Removal of Trace Levels of Arsenic and Selenium from Aqueous Solutions by Calcined and Uncalcined Layered Double Hydroxides (LDH)

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The adsorption of As and Se from dilute aqueous solutions, representing model power-plant effluent streams, by calcined and uncalcined layered double hydroxide (LDH) adsorbents has been investigated. The results indicate that As(V) has a greater adsorption capacity than Se(IV) for both calcined and uncalcined LDHs. An *m*th-order kinetic rate equation describes the adsorption kinetics of As and Se on these adsorbents. The adsorption isotherms obey the Freundlich model. The adsorption capacities of As(V) and Se(IV) on the calcined LDH are higher than those on the uncalcined LDH. The starting solution pH does not significantly influence adsorption of As and Se on calcined LDH, as long as it is higher than 4; As and Se adsorption on uncalcined LDH is, however, more sensitive to variations in the initial pH. Studies of the effect of the metal oxidation state on adsorption reveal that As(III) is more difficult to remove than As(V) by both the calcined and uncalcined LDHs. However, the adsorption of Se(IV) and Se(VI) is relatively similar on both calcined and uncalcined LDHs. Competing ions have a greater effect on Se(IV) uptake than on As(V) uptake. Desorption of As(V) and Se(IV) from the LDH depends on the type of ion species and their concentration in the desorbing solutions.

1. Introduction

Electric utilities are heavy users of water in the United States, putting the industry on an equal footing, in terms of its water needs, with farm irrigation. Most of the water that is utilized during power generation is for steam generation and cooling. As demand for electricity increases with the growing economy, so will the need for water. As a result, the electric power generation industry is likely to find itself in direct competition for new sources of water with the other growing sectors of the economy. In the future, utilities may have to look for alternative sources of cooling water, such as "gray" and underground waters, rather than today's conventional sea- or freshwater supplies. Potential utilization of such waters and the ability to reclaim and reuse spent (discharged) water throughout the power plant (e.g., boiler blow-down water) are likely to reduce the pressure for finding additional sources of conventional cooling water. However, unanswered questions still remain, including the cost of acquisition and treatment and environmental and health issues, e.g., human exposure to heavy metals found in blow-down waters and other plant discharges. At the same time, renewed concerns exist today about the environmental fate of heavy metals, such as mercury (Hg), arsenic (As), and selenium (Se), that are found in many of these effluents, which negatively impact their disposal. Most of the power-plant discharges fall today under the category of high volume, "too clean to clean" effluents. These require highly efficient treatment techniques, particularly for the removal of trace-level metal contaminants. Very little emphasis has, so far, been placed on such discharges.

As and Se are found in waters in the form of oxyanions. Se in waters from power plants exists in the 4+ (Se(IV), selenite) and 6+ (Se(VI), selenate) oxidation state forms.[1] Se is toxic to humans, and acute exposure may lead to severe respiratory problems and neurological effects.[2] In drinking water, for example, the limit is 0.05 ppm in the United States (soon to be lowered to 0.01 ppm) and 0.01 ppm in Europe and Japan.[3,4] Relatively high concentrations of As have been reported both in power-plant discharges and in freshwater supplies. Inorganic As may be present in the 3+ (As(III), arsenite) and 5+ (As(V), arsenate) oxidation states.[5] Protracted contact with As-containing waters is thought to cause arsenicosis, a form of poisoning for humans.[6] The International Agency for Research on Cancer (IARC) currently classifies As as a group 1 chemical, which is thought to be carcinogenic to humans. A recent Southern California Coastal Water Research project report for the year 2000 on 13 power-generating stations located on the Southern California Coast[7] indicates the presence of As and Se in power-plant discharges, usually in small concentrations up to 50 ppb; such levels may still be too high, however, to permit safe environmental discharge in the future.

Methods for reducing As and Se concentrations in waters include precipitation−filtration, adsorption, ion exchange, and reverse osmosis. Of these, adsorption is the simplest and most direct approach. The development of effective adsorbents with applications in water decontamination is of current interest. So far, conventional adsorbents such as clay minerals,[8] activated alumina,[9−11] mesoporous alumina,[12] ferric hydroxide,[13] ferrihydrite,[14]

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and geological materials,[15] etc. have been investigated. Layered double hydroxides (LDHs), which offer a large interlayer surface to host diverse anionic species[16] with the additional advantage that they can be easily recycled, are also attracting current research interest. Recently, for example, researchers at Media and Process Technologies, Inc. (M&P) reported the development and use of LDHs for the separation of As for drinking water applications with significantly improved adsorption capacities.

LDHs (also known as hydrotalcites) have the structural formula $[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}A_{x/n}^{n-}\cdot yH_2O$, where M^{II} and M^{III} denote divalent (e.g., Mg, Ni, and Zn) and trivalent metals (e.g., Al, Fe, and Cr), respectively; A^{n-} represents interlayer anions, such as NO_3^-, SO_4^{2-}, and CO_3^{2-}, and x typically ranges from 0.17 to 0.33.[17] These materials consist of positively charged, brucite-like octahedral layers and a negatively charged interlayer region containing anions and water molecules. Because of the presence of large interlayer spaces and the significant number of exchangeable anions, LDHs have the potential to be good ion-exchangers and adsorbents. They (and their calcined products) have, indeed, been reported as adsorbents for the removal of surfactants,[18] trinitrophenol,[19,20] various pesticides,[21] and chromate[22,23] from aqueous solutions. LDHs can uptake anions from a solution by three different mechanisms: (1) adsorption, (2) intercalation by anion exchange, and (3) intercalation by reconstruction of the structure of the calcined LDH. The latter phenomenon is known as the "memory effect", which takes place when an LDH, usually containing carbonates in its interlayer, is calcined at temperatures that are high enough to eliminate most of the interlayer anions and is then put in a solution of the same or different anions. While in solution, rehydration and reconstruction of the layered structure occurs with incorporation of anions from the solution. The ability of LDHs to "recover" their structure provides, at least in principle, the potential for reuse and recycle of the adsorbent, which is important for these large-volume applications.

In addition to the preliminary investigation by M&P, we know of only a limited number of other publications that report on the adsorption of arsenic and selenium by LDH.s[24−27] These studies focused on the adsorption of the metals on LDHs from concentrated (ppm level) solutions. To the best of our knowledge, there are no published studies, however, on the adsorption behavior of an LDH from dilute (trace ppb level) As and Se solutions. Little concrete is known, furthermore, on the effects of factors such as the As and Se oxidation states, the solution pH, and the temperature and the presence of various other anion species on the adsorption on LDHs and their calcined products.

The focus of the present work is on a systematic study of the adsorption of As and Se by calcined and uncalcined LDHs from dilute aqueous solutions, representing "too clean to clean" model power-plant effluent streams, whose contaminant levels are expected to be in the trace ppb level; such a study is, so far, lacking in this area. The adsorptive behavior of As and Se on both calcined and uncalcined LDHs is evaluated by batch techniques in order to study the adsorption kinetics and the adsorption/desorption isotherms. The effects of such factors as the As and Se oxidation state, the pH, the temperature, and the presence of competing anions are also investigated. In our investigation, we utilize an $Mg-Al-CO_3$ LDH, as it is the most commonly studied LDH (though it is still unclear whether it is the best-suited LDH for this particular application). We believe, however, that the results obtained are instructive toward a better understanding of the potential applications of other calcined and uncalcined LDHs for environmental cleanup and the remediation of trace levels of arsenic and selenium found in contaminated waters.

2. Experimental Section

2.1. Reagent. To prepare As(V) and Se(IV) solutions for the adsorption experiments, we utilized 1000 ppm ICP (inductively coupled plasma) standard solutions (As(V) in 2% HNO_3 and Se(IV) in 2% HNO_3) purchased from Exaxol. Solutions of selenate, Se(VI), were also prepared using Na_2SeO_4 (Sigma Aldrich) for use during the study of the effects of the Se oxidation state on adsorption. To study the effect of the As oxidation state on adsorption, As(III) ASS standard solution (Aldrich) was used as the arsenite source and the As(V) ICP standard was used as the arsenate source.

2.2. Preparation of LDH. The $Mg-Al-CO_3$ LDH was prepared by the coprecipitation method, following a method proposed by Jules et al.[28] in which a solution (140 mL) containing 0.7 mol NaOH and 0.18 mol Na_2CO_3 was added all at once to a second solution containing 0.115 mol of $Mg(NO_3)_2\cdot 6H_2O$ (90 mL) and 0.04 mol of $Al(NO_3)_3\cdot 9H_2O$ (90 mL) (corresponding to a Mg/Al ratio = 2.87) under vigorous stirring. The thick gel obtained was aged for 24 h at 333 K, followed by filtration and washing with distilled water, and was then dried at 393 K. ICP-MS (inductively coupled plasma mass spectroscopy) analysis of the resulting LDH material indicated that its Mg/Al mole ratio is ~2.9, very close to the Mg/Al ratio of the starting salts. The calcined Mg−Al LDH was obtained by heating the original LDH in a muffle furnace at 773 K for 4 h in an air atmosphere with heating and cooling rates of 2 $K\cdot min^{-1}$. Both the calcined and uncalcined LDHs were ground to fine powders before being utilized in the batch adsorption experiments. Two different adsorbent batches (hereinafter referred to as batches #1 and #2) were used for the experiments reported in this paper, each prepared by the same procedure and having very similar Mg/Al ratios. The adsorption isotherm and kinetic experiments used adsorbent from batch #1, while the rest of the experiments were carried out using adsorbent from batch #2.

2.3. Sorption Experiments. The solutions used for the adsorption experiments were prepared by dilution from the standard solutions described above using ASTM Type II water (VWR International). No effort was made to minimize contact with the atmospheric air during the preparation of the various solutions. In addition to the fact that it is exceedingly difficult to completely avoid contact of the various samples with the laboratory atmosphere during the kinetic rate measurements, it is impossible in real life applications to exclude the contact of the various wastewaters with air. Successful adsorbents must be capable of functioning in the presence of carbonate anions because of the contact of water with atmospheric CO_2. All the experiments were performed at 298 K and with an adsorbent loading (dose) of 0.12 g/L (unless otherwise noted).

2.3.1. Adsorption Isotherms. Batch adsorption studies were performed at 298, 318, and 338 K to obtain the equilibrium adsorption isotherms. Aqueous solutions

of As(V) and Se(IV) of a predetermined concentration ranging from 10 to 200 ppb were prepared by diluting the 1000 ppm ICP standard solutions. The initial pH of these solutions ranged from 4.2 to 5.4. No pH adjustment was carried out in order to avoid any possible interference of foreign anions during the adsorption process. For these experiments, a constant mass of the LDH was added to a 13 mL snap-seal polyethylene bottle, which was then filled with a 10 mL aqueous solution of As or Se of a given concentration. The bottles containing the LDH suspension and the As and Se containing solutions were kept closed for the whole period of the adsorption experiment. They were placed in a reciprocal shaking water-bath (Precision model 25) and were shaken at 150 rpm (rotations per minute) for 5 days in order for adsorption on the LDH to reach equilibrium. The mixture in each bottle was then centrifuged immediately, and the As and Se concentrations in the supernatant solutions were determined by ICP-MS (Perkin-Elmer ELAN-9000).

2.3.2. Kinetics of Adsorption. For these experiments, the solutions were prepared by the addition of 90 mg of LDH to 750 mL of 20 ppb As or Se solutions in a 1 L screw-top bottle (equivalent to 0.12 g/L). The starting solution pH for all these experiments was ~5.4. During the experiments, the mixture was shaken at 150 rpm, and at selected time intervals, 4 mL samples were extracted and centrifuged and the As or Se concentrations were determined by ICP-MS. During the experiments some dissolution of the LDH occurs, as manifested by the presence of soluble Al and Mg in the supernatant solution. This typically corresponds to <10 wt % of the original LDH and is more pronounced for the calcined LDH (preconditioning of the calcined LDH, by allowing it to stand in deionized water for ~24 h, significantly reduces the dissolution). Independent experiments using Al and Mg soluble salts have shown that the Al and Mg present have no influence on the As and Se adsorption and that they do not interfere with the ICP-MS analysis.

2.3.3. Effect of pH. The effect of the starting solution pH on the adsorption of As or Se was evaluated using 20 ppb As and Se solutions. The starting solution pH was initially adjusted with 0.01−1 M HNO_3 and NH_4OH solutions and was determined by an Accumet Basic AB 15 pH meter. The resulting LDH suspensions were shaken at 150 rpm for 24 h and centrifuged; the concentrations of As or Se remaining in solution were then determined.

2.3.4. Effect of Competing Ions. For these experiments, the LDHs were accurately weighed and added to 10 mL of 20 ppb As or Se solutions containing additional competing ions, such as NO_3^-, CO_3^{2-}, SO_4^{2-}, and HPO_4^{2-}, with concentrations ranging from 40 ppb to 1000 ppm; these were prepared using $NaNO_3$, Na_2CO_3, Na_2SO_4, and K_2HPO_4, respectively. The samples were shaken for 24 h and centrifuged; the concentrations of As or Se still remaining in solution were then determined.

2.3.5. Desorption Experiments. Desorption experiments were also conducted, in which the effect of using different desoprtion solutions containing various anions, with concentrations ranging from 100 ppb to 1000 ppm, were investigated. Initially, 10 mL of 20 ppb As or Se solutions were equilibrated with the calcined LDH, as described in Section 2.3.1 above. After centrifuging, 4 mL of the equilibrated solution was removed for ICP-MS analysis and was substituted by 4 mL of the solution containing other anions (e.g., NO_3^-, CO_3^{2-}, SO_4^{2-}, and HPO_4^{2-}), which was then shaken for 2 h and centrifuged again. The supernatant solution (4 mL) was again substituted by 4 mL of the solution containing the other anions, and the process was repeated; the overall desoprtion experiment consisted of five such dilution cycles.

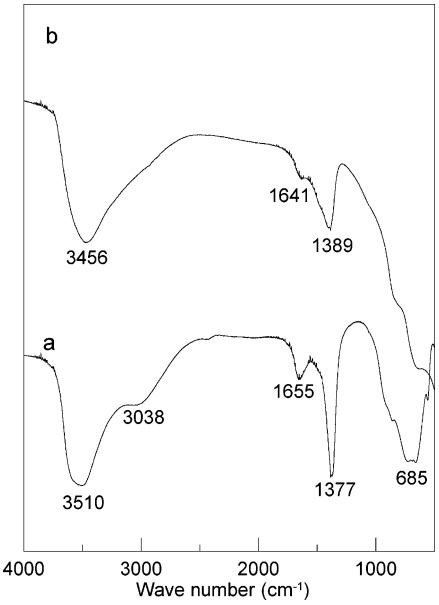

Figure 1. FT-IR spectra of (a) LDH and (b) calcined LDH.

2.4. Characterization. IR spectra of the LDH materials were recorded in the room environment using an FT-IR Mattson Genesis II spectrophotometer with the samples diluted in KBr disks. N_2 adsorption/desorption isotherms are acquired using a Micrometritics ASAP 2010 apparatus. The surface area was determined by the BET method. The As and Se concentrations in the solutions were determined from elemental analyses using a Perkin-Elmer ELAN-9000 ICP-MS system. The instrument detection limit was found to be 0.043 μg/L for As and 0.172 μg/L for Se using the EPA 200.8 method. The 99% confidence interval for the As and Se with a concentration of 20 ppb with 10 sequential measurements is 20.54 ± 0.15 for As and 21.12 ± 0.09 for Se.

3. Results and Discussion

3.1. Characterization of the Calcined and Uncalcined LDHs. The temperature at which the calcination of the LDH is carried out should be sufficiently high to eliminate most of the carbonate anions in the interlayer region and low enough that it does not preclude the structural reconstruction. According to the data reported previously by our group,[29] decarbonation occurs in the temperature range of 405−580 °C. As noted in Section 2.2 above, we chose 500 °C as the calcination temperature.

FT-IR spectra of the calcined and uncalcined LDHs in the room environment are shown in Figure 1. The broad absorption peak in the uncalcined LDH spectra (see Figure 1a) between 3600 and 3300 cm^{-1} is due to the vibration of structural OH^- groups from the brucite-like layers. The peaks around 1655 and 3038 cm^{-1} are due to the interlayer water molecules. The peaks around 1377, 874, and 685 cm^{-1} are due to the carbonate ions.

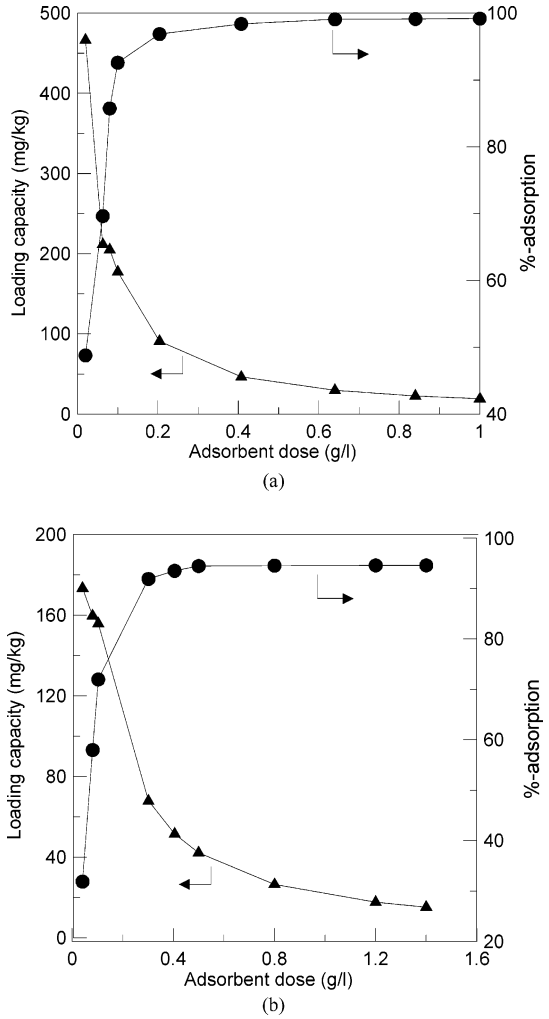

Figure 2. Adsorption of (a) As(V) and (b) Se(IV) in 20 ppb solutions on calcined LDH as a function of adsorbent dose.

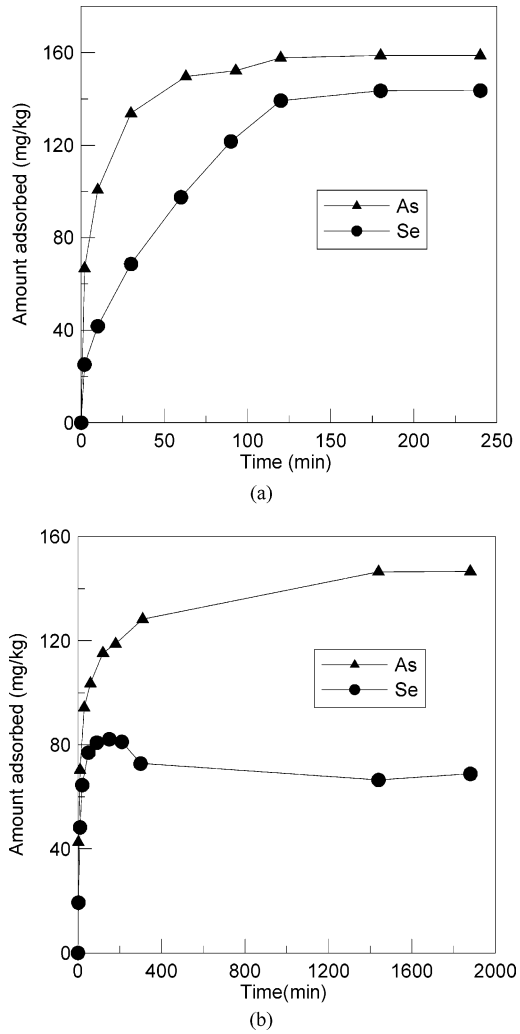

Figure 3. Adsorption of As(V) and Se(IV) on (a) calcined and (b) uncalcined LDHs as a function of time in 20 ppb solutions.

FT-IR spectra of calcined LDH suggest that most of the interlayer water bands have disappeared, but some of the carbonate anions are still present after calcination (e.g., bands at ~1389 cm^{-1} in Figure 1b). However, these may also be due to the carbonate species adsorbed when the LDH sample is cooling in the atmosphere during the calcination.

The specific surface areas of uncalcined and calcined LDHs were determined by the single-point BET method and were found to be 47 and 198 m^2/g, respectively. That the calcined LDH has the higher surface area has also been previously reported by other investigators and is believed to be due to the additional mesoporous region, which is created by the formation of channels and pores resulting from the removal of water and carbon dioxide.[30] However, the surface areas probed by N_2 adsorption are generally thought not to be reflective of the interlayer region in the LDH.

3.2. Effect of Adsorbent Dose. The effect of the LDH adsorbent dose on the adsorption of As(V) and Se(IV) in 20 ppb solutions is shown in Figure 2 (batch #2 adsorbent was used in these experiments). For these experiments, the metal solutions containing the appropriate adsorbent dose were loaded in 13 mL snap-seal polyethylene bottles, which were then placed in the reciprocal shaking water-bath and shaken at 150 rpm for 24 h. The mixture in each bottle was then centrifuged immediately, and the As and Se concentrations in the supernatant solutions were determined by ICP-MS. As expected, the fraction of As(V) and Se(IV) removed first increases sharply with an increase in LDH dose, at fixed initial adsorbate concentrations, and then levels off at an adsorbent dose above ~0.2 g/L (for As) and ~0.4 g/L (for Se). The loading capacity of the material, on the other hand, decreases with increasing LDH dose, as expected based on the simple model of metal adsorption presented below (Das et al.[31] also recently reported a decrease in the loading capacity with an increase in adsorbent dose for a Zn/Al LDH-like compound during the removal of fluorides from an aqueous solution). On the other hand, we have observed that the adsorbent dose seems to also affect the adsorption isotherms. The reasons for this are still not clear and are currently under investigation. As a result, for all experiments reported here (other than those in Figure 2), a common adsorbent dose of 0.12 g/L was utilized.

3.3. Kinetics of Adsorption. The amounts of metal (As(V) and Se(IV)) adsorbed as a function of the time of adsorption on calcined and uncalcined LDHs (adsorbent batch #1) are shown in Figure 3. Though the initial uptake is fairly fast for all metal species, it takes typically 2−3 days for the final concentration in solution (and the adsorbed amount) to completely level off (the adsorption isotherms reported below were generated after 5 days of continuous metal−adsorbent contact, as

noted previously). Though the adsorption rate of Se(IV) on an uncalcined LDH is faster than that of As(V), the equilibrium adsorption capability of Se(IV) is only half of that for As(V). The differences in behavior between calcined and uncalcined LDHs may be related to the additional surface area that is created by the calcination process but are also likely due to the fact that the interlayer of the calcined LDH contains fewer carbonate anions than that of the uncalcined LDH. Selenite and arsenate are both capable of incorporating themselves in this interlayer region. For these low initial As and Se concentrations (<20 ppb), there is some scatter in the measured concentration data, after the adsorption has reached its plateau (particularly for the calcined LDH and Se), and the values reported in Figure 3a represent averages among several such duplicate experiments. For Se on uncalcined LDH, there is a range of nonmonotonic adsorption behavior prior to reaching saturation (similar behavior was also observed with adsorbent #2), which persists over all duplicate experiments and which does not disappear upon varying the initial pH. The reason for this behavior is still unclear, and is currently under investigation.

Adsorption kinetics models correlate the solute uptake rate with the bulk concentration of the solute to be adsorbed; these models are important in water treatment process design and optimization. To develop intrinsic kinetic rate models, one must ascertain first that the experimental data are free of external mass transport limitations by providing sufficient solution and particle agitation during adsorption. In our experiments, we determined the rate of agitation above which external limitations are no longer important by varying the rate of agitation and measuring the corresponding rates of adsorption. An agitation rate of 150 rpm was sufficient to eliminate external mass transport limitations. To fit the experimental data, we have utilized an mth-order kinetic rate equation of the form

$$\mathrm{d}q_t/\mathrm{d}t = k(q_e - q_t)^m \tag{1}$$

where q_e is the amount of solute adsorbed ((mg of solute)/(kg of adsorbent)) at equilibrium with the corresponding bulk concentration of the solute, q_t is the amount of solute adsorbed on the LDH at any time, m is the adsorption rate order, and k [((mg of solute)/(kg of adsorbent))$^{1-m}$·min^{-1}] is the effective adsorption rate constant. Equation 1 must be coupled with the mass-balance equation below for the batch reactor system

$$V\frac{\mathrm{d}C}{\mathrm{d}t} = -W\frac{\mathrm{d}q_t}{\mathrm{d}t} \tag{2}$$

where C is the bulk concentration for the solute (μg/L) at time t, V (mL) is the volume of the reactor, and W (mg) is the amount of the adsorbent present. Equations 1 and 2 must also be coupled with the Freundlich adsorption equilibrium relationship (see further discussion below).

$$q_e = KC^{1/n} \tag{3}$$

A Genetic algorithm which uses selection, crossover, and mutation steps to update the parameter values was utilized to calculate the optimal values of parameters which are consistent with the experimental data. During parameter estimation, the 4th-order Runge−Kutta method was used to solve the set of coupled differential equations (eqs 1−3) above. Figure 4 shows the raw experimental data for As(V) and Se(IV) on calcined and uncalcined LDHs in the form of concentration remaining in the solution versus time, together with the calculated theoretical lines based on the estimated parameters. The estimated values of k and m, together with the corresponding coefficient of determination R^2, are shown in Table 1 (the R^2 values for Se on uncalcined LDH are calculated without taking into account the four points at the minimum of the concentration curve). The empirical exponential rate model provides a satisfactory fit for the adsorption of both As and Se on calcined and uncalcined LDHs. The adsorption kinetics seem to be approximately second order except for the case of Se(IV) on a calcined LDH (similar conclusions were drawn in adsorption studies with adsorbent batch #2).

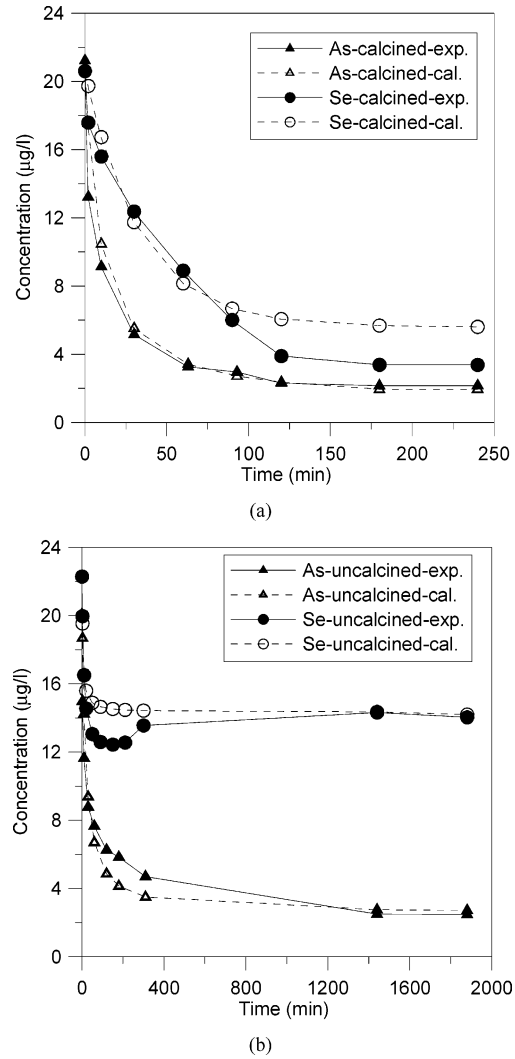

Figure 4. Comparison between the measured and modeled time profiles for adsorption of As(V) and Se(IV) on (a) calcined and (b) uncalcined LDHs.

Table 1. Kinetic Parameters for the Adsorption Experiments

	k	m	R^2
As/calcined LDH	1.00 E−6	2.14	0.941
Se/calcined LDH	1.01 E−2	0.98	0.936
As/uncalcined LDH	1.26 E−6	2.24	0.901
Se/uncalcined LDH	2.00 E−3	1.98	0.975

3.4. Isotherms for As(V) and Se(IV) Uptake. The adsorption isotherms for As(V) and Se(IV) on both

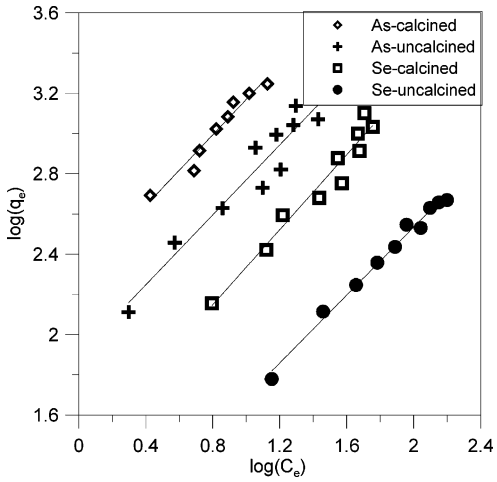

Figure 5. Adsorption isotherms for As(V) and Se(IV) on calcined and uncalcined LDHs.

Table 2. Freundlich Adsorption Constants for Adsorption of As and Se on LDH

	K	$1/n$	R^2
As/calcined LDH	194.4	0.880	0.956
Se/calcined LDH	25.1	0.934	0.952
As/uncalcined LDH	79.4	0.870	0.920
Se/uncalcined LDH	6.99	0.845	0.989

calcined and uncalcined LDHs were also investigated using adsorbent from batch #1. For the range of concentrations studied, the isotherms show no apparent plateau, indicating how effective such materials are for the adsorption of these metals. The data are shown in Figure 5 together with their fit to the Freundlich adsorption isotherm (in the form $\log(q_e) = \log K + {}^1/_n \log(C_e)$). The data show a satisfactory fit to the Freundlich isotherm (better than the fit to the Langmuir isotherm model,) particularly for adsorption on the calcined LDH ($R^2 > 0.95$) and for Se on the uncalcined LDH ($R^2 = 0.989$), and somewhat less so for As on the uncalcined LDH ($R^2 = 0.92$). The estimated K [((mg of solute)/(kg of adsorbent))(L/(μg of solute))$^{1/n}$] and n values are shown in Table 2. In the Freundlich model, K is a measure of the adsorption capacity (larger K indicates a larger overall capacity), whereas the parameter $1/n$ is a measure of the strength of adsorption (larger n indicates higher sorption affinity). As can be seen in Table 2, As(V) has a larger sorption capacity than Se(IV) for both the uncalcined and calcined LDHs. The isotherms also indicate that the adsorption capacity of As(V) and Se(IV) on the calcined LDH is considerably higher than that on the uncalcined LDH. The higher adsorption capacity on calcined LDH may be explained by the overall higher surface area resulting from calcinations; it is also likely due to the fact that the interlayer of the calcined LDH contains fewer carbonate anions than that of the uncalcined LDH and that the calcined LDH, when put in water, can reconstitute the hydrotalcite structure with the incorporation of As and Se anions from the aqueous solution. The LDHs show good promise for the treatment of trace levels of As and Se from power-plant effluents. For example in our study, the 5 day adsorption saturation capacity (calculated by a Langmuir isotherm fit of the experimental data for an initial As concentration range of 20−200 ppb) of As on uncalcined and calcined LDHs is found to be 4545 and 5609 (μg of As(V))/g, respectively. For the adsorption of trace ppb levels of As from aqueous solutions,

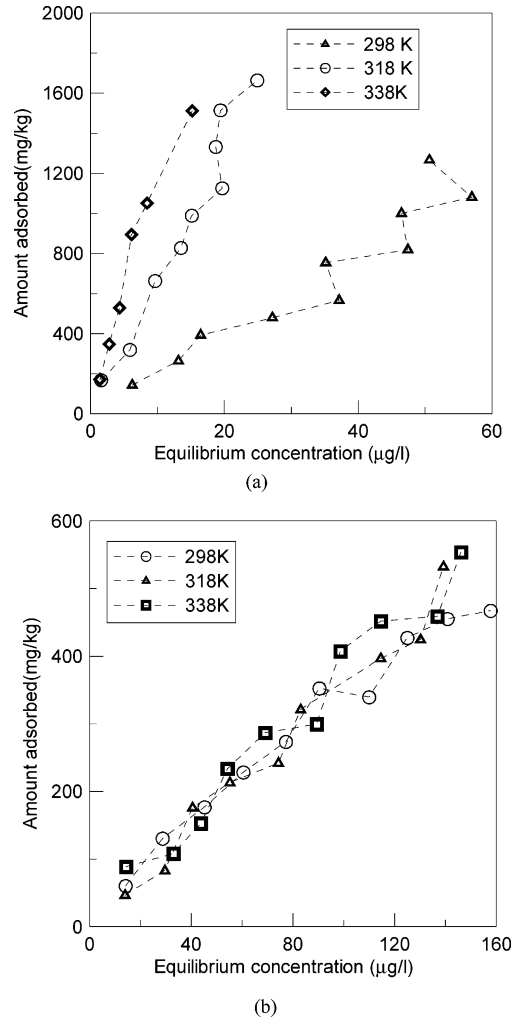

Figure 6. Adsorption of Se(IV) on (a) calcined and (b) uncalcined LDHs as a function of temperature.

adsorption capacities reported in the literature for ferrihydride[32] are ~300 (μg of As(V))/g, while for adsorption on iron oxide-coated sand (IOCS)[33] at pH 7.6, capacities are ~45 (μg of As)/g.

The effect of temperature on the adsorption capacity of As(V) and Se(IV) on calcined and uncalcined Mg−Al−CO_3 LDHs has also been investigated. Figure 6 shows the adsorption of Se(IV) on calcined and uncalcined LDHs at 298, 318, and 338 K. Surprisingly, the amount of Se(IV) adsorbed on the calcined LDH increases with increasing temperature, suggesting that adsorption of Se(IV) on calcined LDH is apparently an endothermic process. Misra and Adutwum[34] have also reported that Se adsorption on activated alumina is an endothermic process, and Pavan et al.,[35] who studied the adsorption of sodium dodecyl sulfate (SDS) on Mg−Al−CO_3 LDH, also found that the adsorbed amount of SDS increases with increasing temperature. Another possible explanation for the effect of temperature on adsorption is that it may be due to the presence of carbonate ions that may be present in the solution prior to placing it in the batch reactors. Increasing the temperature may decrease the concentration of such anions, which would then cause less interference with the adsorption of the metals. Thermodynamic calculations, however, based on the assumption that the solution equilibrates with the atmospheric CO_2 and using the dissociation constants of H_2CO_3[36] and for the

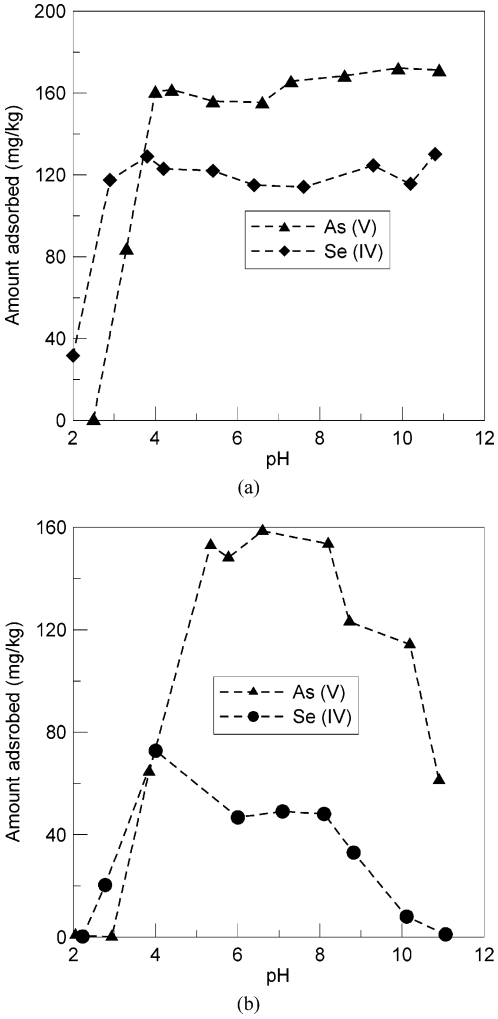

Figure 7. Effects of pH on the uptake of As(V) and Se(IV) in 20 ppb solutions on (a) calcined and (b) uncalcined LDHs.

range of experimental pH values, indicate that the total ($HCO_3^- + CO_3^{2-}$) concentration is at most in the range of a single digit ppb at 298 K. Such concentrations of carbonate anions have been shown (see the discussion in Section 3.7) to have little effect on the adsorption of Se.

In contrast to Se(IV) adsorption on the calcined LDH, temperature has little effect on the adsorption of the same metal on the uncalcined LDH. And though not shown here, As(V) adsorption on calcined and uncalcined LDHs (investigated using a lower dosage of 0.02 g/L) decreases with increasing temperature, indicating an exothermic process.

3.5. The Effect of pH. The effect of starting solution pH on the adsorption of As(V) and Se(IV), from solutions with an initial concentration of 20 ppb, on calcined and uncalcined LDHs (from adsorbent batch #2) is shown in Figure 7. (To lower the pH we introduced 2−60 ppm of NO_3^-; this concentration of NO_3^- anions will not affect the adsorption behavior of As and Se in the solution. See the discussion in Section 3.7.) The data indicate that the amounts of As(V) and Se(IV) adsorbed on calcined LDH (Figure 7a) decrease with decreasing pH for a starting solution pH <4, while for pH >4, the adsorption seems to be pH-independent. The decrease in adsorption with decreasing pH in the low-pH range may be due to the dissolution of LDH in the low-pH solutions.[20] This was confirmed by the presence of Mg and Al in the final solution using the ICP-MS analysis. The adsorption of As(V) and Se(IV) on uncalcined LDH shows a different behavior with respect to the starting solution pH than the adsorption on the calcined LDH. As Figure 7b indicates, there is a certain range of pH values for which the adsorbed amount is maximized. For As(V), adsorption is fairly high in a starting pH range from 5 to 8. Below pH 5, adsorption decreases sharply with decreasing pH (this again may be due to the dissolution of the LDH structure), and the same is true with increasing pH above 8 (see explanation below). Adsorption of Se(IV) on uncalcined LDH first increases with increasing pH and reaches its maximum at ~pH 4. Then, the adsorption decreases and appears to reach a plateau in the pH range of 6−8; the adsorption decreases again with increasing pH, above 8. The effect of pH on As(V) and Se(IV) adsorption using solutions with a higher initial concentration (i.e., 50 ppb) exhibits similar trends.

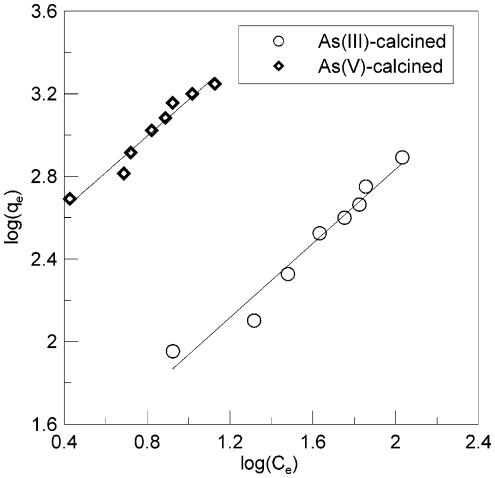

Figure 8. Adsorption isotherms of As(III) and As(V) on calcined LDHs.

The effect of pH on adsorption on uncalcined LDH can be explained as follows. Since the point of zero charge (pH_{pzc}) for the uncalcined LDH was reported to be in the range 6.8−8.9,[31,37] the surface of the LDH is negatively charged when pH > pH_{pzc}. Therefore, in the higher pH range, the arsenate and selenite anionic species will be repelled by the LDH surface. For pH < pH_{pzc}, the LDH surface is positively charged, which is normally beneficial for the adsorption of the negatively charged anionic species. On the other hand, as previously noted, very low pH negatively impacts the stability of the LDH structure and, therefore, results in a decrease of the uptake of As and Se anions. The negative effect of pH at the higher pH range may be further compounded by the increasing competitive effect of OH^- adsorption on LDH. Miyata[38] reported that OH^- has the highest LDH affinity among monovalent anions such as Cl^-, Br^-, and NO_3^-.

3.6. The Effect of the As and Se Oxidation States. Adsorption behavior of As(III) and Se(VI) on calcined and uncalcined LDHs was also investigated in this study. The adsorption isotherm data for As(III) and Se(VI), together with the corresponding data for As(V) and Se(IV), are shown in Figures 8 and 9, respectively (for adsorbent batch #1). As one notes from Figure 8, As(III) adsorbs less from aqueous solutions than As(V); in fact, though we do not include the data here, uncalcined LDH adsorbs almost no As(III). The differ-

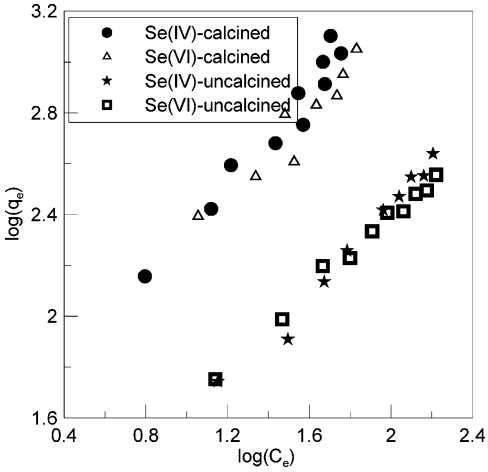

Figure 9. Adsorption isotherms of Se(IV) and Se(VI) on calcined and uncalcined LDHs.

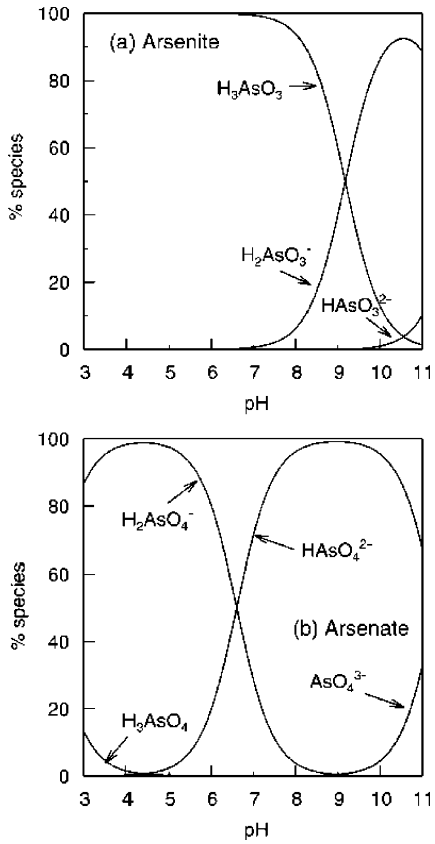

Figure 10. (a) Arsenite, As(III), and (b) arsenate, As(V), speciation as a function of pH.[39]

ence in the total amounts adsorbed of As(III) and As(V) on the LDH adsorbents may be related to the different species found in solution for these two forms of As with different oxidation states. Figure 10 show the speciation diagrams for arsenate and arsenite with respect to pH. Arsenate is present as negatively charged ionic species (either $H_2AsO_4^-$ or $HAsO_4^{2-}$) in a broader range of pH conditions than arsenite, which is mostly found in the nonionic form (H_3AsO_3). Since the LDHs above their isoelectric point are positively charged, one expects the negatively charged As(V) species to be more easily adsorbed by the LDH structure, either through anion exchange for the uncalcined LDH, or by rehydration and incorporation into the calcined LDH, to rebuild the initial LDH structure. In contrast, Se(IV) and Se(VI)

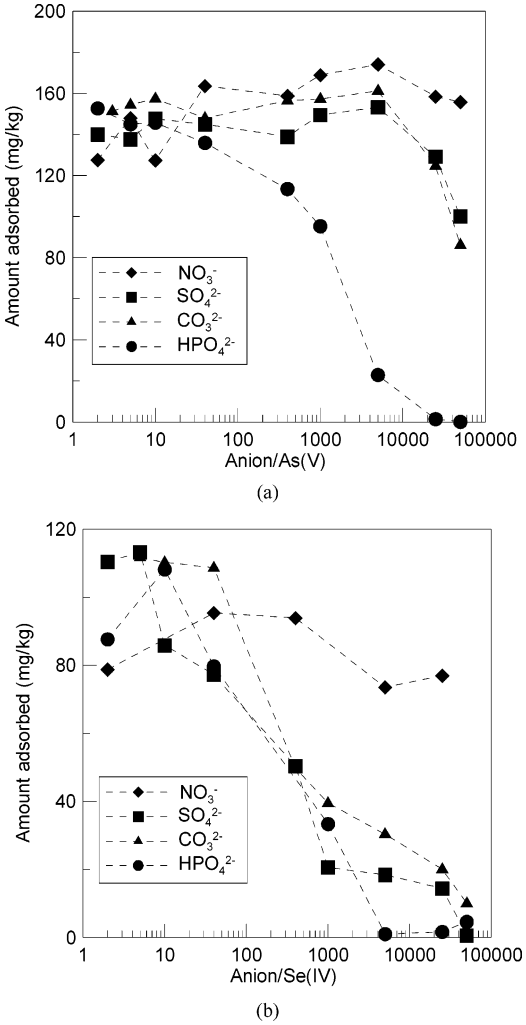

Figure 11. The effects of competitive anions on the uptakes of (a) As(V) and (b) Se(IV) on calcined LDH in 20 ppb solutions.

adsorption is very similar on both calcined and uncalcined LDHs, as shown in Figure 9.

3.7. Effects of Competitive Anions on As(V) and Se(IV) Uptake. Figure 11 shows the effect of competitive anions on the uptake of As(V) and Se(IV) by the calcined LDH. The experimental data indicate that NO_3^- has almost no effect on the adsorption of As(V) on the calcined LDH up to a concentration of 1 000 ppm (50 000 times higher than the initial concentration of As(V) of 20 ppb). SO_4^{2-} and the carbonates (these are introduced in the solution through the use of Na_2CO_3; CO_3^{2-} and HCO_3^- coexist in the solutions for the concentration range studied, so the term carbonates is used to represent both CO_3^{2-} and HCO_3^-) have a modest effect, causing only 14% and 20% reductions when their concentration is 500 ppm, and 33% and 45% reductions, respectively, when the concentration is 1000 ppm. HPO_4^{2-} (these are introduced through the use of K_2HPO_4; HPO_4^{2-} is the main anion that results, with only minor amounts of $H_2PO_4^-$ or PO_4^{3-} being present in the solution) appears to be the anion that most negatively impacts the adsorption of As(V). When its concentration is 20 ppm, adsorption of As is 34% less than when HPO_4^{2-} is absent from the solution. As(V) adsorption completely stops when the HPO_4^{2-} concentration is >500 ppm. The presence of HPO_4^{2-} does not appear to be a serious issue for power-plant effluents, however; we have analyzed the concentration in two power-plant

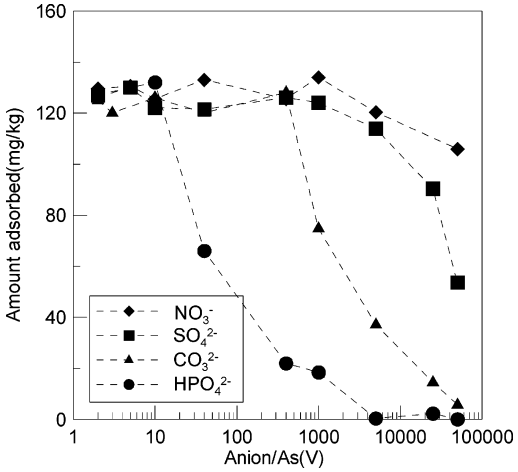

Figure 12. The effects of competitive anions on the uptakes of As(V) on uncalcined LDH in 20 ppb solutions.

effluents—Harbor cogeneration station and the Redondo generating station—using ICP-MS and found that the HPO_4^{2-} concentration was <150 ppb, which means that the uptake of As and Se in such effluents will not be affected by its existence. To summarize, the effect of competing anions on the adsorption of As(V) decreases in the order: HPO_4^{2-} > carbonate > SO_4^{2-} > NO_3^-.

Competitive anions have a stronger effect on Se(IV) uptake than on As(V) uptake. As shown in Figure 11b, SO_4^{2-}, carbonate, and HPO_4^{2-} have a significant effect on Se uptake, even when their concentrations are only 400 times higher than that of Se. The effect of competing anions on the adsorption of Se(IV) decreases in the order HPO_4^{2-} > SO_4^{2} > carbonate > NO_3^-. However, in the case of Se, the negative impact of HPO_4^{2-} is not as significantly different from the impacts of carbonate and SO_4^{2-} as in the case of As(V). The differences in behavior between As(V) and Se(IV) on the effect of competitive ions are consistent with the differences in their sorption affinities (see Table 2) toward the LDH. In a previous study on the sorption of the same metals on LDH, You et al.[25] reported that Se uptake by Mg−Al LDHs from 20 ppm solutions is also seriously impacted by competitive ions, such as SO_4^{2-}, CO_3^{2-}, and HPO_4^{2-}, when the ratio of the concentration of such anions to Se was >20.

The competing ions have a stronger effect on the adsorption on uncalcined LDH than on that of calcined LDH. The adsorption of As(V) on the uncalcined LDH is shown, as an example, in Figure 12. Comparing Figure 12 with Figure 11a, the carbonates, for example, cause an ~69% reduction when their concentration is 100 ppm, 5000 times higher than the initial 20 ppb concentration of As(V) in the solution.

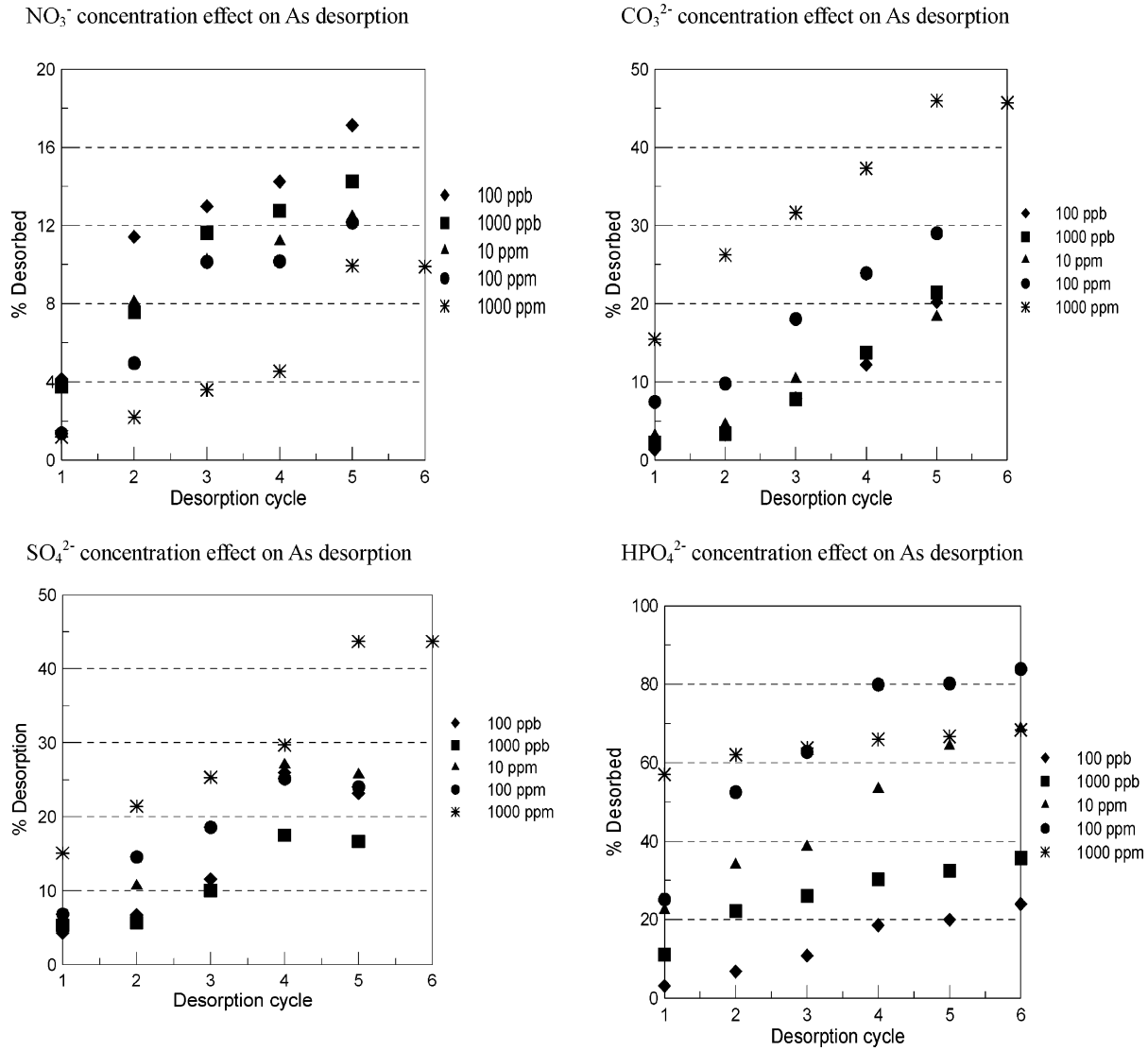

Figure 13. Desorption of As(V) from calcined LDH as a function of different anions and concentrations.

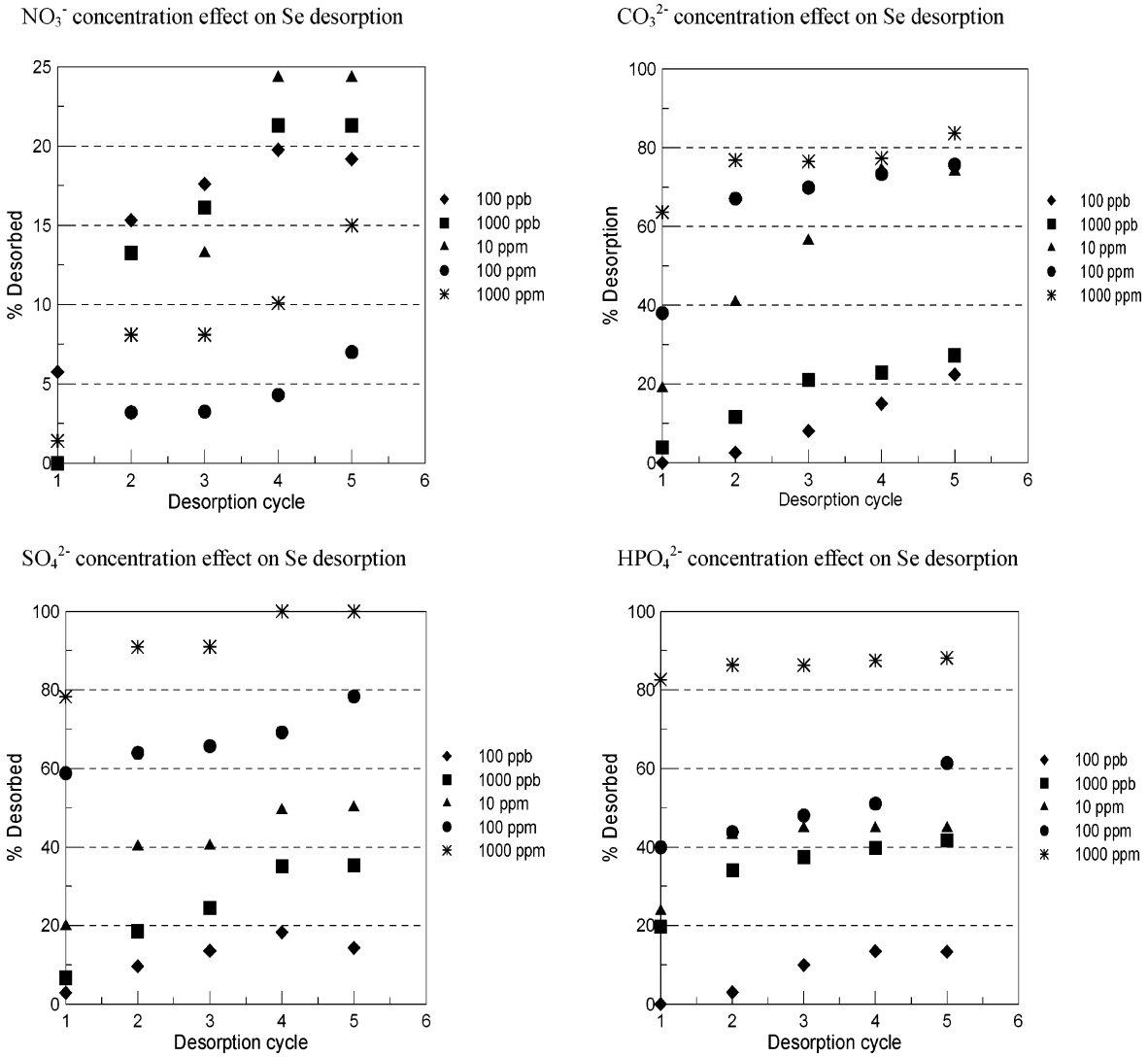

Figure 14. Desorption of Se(IV) from calcined LDH as a function of different anions and concentrations.

3.8. Desorption Results. Figure 13 shows the effect of solutions containing various anions with differing concentrations on the desorption of As(V) from calcined LDH. This figure indicates that different metal amounts can be desorbed by the different anions and that the type of the anion species present, as well as its concentration in the solution, can affect the desorption process. In the NO_3^- solution, only up to 17% of the adsorbed As(V) is desorbed after five desorption cycles. Although the data are somewhat scattered, it is interesting to note that the fraction of As that is desorbed appears to decrease with increasing NO_3^- concentration. This might be due to the effect of ionic strength on the adsorption. Lazaridis et al.[40] reported that arsenate adsorption increased with increasing ionic strength (potassium nitrate is used for regulating the solution ionic strength). Therefore, the higher the NO_3^- concentration in the solution, the better is the adsorption interaction between the arsenate ions and the adsorbent and the smaller is the amount of arsenate desorbed. For the carbonate and SO_4^{2-} solutions, the fraction of As(V) that desorbs from the LDH does not depend on the anion concentration for concentrations of <10 ppm, while at >10 ppm, the fraction of As(V) that desorbs increases with increasing carbonate and SO_4^{2-} concentration. After five cycles with the 1000 ppm carbonate and SO_4^{2-} solutions, for example, 46% and 43% of As(V) are desorbed, respectively. The release of As(V) in HPO_4^{2-} solutions is faster and more concentration dependent. Almost 84% of As(V) desorbs in the 100 ppm HPO_4^{2-} solution after the five desorption cycles. Note that the desorption of As(V) in the 1000 ppm HPO_4^{2-} solutions is very fast; ~57% of As desorbs after the first desorption cycle, and the desorption amount does not significantly increase with increasing desorption cycles. The reason for this is not clear at the present time. The desoprtion results for As(V) in the presence of various anions are consistent with the adsorption behavior in the presence of the same competitive anions. We have found previously that the effect of various competitive anions on the adsorption of As on calcined LDH decreases in the order HPO_4^{2-} > carbonate > SO_4^{2-} > NO_3^-; we noted in the discussion that the reason for such a behavior is most likely the different affinities of the same anions for the LDH, which also follow the same order. As Goswamee et al.[41] noted previously, when an anion is better suited stereochemically for inclusion into the interlayer of LDH, it also has a greater ability to cause the release of interlayer anions already present in the LDH.

Desorption of Se as a function of various anions and concentrations is shown in Figure 14. Both the desorption rate and the fraction of Se(IV) that is desorbed from the calcined LDH are higher in this case than in the

case of As(V). For HPO_4^{2-}, SO_4^{2-}, and carbonate (and for the nitrate case for lower NO_3^- concentrations), for example, it takes about three desorption cycles for the fraction of metal desorbed to reach a plateau. This behavior is consistent with the lower sorption affinity of Se toward the calcined LDH, since the lower the affinity of a given metal to the calcined LDH, the easier it is for the same metal to be released in the solution. In general, the release rates and the fraction of Se metal removed in HPO_4^{2-}, SO_4^{2-}, and carbonate solutions increase with an increase in the metal concentrations. In the case of the NO_3^- solutions, only small fractions of the Se(IV) are removed and the behavior with respect to concentration is rather complex. The maximum amount of desorption of Se is found in the 1000 ppm SO_4^{2-} solution, for which 100% of adsorbed Se is desorbed.

Summary and Conclusions

From the results reported here, one concludes that calcined Mg−Al−CO_3 LDH is a promising adsorbent for the removal of trace levels of As and Se from aqueous solutions, even in the presence of competing ions, such as CO_3^{2-} and HPO_4^{2-}. The empirical exponential rate model provides a satisfactory fit for the adsorption of both As and Se on calcined and uncalcined LDHs. As(V) has a higher affinity to both calcined and uncalcined LDHs than Se(IV). The adsorption of Se(IV) on the calcined LDH is a endothermic process, while the adsorption of As(V) on both calcined and uncalcined LDHs is exothermic. The results also indicate that pH does not significantly influence the adsorption of As and Se on calcined LDHs when pH > 4, while As and Se adsorption on uncalcined LDH is more sensitive to changes in the pH. As(III) is much more difficult to remove than As(V) both by calcined and uncalcined LDHs. In contrast, Se(IV) and Se(VI) adsorption is very similar on both calcined and uncalcined LDHs. Desorption of As(V) and Se(IV) depends on the anion species and concentrations in the desorbing solutions. Both the desorption rate and the desorption amounts of Se(IV) from calcined LDH are higher than those of As(V). The maximum amounts of As(V) and Se(IV) desorbed are found in 100 ppm HPO_4^{2-} and in 1000 ppm SO_4^{2-} solutions, respectively, for which ~84% and 100% of the As(V) and Se(IV) adsorbed are desorbed.

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