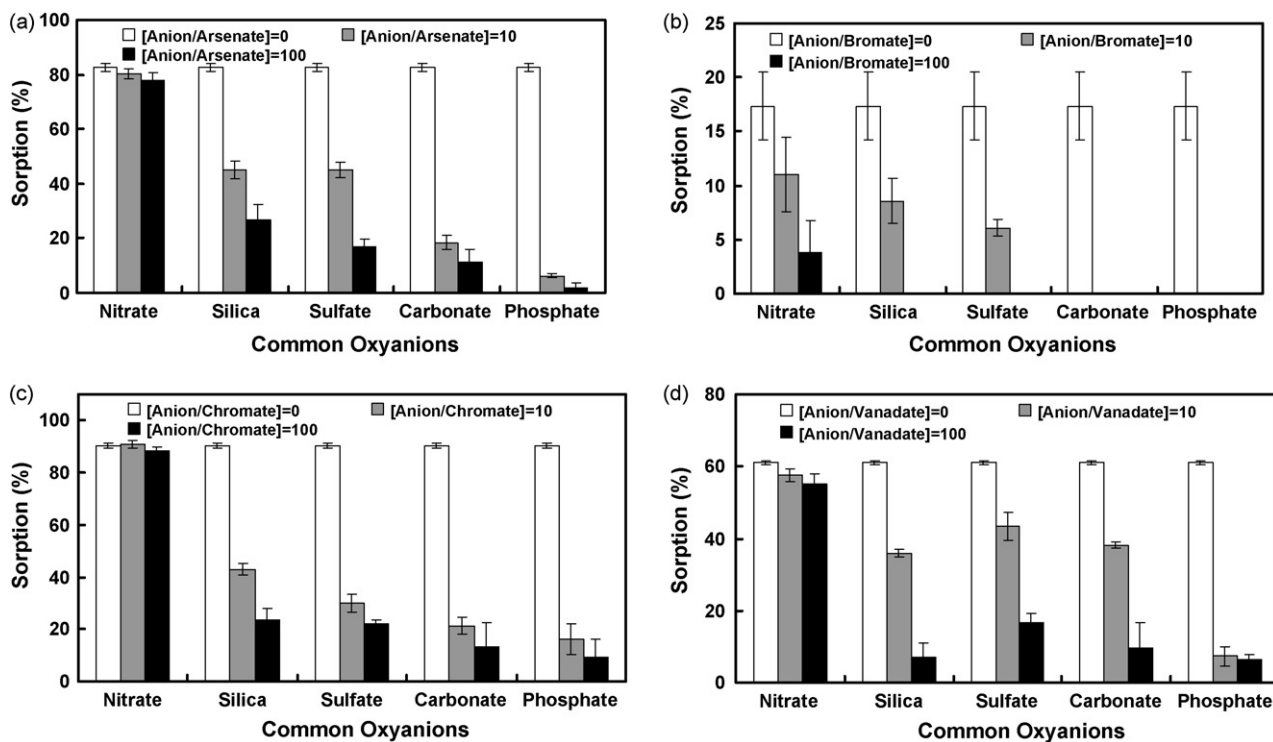


Fig. 4. Influences of common oxyanions on the sorption of (a) arsenate, (b) bromate, (c) chromate, and (d) vanadate by LDH (pH 8–11.5, time = 24 h, dose = 0.4 g/L, toxic oxyanion concentration = 0.4 mM).

trum of the reacted sample in the presence of carbonate could be assigned to C–O bending vibration of CO_3^{2-} [16], thereby suggesting the intercalation of carbonate into LDH. The spectral features at 1115 and 1067 cm^{-1} in the third region could be attributed to the S–O vibration and P–O vibration [17], respectively, indicating the sorbed sulfate and phosphate on the LDH surface after reaction in sulfate and phosphate solutions. The bands recorded at 795, 668, 556, and 447 cm^{-1} are due to the M–O vibrations and M–O–H bending. Though rather weak, arsenic peaks seem to appear at 820–830 cm^{-1} which corresponding to As–O stretching vibration [18] after LDH reacted with arsenate in ultrapure water and nitrate solution.

3.2. Effects of common oxyanions

3.2.1. Investigation on the sorption of toxic oxyanions having different molecular properties

Fig. 4 clearly shows that the sorption of arsenate, bromate, chromate, and vanadate on LDH was affected by both the type and concentration of the co-existing common oxyanions. Increasing the concentrations of the common oxyanions generally resulted in the decrease in toxic oxyanion sorption by LDH, indicating that the common oxyanions might compete with the target oxyanions for the same positively charged sites on LDH due to their comparable molecular structures (Table 1). With an initial arsenate concentration of 0.4 mM and LDH dosage of 0.4 g/L, about 83% of arsenate was sorbed by LDH in the absence of common oxyanions (Fig. 4a). The sorption of arsenate on LDH only declined marginally to 80 and 78% when the nitrate/arsenate molar ratio was increased to 10 and 100, respectively. Nitrate also induced marginal decreases in chromate and vanadate sorption by LDH.

In the contrary, a more significant adverse effect on arsenate sorption could be induced by silica, sulfate, carbonate, and phosphate. Based on the detrimental effects on arsenate sorption, the common oxyanions can be ranked in the order of:

nitrate < silica ≤ sulfate < carbonate < phosphate. The similar order was also generally valid for the cases of bromate, chromate, and vanadate sorption by LDH (Fig. 4b–d). On the other hand, based on their abilities to outcompete co-existing common oxyanions for LDH sorption sites, the toxic oxyanions followed the order of: bromate < arsenate ≈ chromate ≤ vanadate. This generally suggested that the adverse effects of common oxyanions were more profound on the sorption of monovalent toxic oxyanion (i.e. bromate with $\mu = 4.7 \text{ nm}^{-1}$) than the sorption of polyvalent toxic oxyanion (i.e. vanadate, arsenate, and chromate with $\mu > 7.6 \text{ nm}^{-1}$).

Our preliminary macroscopic and microscopic studies showed that monovalent oxyanion with $\mu < 5 \text{ nm}^{-1}$ formed outer-sphere complexes on nanocrystalline LDH and had a lower degree of specific sorption by the nanocrystalline LDH than the polyvalent oxyanion with $\mu > 7 \text{ nm}^{-1}$ which formed both outer-sphere and inner-sphere complexes with LDH. Therefore, bromate sorption on the LDH was subjected to the greater adverse impact of sorption competition with common oxyanions (generally possessed $\mu > 4.7 \text{ nm}^{-1}$) compared to the sorption of arsenate, chromate, and vanadate.

3.2.2. Competitive sorption of arsenate with common oxyanions

The sorption reaction of arsenate with the LDH was suitably expressed by Langmuir isotherm and was believed to occur through two mechanisms, i.e. primary anion exchange mechanism and secondary ligand exchange mechanism [15]. The anion exchange mechanism involved stoichiometric and reversible electrostatic interaction between arsenate and the intercalated anion (i.e., nitrate) in the interlayer region of LDH. The ligand exchange mechanism involved the exchange of OH groups on LDH surface with arsenate. Fig. 5 illustrates the oxyanion sorption mechanisms on LDH. The common oxyanions in aqueous system can potentially inhibit these mechanisms at different degrees by competing for sorption sites, blocking or reducing available sorption sites, or altering the surface electronic charge of LDH.

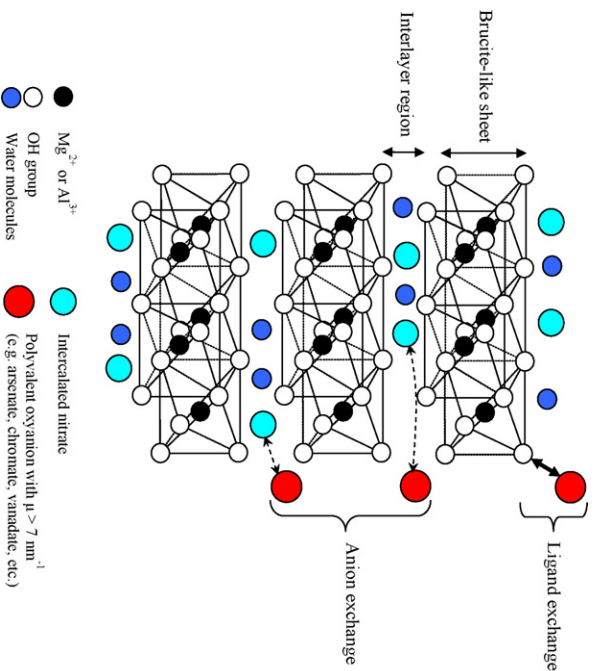


Fig. 5. Schematic representation of oxyanion sorption mechanisms on LDH.

Fig. 6 illustrates the time-dependent arsenate sorption on LDH in the presence of various common oxyanions of different concentrations (at oxyanion/arsenate molar ratios of 1 and 10). In the ultrapure water and also the solutions containing a co-existing species, the sorption kinetics can be best described by the Elovich model on the basis of the statistical parameters ($R^2 > 0.95$, $\chi^2 < 2.8$, $\Delta q < 35$) among the examined kinetic models (Table 2). The Elovich equation can be expressed as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (1)$$

where q_t is the amount of sorbate per unit mass of sorbent at time t (cmol/kg), α is the initial sorption rate (cmol/kg min), and β is related to the extent of surface coverage (kg/cmol). Integration of Eq. (1) with boundary condition $q = q_t$ at sorption time t and $q = 0$ at $t = 0$ yields

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t + t_0) \quad (2)$$

where $t_0 = 1/\alpha\beta$. The value of the constant β can be obtained from the slope of the straight line plot of q_t versus $\ln(t + t_0)$ and the constant α can be calculated from the t_0 and β values [19]. The Elovich equation, which accounts for the characteristics of heterogeneous sorptive sites [20], is appropriate for LDH since there were external

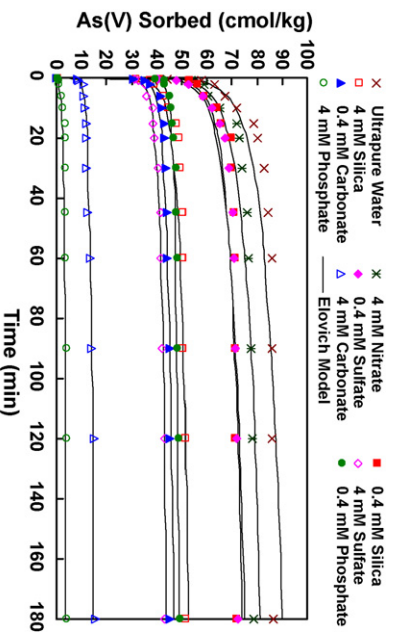


Fig. 6. Time-dependent sorption of arsenate by LDH in the presence of various common oxyanions (dose = 0.4 g/L, arsenate concentration = 0.4 mM).

Table 2 Kinetic and statistical parameters of three kinetic models for arsenate sorption in various matrix solutions and the corresponding pH changes and metals released.

Co-existing species	Pseudo-first-order $\frac{dq_t}{dt} = k_1(q_e - q_t)$					Pseudo-second-order $\frac{dq_t}{dt} = k_2(q_e - q_t)^2$					Elovich $\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$					pH		Metals released ^a (wt%)	
	$q_{e, cal}$ (cmol/kg)	$k_1 \times 10^{-2}$ (min ⁻¹)	R^2	χ^2	Δq (%)	$q_{e, cal}$ (cmol/kg)	$k_2 \times 10^{-3}$ (kg/cmol min)	R^2	χ^2	Δq (%)	α (cmol/kg min)	β (kg/cmol)	R^2	χ^2	Δq (%)	Initial	Final	Mg	Al
Ultrapure water ^b	86.8	1.38	0.603	8913	68.4	87.0	10.75	0.970	2.01	13.3	56.9	0.16	0.984	1.93	6.9	9.5	9.9	0.09	0.04
4 mM nitrate	79.1	1.53	0.723	7464	66.8	79.4	9.51	0.955	3.29	17.0	51.6	0.18	0.986	1.47	6.3	9.4	9.8	0.08	0.04
0.4 mM silica	73.3	0.77	0.424	15995	75.8	71.4	16.61	0.969	1.11	12.2	51.5	0.23	0.984	1.34	6.5	10.1	10.4	0.03	0.06
4 mM silica	51.4	1.11	0.657	7387	70.5	51.5	17.84	0.951	0.99	16.0	37.0	0.32	0.990	0.71	4.5	11.0	11.5	0.02	0.05
0.4 mM sulfate	72.6	1.12	0.664	8917	70.0	73.0	11.04	0.960	1.59	16.1	48.7	0.20	0.989	1.17	5.0	10.0	10.4	0.06	0.06
4 mM sulfate	45.6	0.56	0.546	16467	78.4	45.2	8.07	0.827	15.06	29.8	32.7	0.47	0.999	0.09	1.4	10.3	10.8	0.07	0.04
0.4 mM carbonate	45.6	1.43	0.784	6110	67.8	45.7	9.07	0.955	0.70	13.4	35.1	0.48	0.990	0.52	4.4	10.5	10.8	0.03	0.04
4 mM carbonate	15.8	0.61	0.776	2904	75.4	15.8	7.13	0.864	10.70	34.5	8.8	0.87	0.992	0.26	4.0	10.9	11.3	0.02	0.05
0.4 mM phosphate	49.1	0.88	0.604	14584	74.2	49.0	7.74	0.876	2.55	19.1	41.3	0.71	0.999	0.05	1.5	9.1	9.4	0.18	0.11
4 mM phosphate	4.0	0.59	0.583	43	67.5	4.0	5.12	0.987	0.26	11.6	0.6	1.58	0.959	0.84	35.0	7.2	7.6	2.45	0.44
10 mg/L NOM	76.8	1.11	0.759	4480	67.7	77.5	5.07	0.979	1.81	18.8	35.4	0.12	0.985	2.79	6.8	9.6	9.7	0.10	0.09
100 mg/L NOM	11.6	0.38	0.681	113	62.4	11.6	5.15	0.969	2.85	31.6	1.0	0.55	0.988	0.49	33.7	9.2	9.4	0.36	0.26

Note: q_e is the amount of arsenate sorbed at equilibrium, q_t is the amount sorbed at time t , k_1 is the pseudo-first-order constant, k_2 is the pseudo-second-order constant, α and β are the Elovich constants.

^a Mg and Al released from the LDH samples after reaction for 24 h.

^b Control experiment.

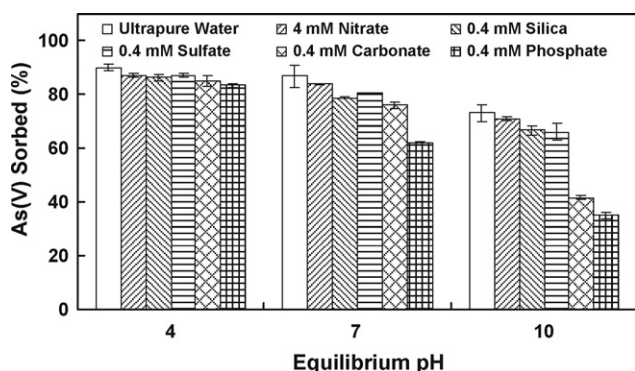


Fig. 7. Influences of common oxyanions on arsenate sorption by LDH as a function of pH (time = 4 h, dose = 0.4 g/L, arsenate concentration = 0.4 mM).

surface sorption sites as well as the interlayer ion exchange sites for the target oxyanions that resulted in heterogeneous sorption process. The kinetic data are presented in Table 2.

Nitrate is commonly present in many water resources and polluted runoffs. It was found that the decrease in arsenate sorption by LDH was marginal (<8%) when 4 mM nitrate (10 times higher than arsenate concentration) was spiked as a co-existing species, relative to the ultrapure water (Fig. 6). Yang et al. [7] also reported that nitrate had almost no effect on the sorption of arsenate by a calcined LDH up to a concentration of 1000 mg/L. Furthermore, the presence of nitrate only slightly affected the sorption rate of arsenate on LDH (indicated by α value of the best-fitted Elovich model in Table 2). Indeed, over the entire pH range investigated, the presence of nitrate at 10 times of arsenate could only induce less than 3% reduction of arsenate sorption achieved in ultrapure water (Fig. 7). At pH 4, arsenate existed predominantly as H_2AsO_4^- , H_2AsO_4^- and HAsO_4^{2-} at pH 7, and HAsO_4^{2-} at pH 10 whereas nitrate has a pK_a of 1.4 and existed as a monovalent anion species over the investigated pH range (Table 1). The insignificant effect of nitrate on arsenate sorption by LDH could be ascribed to the fact that nitrate is a nonspecific anion in solid-liquid interfacial reactions [21]. It generally has a lower ionic potential than arsenate, resulting in its weaker competition ability with arsenate for binding sites on LDH.

Silica and sulfate are omnipresent in groundwaters, surface waters, and seawaters. Fig. 6 reveals that both silica and sulfate had modest effect on arsenate sorption by LDH. The amount of arsenate sorbed at 3 h (near sorption equilibrium) reduced substantially from 71.3 to 51.2 cmol/kg when the silica concentration increased from 0.4 to 4 mM (equivalent to the increment of silica/arsenate molar ratio from 1 to 10). Likewise, arsenate sorption dropped from 72.5 to 43.1 cmol/kg with increasing molar ratio of sulfate/arsenate from 1 to 10. Similar observations of significant reduction in arsenate removal with increasing silica or sulfate concentration have also been reported for arsenate sorption on iron and aluminium oxides [22] and calcined LDH [7]. The α values for arsenate sorption in 0.4 mM silica and sulfate solutions were only slightly smaller than that in ultrapure water but decreased by about 40% in 4 mM silica and sulfate solutions, implying that arsenate sorption rate on LDH was only retarded by the overwhelming presence of silica and sulfate (Table 2).

The effects of silica and sulfate on arsenate sorption by LDH appeared to be more pH-dependent than that of nitrate (Fig. 7). The presence of silica decreased arsenate sorption by 3.7%, 8.0%, and 6.2% whereas the presence of sulfate decreased arsenate sorption by 2.9%, 6.3%, and 6.9% at pH 4, 7, and 10, respectively. The effect of silica on arsenate sorption by LDH became more significant at $\text{pH} \geq 7$, probably due to the change in speciation of silicic acid with pH. Silica exists as neutral molecules (H_2SiO_3) at $\text{pH} < 7$ and they generally have weak affinities for sorbent surface. At $\text{pH} \geq$

7, silica dissociates into HSiO_3^- and SiO_3^{2-} and these molecules have greater affinities for the positively charged sorbent surface, contributing to a stronger competition with arsenate. An enhanced detrimental effect of silica on arsenate sorption at higher pH has also been reported for other sorbents such as iron oxide hybrid media, amorphous ferric hydroxide, and activated alumina [23,24]. On the other hand, SO_4^{2-} is the prevalent sulfate species at pH 4, 7, and 10, and the decrease in arsenate removal with increasing pH could be ascribed to the competition of arsenate with sulfate and hydroxide ions. Examinations of the FTIR spectral feature for the LDH reacted in silica solution however did not show noticeable presence of any silicon compound, suggesting marginal sorption of silica on LDH surface upon its competition with arsenate (Fig. 3). In contrast, sulfate was evidenced in the LDH reacted in sulfate solution. The FTIR spectra revealed that sulfate caused a slightly larger competition effect on arsenate sorption than silica. In summary, the results suggested that both silica and sulfate could compete with arsenate for sorption by LDH, especially at $\text{pH} \geq 7$ over which arsenate has weak affinity with increasing pH.

The carbonate solution chemistry may affect the fate of toxic oxyanions in aqueous system. For example, the release of arsenic into groundwaters has been found related to the carbonate concentration in the leaching solution [25–27]. In the present study, the presence of carbonate generally caused a remarkable reduction in arsenate sorption efficiency and sorption rate on LDH (Fig. 6 and Table 2). At pH 4, arsenate sorption was reduced by about 5% in the presence of carbonate (Fig. 7). At pH 7 and 10, carbonate caused a greater drop in arsenate sorption, i.e. 10.7% and 31.4%, respectively, mainly owing to the prevalence of monovalent HCO_3^- and divalent CO_3^{2-} compared to the uncharged H_2CO_3 at pH 4. The evidence of carbonate intercalation into nanocrystalline LDH is shown in the XRD pattern and the FTIR spectrum of the reacted LDH samples in carbonate solution (Figs. 2 and 3). Compared to silica and sulfate, carbonate exerted a larger detrimental effect on arsenate sorption due to the relatively strong electronic forces of its attraction with the host lattice of LDH and the orientation of carbonate molecule parallel to the principal layers (this facilitated sorption within interlayer region). In short, at higher carbonate concentration and at alkaline condition, carbonate outcompeted arsenate in the sorption process and subsequently reduced the amount of binding sites available for arsenate.

Phosphate is believed to be competing directly with arsenate for sorption sites on LDH mainly due to their similarities in molecular structure and dissociation constants. Several researchers have reported that the presence of phosphate substantially reduced the amount of arsenic sorbed on the surfaces of mineral sorbents such as aluminosilicate minerals, iron oxides, and soils [28–30]. Compared to carbonate and all other common oxyanions, phosphate generally caused a more significant reduction in sorption efficiency and kinetic suppression for arsenate sorption by LDH (Fig. 6 and Table 2).

The decrease in arsenate sorption in phosphate solution was highly dependent on pH values (Fig. 7). At pH 4, 7, and 10, arsenate sorption was reduced by 6.7%, 24.5%, and 38.2%, respectively, in the presence of phosphate at a similar molar concentration. The characteristic peak for P–O vibration evidenced in the FTIR spectrum of the reacted LDH was probably corresponded to the phosphate intercalated into the interlayer surface sites and also those sorbed on the external surface sites (Fig. 3). Phosphate has also been reported to form inner-sphere complexes upon specific adsorption on various mineral surfaces [14,31,32]. Based on these results, it could be deduced that the great decrease in arsenate sorption caused by the presence of phosphate under neutral and alkaline conditions was primarily associated with the competition between phosphate and arsenate for the same group of sorption sites on LDH due to their comparable chemistry.

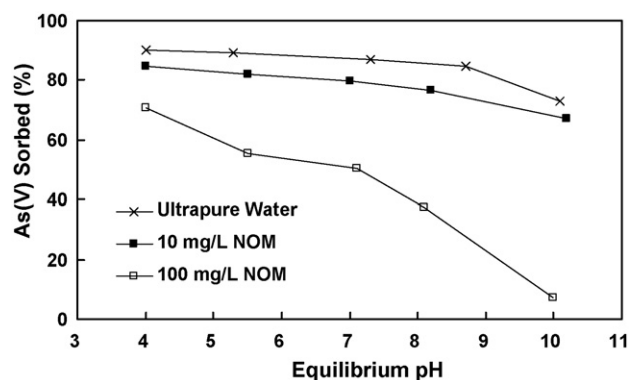


Fig. 8. Influence of NOM on arsenate sorption by LDH as a function of pH (time = 4 h, dose = 0.4 g/L, arsenate concentration = 0.4 mM).

In summary, the effects of co-existing common oxyanions on the sorption of toxic oxyanions by LDH increased in the order: nitrate < silica \leq sulfate < carbonate < phosphate. These common oxyanions can be categorized into two groups based on their ionic potentials and their competitive effects on the sorption reaction: (1) oxyanions with $\mu \leq 5 \text{ nm}^{-1}$, such as nitrate ($\mu = 5 \text{ nm}^{-1}$) and silica ($\mu = 4.9 \text{ nm}^{-1}$) that have negligible to moderate competitive effects on toxic oxyanion sorption, and (2) oxyanions with $\mu > 5 \text{ nm}^{-1}$, such as sulfate ($\mu = 8.7 \text{ nm}^{-1}$), carbonate ($\mu = 6.1 \text{ nm}^{-1}$), and phosphate ($\mu = 8.4 \text{ nm}^{-1}$) that have moderate to significant competitive effects on toxic oxyanion sorption. Relative to cases of reaction in the ultrapure water and nitrate solution, there seemed to be weaker peak associated with As–O stretching vibration at 820–830 cm^{-1} of the FTIR spectra for the LDH reacted in silica, sulfate, carbonate, and phosphate solutions, indicating lesser arsenate sorbed on the surface of LDH particles. The pH of the aqueous solutions increased slightly after 24 h reaction in all cases (Table 2). The pH increase was expected because sorption of oxyanions would release OH groups from LDH as a result of the ligand exchange mechanism.

3.3. Effect of natural organic matter

Humic acid and fulvic acid generally represent about 60% of the NOM in aquatic systems [33]. Humic acid consists of a large number of functional moieties including carboxylic, phenolic, and alcoholic groups that interact with dissolved ions and surface functional groups of solids in aqueous system, thus it potentially interferes with the oxyanion sorption.

In this study, the time-dependent sorption experiment revealed that the kinetics of oxyanion sorption in the presence of NOM could be still best represented by the Elovich model (Table 2). The equilibrium sorption of arsenate by the LDH was slightly affected by the presence of 10 mg/L NOM from pH 4 to 10 (as shown in Fig. 8). However, at 100 mg/L, NOM dramatically decreased arsenate sorption, particularly at alkaline condition. The decrease in arsenate sorption could be owing to the large NOM molecules, typically 1–1000 nm

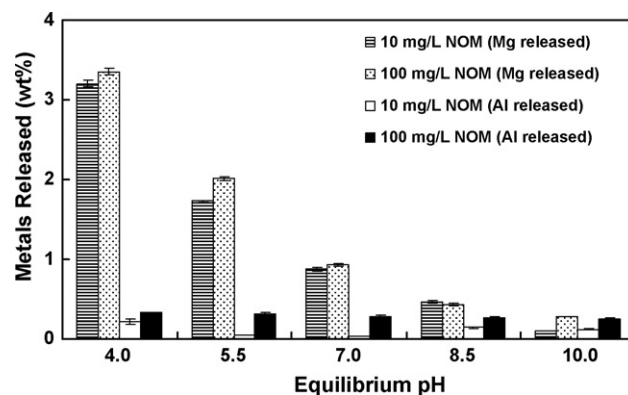


Fig. 9. The amount of Mg and Al released from LDH at different pH in the presence of NOM.

diameter for humic acid [34], that occupied a large fraction of sorption sites on the LDH. This phenomenon caused steric congestion on the LDH surface and formation of physical barrier to mass transfer of arsenate to the LDH surface. The FTIR spectrum (Fig. 3) for the NOM-reacted LDH also indicated diminution of the characteristic peak for the LDH (at 1384 cm^{-1}) with concurrent emergence of new peaks (at 1390 and 1559 cm^{-1}) corresponding to carboxylate, which confirmed the possible coverage of NOM on the LDH. In addition, direct competition between NOM and arsenate for sorption sites on the LDH might also contribute to the decrease in arsenate sorption. For the sorption experiments with 100 mg/L of NOM conducted at pH 7–10, the formation of LDH–NOM precipitate was observed. Apparently, the NOM precipitation at alkaline condition might trap and settle out the LDH particles from the aqueous solution. This resulted in the drastic reduction in arsenate sorption (Fig. 8).

3.4. Stability of nanocrystalline Mg/Al LDH in aqueous matrix

The releases of Mg and Al from the freshly synthesized nanocrystalline LDH were monitored during the sorption experiments. The Mg and Al released were negligible at pH 10 (Table 3), indicating that the LDH was stable at its natural pH of ~ 9.5 . Under the neutral and alkaline conditions, the Mg released was in the range of 0.1–1.3% whereas the Al released was lower than 0.2%. As the solution became more acidic, increasing releases of Mg and Al were observed. Nevertheless, our previous study revealed that if the LDH was regenerated and reused in the subsequent cycles, it would become rather stable with negligible further releases of Mg and Al [15]. Thus, the Mg and Al releases from the freshly synthesized LDH could be attributed to the dissolution of the small fraction of poorly crystalline LDH or the residual Mg or Al precursor salts that still remained in the synthesized LDH. Overall, it can be generally concluded that the presence of different electrolyte solutions and NOM did not appear to affect the mineral stability of the nanocrystalline LDH, as can be inferred from Table 3 and Fig. 9.

Table 3

The amount of Mg and Al released from LDH at different pH in the presence of different electrolyte solutions.

Background electrolyte	Mg released (wt%)			Al released (wt%)		
	pH 4	pH 7	pH 10	pH 4	pH 7	pH 10
Ultrapure water (control)	2.88 \pm 0.25	1.17 \pm 0.08	0.07 \pm 0.00	0.76 \pm 0.06	0.05 \pm 0.00	0.08 \pm 0.01
4 mM nitrate	2.81 \pm 0.24	1.27 \pm 0.02	0.07 \pm 0.00	0.78 \pm 0.04	0.04 \pm 0.00	0.09 \pm 0.01
0.4 mM silica	2.35 \pm 0.16	1.20 \pm 0.05	0.10 \pm 0.00	0.46 \pm 0.03	0.04 \pm 0.00	0.05 \pm 0.00
0.4 mM sulfate	4.25 \pm 0.29	0.88 \pm 0.05	0.10 \pm 0.00	0.90 \pm 0.04	0.04 \pm 0.00	0.10 \pm 0.00
0.4 mM carbonate	3.02 \pm 0.17	0.94 \pm 0.03	0.06 \pm 0.00	1.33 \pm 0.05	0.04 \pm 0.00	0.06 \pm 0.01
0.4 mM phosphate	2.69 \pm 0.17	1.07 \pm 0.07	0.18 \pm 0.00	0.11 \pm 0.01	0.04 \pm 0.00	0.10 \pm 0.00

4. Conclusions

Both common oxyanions and NOM exhibit varying degrees of competition or inhibition to the sorption of toxic oxyanions by the nanocrystalline Mg/Al LDH. The competitive and inhibitive effects were dependent on pH which regulates protonation/deprotonation of oxyanions or dissolution/precipitation of NOM. In general, based on their sorption competitiveness with the toxic oxyanions, the common oxyanions can be ranked in the order of nitrate < silica ≤ sulfate < carbonate < phosphate, while the affinities of the toxic oxyanions for the LDH in the presence of common oxyanions followed the order of bromate < arsenate ≈ chromate ≤ vanadate. This indicates that the oxyanions with lower ionic potentials tend to be less preferably sorbed by the LDH. The competition of the common oxyanions for common sorption sites on the LDH is predominantly occurred through ion exchange mechanism, the extent of which can be predicted by the ionic potentials of the competing oxyanions. NOM can induce sorption inhibition of the oxyanions through obstruction of the LDH surface, direct competition for sorption sites, and settle out LDH from aqueous solution at alkaline condition. The common oxyanions and NOM do not appear to affect the mineral stability of the nanocrystalline LDH.

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