The removal and recovery of Cr(VI) by Li/Al layered double hydroxide (LDH)

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Abstract

Hexavalent Cr has been identified as one of the toxic metals commonly present in industrial effluents. Among the treatment techniques developed for removing Cr(VI) from waste waters, sorption is most commonly applied, due to its simplicity and efficiency. However, few adsorbents can be recycled and reused cost-effectively. In this study, the removal and recovery of Cr(VI) from water using Li/Al LDH was investigated. The removal of Cr(VI) by Li/Al LDH was evaluated in a batch mode. The results demonstrated that Cr(VI) adsorption onto Li/Al LDH occurs by replacing the Cl^- that originally exists in the interlayer of the adsorbent. The degree of Cr(VI) adsorption observed for Li/Al LDH was relatively high and the process occurred rapidly; however, a portion of adsorbed Cr(VI) was gradually desorbed, due to the Li de-intercalation of Li/Al LDH. Lithium de-intercalation from Li/Al LDH with interlayer Cl^- and interlayer Cr(VI) follows the first order kinetics and has the activation energies of 76.6 and 41.5 kJ mol^{-1}, respectively. The properties of thermal unstablility and the high adsorption capacity of Li/Al LDH may lead to the development of an innovative technique for the removal of Cr(VI) from Cr(VI)-containing wastewater. That is, Li/Al LDH may be used as an effective adsorbent for the adsorption of Cr(VI) in an ambient environment. Following the adsorptive process, the adsorbed Cr(VI) may be released, using heated water to treat the Cr(VI)-containing Li/Al LDH particles. Through this hydrothermal treatment of the used adsorbent, Cr(VI) can be recovered and the solid product (gibbsite) can be recycled for further use.
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1. Introduction

In the environment, chromium predominantly exits in two oxidation states, trivalent chromium [i.e., Cr^{3+}, $Cr(OH)^{2+}$, or $Cr(OH)_2^+$ etc., usually denoted as Cr(III)] and hexavalent chromium [i.e., $HCrO_4^-$, CrO_4^{2-}, or $HCr_2O_7^-$ etc., usually denoted as Cr(VI)]. Chromium(III) naturally occurs in the environment and is an essential micronutrient for human beings. A dietary supplement of 200 μg Cr(III) d^{-1} is recommended for adult-onset diabetes mellitus and insulin resistance [1]. Conversely, Cr(VI) is generally produced via industrial processes and is commonly found at contamination sites. For example, previous studies have shown that the uncontrolled discharge of Cr-containing wastewater from metal finishing and leather tan-ning contribute significant amounts of Cr(VI) to surface waters [2]. Chromium(VI) is toxic to both plants and animals [3,4]. In particular, exposure to Cr(VI) may increase one's risk of con-tracting cancer or of developing hypersensitivity of the skin or respiratory system [5,6]. Moreover, because Cr(VI) exhibits high mobility in most neutral to alkaline soils, it poses a great threat to surface water and groundwater [7]. Therefore, it is necessary to eliminate Cr(VI) from the environment, in order to prevent the deleterious impact of Cr(VI) on ecosystems and public health. Sorption is one of the common methods used to remove Cr(VI) from wastewaters [8,9]. However, previous studies largely have focused on the removal efficiency of adsorbents; less attention has been paid to the disposal or recycling of Cr(VI)-containing adsorbents. The mishandling of used adsorbents may result in desorption of Cr(VI) from the adsorbents and secondary contam-ination with Cr(VI). Therefore, the development of a technique to recover Cr(VI) from adsorbents and recycle used adsorbents has become vital.

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Layered double hydroxides (LDHs) have a structure that is analogous to naturally occurring hydrotalcite [10]. The formula of LDHs is generally expressed as $[M_{1-x}{}^{z+}M_x{}^{3+}(OH)_2]^{y+}A_{y/n}{}^{n-} \cdot H_2O]$. The hydroxide layers in LDHs contain either divalent cations ($z = 2$) or monovalent cations ($z = 1$) with trivalent cations. In the case of $z = 2$, which is the major group of LDHs, the isomorphous substitution of divalent cations (Ca^{2+}, Cd^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, or Ni^{2+}) by trivalent cations (Al^{3+}, Cr^{3+}, Fe^{3+}, or, V^{3+}) results in positive charges within the hydroxide layers, and gives the formula $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}A_{x/n}{}^{n-} \cdot H_2O]$ [11–18]. The structure of LDHs consists of positively charged hydroxide layers [10,12]. The positive charges result from the isomorphous substitution of divalent cations by trivalent cations, and are counterbalanced by anions intercalating between adjacent layers [10,12]. In the case of $z = 1$, where M^+ and M^{3+} are limited to Li^+ and Al^{3+}, respectively, the general chemical composition is $[LiAl_2(OH)_6]A \cdot H_2O$ (A = Cl, Br, NO_3) [12,19,20]. Unlike the LDHs with $z = 2$, which are synthesized primarily by co-precipitation methods [10,21,22], Li/Al LDHs are often prepared through the intercalation of lithium salts into the structure of aluminum hydroxide (i.e., gibbsite, bayerite or nordstrandite) [19,20,23]. Lithium cations are inserted into the vacant octahedral sites of the $Al(OH)_3$ layers and contribute the positive charges of the hydroxide layers. In this case, the positive charge centers are distributed in an orderly fashion through the hydroxide layers, which is different from LDHs with $z = 2$, wherein the distribution of positive charge sites is not ordered [10,12].

LDHs have been applied in a variety of scientific fields in recent years, because of their high anion exchange capacities [10,12]. The use of LDHs to remove anionic contaminants—like oxometallate ions [24], chromate [22,25,26] and other harmful organics [27–29]—from water previously has been studied. These results have yielded the positive perspective that LDHs potentially could be applied to treat waste streams containing anionic contaminants. However, industrial effluents and polluted water bodies usually contain mixed compounds with a variety of chemical and physical conditions (e.g., different pHs, ionic strengths, and temperatures). Thus, the stability of LDHs in waste streams must be investigated to determine whether these materials are suitable for use in real-life situations. In our previous work, Li/Al LDH was found to be an efficient adsorbent for Cr(VI) removal [26]. However, due to the de-intercalation of Li^+ from the Li/Al LDH structure, a portion of the adsorbed Cr(VI) was gradually released from used adsorbent into the solution [26]. This unstable characteristic of Li/Al LDH was deemed unfavorable for an absorbent; nevertheless, it was hypothesized that the unstability of Li/Al LDH could be utilized to develop a technique for the recovery and reuse of the adsorbent. Therefore, in the current work, the release of Li^+ and Cr(VI) at various temperatures was studied, in addition to the Cr(VI) adsorption of Li/Al LDH. One practical application of Li/Al LDH to treat Cr(VI)-containing water was demonstrated. The aim was to determine the feasibility of using Li/Al LDH for the storage, condensation, and controlled release of adsorbed Cr(VI), a finding that might lead to the further development of a cost-effective method for treating Cr(VI)-containing water and recycling the used adsorbent.

2. Materials and methods

2.1. The synthesis of Li/Al LDH

All chemicals were purchased and utilized without further purification. Deionized (DI) water was boiled to eliminate dissolved carbonate prior to its use in all experiments. The layered double hydroxide $[LiAl_2(OH)_6]Cl \cdot H_2O$ was synthesized by stirring 5 g of gibbsite (from Merck Co.) in 25 ml 10 M LiCl solution. The suspensions were heated at 90 °C for 14 h. The product was then washed free of salts, centrifuged, and dried at 90 °C for 24 h. Ice water was used during the washing process to prevent the de-intercalation of Li/Al LDHs that had been observed in preliminary experiments.

2.2. Temperature effect

The influence of temperature on the stability of Li/Al LDH was conducted by adding 0.5 g of Li/Al LDH to 500 mL DI water. The suspension, with $1\,g\,L^{-1}$ LDH, was stirred in a 1 L water-jacked reaction vessel, which was connected to a temperature-regulated water bath to maintain specific suspension temperatures (i.e., 10, 25, 40, 60, or 90 °C) during the experiments. Periodically, 10 mL of suspension were extracted and passed through a 0.45 μm membrane filter. The filtrate was collected for Cl^- and Li^+ analysis. At the completion of the experiment at each temperature, the Li/Al LDH particles were filtered, air-dried, and ground to allow for X-ray diffraction (XRD) and FTIR measurements.

2.3. Chromium(VI) adsorption kinetics

Adsorption kinetics of Cr(VI) were observed at five temperature levels (i.e., 10, 25, 40, 60, and 90 °C) in a 1 L water-jacked reaction vessel. 0.5 g of Li/Al LDH powder was added to 500 mL $600\,mg\,L^{-1}$ Cr(VI) solution, pre-adjusted to the desired temperature. Under constant stirring, the suspensions were extracted at different time intervals and filtered through a 0.45 μm membrane filter. The Cr(VI) concentration in the filtrates was determined using the DPC (s-diphenylcarbazide) method [30]. At the end of each experiment, the residual Li/Al LDH particles were washed with ice water, air-dried, and ground prior to XRD and FTIR analyses.

2.4. Chromium(VI) desorption kinetics

To conduct a Cr(VI) desorption experiment, Cr(VI)-containing Li/Al LDH was initially prepared by adding 0.5 g Li/Al LDH to 500 mL $600\,mg\,L^{-1}$ Cr(VI) solution at 10 °C. The suspensions were continuously stirred for 12 h and the solution temperature maintained at 10 °C. Subsequently, the suspensions were filtered using a 0.45 μm membrane filter (47 mm in diameter). The Cr(VI)-containing Li/Al LDH particles on the filter were washed off using a small amount of ice water, and then

immediately transferred to DI water with a pre-adjusted temperature of 10, 25, 40, 60, or 90 °C. The suspensions were stirred, periodically extracted, and passed through a 0.45 μm membrane filter to collect filtrates. The Cr(VI) concentrations in the filtrates were analyzed using the DPC method [30] and recorded as a function of time. At selected times during the desorption experiments, Li/Al LDH solids were filtered and collected for XRD and FTIR analyses.

2.5. X-ray diffraction and FTIR analysis

The original and Cr(VI)-containing Li/Al LDH samples were examined using an X-ray diffractometer (Rigaku Miniflex) with Cu Kα radiation. XRD patterns were recorded in the range of 2–60° 2θ with a scanning rate of 2° 2θ min^{-1}. Infrared spectra were collected for LDH samples on Nicolet Nexus 470 FTIR spectrometer, employing the KBr dilution technique (1.5%, w/w). Chloride and Li ions were determined using ionic chromatography (IC) and atomic absorption spectroscopy (AAS), respectively.

3. Results and discussion

3.1. Synthesis of Li/Al LDH

Upon the addition of LiCl to gibbsite suspensions, the XRD peaks of gibbsite at 0.485 nm gradually decreased, which indicated that the intercalation of Li$^+$ into gibbsite structures proceeded readily. Concomitant with the decreasing intensities of gibbsite reflections, the intensities of the peaks at 0.761 and 0.383 nm, which refer to the 0 0 2 and 0 0 4 reflections of Li/Al LDH, respectively, gradually increased. The d-spacing values of the Li/Al LDH agree well with those previously reported [19,31]. After a 14 h reaction, the disappearance of the 0.485 nm reflection indicated complete transformation from gibbsite to Li/Al LDH (Fig. 1). However, the time required for the transformation is not in compliance with a previous report [31], in which a small proportion of unchanged gibbsite remained, even after 40 h, under the same experimental conditions (i.e., 10 M LiCl and 90 °C), as identified using a time-resolved in situ X-ray diffraction technique. This incongruity probably is due to the difference in the initial solid/liquid ratio, since the solid/liquid ratio of 0.2 g mL^{-1} (0.2 g gibbsite per mL 10 M LiCl) used in the current study was higher than the 0.042 g mL^{-1} used by Fogg and O'Hare [31].

3.2. Temperature effect on de-intercalation rates of Li$^+$ and Cl$^-$

Our previous study demonstrated that, upon Cr(VI) adsorption, Li$^+$ de-intercalation of Li/Al LDH simultaneously occurred, albeit at a slower reaction rate [26]. The de-intercalation of Li$^+$ resulted in the release of adsorbed Cr(VI) from the Li/Al LDH structure to the solution, and this release rate seemed to be temperature-dependent. In order to elucidate the temperature effect in both reactions, we first conducted kinetic measurements for the de-intercalation of Li$^+$ in the absence of
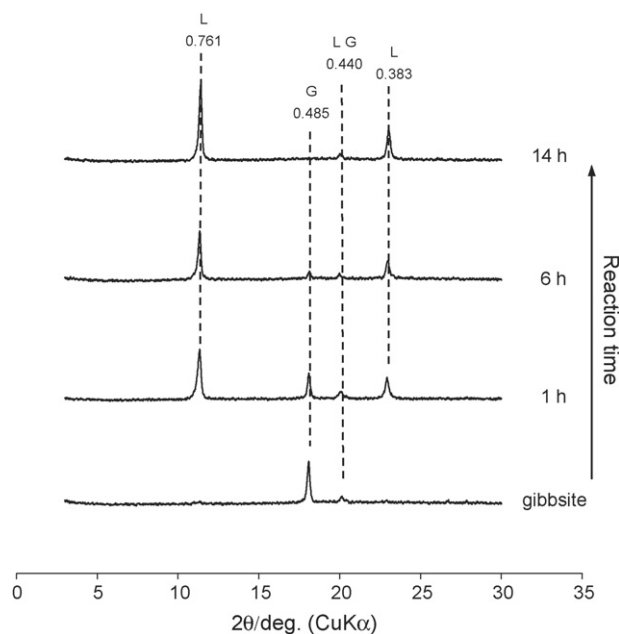

Fig. 1. X-ray diffractograms for the synthesis of Li/Al LDHs as a function of time. The unit of d-spacings is nm. L: Li/Al LDHs; G: gibbsite.

Cr(VI). In the next section, Li$^+$ de-intercalation would be monitored during Cr(VI) adsorption.

3.2.1. XRD diffractogram

The effect of solution temperature on the stability of the Li/Al LDH structure was first investigated using X-ray diffraction. Li/Al LDH has two major diffraction peaks at 0.761 and 0.383 nm. There were no other peaks observed when Li/Al LDH was collected after 12 h at 10 °C. After 24 h, a small peak appeared at 0.483 nm (Fig. 2). This peak corresponds to gibbsite, which was the precursor used for synthesizing Li/Al LDH. The peak's appearance indicated the occurrence of Li$^+$ de-intercalation. At a higher solution temperature (i.e., at 25 °C), a significant increase in the intensity of the diffraction peak for gibbsite was observed (Fig. 2). When the temperature was
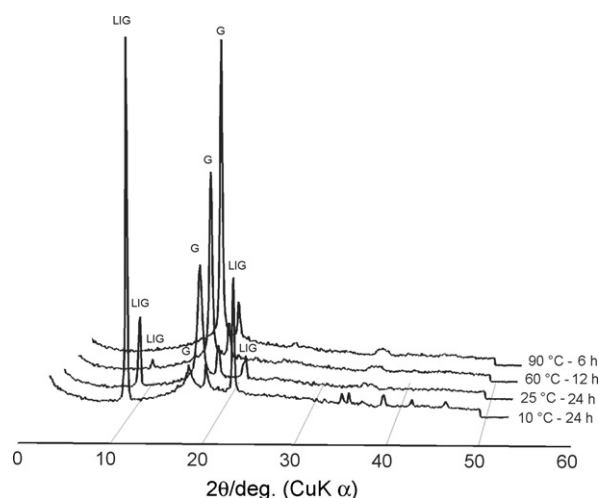

Fig. 2. X-ray diffraction pattern of Li/Al LDH collected after suspension at 10 and 25 °C for 24 h, 60 °C for 12 h, and 90 °C for 6 h.
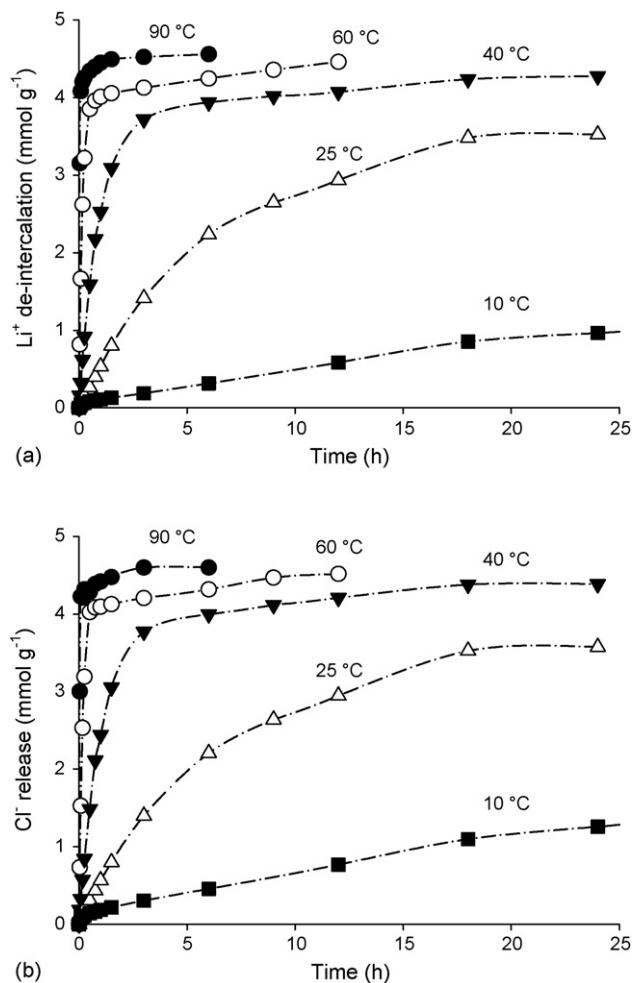
Fig. 3. The influence of solution temperature on (a) the de-intercalation of Li$^+$, and (b) the release of Cl$^-$ from 1 g L^{-1} Li/Al LDHs as a function of time.

Fig. 4. The adsorption of 11.54 mM Cr(VI) on 1 g L^{-1} Li/Al LDHs, as influenced by solution temperature (a) is enlarged from (b).

increased to above 60 °C, the influence of temperature on the stability of Li/Al LDH was even more significant (Fig. 2). For example, the diffractogram of a more intense gibbsite peak was observed when Li/Al LDH was hydro-heated at 60 °C for 12 h (Fig. 2). When we hydro-heated Li/Al LDH samples at 90 °C for 6 h, only gibbsite diffraction patterns were observed, which suggests that Li/Al LDH structures no longer were present. At elevated temperatures, de-intercalation of LiCl occurred more rapidly, which caused greater proportions of Li/Al LDH to be converted into gibbsite.

3.2.2. Solution compositions

The effects of temperature on the de-intercalation of Li$^+$ and Cl$^-$ from the suspended Li/Al LDHs are shown in Fig. 3. As the reaction time increased, the concentration of Li$^+$ released from the Li/Al LDH structure gradually increased, and the release rate increased upon increasing temperature (Fig. 3a). Concomitant with Li$^+$ de-intercalation, Cl$^-$ was detected in the solutions (Fig. 3b). The release of Cl$^-$ followed the same tendency as that of Li$^+$ at each reaction temperature. Lithium de-intercalation occurred more readily when the suspension temperature was 40 °C or higher. For example, as much as 4.41
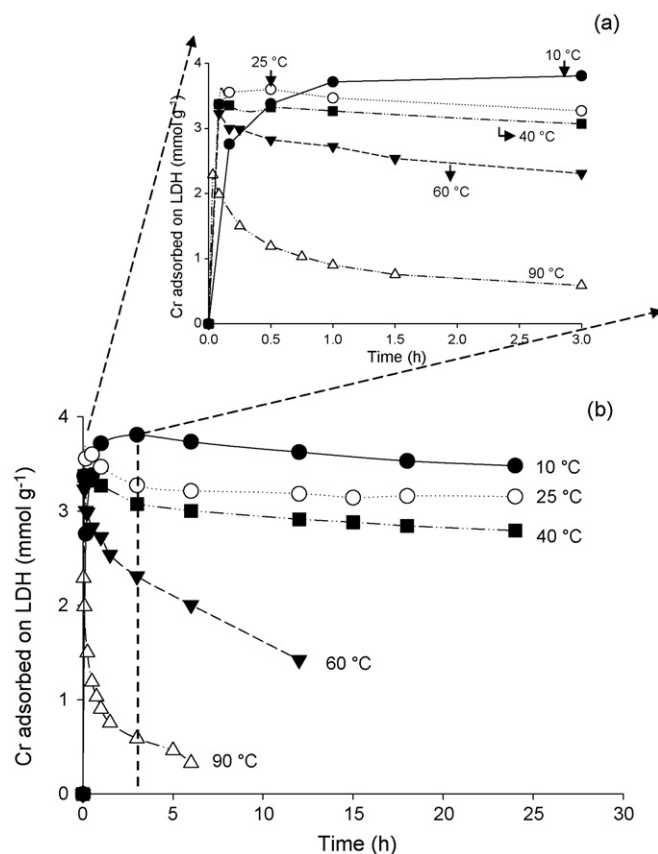
and 4.43 mmol g^{-1} of Li$^+$ were de-intercalated at 60 and 90 °C within 12 and 6 h, respectively. These results were consistent with those observed using XRD, and showed that the Li$^+$ located in the octahedral sites of gibbsite-like layers became unstable upon exposure to a dilute solution at elevated temperatures.

3.3. Adsorption of Cr(VI) by Li/Al LDH

3.3.1. Effect of temperature on Cr(VI) adsorption kinetics and capacity

Chromium(VI) adsorption on Li/Al LDH at various temperatures is shown in Fig. 4. As the reaction time increased, the adsorption of Cr(VI) first reached a maximum and then gradually decreased. With increasing temperature, the time required to reach the adsorption maximum followed the order of 10 °C > 25 °C > 40 °C > 60 °C > 90 °C (Fig. 4a). That is, maximum adsorption of Cr(VI) was more rapidly achieved at higher temperatures. For example, the maximum adsorption of Cr(VI) occurred in less than 5 min at 90 °C versus 3 h at 10 °C.

Even though Cr(VI) adsorption on Li/Al LDH occurred more rapidly at higher temperatures, a lower adsorption capacity for Cr(VI) was observed (Fig. 4a). For example, the maximum adsorption of Cr(VI) by Li/Al LDH was 3.81 mmol g^{-1} at 10 °C compared with 3.60, 3.41, and 3.23 mmol g^{-1} at 25, 40, and 60 °C, respectively. At 90 °C, Cr(VI) adsorption dropped to its lowest value of 2.29 mmol g^{-1} (Fig. 4a).
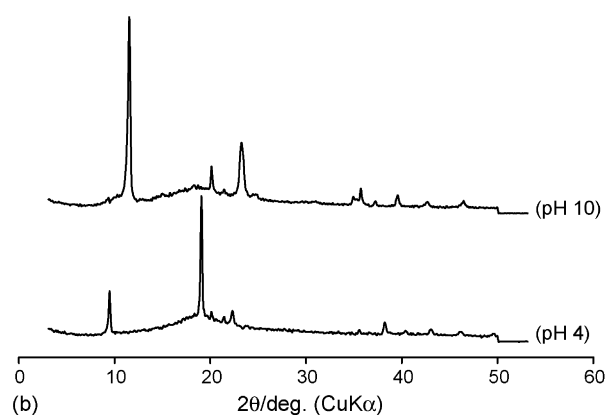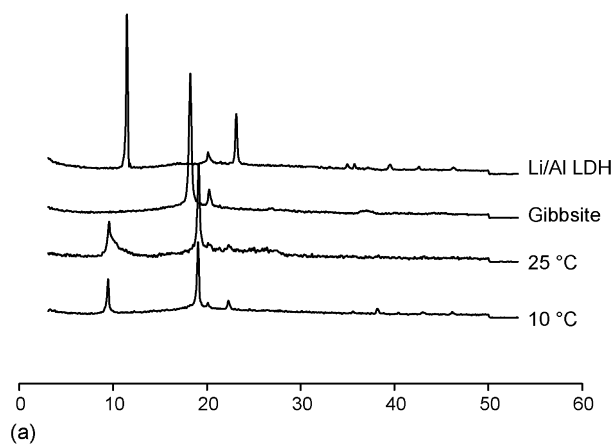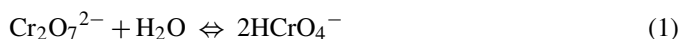
Fig. 5. X-ray diffractograms for (a) Li/Al LDH, gibbsite, and 11.54 mM Cr(VI) (pH 4.3 ± 0.5) treated Li/Al LDHs at 10 and 25 °C; (b) Li/Al LDHs treated with 11.54 mM Cr(VI) at pH 10.0 and pH 4.0 at 10 °C.

Fig. 6. The influence of the adsorption of 11.54 mM Cr(VI) and solution temperature on the de-intercalation of (a) Li$^+$ and (b) Cl$^-$ (the small figure is enlarged from the shaded rectangle).

Theoretically, the calculated positive charges of Li/Al LDH used in the study are 4.62 mmol g^{-1}. However, the maximum adsorption of Cr(VI) obtained at each temperature was less than the theoretical value. Two possible explanations exist for this phenomenon. (1) First, de-intercalation of Li$^+$ and Cl$^-$ from Li/Al LDH has been reported previously [26,32]. This property led to decreases in both the positive charges and the anion-exchange capacity of Li/Al LDH. (2) A small proportion of interlayer Cl$^-$ could not be exchanged easily under current experimental conditions, which consequently resulted in a lower level of Cr(VI) adsorption. Meanwhile, within the interlayer space of Li/Al LDH, the replacement of Cl$^-$ by larger HCrO$_4^-$ or Cr$_2$O$_7^{2-}$ ions may be limited, due to steric hindrance. Chromate would dimerize to form dichromate with a Cr concentration > 10 mM at low pH [33]. As indicated in Cotton [34], HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ are in equilibrium at a pH between 2 and 6:

$$Cr_2O_7^{2-} + H_2O \Leftrightarrow 2HCrO_4^- \tag{1}$$

In the current study with an initial Cr concentration of 11.54 mM at pH 4.3 ± 0.5, HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ may exist simultaneously and be incorporated into Li/Al LDH by means of an anion exchange reaction. An increase in the basal spacing of Li/Al LDH from 0.76 to 0.93 nm may be due to the occurrence of
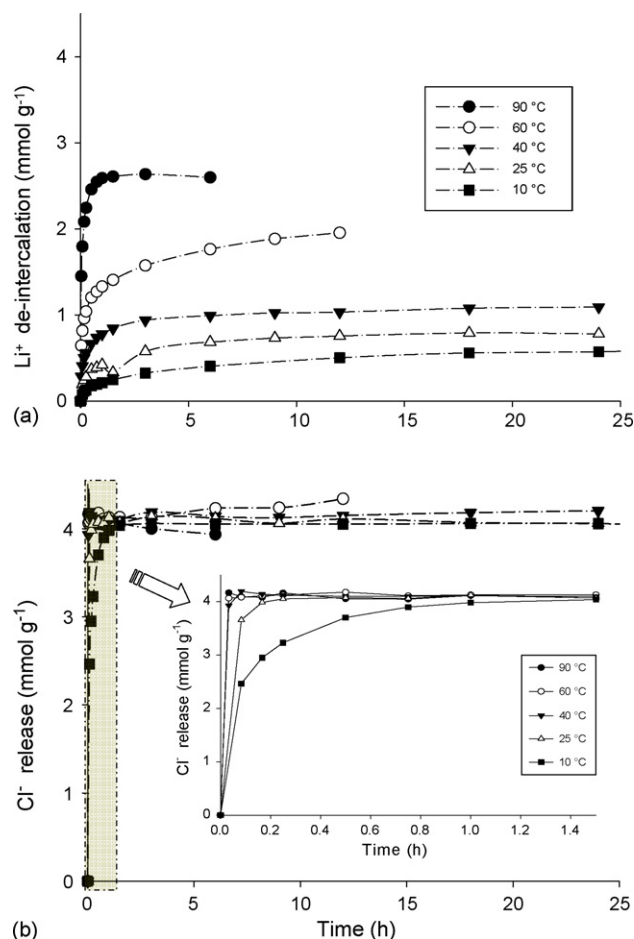
Cr$_2$O$_7^{2-}$ in the interlayer of Li/Al LDH (Fig. 5a). Conversely, such an increase in basal spacing was not observed at pH 10, at which CrO$_4^{2-}$ dominates (Fig. 5b). Thus, the increase in basal spacing of Cr(VI) containing Li/Al LDH at pH 4 is due to the adsorption of larger dichromate anions. This result is consistent with results reported previously [25,35].

3.3.2. Cl$^-$ release

When Cr(VI) is removed from aqueous solutions by Li/Al LDH, Cr(VI) enters the interlayer of the Li/Al LDH and replaces the interlayer Cl$^-$. This anion exchange reaction results in an increase in Cl$^-$ concentrations in the solution. Although the de-intercalations of Li$^+$ and Cl$^-$ occur simultaneously, the released Cl$^-$ concentration may be predominantly attributed to an anion exchange reaction, particularly at 10 and 25 °C (compare the curves for 10 and 25 °C in Fig. 3b with those of Fig. 6b, Table 1). As the reaction temperature was increased, the contribution of the de-intercalation reaction to the concentration of released Cl$^-$ became comparable to that of the anion exchange reaction. Because the release of Cl$^-$ was rapid in both Cr(VI)-absent (Fig. 3b) and Cr(VI)-present (Fig. 6b) systems at temperatures higher than 40 °C, it was difficult to differentiate the proportion of released Cl$^-$ attributable to Cr(VI) adsorption.

Table 1
The amount of Cl⁻ release from Li/Al LDHs at different temperature

Temperature (°C)	Reaction time (h)	Cl⁻ release[a] (mM)	
		In water	With Cr(VI)
10	24	1.47	4.02
25	24	3.56	4.07
40	24	3.95	4.19
60	12	4.02	4.25
90	6	4.26	4.33

[a] Theoretic calculation of Cl⁻ content in 0.5 g LDHs is 4.62 mM.

3.3.3. Chromium(VI) release and Li⁺ de-intercalation

Following a rapid adsorption process that took place within several minutes to hours, depending upon the reaction temperature, the release of adsorbed Cr(VI) was observed. At each temperature, this occurred at a different rate (Fig. 4b). The release of adsorbed Cr(VI) was a slow process at lower reaction temperatures. About 8.7 and 12.5% of the adsorbed Cr(VI) were released at 10 and 25 °C, respectively, after 24 h; however, as much as 85.6% of the adsorbed Cr(VI) was released at 90 °C after only 6 h. The release of adsorbed Cr(VI) was much slower than that of Cl⁻ in pure water (compare Fig. 4b with Fig. 3b). For instance, the release of Cl⁻ equaled 27.2 and 77.4% of total interlayered Cl⁻ at 10 and 25 °C, respectively, after 24 h of reaction. Coincident with Cr(VI) release, Li⁺ was detected in the solutions (Fig. 6a). At each temperature, the de-intercalation of Li⁺ generally followed the same tendency as that of Cr(VI) release (Figs. 4b and 6a). The results illustrate that adsorbed Cr(VI) was electrically attracted by octahedral Li⁺. Once Li⁺ de-intercalation occurs, adsorbed Cr(VI) is simultaneously released from the structure.

With respect to a kinetic analysis of Li⁺ release from Li/Al LDH, such release generally follows a first order kinetic model with Cl⁻ or Cr(VI) as the interlayer anions. The kinetic model is expressed as

$$\frac{dC_{Li}}{dt} = -kC_{Li} \tag{2}$$

$$[C_{Li}] = [C_{Li}]_0\, e^{-kt} \tag{3}$$

where k is the reaction rate constant, and $[C_{Li}]$ and $[C_{Li}]_0$ are the residual Li⁺ in the gibbsite structure at reaction time t and the total structural Li⁺, respectively. Thus, $[C_{Li}]_0 - [C_{Li}]$ yields $[C_{Li}]_{sol}$:

$$[C_{Li}]_0 - [C_{Li}] = [C_{Li}]_0(1 - e^{-kt}) \tag{4}$$

$$[C_{Li}]_{sol} = [C_{Li}]_0(1 - e^{-kt}) \tag{5}$$

where $[C_{Li}]_0$ is a constant, and $[C_{Li}]_{sol}$ is the Li⁺ concentration in the solution at reaction time t. Eq. (5) can be described in the form:

$$\ln\left\{1 - \frac{[C_{Li}]_{sol}}{[C_{Li}]_0}\right\} = -kt \tag{6}$$

By plotting $\ln\{1 - [C_{Li}]_{sol}/[C_{Li}]_0\}$ against reaction time t, a straight line was obtained. The kinetic parameters are summarized in Table 2. It appears that the rate constant for Li⁺

Table 2
Summary of the kinetic constants obtained for the de-intercalation of Li⁺ from Li/Al LDH at various temperatures

T (°C)	Anion	K (×10⁻⁴ s⁻¹)	R^2	H₂O/LDH ratio (g g⁻¹)
10	Cl⁻	0.02	0.98	1000
	Cr(VI)	0.14	0.98	1000
25	Cl⁻	0.26	0.98	1000
	Cr(VI)	0.27	1.00	1000
40	Cl⁻	2.56	0.99	1000
	Cr(VI)	0.82	0.97	1000
60	Cl⁻	10.3	0.97	1000
	Cr(VI)	1.35	0.99	1000
90	Cl⁻	65.1	1.00	1000
	Cr(VI)	3.76	0.96	1000
	Cl⁻	18.0[a]	–	1000
92	Cl⁻	23.0[a]	–	100
	Cl⁻	16.0[a]	–	50

[a] Data was obtained from Ref. [32].

de-intercalation from Li/Al LDH, with Cl⁻ as the interlayer anion, increased as the reaction temperature increased. At 90 °C, the kinetic constant reached 65.1×10^{-4} s⁻¹, which was two- to three-fold higher than the values reported by Tarasov et al. [32], using the same temperature and interlayer anions. This discrepancy is probably due to the high water/LDH ratio of 1000 (g g⁻¹) used in the current study, compared with that of 50 (g g⁻¹) used by Tarasov et al. [32]. With Cr(VI) as the interlayer anion, Li⁺ de-intercalation from Li/Al LDH also occurs relative to reaction temperature (Table 2). At lower reaction temperatures (i.e., ≤25 °C), the Li⁺ de-intercalation rate with interlayer Cr(VI) is higher than that observed with interlayer Cl⁻ (Table 2). On the other hand, at temperatures ≥40 °C, the quantity and rate of Li⁺ de-intercalation observed with Cr(VI)-containing Li/Al LDH are much lower than those observed with Cl⁻-containing Li/Al LDH (Fig. 6a and Table 2). The apparent activation energy (E_a) for the de-intercalation of Li⁺ from Li/Al LDH was obtained

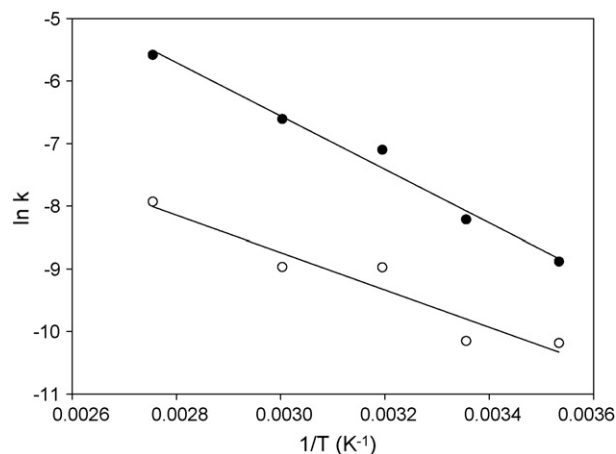Fig. 7. Arrhenius dependence for the determination of activation energy for the de-intercalation of Li⁺ from (a) Cl⁻, and (b) Cr(VI)-containing Li/Al LDH.
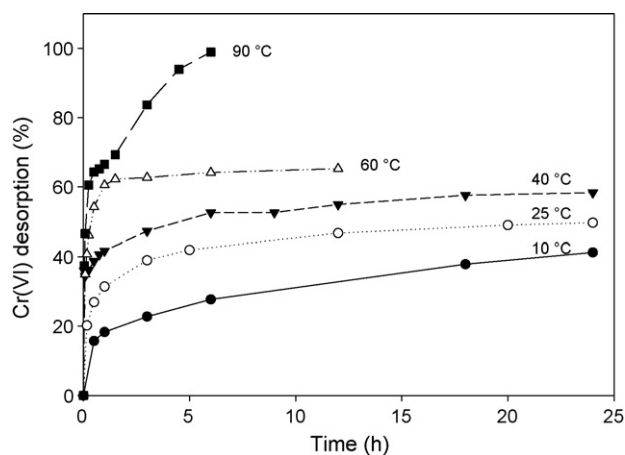
Fig. 8. The kinetic release of adsorbed Cr(VI) from Cr(VI)–Li/Al LDHs at different temperatures. Cr(VI)–Li/Al LDHs were obtained by treating $1 \, g \, L^{-1}$ Li/Al LDHs with 11.54 mM Cr(VI) at 10 °C for 12 h.

using Arrhenius expression:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{7}$$

The dependence of $\ln k$ versus reciprocal temperature for both the Cl^- and Cr(VI)-forms of LDH is shown in Fig. 7, and the values of E_a are 76.6 and 41.5 kJ mol^{-1}, respectively.

3.4. Release of absorbed Cr(VI) at different temperatures

Following the rapid adsorption of Cr(VI) at 10 °C, water at different temperatures was added into the Cr(VI)-containing LDHs to evaluate the degree of Cr(VI) release over reaction time, and the results are shown in Fig. 8. The quantity and rate of Cr(VI) release increased with increasing solution temperature. For instance, 41.2% of the adsorbed Cr(VI) was released at 10 °C after 24 h; however, almost all of the adsorbed Cr(VI) was released at 90 °C after 6 h. Compared with the data obtained at each reaction temperature in the Cr(VI) adsorption experiment, a much higher proportion of adsorbed Cr(VI) was released, particularly at 10 and 25 °C. This illustrates that not only the solution temperature but also the concentration of Cr(VI) in the bulk solution influences the release of adsorbed Cr(VI). That is, Cr(VI)-containing LDH suspended in de-ionized water would accelerate the release of adsorbed Cr(VI) (Fig. 8) versus that suspended in a Cr(VI)-containing solution (Fig. 3).

Based upon the results described here, a method for the treatment of Cr(VI)-containing waste streams may be developed. Because at low temperatures the Cr(VI) adsorption of Li/Al LDH is much faster than the de-intercalation reaction, Cr(VI) can be removed from solution at low temperatures. Subsequently, Cr(VI)-containing Li/Al LDH could be suspended in heated water to release the adsorbed Cr(VI) through Li de-intercalation. To accelerate the recovery process, Cr(VI)-containing Li/Al LDH might be treated with heated water several times. Fig. 9 shows the recovery of adsorbed Cr(VI) from Li/Al LDH using various amounts of heated water. At a water/LDH ratio of $1000 \, g \, g^{-1}$, 99% of the adsorbed Cr(VI) could be released within
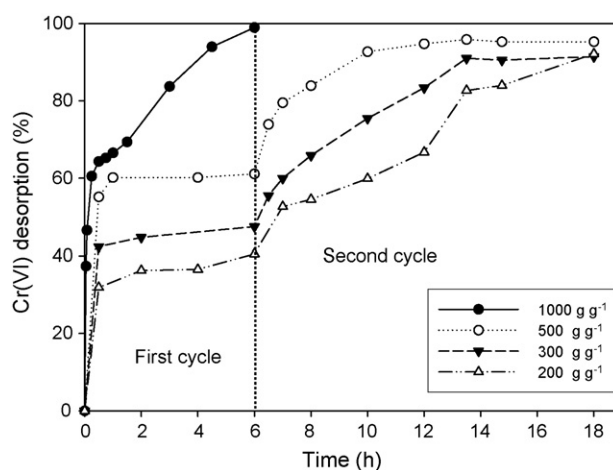

Fig. 9. The recovery of adsorbed Cr(VI) from Li/Al LDH treated with 11.54 mM Cr(VI), using heated water (90 °C) and various water/LDH ratios.

6 h. However, with water/LDH ratios $\leq 500 \, g \, g^{-1}$, two cycles of the thermal-treatment process were required to recover more than 97% of the adsorbed Cr(VI). Accordingly, hydrothermal treatment of Cr(VI)–Li/Al LDH might not only recover the adsorbed Cr(VI) but also recycle the de-intercalation product, gibbsite, for further use.

4. Conclusions

Li/Al LDHs can be synthesized readily by intercalating Li$^+$ into the octahedral structure of gibbsite, with Cl^- as the counterbalancing anion. Because the interlayer Cl^- is exchangeable, Li/Al LDH exhibits anion exchange properties that can be utilized to scavenge anionic contaminants. However, Li/Al LDH is unstable at elevated temperatures. Upon exposure of Li/Al LDH particles to a solution at any temperature higher than 40 °C, a great amount of Cl^- is rapidly released, accompanied with Li$^+$ de-intercalation. As a result, the layered structures of Li/Al LDH would be converted to its synthetic precursor, gibbsite.

We found that the adsorption of Cr(VI) on Li/Al LDH via an ion-exchange reaction with Cl^- was relatively rapid at each selected temperature. Nevertheless, the maximum adsorption of Cr(VI) on Li/Al LDH occurred at temperatures ≤ 25 °C, due to the low Li$^+$ de-intercalation rate. Although Li/Al LDH exhibited relatively high Cr(VI) adsorption capacity, adsorbed Cr(VI) was gradually released over the reaction time, particularly at high temperatures. The release of adsorbed Cr(VI) was accompanied with Li$^+$ de-intercalation, but at a lower rate than in a Cr(VI)-free system. According to the current results, high temperatures associated with a dilute solution would accelerate Cr(VI) release from Li/Al LDH.

The properties of high adsorption rate and thermal unstability of Li/Al LDH may lead to its potential application in the treatment of Cr(VI)-containing wastes. That is, Li/Al LDH can be used as an adsorbent for the rapid removal of Cr(VI) in water. Then the Cr(VI)-LDH particles could be collected and resuspended in water by elevating the water temperature. Through this hydrothermal process to enhance the Li de-intercalation

reaction of Li/Al LDH, Cr(VI) could be desorbed back into the aqueous phase and be recovered; the solid product, gibbsite, also could be recovered for further use.

Acknowledgments

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