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Effective removal and fixation of Cr(VI) from aqueous solution with Friedel's salt

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ABSTRACT

Friedel's salt ($3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$ or $Ca_4Al_2(OH)_{12}Cl_2(H_2O)_4$) is a calcium aluminate hydrate formed by hydrating cement or concrete in seawater at a low cost. In the current study, we carefully examined the adsorption behaviors of Friedel's salt for Cr(VI) from aqueous solution at different concentrations and various initial pHs. The adsorption kinetic data are well fitted with the pseudo-first-order Lageren equation at the initial Cr(VI) concentration from 0.10 to 8.00 mM. Both the experimental and modeled data indicate that Friedel's salt can adsorb a large amount of Cr(VI) (up to 1.4 mmol Cr(VI)/g) very quickly ($t_{1/2}$ = 2–3 min) with a very high efficiency (>99% Cr(VI) removal at [Cr] < 4.00 mM with 4.00 g/L of adsorbent) in the pH range of 4–10. In particular, the competitive adsorption tests show that the Cr(VI) removal efficiency is only slightly affected by the co-existence of Cl^- and HCO_3^-. The Cr(VI)-fixation stability tests show that only less than 0.2% adsorbed Cr(VI) is leaching out in water at pH 4–10 for 24 h because the adsorption/exchange of Cr(VI) with Friedel's salt leads to the formation of a new stable phase ($3CaO{\cdot}Al_2O_3{\cdot}CaCrO_4{\cdot}10H_2O$). This research thus suggests that Friedel's salt is a potential cost-effective adsorbent for Cr(VI) removal in wastewater treatment.

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1. Introduction

Hexavalent chromium (Cr(VI)) is a primary contaminant of concern in water purification due to its high toxicity. On one hand, a variety of industrial processes, including metal plating, tanning, and textile production, produce the effluents with high concentrations of chromium. Once such effluents are not well treated and directly discharged to the rivers and lakes, the public water system will be then Cr-contaminated. On the other hand, however, prolonged exposure to the chromium even at very low concentrations can cause lung cancer [1], and thus US-EPA has set up a maximum contaminant level of 100 μg/L of total chromium in drinking water [2]. Therefore, the technology for the effective removal of Cr(VI) from water and wastewater is urgently needed.

In the recent years, various methods have been developed to remove Cr(VI), including adsorption [3–7], chemical reduction [8] and membrane separation [9,10]. Among these methods, the adsorption technique using various absorbents (iron-complexed protein waste, modified active carbons, composite chitosan biosorbent, modified zeolite, maghemite and some clay materials) has been recognized as an effective and potential method. However, the removal effectiveness, i.e. the adsorption capacity of Cr(VI) and/or the adsorption time, seems not to be ideal, and is often pH dependent. The adsorption amount of Cr(VI) in most cases was 0.1–1.0 mmol Cr(VI)/g with the pH being often selected in the range of 1–4 [3–7]. Therefore, it is very much desirable if an adsorbent can effectively adsorb Cr(VI) in a wider pH range since the effluent pH in various industries normally fluctuates from pH 3.0 to 12.0 [11]. To this end, layer double hydroxides (LDHs), especially, Friedel's salt, appear to be the cost-effective candidate.

Layer double hydroxides (LDHs) are a family of anionic clay minerals consisting of cationic brucite layers and exchangeable interlayer anions, and most can be nominally expressed as a chemical formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}mH_2O$, where M^{2+} represents any divalent metal cation, M^{3+} any trivalent metal cation and A^{n-} an anion (inorganic or organic) [12]. Various LDHs with easily exchangeable anions, such as chloride-LDHs, have been explored as adsorbents to remove chromate contaminants in recent years [13–19]. For example, ZnAl-, MgAl- and ZnCr-Cl-LDHs were reported to adsorb *ca.* 1.0 mmol Cr(VI)/g by Houri et al. [16]. Carriazo et al. found that the adsorption capacity of MgAl- and ZnAl-Cl-LDHs (up to 1.2–1.4 mmol Cr(VI)/g) is higher than calcined MgAl- and ZnAl-LDHs for Cr(VI) [14]. These reports demonstrate that chloride-LDHs is a good adsorbent for the removal of Cr(VI). However, the adsorption (anion exchange) took very long time (normally

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more than 24 h) to reach the adsorption equilibrium [14]. Tzou and co-workers reported that $LiAl_2(OH)_6Cl$-LDH can even take up 3.81 mmol Cr(VI)/g [17]. However, the intercalated Cr(VI) can be easily leached out (40–80%) within a few hours.

In particular, Friedel's salt ($Ca_4Al_2(OH)_{12}Cl_2(H_2O)_4$ or $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$), known as chloride hydrocalumite, is a major and stable hydration product of cement/concrete subjected to sea water or other chemical aggressive attacks, so this salt can be easily and cheaply made via the simple hydration reaction between cement paste and Cl-bearing salt solution [20,21]. The cement paste (the basic chemical composition is $CaO–Al_2O_3–SiO_2–H_2O$) was reported to take up Cr(VI), but the adsorption capacity was quite low (0.16 mmol Cr(VI)/g) [22]. On the contrary, Qian et al. reported that Friedel' salt can strongly fix heavy metals from electronic sludge wastes [23]. Therefore the objective of this research was particularly to investigate the Cr(VI) adsorption behaviors of Friedel's salt in detail. We found that this special mineral salt can very quickly adsorb a larger amount of Cr(VI) (1.3–1.4 mmol Cr(VI)/g in practice) in a wider pH range and can strongly fix the chromate within its lattice.

2. Materials and methods

2.1. Preparation and characterization of Friedel's salt

Friedel's salt (Ca_4Al_2-Cl-LDH) was prepared by precipitation method as reported elsewhere [24]. In brief, 22 mmol of powdered $3CaO{\cdot}Al_2O_3$ (prepared at 1400 °C in our lab) was slowly added to a solution containing 22 mmol of $CaCl_2{\cdot}6H_2O$ (GA, Riedel-dehaen) under vigorous stirring. The $CaCl_2$ solution was made by dissolving $CaCl_2{\cdot}6H_2O$ in distilled water, having an initial pH of *ca.* 6.5. The mixed suspension was aged at 45 °C for 24 h under stirring, having a final pH of *ca.* 10.5. The precipitate was then collected via filtration, thoroughly washed with deionized water and dried at 100 °C in an oven.

The synthesized Friedel's salt was identified with the powder X-ray diffraction pattern recorded on a Dmax/RB diffractometer (Rigaku Co.) with Cu Kα radiation ($\lambda = 0.15418$ nm) at 34 kV and 20 mA, and further characterized with the FTIR spectrum collected on a Perkin-Elmer 2000 FTIR in the range of 4000–400 cm^{-1} with resolution of 4 cm^{-1} using the KBr pellet technique. The morphological images of as-prepared Friedel's salt were recorded on a scanning electron microscope (JSM-6360). The specific surface area was derived using BET method to analyze the low temperature N_2 adsorption isotherm on a Quantachrome NOVA-1200 gas absorption analyzer.

2.2. Adsorption of Cr(VI)

In all adsorption tests, 4.00 g/L of Friedel's salt was used. To investigate the adsorption equilibrium, a series of Cr(VI) solutions were prepared by dissolving K_2CrO_4 (AR, UnivaR) with the initial Cr(VI) concentration from 0.10 to 8.00 mM and adjusting the initial pH to 4.0, 6.0, or 10.0 with dilute HCl or NaOH solution. In general, 50 mL of Cr(VI) solution and 0.200 g of Friedel's salt were added into a 100-ml sealed conical flask that was shaken at a speed of 150 rpm in a thermostatic water bath at 25 ± 1 °C. After 24-h adsorption, the remaining Cr(VI) concentration was determined. All the experiments were carried out in duplicate with the reproducibility within ±5%.

To examine the adsorption kinetics of Cr(VI) over Friedel's salt, the initial Cr(VI) concentration of 0.40, 2.00, or 8.00 mM with the initial pH of 10.0 was selected and the adsorption was conducted under the similar conditions. At the selected time points (0.25, 0.5, 1, 2, 3, 4, 8, 16, and 24 h), an aliquot of 1.0 mL was withdrawn through a 0.22-μm filter for the Cr(VI) concentration determination. In particular, the competitive adsorption of Cr(VI) with Cl^- and HCO_3^- was further conducted by adding NaCl (2.00 mM), $NaHCO_3$ (2.00 mM), or NaCl (1.00 mM) plus $NaHCO_3$ (1.00 mM) into the Cr(VI) solution (2.00 mM Cr) under similar conditions.

During the adsorption, the pH was monitored with an Elico digital pH meter (Model LI-120) using a combined glass electrode (Model CL 51). The final precipitate was collected and analyzed with XRD. The Cr(VI) concentration was determined spectrophotometrically at 540 nm, following the 1,5-diphenylcarbazide method [25] in a Varian Cary 1E UV-spectrophotometer (Model EL96043181). The Cl^- concentration was monitored following the method in the literature in a Flow Injection Analyzer (Lachat Quikchem 8000).

2.3. Fixation stability evaluation

The stability of Cr(VI)-adsorbed Friedel's salt was evaluated by modified toxicity characteristic leaching procedure (TCLP) [26]. The Cr(VI)-loaded Friedel's salt (2.50 g, the final adsorption product from a solution containing the initial [Cr] = 8.00 mM and initial pH 10.0) was placed in 50 mL of deionized water with pH being previously adjusted to 4.0, 7.0, 10.0, or 13.0 using dilute HCl or NaOH. At the selected time points (1, 2, 3, 4, 8, 16 and 24 h), an aliquot of 1.0 mL was withdrawn to determine the concentration of released Cr(VI).

3. Results and discussion

3.1. Structural features of Friedel's salt

The as-prepared sample was identified with the XRD pattern (Fig. 1A) to be a pure Friedel's salt with the approximate formula of *formula of* $Ca_{3.6}Al_2(OH)_{11.2}Cl_{1.9}(CO_3)_{0.05}(H_2O)_{3.8}$, since the pattern was well matched with the reported one (JCPDS No 78-1219), with the layer spacing of 7.81 Å. Similarly, such a mineral phase was also confirmed by the FTIR spectrum (Fig. 1B) which shows all the characteristic vibrations of the salt, such as 3636 and 3480 cm^{-1} (ν_{OH}), 1621 cm^{-1} (δ_{H_2O}), and 785, 620 and 532 cm^{-1} (M–O vibrations and M–O–H bending in lattice) [24,27]. In particular, the band at 1442 cm^{-1} due to the stretching vibration of CO_3^{2-} indicated the adsorption of CO_2 from air during the synthesis [28]. In addition, the as-prepared Friedel salt has the specific surface area of *ca.* 10 m^2/g.

3.2. Adsorption isotherms

Fig. 2A shows the isotherms of Cr(VI) adsorption on Friedel's salt at 25 °C with different initial pH values. Seemingly, the three curves are quite close one another, indicating that the adsorption behaviors at different pH are similar. This is largely due to the pH buffering capacity of Friedel's salt, as reported for MgAl-LDH elsewhere [29]. As also shown in Fig. 3, pH of the aqueous mixture (4.00 g/L of Friedel's salt in pure water and Cr(VI) solution, the initial pH 4.0) was almost immediately jumped to *ca.* 10.0, as a consequence of a small portion of Friedel's salt dissolution [30,31,32], and finally increased to 10.5–11.4. Similarly, such dissolution takes place also at the initial pH of 6.0 or even 10.0. Although the initial pH is 4.0, 6.0, or 10.0, the dissolution of Friedel's salt in a small portion leads to a very similar final pH, i.e. 10.3–11.3 [32]. However, the equilibrium adsorption capability at pH 10.0 is always slightly higher than those at pH 4.0 and 6.0 at the same equilibrium concentration under the same conditions, because much less Friedel's salt is dissolved at pH 10.0. In the experiments, the practical maximum adsorption capability is 1.34, 1.36 and 1.45 mmol Cr(VI)/g at pH 4.0, 6.0 and 10.0, respectively (Fig. 2A).

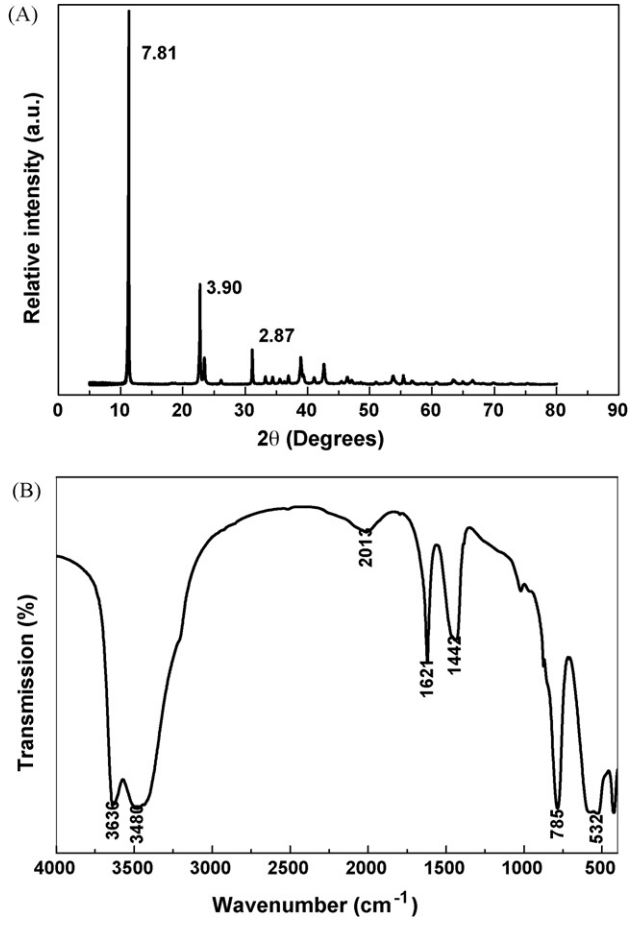

Fig. 1. The XRD pattern (A) and FTIR spectrum (B) of as-prepared Friedel's salt. The marked number in (A) is in Å.

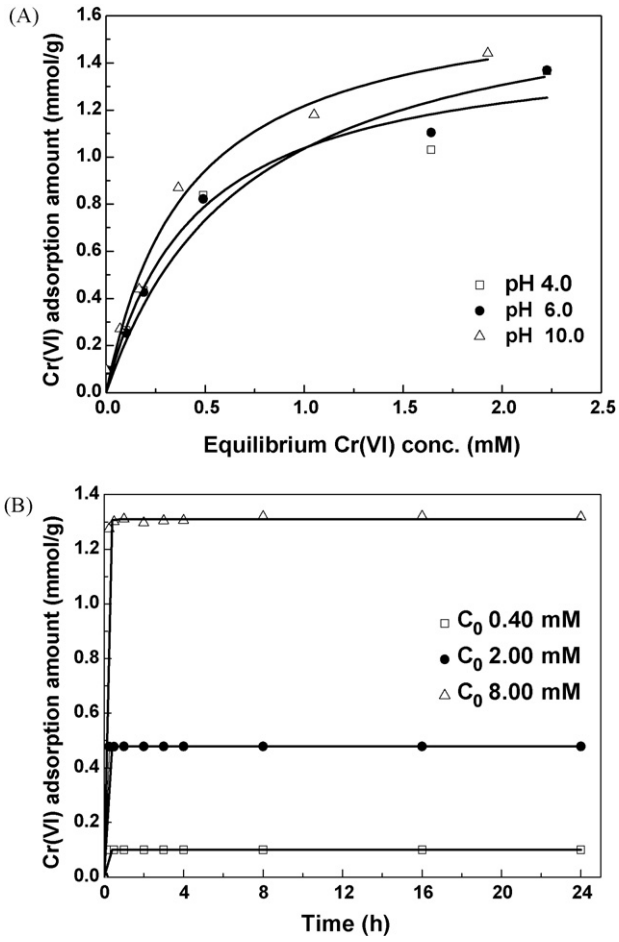

Fig. 2. Cr(VI) adsorption isotherms (A) and kinetics (B) over Friedel's salt.

3.3. Adsorption kinetics

As Cr(VI) adsorption at pH 10.0 is a bit more efficient in the test concentration range, we further investigated the adsorption kinetics at the initial pH of 10.0. Fig. 2B shows the time-adsorption profile of Cr(VI) at the initial concentration of 0.40, 2.00 and 8.00 mM. Obviously, Cr(VI) adsorption on Friedel's salt took place mainly within the first half hour and then reached the saturate plateau. Increasing the adsorption time to more than 1 h seemed not to bring any further benefit.

The kinetic data are well fitted to the first-order Lageren equation:

$$Q_t = Q_e(1 - e^{-kt})$$

where Q_e is the Cr(VI) amount adsorbed on Friedel's salt at the equilibrium (mmol Cr(VI)/g), Q_t the Cr(VI) amount adsorbed at time t (mmol Cr(VI)/g), and k the adsorption rate constant (min^{-1}). As summarized in Table 1, the rate constant (k) at the initial [Cr] = 0.40 and 2.00 mM is very similar (0.415–0.432 min^{-1}), indicating the similar adsorption behavior, while k for [Cr] = 4.00 and 8.00 mM is also similar (0.257–0.283 min^{-1}), but a bit smaller. Even though there is only 1–2 data points before the curve reaches a plateau and the k value may not be so exact, however, it still reveal that Cr(VI) adsorption is a very fast process ($t_{1/2} = 0.693/k = 2$–3 min). In this connection, the Cr(VI) adsorption and the pH jumping (Fig. 3) seem to occur simultaneously and mainly in the first 5–15 min.

Table 1
The parameters from the kinetic modeling of Cr(VI) adsorption on Friedel's salt.

C_0 (mM)	k (min^{-1})	Q_e (mmol Cr(VI)/g)	R^2
0.40	0.415	0.100	1.000
2.00[a]	0.432	0.478	1.000
4.00	0.283	0.986	1.000
8.00	0.257	1.310	0.999

[a] The real [Cr] concentration is 1.92 mM in 100 ppm Cr(VI) solution.

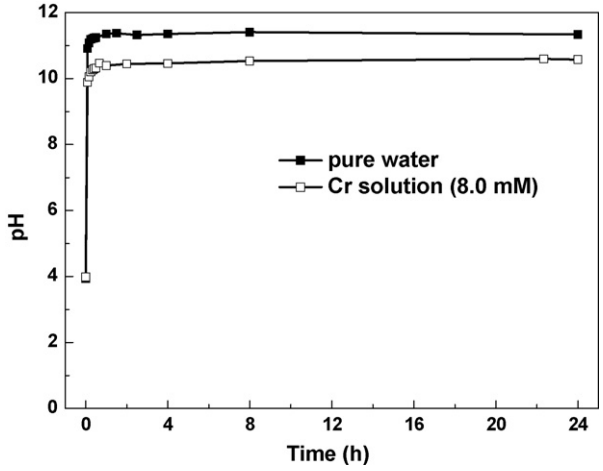

Fig. 3. pH change profile after adding 4.00 g/L Friedel's salt into water or Cr(VI) solution.

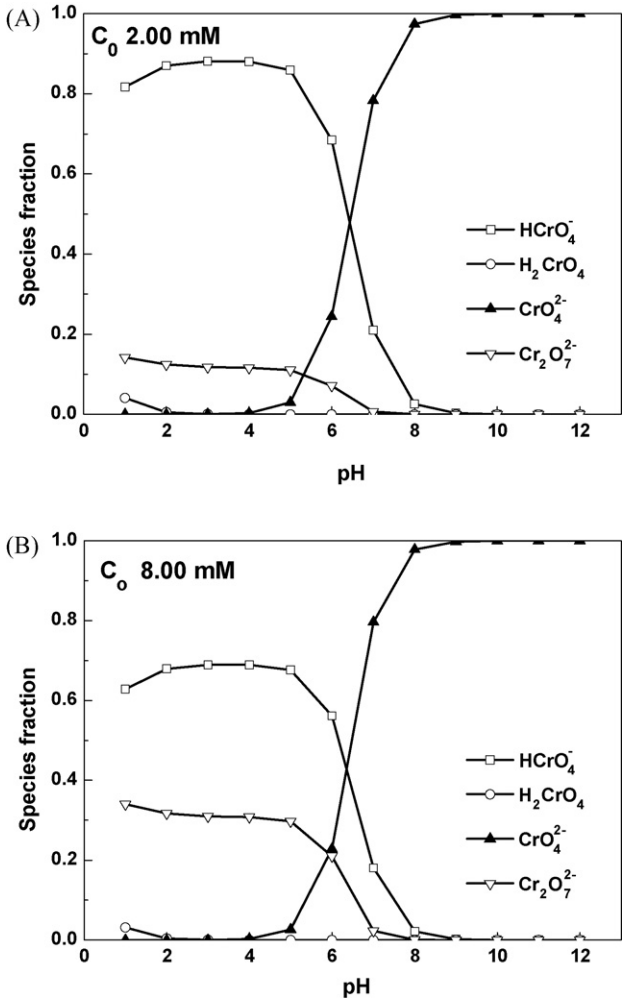

Fig. 4. Chromate species distribution at different pH with initial [Cr(VI)] = 2.00 (A) and 8.00 mM (B).

Not surprisingly, a higher percentage (>99%, estimated with $100 \times 4.00 \times Q_t/C_0$) of Cr(VI) was removed at the initial concentration of 0.40 and 2.00 mM while only 65% Cr(VI) was adsorbed at the initial [Cr] = 8.00 mM. The lower percentage of Cr removal at the initial [Cr] = 8.00 mM is because the amount of Cr(VI) in the solution is exceeding the maximum capability that Friedel's salt is expected to demonstrate. In theory, 1.00 g chloride hydrocalumite (MW = 524, $Ca_{3.6}Al_2(OH)_{11.2}Cl_{1.9}(CO_3)_{0.05}(H_2O)_{3.8}$) can at most adsorb 1.81 mmol CrO_4^{2-} (suppose that carbonate cannot be exchanged), corresponding to 7.24 mM under current conditions. The practical maximum adsorption amount is close to the theoretical limit considering that the as-prepared chloride hydrocalumite contains a bit carbonate, indicating that this material is a very efficient absorbent for Cr(VI). The adsorption at the initial [Cr] = 4.00 mM was an in-between case. The removal percentage was as high as 98.6%, like at the lower concentrations. However, the adsorption rate constant was close to that at a higher concentration.

3.4. Adsorption process

As shown in Fig. 4, at pH above 8.0, chromate (Cr(VI)) exists only in the form of CrO_4^{2-}. Therefore, in the case of the initial pH 10.0, CrO_4^{2-} is the only Cr(VI) species that involves the adsorption/exchange, as expressed in the following reaction:

$$Ca_4Al_2(OH)_{12}Cl_2(H_2O)_4{\cdot}xH_2O + CrO_4^{2-} \rightarrow Ca_4Al_2(OH)_{12}CrO_4(H_2O)_4{\cdot}xH_2O + 2Cl^- . \quad (1)$$

When the initial pH is 4.0 or 6.0, the pH quickly jumps to over 10.0 as the consequence of the quick dissolution of Friedel's salt (refer to Fig. 3) [31,32]. Simultaneously, the Cr(VI) adsorption occurs also very quickly (Fig. 2B), so both two forms of chromates ($Cr_2O_7^{2-}$ and CrO_4^{2-}) involve the adsorption, which should result in a higher Cr(VI) adsorption amount at the initial pH 4.0 than pH 10.0. However, pH rising from 4.0 to 10.0 needs more Friedel's salt to dissolve, which reduces the effective adsorbent and thus decreases the Cr(VI) adsorption amount.

Presumably, $Cr_2O_7^{2-}/CrO_4^{2-}$ are first adsorbed onto the surface by replacing surface Cl^-. During this period, as the pH is quickly increased, the adsorbed $Cr_2O_7^{2-}$ is thus expected to convert to CrO_4^{2-}. These CrO_4^{2-} are then intercalated into the interlayer via exchanging with interlayer Cl^-. The intercalation of CrO_4^{2-} results in the phase transform of Friedel's salt. As indicated by XRD patterns (Fig. 5A) of Cr(VI)-adsorbed Friedel's salts collected from the chromate solution with initial [Cr] = 4.0 mM and initial pH 10.0, the original chloride hydrocalumite was the major phase after 2-h adsorption, with the d(0 0 3) and d(0 0 6) being 0.78–0.79 and 0.39 nm, respectively. This phase started to transfer to a new phase after 18 h, and the transformation completed after 24-h adsorption/exchange. In contrast, when the initial [Cr] = 8.00 mM

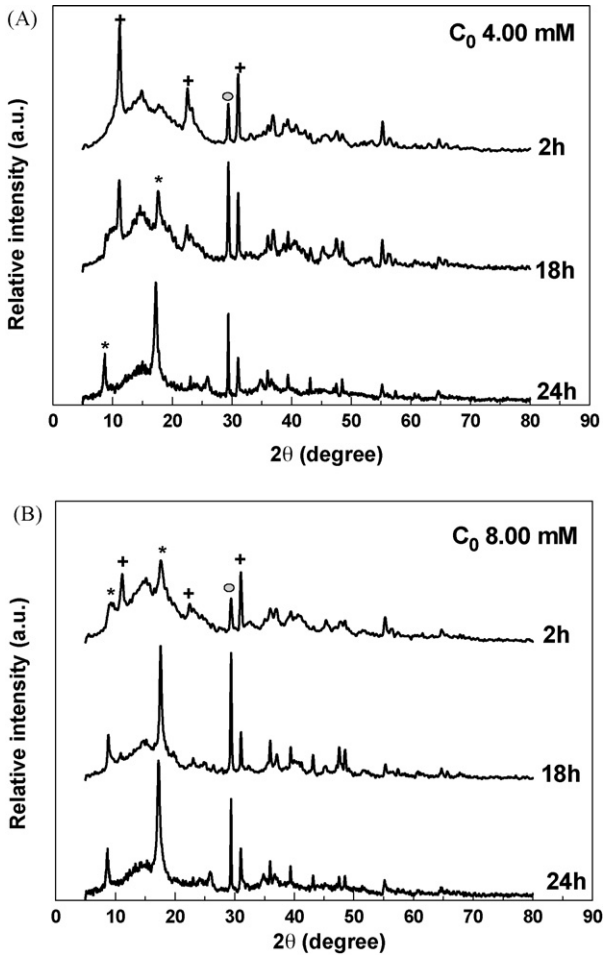

Fig. 5. XRD patterns of adsorbents after adsorption of CrO_4^{2-} vs. reaction time at pH 10.0 with initial [Cr] = 4.00 (A) and 8.00 mM (B), where the original Friedel's salt was marked as "+", the newly formed hydrocalumite as "*", and $CaCO_3$ as "○".

(Fig. 5B), the new phase appeared at as early as 2 h, and the initial chloride Friedel's salt disappeared after 18 h. The XRD pattern of the new phase is identical to that of chromate hydrocalumite ($Ca_4Al_2(OH)_{12}CrO_4(H_2O)_4$, JCPDS 42-0063), with two characteristic *d* values of 0.51 and 1.00 nm, corresponding to the (0 0 4) and (0 0 2) diffraction, respectively. The expansion of the layer space from 0.78–0.79 to 1.00 nm is due to the intercalation of larger CrO_4^{2-}. The layer space of Cr(VI)-intercalated sample is in excellent agreement with the report elsewhere [32,33].

In terms of the time scale, the adsorption of most Cr(VI) occurs within the first 5–15 min while the new phase becomes predominant only after 2 h (Fig. 5B). It has been observed that the anion intercalation takes place within a few minutes via the adsorption on the edges and surfaces [34,35], so the adsorption/intercalation of chromate is very fast. However, the formation of a new phase (i.e. chromate hydrocalumite) that can be detected with XRD needs a longer period of time as the reconstruction of the new LDH structure via the so-called 3D process [36] is a process slower than the adsorption/exchange. This may also be the reason that the adsorption of Cr(VI) over MgAl- and ZnAl-Cl-LDHs [14] is very slow (10 h to 7 days). Since quick pH rising (Fig. 3) gives a certain level of Ca^{2+}, $Al(OH)_4^-$ and OH^-. These ions in solution, together with CrO_4^{2-}, may facilitate the dissolution/re-crystallization of the LDH structure [36], and thus speed up the exchange/adsorption of Cr(VI).

The phase change was also indicated by the XRD patterns of the equilibrium products with different initial Cr(VI) concentrations. As shown in Fig. 6, chloride hydrocalumite was the major phase when initial [Cr] ≤ 2.0 mM. Supposing all Cr(VI) joins the exchange, about 28% Cl^- is expected to be replaced at initial [Cr] = 2.0 mM. When the initial [Cr] increases to ≥4.00 (pH 4.0 and 6.0) or 3.20 mM (pH 10.0), the characteristic peaks of chromate hydrocalumite appeared and the peak intensities increased with the initial Cr(VI) concentration.

If CrO_4^{2-} adsorption were all attributed to the exchange with Cl^- ions (Eq. (1)), then each CrO_4^{2-} would release two Cl^- into the solution. However, as shown in Fig. 7A, the molar ratio of Cl^-/CrO_4^{2-} is only 0.8–0.9 if a straight line is used to fit the data. This small molar ratio suggests that CrO_4^{2-} replaces some other species. One possibility is the exchange of CrO_4^{2-} with hydroxide hydrocalumite, without releasing Cl^-:

$$Ca_4Al_2(OH)_{12}(OH)_2(H_2O)_4{\cdot}xH_2O + CrO_4^{2-} \rightarrow Ca_4Al_2(OH)_{12}CrO_4(H_2O)_4{\cdot}xH_2O + 2OH^- \quad (2)$$

We believe this is a possible process. At the beginning of Cr(VI) adsorption, we note that [Cl^-] is already 8–10 mM (Fig. 7B), which may come from the residue NaCl in the adsorbent (ignorable) and those replaced by OH^- and CrO_4^{2-}. Since the pH is sharply increased to over 10.0, the freshly formed OH^- could probably replace interlayer Cl^- more quickly than CrO_4^{2-}, and intercalate into the interlayer spacing and release some Cl^- prior to Cr(VI) adsorption. Therefore Eq. (2) is a possible adsorption process, without Cl^- release.

It is worth mentioning that calcite ($CaCO_3$) is formed in all cases, as identified by the XRD peak at 29.1° (Figs. 5 and 6) Since the pH increases to above 10.0, the solution can readily absorb CO_2 from air and transfer to CO_3^{2-} that combines with the dissolved Ca^{2+} to produce $CaCO_3$. As [Ca^{2+}] was determined to be 1–2 mM in the experiments, so CO_3^{2-} at $2–4 \times 10^{-6}$ M could result in $CaCO_3$ precipitation. Such a low CO_3^{2-} concentration could drive the following exchange of CrO_4^{2-} with the original carbonate hydrocalmite (IR in Fig. 1B) to happen:

$$Ca_4Al_2(OH)_{12}CO_3(H_2O)_4{\cdot}xH_2O + CrO_4^{2-} \rightarrow Ca_4Al_2(OH)_{12}CrO_4(H_2O)_4{\cdot}xH_2O + CO_3^{2-}, \quad (3)$$

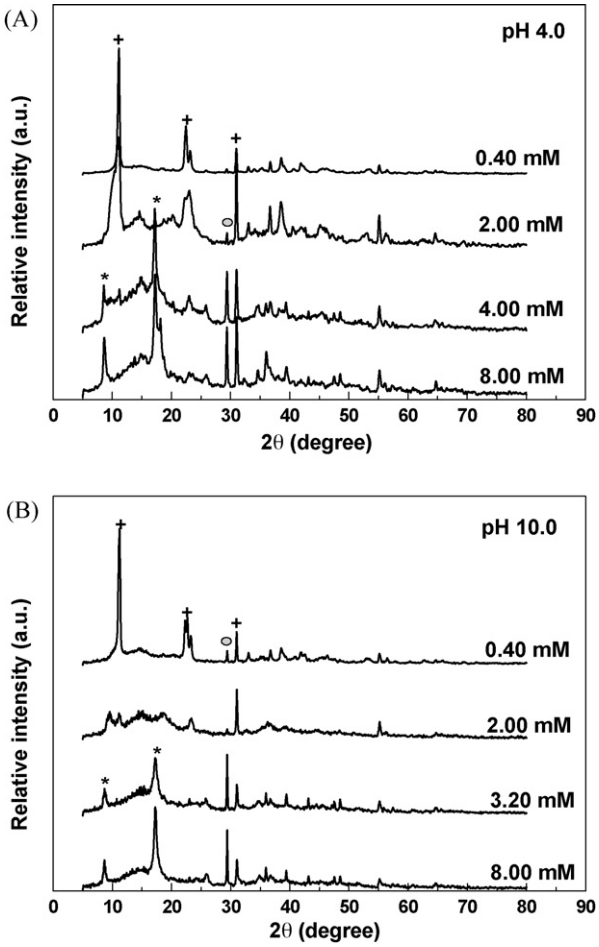

Fig. 6. XRD patterns of adsorbents after adsorption of CrO_4^{2-} vs. initial Cr(VI) concentration at initial pH 4.0 (A) and 10.0 (B) after 24-h adsorption, where the original Friedel's salt was marked as "+", the newly formed hydrocalumite as "*", and $CaCO_3$ as "○".

which adsorbs CrO_4^{2-}, but does not release Cl^-. Actually, the complete disappearance of the diffraction peak at 10.9° (assigned to (0 0 2) of either chloride or carbonate hydrocalumite) after 24-h exchange (Figs. 5 and 6) may demonstrate the happening of Eq. (3).

3.5. Effect of co-existing anions on the Cr(VI) adsorption

Since in the wastewater there are always some anions existing, such as Cl^-, HCO_3^- as well as phosphates, we further investigated the effects of some common anions for the competitive adsorption onto Friedel's salt. As shown in Fig. 8, the presence of Cl^- (2.00 mM) does not affect Cr(VI) adsorption in aqueous solution at all (initial [Cr] = 2.00 mM and initial pH 10), as reflected by the same time-adsorption profile as that without any anion existing. When $NaHCO_3$ is added into solution, HCO_3^- is supposed to change to CO_3^{2-} because pH quickly increases to above 10, therefore it is CO_3^{2-} (2.00 mM) that competes with CrO_4^{2-} (2.00 mM) in the exchange with Friedel's salt. Fig. 8 indicates that *ca.* 97% CrO_4^{2-} was first adsorbed within 15 min under the existence of 2.00 mM CO_3^{2-}. The removal percentage of CrO_4^{2-} was then decreased to 90% after 24-h adsorption, probably due to the continuous increase of CO_3^{2-} that comes from the capture of air CO_2 by this alkaline solution (pH 10–11). The increased CO_3^{2-} replaces CrO_4^{2-}, resulting in the removal percentage decrease. The decrease of Cr(VI) removal percentage with the adsorption time demonstrates that CO_3^{2-} has a higher affinity to hydrocalmite than CrO_4^{2-}. Predictably, the

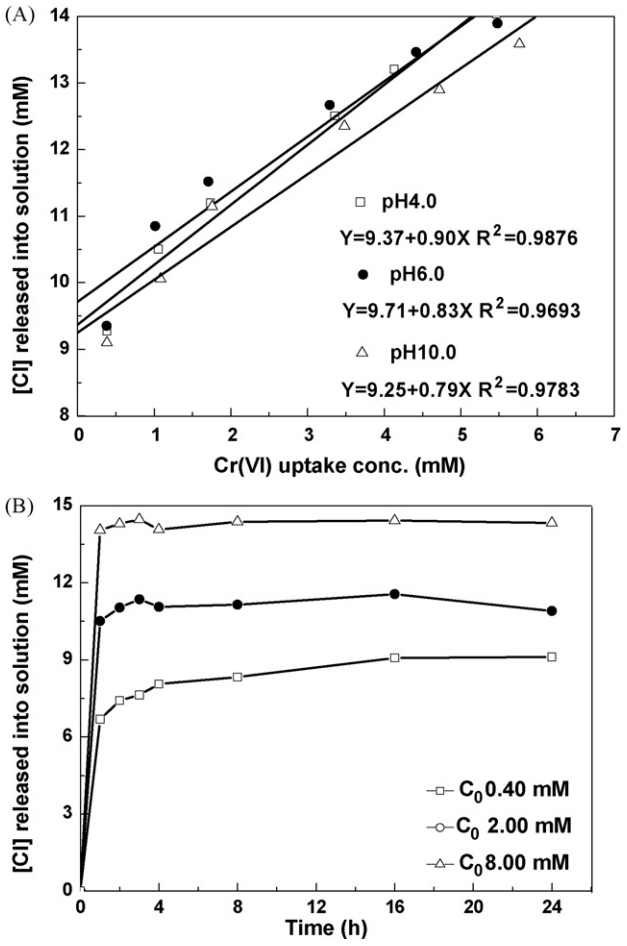

Fig. 7. Chloride release profile during the adsorption of Cr(VI) at different pHs (A) and different initial Cr(VI) concentration (B).

co-existence of Cl^- (1.00 mM) and CO_3^{2-} (1.00 mM) reduces the Cr(VI) removal percentage but to a very limited extent (>97% Cr(VI) removal) because of the competitive adsorption of less amount of CO_3^{2-}. Based on these observations, the co-existence of common anions in the wastewater containing chromate has a limited influence on the Cr(VI) removal with Friedel's salt, particularly for the adsorption in the first half hour.

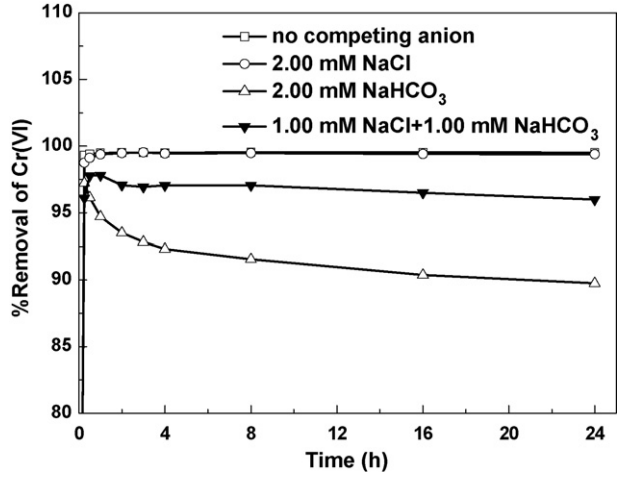

Fig. 8. The effect of co-existing Cl^- and/or HCO_3^- on the removal of Cr(VI). Note that the curve for no competing anion is overlapping with that with 2.00 mM NaCl.

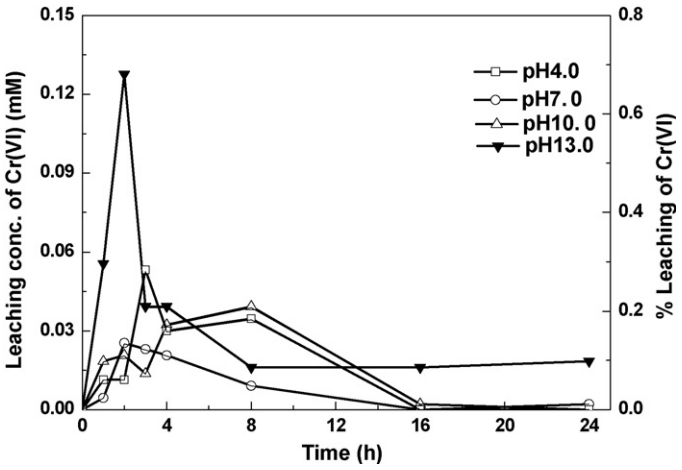

Fig. 9. Chromate release from Cr(VI)-adsorbed Friedel's salt in water.

3.6. Fixation stability of chromate with hydrocalumite

In order to evaluate the aqueous stability of chromate fixed onto hydrocalumite, i.e. the adsorption product collected from the solution with initial pH 10.0 and initial [Cr] = 8.00 mM after 24-h adsorption, the modified TCLP method was employed to examine the release behavior of chromate from the adsorbed product in water at different pHs. As shown in Fig. 9, the leaching concentration of Cr(VI) at pH 4–10 was only 0.03–0.06 mmol Cr(VI)/L, i.e. 1.6–3.1 mg Cr(VI)/L, after 10-h stirring, but then decreased to less than 0.01 mmol Cr(VI)/L afterwards, in comparison with 1–2 mM of Ca^{2+} and 0.1–0.2 mM $Al^{3+}/Al(OH)_4^-$ leached out simultaneously (unpublished data). The release amount corresponds to less than 0.2–0.3% of chromate adsorbed by Friedel's salt. In comparison with the competitive adsorption test (Fig. 8), the lower leach percentage of chromate may be due the much smaller concentration of carbonate in water as well as relative larger amount of chromate hydrocalumite (50 g/L). The chromate leaching profile suggests that its leaching process involves: (1) dissolution of chromate hydrocalumite that causes the increase of chromate leaching in 10 h and (2) re-precipitation/re-crystallization of chromate into the hydrocalumite matrix that leads to the decrease of chromate concentration afterwards. Only at pH 13.0 was the leaching CrO_4^{2-} amount a bit more, being maximum at 2 h (0.13 mmol Cr(VI)/L), i.e. 0.7% of chromate in the initial Cr-loaded hydrocalumite, probably caused by the dissolution of '$Al(OH)_3$' as $Al(OH)_4^-$ at a higher pH [36]. Generally speaking, Cr(VI) is well stabilized and fixed by Friedel's salt within a wider pH range. The stable fixation of Cr(VI) by Friedel salt presents a striking contrast to the case by $LiAl_2(OH)_6Cl$-LDH which can take up 3.81 mmol Cr(VI)/g but quickly release more than 40% of adsorbed Cr(VI) in a few hours [17].

4. Conclusion

Cr(VI) can be effectively adsorbed over Friedel's salt in the form of CrO_4^{2-} in the initial pH range of 4.0–10.0, with the practical adsorption capacity up to 1.3–1.4 mmol Cr(VI)/g. The initial pH of the chromate solution has a minor effect on the Cr(VI) adsorption amount due to the buffer capability of Friedel's salt. At [Cr] = 0.20–2.00 mM (Cr), this salt can remove over 99% Cr(VI) from the aqueous solution, and this effectiveness is only slightly affected by the co-existence of the common anions, such as Cl^- and HCO_3^-. The adsorption kinetics follows the pseudo-first-order Lageren process. The fixation of Cr(VI) probably involves the adsorption/exchange, leading to the formation of chromate hydrocalumite phase. Our tests have also indicated a higher fixation stability of

chromate in the hydrocalumite lattice at pH 4.0–13.0. The present research indicates that Friedel's salt is a potential cost-effective adsorbent for Cr(VI) removal from the wastewater.

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