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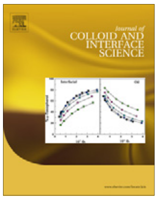

Complexation at the edges of hydrotalcite: The cases of arsenate and chromate

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ABSTRACT

Sorption of CrO_4^{2-} and $HAsO_4^{2-}$ by hydrotalcite, in its chloride form, was studied as a function of anion concentration. In both cases, the shape of the isotherms is langmuirian. The maximum uptake of CrO_4^{2-} equals the ion-exchange capacity of the solid, whereas sorption of $HAsO_4^{2-}$ saturates at a higher value. Chloride ions inhibit the uptake of both anions, the amount of sorbed CrO_4^{2-} declining rapidly to zero. The uptake of $HAsO_4^{2-}$, however, attains a constant value at high chloride concentrations. The excess of arsenate uptake follows, at constant pH, a langmuirian dependence with equilibrium concentration and decreases with increasing pH, depicting a marked change in slope at $pH \approx pQ_{a3}$. CrO_4^{2-} and $HAsO_4^{2-}$ have notable, albeit different, effects on the electrophoretic behavior of hydrotalcite; the positive particle charge is screened almost completely by CrO_4^{2-}, whereas sorption of $HAsO_4^{2-}$ produces charge reversal. These results reflect the formation of inner-sphere arsenate surface complexes at the edges of hydrotalcite particles. The underlying rationale is discussed in terms of the crystal structure of hydrotalcite surfaces.

1. Introduction

Layered double hydroxides (LDHs) are stacks of hexagonal $M(OH)_2$ layers containing divalent and trivalent metal ions in mole ratios that span typically from 2 to 4. These slabs are held together by intercalated anions, which counterbalance their excess positive charge and determine the basal spacing of the solid [1]; water molecules, as well, occupy the interlamellar space. Whereas natural LDHs are rather scarce, the variety of synthetic LDHs is nowadays huge [2,3]. Small inorganic interlamellar anions, except carbonate, are readily exchangeable [4]. For this reason, these materials are regarded as promising sorbents for the removal of dissolved toxic anions [5–11]. Anion uptake is dominated by ion-exchange; thus, maximum uptake capacities are determined by the composition of the brucite-like layers (i.e., by their M(II)/M(III) mole ratios) and by the charge number of the incoming anion. Affinities, on the other hand, are influenced by anion charge/size ratios [12], as well as by enthalpic and entropic contributions [13,14].

Clearly, anion exchange is a phenomenon that involves the bulk of LDHs. However, it has been recently suggested that adsorption at the edges of LDHs particles may also be of importance. Wang and Gao [15], based on structural considerations, argued that sorption at edges is driven by a *cage effect*; according to them, the interlaminar space and the voids between corner-sharing $M(OH)_6$ octahedra at edges of the brucite-like layers define a cage, which should provide a suitable sorption chemical environment for fitting anions. On the other hand, Goh et al. [16], based on the ideas set by the well-known surface complexation approach [17–19], suggested that oxyanions form also inner-sphere complexes at the edges of hydrotalcite. Despite the latter suggestion is indeed sound, the evidence advanced by the authors is rather feeble.

Aiming at assessing the actual role of the edges of LDHs particles in the uptake of oxyanions, this work presents a detailed study of the effect of chloride concentration on the sorption of arsenate and chromate by Cl-hydrotalcite and reports the electrophoretic behavior Cl-hydrotalcite immersed in arsenate and chromate aqueous solutions.

2. Experimental

Chloride-hydrotalcite was synthesized by coprecipitation as described previously [20]. The so-prepared solid is composed of ca. 100 nm size hexagonal platelets. Its XRD pattern depicts reflections that are typical of LDHs, the basal spacing being 0.786(2) nm, and $d_{110} = 0.305(1)$ nm. Its chemical composition, which was assessed by elemental analyses, is given by the formulae $Mg_{0.73}Al_{0.27}(OH)_2Cl_{0.19}(CO_3)_{0.04}\cdot H_2O$.

Chromate and arsenate sorption experiments were performed as follows: weighted aliquots of a 4 g L^{-1} aqueous dispersion of

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hydrotalcite were placed in Pyrex flasks, to which measured volumes of solutions containing K_2CrO_4 (or Na_2HAsO_4) and KCl in known concentrations were added. The pH of the resulting suspensions was measured and adjusted (when required) by adding a small volume of a KOH solution of appropriate concentration. The systems were then left to equilibrate under constant stirring for 1 h at room temperature (23 ± 1 °C); preliminary experiments showed that sorption equilibrium is attained in ca. 20 min. Afterward, the suspensions were filtered throughout 0.22 μm pore-size nitrocellulose membranes, and the supernatants stored for analyses. Chromate and arsenate concentrations were measured by ICP-AES in a Perkin Elmer Optima 5100 spectrometer. The amount of Cr(VI), or As(V), taken up per gram of hydrotalcite (q) was then determined solving the mass balance of the systems, that is,

$$q = \frac{(C_0 - C)V}{m} \tag{1}$$

where C_0 is the total Cr(VI), or As(V), concentration, C is the concentration of the equilibrated solution, V is the volume of the aqueous phase, and m is the mass of hydrotalcite in the system.

Electrophoretic mobility measurements were carried out using a Malvern Zeta Sizer 2000 apparatus. For this purpose, Cl-hydrotalcite particles were dispersed in 5×10^{-3} M KCl, 5×10^{-3} M K_2CrO_4, and 5×10^{-3} M Na_2HAsO_4 solutions of prefixed pH and let to equilibrate for at least 1 h before the measurements; all solutions were pre-filtered through 0.22 μm pore-size membranes. All suspensions were extremely diluted to avoid possible artifacts due to multiple scattering. Consequently, the concentrations of Cr(VI) and As(V) in equilibrium with the solid can be safely assumed to be equal to the total concentration of the salts. Measured electrophoretic mobility values were cast as zeta potential (ζ) using von Smoluchowski's equation. Despite these experiments were performed at a different ionic strength, the observed electrophoretic behaviors can be safely compared; in the studied range, the influence of ionic strength on ζ is negligible.

To avoid dissolution of the solid phase [21], all experiments were carried out at pH ⩾ 9.3, which is the natural pH of hydrotalcite aqueous suspensions; it is worth mentioning that dissolution may blur the interpretation of the data.

Analytical grade reagents and deionized water (18 MΩ cm^{-1}), obtained from an E-pure apparatus, were used in all experiments. They were performed under a CO_2-free nitrogen blanket to avoid carbonate contamination. pH values were measured using a combined glass electrode and a Metrohm 654 pH-meter.

3. Results and discussion

Figs. 1 and 2, which show respectively the sorption isotherms of CrO_4^{2-} and $HAsO_4^{2-}$ at pH 9.3, indicate that Cl-hydrotalcite sorbs both anions very efficiently. At this pH value, both chromate ($pK_{a2} = 6.51$) and arsenate ($pK_{a2} = 6.96$; $pK_{a3} = 11.50$) are present as dianions (see Supplementary data), thus the uptake of Cr(VI) and As(V) must be accounted for by the following anion exchange equilibria:

$$1/2CrO_4^{2-}(aq) + HTCl(s) = Cl^-(aq) + HT(CrO_4)_{1/2}(s) \tag{2}$$

$$1/2HAsO_4^{2-}(aq) + HTCl(s) = Cl^-(aq) + HT(HAsO_4)_{1/2}(s) \tag{3}$$

where HT stands for $[Mg_{3.84}Al_{1.42}(OH)_{10.52}(CO_3)_{0.21}]^+$; interlamellar water molecules were omitted. Note that carbonate ions are not exchangeable [4,20]

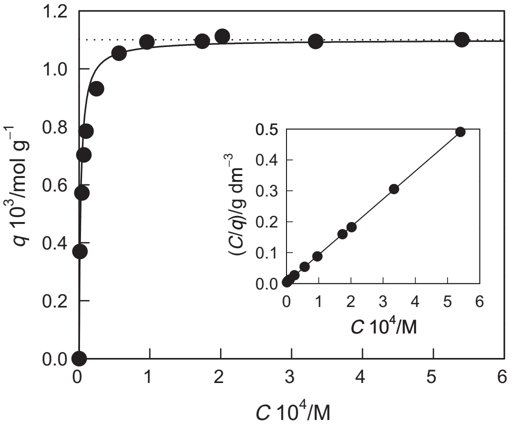

Fig. 1. Uptake of Cr(VI) as a function of the chromate equilibrium concentration; hydrotalcite load: 0.8 g L^{-1}; pH = 9.3 ± 0.1. The dotted line shows the value of the maximum exchange capacity. Inset: data re-plotted in terms of Eq. (4).

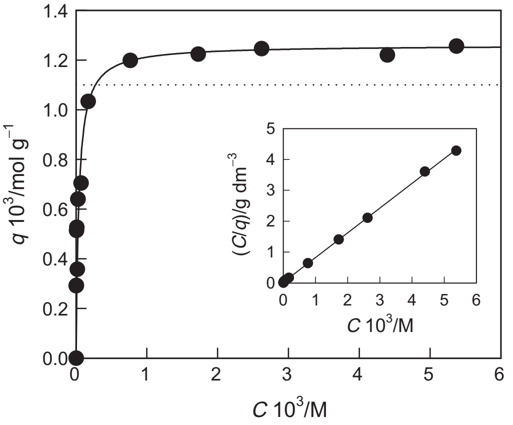

Fig. 2. Uptake of As(V) as a function of the arsenate equilibrium concentration; hydrotalcite load: 3.1 g L^{-1}; pH = 9.3 ± 0.1. The dotted line shows the value of the maximum exchange capacity. Inset: data re-plotted in terms of Eq. (4).

Table 1
Langmuirian parameters describing the uptake of chromate and arsenate by chloride-hydrotalcite.

Anion	K_L (M^{-1})	q_m (mmol g^{-1})	$q_m - mec_{1:2}$
CrO_4^{2-}	4.0×10^5	1.11	0
$HAsO_4^{2-}$	2.5×10^4	1.26	0.15

Both sorption profiles, however, can be well described by the Langmuir adsorption model, from which the parameters listed in Table 1 were derived; maximum uptake capacities, q_m, were determined from the reciprocal of the slopes of the straight lines (Eq. (4)) shown in the insets of Figs. 1 and 2. For anion exchange reactions (Eqs. (2) and (3)), compliance of the data presented in latter figures with the Langmuir adsorption model is fortuitous [20], thus the derived K_L values ought to be regarded as operational ones [22]. Nonetheless, Eq. (4) allows for the accurate determination of q_m, on which we shall center our attention.

$$\frac{C}{q} = \frac{1}{q_m K_L} + \frac{1}{q_m} C \tag{4}$$

For chromate, the maximum uptake matches exactly $mec_{1:2}$, which is the value of the maximum exchange capacity that results from the chemical composition of the exchanger phase and the anticipated 1:2 anion exchange stoichiometry (Eq. (2)). For $HAsO_4^{2-}$, on the other hand, q_m is larger than $mec_{1:2}$. The excess, which is about 14%, cannot be attributed to a departure from the exchange stoichiometry. Deviations from the expected anion ex-