Available online at www.sciencedirect.com
ScienceDirect
Applied Clay Science 37 (2007) 107–114
Applied CLAY Science
www.elsevier.com/locate/clay

Deintercalation of Li/Al LDH and its application to recover adsorbed chromate from used adsorbent

Yu-Min Tzou [a], Shan-Li Wang [a,b,*], Liang-Ching Hsu [a], Rung-Rung Chang [a], Chenfang Lin [a]

[a] *Department of Soil and Environmental Sciences, National Chung Hsing University, Taichung, Taiwan 40227, Taiwan*
[b] *Center of Nanoscience and Nanotechnology, National Chung Hsing University, Taichung, Taiwan 40227, Taiwan*

Received 21 March 2006; received in revised form 7 August 2006; accepted 20 October 2006
Available online 12 December 2006

Abstract

Layered double hydroxides (LDHs) have been shown to be potential adsorbents for anionic contaminants, but less studies have focused on how to treat the used adsorbents to recover adsorbed contaminants. In this study, we investigated the chromate ($HCrO_4^-$) adsorption on Li/Al LDH and the recovery of adsorbed chromate, achieved through the Li deintercalation reaction of Li/Al LDH. The adsorption of chromate on LDH was a fast process that could be accomplished in minutes at any temperature, ranging from 10 °C–90 °C. On the other hand, the Li deintercalation rate of Li/Al LDH was relatively slow at a temperature ≤ 25 °C and increased as the reaction temperature was increased. More than 95% of structural Li^+ could be deintercalated from the LDH structure within 30 min at a temperature ≥ 60 °C. The Li deintercalation resulted in the loss of positive charges in the hydroxide layers and consequently the releases of counterbalancing chromate and Cl^- in the interlayer. Therefore, practically, the material can be used as an effective adsorbent for chromate when the deintercalation reaction is inhibited at low temperature. After chromate is adsorbed, it can be released from the used material into the solution through deintercalating Li^+ from the structure. This process can be achieved by simply using hot water to treat the used material and no additional chemicals are required. The final products of the deintercalation reaction include gibbsite and a Cr-containing solution. Gibbsite may be reused to synthesize Li/Al LDH and the solution containing Cr may be further treated to recover Cr. An innovative approach to recover adsorbed contaminant and regenerate the used adsorbent was proposed in this study.

Keywords: Layered double hydroxide; Adsorption; Chromate; Deintercalation; Contaminant recovery; Water treatment

1. Introduction

Surface and ground water supplies worldwide are contaminated or threatened by contaminants, produced by natural and human-involved processes (Galvin, 1996). Toxic, anionic contaminants from metals such as arsenic (As) and chromium (Cr) are priority contaminants of major concern in the environment. These elements are highly carcinogenic after long term or high-dose exposure and have caused great public concern due to increased awareness of the health risks associated with the consumption of contaminated water. The Environmental Protection Agency of Taiwan has

* Corresponding author. Department of Soil and Environmental Sciences, National Chung Hsing University, Taichung, Taiwan 40227, Taiwan. Tel.: +886 4 2284 0373x3406; fax: +886 4 2286 2043.
E-mail address: slwang@dragon.nchu.edu.tw (S.-L. Wang).

0169-1317/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2006.10.007

prescribed the maximum contamination levels of 50 ppb for As and Cr in drinking water. The current US-EPA maximum contamination levels of As and Cr in drinking water are 50 ppb and 100 ppb, respectively (US-EPA, 2003). Compliance with these strict standards is very costly, and therefore treatment efficiency and ultimate disposal of removed contaminants are the major concern for risk management in the treatments of drinking water, groundwater and industrial wastewater containing contaminants.

Adsorption or precipitation is a common task for removing contaminants from drinking water and industrial wastewater. In the literature, many studies have suggested that layered double hydroxides (LDHs), which have a high surface area and a high anion exchange capacity, are potential adsorbents for anionic contaminants, such as the oxyanions of As, Cr, Se and Tc (Goswamee et al., 1998; Kang et al., 1999; Kovanda et al., 1999; You et al., 2001; Lazaridis and Asouhidou, 2003; Bhaumik et al., 2004; Alvarez-Ayuso and Nugteren, 2005). LDHs comprise positively charged layers with at least two different metal cations, octahedrally coordinated by hydroxyl groups (Cavani et al., 1991). The positive charges of LDHs are counterbalanced by interlayer anions. The interlayer anions and water, which fill the interlayer space, are often labile. Therefore, LDHs exhibit anion exchange capacity (AEC) and have been studied ultimately in order to demonstrate their role as potential filters for anionic inorganic and organic contaminants from polluted water. However, less attention has been paid to the disposal or recycling of used adsorbents containing contaminants. Whether contaminant-bearing LDHs will be disposed or treated for recovering the contaminants, the secondary pollution from the used materials and/or the pollution generated by the chemicals used to treat the materials should be taken into consideration. Higher treatment efficiency of contaminant-bearing materials will also lower the overall cost in the treatment of contaminated waters.

One of the unique compounds in the LDH group is Li/Al LDH, which has the formula of $[LiAl_2(OH)_6]^+ A^- \cdot xH_2O$ (Cavani et al., 1991). Li/Al LDHs are usually synthesized through intercalation of Li salts into aluminum hydroxides, i.e., gibbsite or bayerite (Nemudry et al., 1986; Poeppelmeier and Hwu, 1987; Isupov et al., 1994; Fogg and O'Hare, 1999). In the hydroxide sheets of Li/Al LDH, Li^+ cations are located in the vacant octahedral sites within the gibbsite-like $Al(OH)_3$ layers and contribute to the positive charge sites in the hydroxide layers (Besserguenev et al., 1997). In gibbsite, each of the $Al(OH)_3$ layers consists of nearly close packed OH^- ions in which the Al^{3+} occupies 2/3 of the octahedral holes between the alternate layers. The positive charge sites in the hydroxide sheets result from Li^+ located in the vacant octahedral holes of the gibbsite-like octahedral Al hydroxide sheet. As such, Li/Al LDH has a maximum charge density ($\sim$4 (+) nm^{-2}) compared with hydrotalcite-like M^{2+}/M^{3+} LDHs (Dutta and Puri, 1989; Borja and Dutta, 1992). Therefore, it is expected that the adsorption capacity of Li/Al LDH for contaminants may be higher than those of M^{2+}/M^{3+} LDHs.

In this study, the removal and recovery of chromate from water using Li/Al LDH were investigated. Chromate is generally produced by industrial processes and commonly found at contaminated sites (Kotas and Stasicka, 2000). It is the dominant form of chromium under oxidizing conditions. Depending on the total Cr concentration and pH value, chromate is present in the forms of CrO_4^{2-}, $HCrO_4^-$ or $Cr_2O_7^{2-}$ in aqueous solutions (Kotas and Stasicka, 2000). The removal of chromate using Mg/Al LDHs was previous studied and the reported value for the Cr adsorption capacity ranged from 0.3 mmol g^{-1} to 2.26 mmol g^{-1}, depending on the type of interlayer anions, Mg/Al molar ratio and calcination temperature (Goswamee et al., 1998; Kovanda et al., 1999; Alvarez-Ayuso and Nugteren, 2005). Kovanda et al. (1999) proposed a calcination–rehydration–anion exchange process to recover adsorbed Cr (VI) and regenerate the used hydrotalcite-like LDHs. In the current work, Li/Al LDH was shown to be an effective adsorbent for chromate and a maximum adsorption of 3.81 mmol g^{-1} was observed under a selected condition. However, the calcination–rehydration procedure proposed by Kovanda et al. (1999) to regenerate Mg/Al LDHs cannot be applied to regenerate Li/Al LDH because, unlike the structure of Mg/Al LDHs, the calcinated product of Li/Al LDH cannot be transformed back to Li/Al LDH upon rehydration (Nayak et al., 1997; Hou and Kirkpatrick, 2001). That is, the dehydroxylation due to calcination is an irreversible process for Li/Al LDH but is reversible for Mg/Al LAH. Therefore, an alternative regeneration process is needed for Li/Al LDH. Our preliminary studies showed a portion of the adsorbed Cr(VI) gradually was released from used adsorbent into the solution upon prolonged reactions. This unstable characteristic of Li/Al LDH was deemed unfavorable for an absorbent; nevertheless, it was hypothesized that the instability of Li/Al LDH could be utilized to recover adsorbed chromate and regenerate the used adsorbent. After chromate ions are fixed in the adsorbent, they may possibly be recovered by deintercalating Li^+ from the structure of Li/Al LDH to 'witch off' its surface charge. In this case, LDHs can

be regenerated for re-use; the recovered chromate can be further concentrated for reprocessing. Therefore, in addition to the adsorption of chromate on Li/Al LDH, the Li deintercalation of chromate-bearing Li/Al LDH in water were studied at different temperatures to show the potential for developing a method to recover Cr and regenerate LDH for reuse.

2. Materials and methods

2.1. Synthesis of Li/Al LDH

Layered double hydroxide, $[LiAl_2(OH)_6]Cl{\cdot}H_2O$, was synthesized by adding 5 g of synthetic gibbsite (α-$Al(OH)_3$) into 25 mL 10 M LiCl solution and the temperature of the suspension was maintained at 90 °C during the synthetic process. After 24 h, the suspension was then centrifuged and the solids collected were washed with iced water until free of chloride. Iced water was used to wash the samples to inhibit the Li deintercalation reaction of Li/Al LDHs that would otherwise occur at higher temperatures. The solid product was subsequently dried at 90 °C for 24 h in an oven and stored in a glass vial prior to further use.

2.2. Li deintercalation of Li/Al LDH

The Li deintercalation reaction of Li/Al LDH was investigated at 10 °C, 25 °C, 60 °C and 90 °C. 0.5 g of Li/Al LDH was added into 500 mL de-ionized water in a water-jacketed reaction vessel, which was connected to a water bath to maintain a constant temperature during the experiments. 10 mL of the suspension was periodically withdrawn from the reaction vessel and passed through a 0.45-μm membrane filter to collect the filtrates. The Cl^- and Li^+ concentrations in the filtrates were analyzed using ion chromatography. The experiments were continued for 24 h or until the concentration of Li^+ reached a constant value. In the end of the experiment, at each temperature, the Li/Al LDH solids that remained in the reaction vessel were filtered, air-dried, grounded, and analyzed using powder X-ray diffraction.

2.3. Chromate adsorption on Li/Al LDH at different temperatures

Chromate adsorption kinetics of Li/Al LDH was studied at four different temperatures (i.e., 10 °C, 25 °C, 60 °C and 90 °C). 0.5 g of Li/Al LDH was added into 500 mL aqueous solution containing 600 mg L^{-1} chromate at pH 4.0, and the temperature of the mixture was maintained constant in a water-jacketed reaction vessel. During the experiment, an aliquot of the suspension was periodically withdrawn and filtered using a 0.45-μm membrane filter to collect the filtrate. The chromate concentration in the filtrate was determined using the *s*-diphenylcarbazide method (Eaton et al., 1995). The amount of adsorbed chromate was calculated using the difference between the initial and measured Cr concentrations. The Cl^- and Li^+ concentrations in the filtrates were also analyzed using ion chromatography to monitor the occurrence of the Li deintercalation reaction during Cr adsorption.

2.4. Recovery of chromate from contaminant-bearing Li/Al LDH

Chromate containing Li/Al LDH was first prepared by adding 0.5 g Li/Al LDH into 500 mL solution of 600 mg L^{-1} chromate at pH 4.0 in a reaction vessel at 10 °C. During this stage, the temperature was maintained at 10 °C in order to inhibit the Li deintercalation of LDH when Cr adsorption occurred. After 3 h of reaction, the solids were filtered using a 0.45-μm membrane filter and washed twice with 200 mL iced water. The filtration process was completed within 1 min and the collected solids were immediately transferred to the reaction vessel containing 90 °C deionized water to recover Cr (VI). The temperature of deionized water in a water-jacketed reaction vessel was maintained at 90 °C, and the suspension was periodically withdrawn from the reaction vessel and filtered using a 0.45-μm membrane filter. The chromate concentrations in the filtrates were subsequently determined using the methods previously described.

2.5. Powder X-ray diffraction

X-ray diffraction patterns of Li/Al LDH samples were obtained on a Rigaku Miniflex diffractometer using Cu-Kα radiation. Data were collected from 2 to 80° 2θ, with a scan rate of 2° 2θ min^{-1}.

3. Results and discussions

Adsorption kinetics of chromate on Li/Al LDH at pH 4.0 was investigated as a function of reaction temperature with simultaneously monitoring the concentrations of Li^+, Cl^- and chromate (Fig. 1). Originally, the positively charged centers in the hydroxide layers of Li/Al LDH are counterbalanced by the interlayer Cl^- anions. After Li/Al LDH interacted with chromate in the solution, chromate was adsorbed by Li/Al LDH through replacing Cl^- in the interlayer. Since the predominant species of chromate is $HCrO_4^-$ at pH 4.0, the exchange of Cl^- by $HCrO_4^-$ is in a 1-to-1 ratio, so that it is easy to observe the stoichiometric correspondence between the chromate and Cl^- concentrations during the reactions. Meanwhile, the dissolution of CO_2 and formation of carbonate, which has high affinity towards LDHs, could be inhibited by setting the pH = 4.0.

A fast removal of chromate from the solution was seen in the beginning of the reaction at any temperature (Fig. 1). For example, at 10 °C, as much as 2.77 mmol g^{-1} Cr, corresponding to approximately 64% of the anion exchange capacity (AEC = 4.3 mmol g^{-1}) of Li/Al LDH, was adsorbed within 10 min. The fast reaction rate is a

characteristic property of ion exchange reactions in comparison with the typically slow rate of surface adsorption reactions (Sposito, 1984). As a result, the concentration of the correspondingly released Cl^- in the solution reached a maximum within the first 10 min (Fig. 1). However, a discrepancy was found between the amounts of adsorbed chromate and released Cl^-, and the discrepancy value became larger at higher temperatures (Fig. 1). Meanwhile, after the chromate adsorption reached a maximum, a portion of adsorbed chromate was subsequently desorbed over the reaction time and the releasing rate was significantly dependent on the reaction temperature. As seen in Fig. 1A, the adsorption reached a maximum of 3.81 mmol g^{-1} at 10 °C but 8.7% of adsorbed Cr was desorbed after 24 h. When the reaction temperature was increased to 25 °C (Fig. 1B), an adsorption maximum occured after 30 min reaction but decreased to 3.60 mmol g^{-1}, which was smaller than that observed at 10 °C. After 24 h, about 13% of adsorbed Cr was released. Further increasing the reaction temperature resulted in a decrease in the maximum adsorption of Cr and increases in the amount and rate of releasing adsorbed Cr. As seen in Fig. 1C, the Cr adsorption reached a maximum value of 3.23 mmol g^{-1} after 5 min reaction at 60 °C, but decreased to 1.42 mmol g^{-1} after 12 h. At 90 °C, Cr adsorption quickly increased to 2.92 mmol g^{-1} within 5 min but as much as 86% of the adsorbed chromate was released into the aqueous solution after 6 h (Fig. 1D). This chromate adsorption phenomenon of Li/Al LDH is different from those reported for chromate adsorption on M^{2+}/M^{3+}-LDHs, in which the adsorption maximums remain constant over time (Kovanda et al., 1999; Lazaridis and Asouhidou, 2003; Alvarez-Ayuso and Nugteren, 2005). As revealed by the increasing Li^+ concentration during chromate adsorption (Fig. 1), the releases of adsorbed Cr and remaining Cl^- in the interlayer are attributed to the deintercalation of Li^+ from the structure. The deintercalation of Li^+ from the LDH structure results in the decrease in the positive charges in the hydroxide layers and consequently the release of adsorbed chromate from the structure.

For comparison, the releases of Li^+ and Cl^- without the presence of chromate are also shown in Fig. 2. The release of the charge-balancing interlayer Cl^- was observed with the amount equivalent to that of released Li^+, and both the concentrations of Li^+ and Cl^- monotonously increased as the reaction time increased. At 10 °C, the deintercalation rate was relatively slow

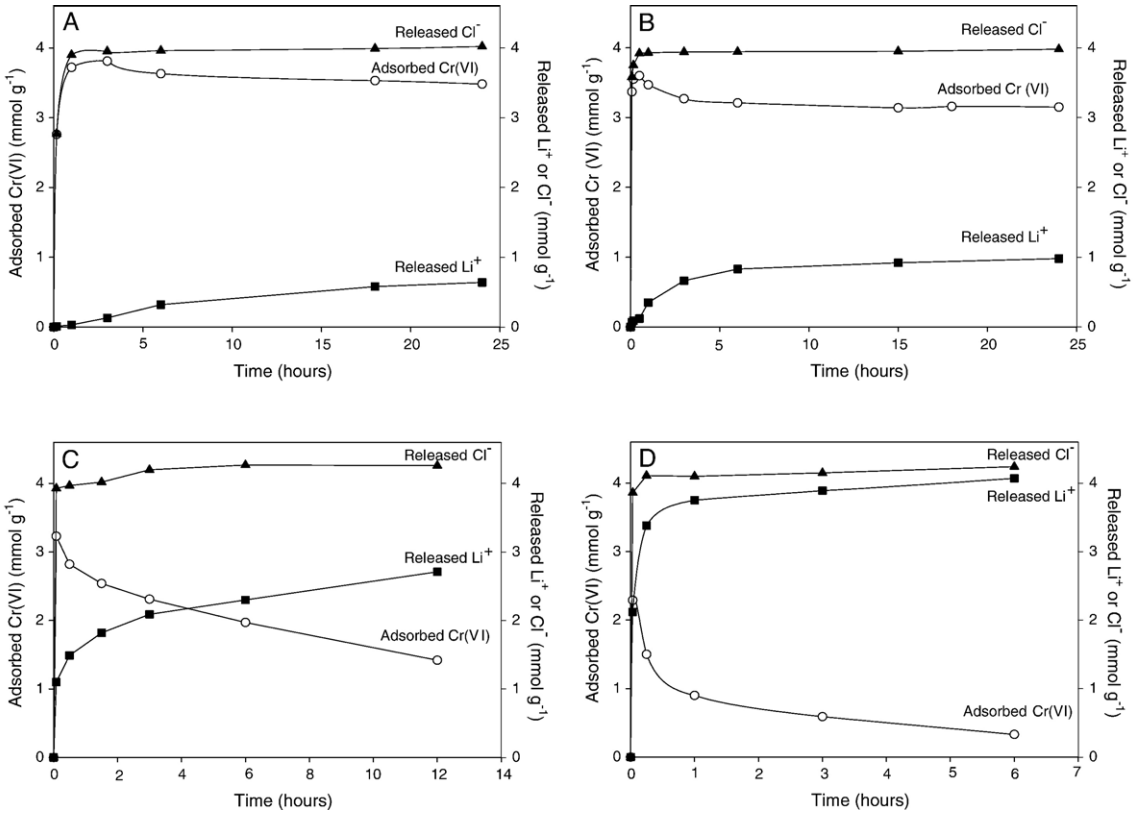

Fig. 1. The concentrations of chromate, Li^+ and Cl^- during the adsorption of chromate on Li/Al LDH at (A) 10 °C, (B) 25 °C, (C) 60 °C and (D) 90 °C.

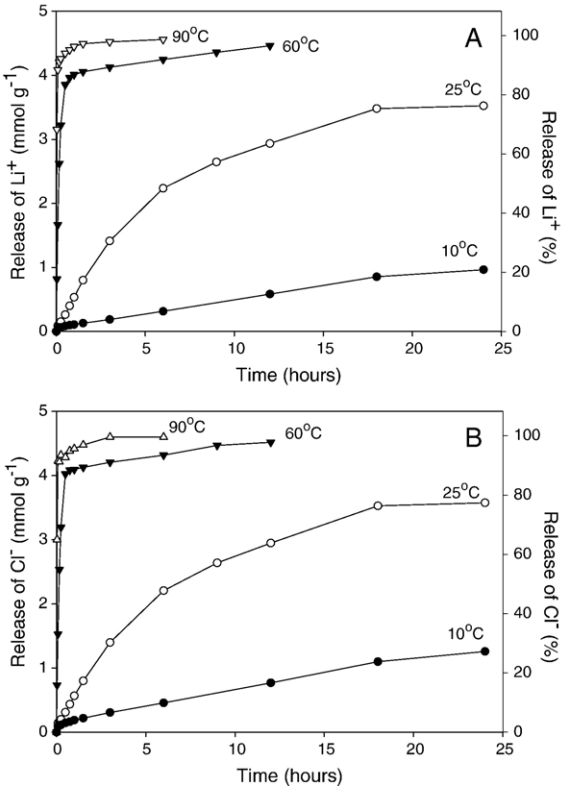

Fig. 2. The concentrations of (A) Li^+ and (B) Cl^- during the deintercalation of Li/Al LDH at 10 °C, 25 °C, 60 °C and 90 °C.

and about 1.0 mmol g^{-1} (≈23%) of Li^+ and Cl^- were released after Li/Al LDH was immersed in water for 24 h. As shown in the X-ray diffractogram, gibbsite was present in the product due to Li deintercalation (Fig. 3). As the reaction temperature was further increased, the deintercalation rates increased (Fig. 2). This is because, at higher temperatures, Li^+ and Cl^- have larger kinetic energies, resulting in the increase in the reaction rate (Tarasov et al., 2004). When the temperature was 60 °C or above, the deintercalation reaction rate was significantly enhanced (Fig. 2). Approximately 100% of Li^+ and Cl^- in the structure were released into the solution after 15 min at 90 °C; only the reflections of gibbsite were observed in the corresponding XRD pattern and those of Li/Al LDH were no longer detected (Fig. 3).

Li/Al LDH is synthesized through the reaction of gibbsite with concentrated LiCl (i.e., 10 M in this work) and Li/Al LDH may become thermodynamically unfavorable in a diluted system. Therefore, Li deintercalation may occur when the LDH particles are in contact with aqueous solutions with low Li concentration. During the chromate adsorption reaction, Li^+ was initially absent in the solution so the Li deintercalation simultaneously occurred (Fig. 1). The Li deintercalation reaction results in a decrease in the layer charges and consequently the release of counterbalancing chromate and Cl^- held in the interlayer. As the reaction temperature was increased, the deintercalation rate increased and became comparable to the chromate adsorption rate (e.g., Fig. 1C and D). In other words, the Li deintercalation reaction counteracts the anion exchange reaction with respect to the chromate removal from water. Because complex time-dependence behaviors were observed for the Li, Cl and Cr concentrations during the reaction, no simple rate law can be applied to describe them.

Losing structural positive charges due to the Li deintercalation would decrease the adsorption capacity of Li/Al LDH. Therefore, for the purpose of using Li/Al LDH in removing contaminants from waters, the deintercalation of Li/Al LDH needs to be inhibited during the adsorption of contaminants in order to sustain maximum adsorption capacity of LDH. In contrast, the contaminant fixed by Li/Al LDH may be recovered through the deintercalation reaction at elevated temperatures, if the presence of contaminants in the interlayer of Li/Al LDH does not interfere the deintercalation of structural Li. During the adsorption of Cr(VI) at 10 °C, the curve of released Cl departed from that of released Li but was similar to that of chromate adsorption, indicating that chromate adsorption has a predominant contribution to Cl release. The deintercalation reaction of Li/Al LDH is slower than the anion exchange reaction between chromate and Cl^-, so an

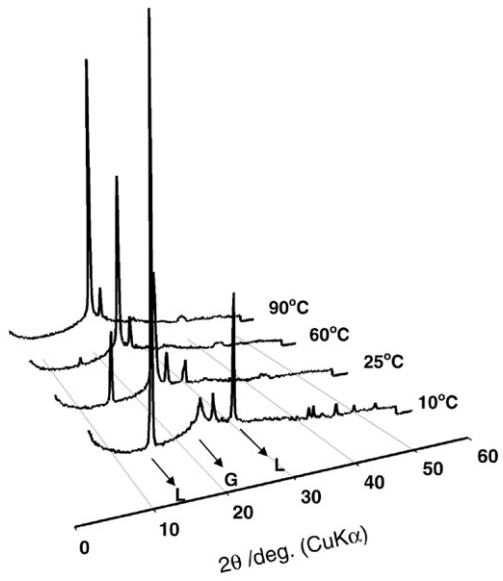

Fig. 3. X-ray diffraction patterns of solid samples collected after the deintercalation experiments of Li/Al LDH at different temperatures.

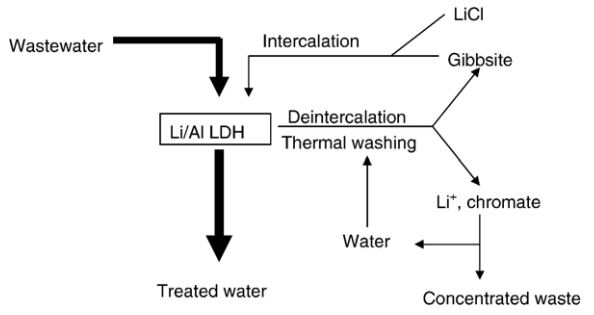

Fig. 4. Schematic representation for the proposed processes to recover Cr from contaminated water using Li/Al LDH and to regenerate the used material.

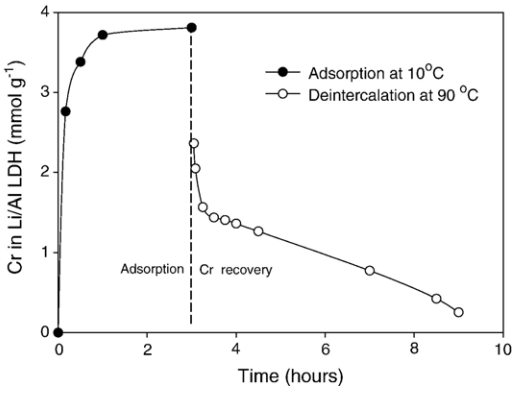

Fig. 5. Evolution of Cr concentration during the adsorption and deintercalation of chromate in Li/Al LDH.

adsorption maximum of 3.81 mmol g^{-1} chromate was reached first and then chromate was slowly released due to the Li deintercalation. This is probably because the anion exchange reaction only involves the replacement of interlayer Cl^- anions with chromate but in the intercalation/deintercalation processes the migrations of Li^+ and counter anions in and out of the structure are required to overcome the higher energetic barriers, especially the reorganization of the hydrogen-bonding network in the structures of gibbsite and LDH during their transformation to each other (Besserguenev et al., 1997; Fogg and O'Hare, 1999; Wang and Johnston, 2000). Therefore, although the deintercalation of structural Li^+ is disadvantageous for Li/Al LDH being an adsorbent, this material can still be an effective adsorbent for chromate if the Li deintercalation is inhibited at low temperature.

On the other hand, the Li deintercalation rate is significantly enhanced when the reaction temperature is increased. When Cr adsorption was preceded at 60 °C and 90 °C, about 24% and 46% of structural Li^+, respectively, were simultaneously released from the adsorbent after 5-min reaction (Fig. 1C and D). The amount of released Li^+ was enlarged over reaction time, which resulted in a significant decrease in the amount of adsorbed chromate. At 90 °C, as much as 86% of the adsorbed chromate can be released from the structure into the aqueous solution after 6 h. Comparatively, without the presence of chromate in the solution, the deintercalation of Li^+ reached 100% within 30 min at 60 °C or above (Fig. 2A). The high concentration of Cr in the solution seems to slow the Li deintercalation rate. Therefore, it is expected that the recovery rate of adsorbed chromate can be higher if the contaminant-bearing material is treated using hot clean water without chromate.

Based on the results above, we proposed a scheme of applying Li/Al LDH for treatment of water containing chromate with the possibility that the contaminant can be recovered and the used material regenerated (Fig. 4). At low temperature, the Cr adsorption of Li/Al LDH is fast while the Li deintercalation is slow. The treatment of water containing Cr using Li/Al LDH can be conducted at low temperature to inhibit the Li deintercalation reaction and increase adsorption capacity of Li/Al LDH (thick lines in Fig. 4). Because the deintercalation rate of structural Li^+ is significantly enhanced at elevated temperatures and a complete deintercalation is achievable, the adsorbed chromate can be potentially

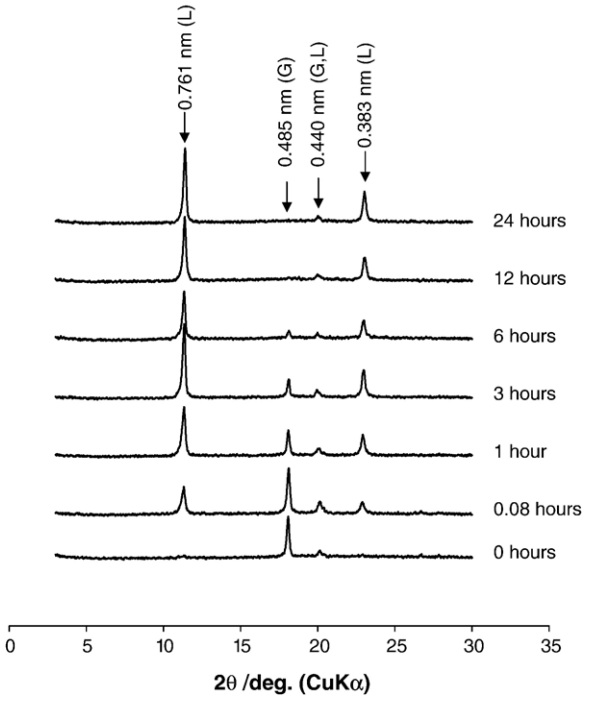

Fig. 6. X-ray diffraction patterns for LiCl intercalation of recycled gibbsite.

recovered through washing the contaminant-bearing LDH with hot water and no additional chemicals are required (thin lines in Fig. 4). An experiment was conducted to demonstrate the feasibility of such a practice (Fig. 5). 0.5 g Li/Al LDH was first reacted with 600 mg L^{-1} chromate at 10 °C and an adsorption maximum was reached within 3 h. Afterward, the solid was separated from the solution and placed into 90 °C water to initiate the deintercalation reaction of LDH to recover Cr. After 6 h at 90 °C, the chromate that remained in LDH was decreased to 0.25 mmol g^{-1}, indicating that 94% of the adsorbed chromate was released from the used adsorbent into the solution. The recovery of Cr can be as high as 100% of adsorbed chromate if the thermal washing process is repeated (data is not shown). The final products of thermal washing are gibbsite and an aqueous solution containing Li^+ and chromate. The solution containing chromate may be further concentrated to eliminate water and reduce the volume of waste. Water may be recovered for the use in thermal washing; concentrated waste may be further treated to recover contaminant (Fig. 4).

The solid product after thermal washing the Cr-bearing LDH is gibbsite, which may be reused to synthesize Li/Al LDH through LiCl intercalation. As seen in Fig. 6, the XRD pattern of gibbsite exhibits two major peaks at 0.485 nm and 0.437 nm, corresponding to the (002) and (110) reflections, respectively (Saalfeld and Wedde, 1974). After gibbsite was treated with 10 M LiCl solution at 90 °C for 5 min, three peaks appeared at 0.761, 0.440 and 0.383 nm, corresponding to the (002), (101) and (004) reflections of Li/Al LDH, respectively (Besserguenev et al., 1997). The 0.440-nm peak overlaps with the (110) reflection of gibbsite at 0.437 nm. As the reaction time increases, the intensities of the reflections of Li/Al LDH gradually increase while those of gibbsite decrease in intensity. The disappearance of the (002) reflection of gibbsite at 0.485 nm after 12 h of reaction indicates the complete transformation of gibbsite into LDH (Fig. 6). Therefore, the recovered gibbsite can be regenerated and reused for synthesizing Li/Al LDH, which can be re-applied to treat water containing chromate.

4. Conclusions

Li/Al LDH, which is synthesized through LiCl intercalation into gibbsite, has exhibited a high adsorption capability of chromate in aqueous solutions. Li/Al LDH could rapidly adsorb chromate within minutes but the adsorption capacity decreases as reaction temperature increases due to the deintercalation of Li^+ from the structure. Treatment with water at elevated temperatures will enhance the deintercalation of Li^+ and, consequently, the loss in the positive charges of LDH. Therefore, the Li deintercalation reaction can be applied to recover adsorbed contaminant from used LDH containing Cr. Accordingly, a new approach is suggested to remove chromate from wastewater using Li/Al LDH at low temperature. After the used adsorbent is separated from wastewater by filtration or centrifugation, it can be treated with hot water to recover the adsorbed Cr. The solid residue after recovering Cr will be gibbsite, which may be recycled and reused for synthesizing Li/Al LDH.

Acknowledgement

The authors thank the National Science Council, Taiwan for the financial support (NSC 92-2211-E-005-006, 93-2313-B-005-055 and 93-2313-B-005-056).

References

Alvarez-Ayuso, E., Nugteren, H.W., 2005. Purification of chromium (VI) finishing wastewaters using calcined and uncalcined Mg–Al–CO_3–hydrotalcite. Water Res. 39, 2535–2542.

Besserguenev, V., Fogg, A.M., Francis, R.J., Price, S.J., O'Hare, D., Isupov, V.P., Tolochko, B.P., 1997. Synthesis and structure of the gibbsite intercalation compounds $[LiAl_2(OH)_6]X$ {X=Cl, Br, NO_3} and $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ using synchrotron X-ray and neutron powder diffraction. Chem. Mater. 9, 241–247.

Bhaumik, A., Samanta, S., Mal, N.K., 2004. Efficient removal of arsenic from polluted ground water. J. Appl. Sci. 4, 467–471.

Borja, M., Dutta, P.K., 1992. Fatty acids in layered metal hydroxides: membrane-like structure and dynamics. J. Phys. Chem. 96, 5434–5444.

Cavani, F., Trifiro, F., Vaccari, A., 1991. Hydrotalcite-type anionic clays: preparation, properties and applications. Catal. Today 11, 173–301.

Dutta, P.K., Puri, M., 1989. Anion-exchange in lithium aluminate hydroxides. J. Phys. Chem. 93, 376–381.

Eaton, A.D., Clesceri, L.S., Greenberg, A.E., 1995. Standard Methods for the Examination of Water and Wastewater. Am. Public Health Assoc., Washington, DC.

Fogg, A.M., O'Hare, D., 1999. Study of the intercalation of lithium salt in gibbsite using time-resolved *in-situ* X-ray-diffraction. Chem. Mater. 11, 1771–1775.

Galvin, R.M., 1996. Occurrence of metals in waters: an overview. Water S.A. 22, 7–18.

Goswamee, R.L., Sengupta, P., Bhattacharyya, K.G., Dutta, D.K., 1998. Adsorption of Cr(VI) in layered double hydroxides. Appl. Clay Sci. 13, 21–34.

Hou, X.Q., Kirkpatrick, R.J., 2001. Thermal evolution of Cl^-–$LiAl_2$ layered double hydroxide: a multinuclear MAS NMR and XRD perspective. Inorg. Chem. 40, 6397–6404.

Isupov, V.P., Mitrofanova, R.P., Chupakhina, L.E., 1994. Intercalation compounds of aluminum hydroxide with lithium salts in synthesis of lithium monoaluminate. Russ. J. Appl. Chem. 67, 1687–1688.

Kang, M.J., Chun, K.S., Rhee, S.W., Do, Y., 1999. Comparison of sorption behavior of I^- and TcO_4^- on Mg/Al layered double hydroxide. Radiochim. Acta 85, 57–63.

Kotas, J., Stasicka, Z., 2000. Chromium occurrence in the environment and methods of its speciation. Environ. Pollut. 107, 263–283.

Kovanda, F., Kovacsova, E., Kolousek, D., 1999. Removal of anions from solution by calcined hydrotalcite and regeneration of used sorbent in repeated calcination–rehydration–anion exchange processes. Collect. Czechoslov. Chem. Commun. 64, 1517–1528.

Lazaridis, N.K., Asouhidou, D.D., 2003. Kinetics of sorptive removal of chromium(VI) from aqueous solutions by calcined Mg–Al–CO_3 hydrotalcite. Water Res. 37, 2875–2882.

Nayak, M., Kutty, T.R., Jayaraman, V., Periaswamy, G., 1997. Preparation of the layered double hydroxide (LDH) $LiAl_2(OH)_7{\cdot}2H_2O$, by gel to crystallite conversion and a hydrothermal method, and its conversion to lithium aluminates. J. Mater. Chem. 7, 2131–2137.

Nemudry, A.P., Isupov, V.P., Kotsupalo, N.P., Boldyrev, V.V., 1986. The formation of double basic salts of aluminum and lithium on crystalline aluminum hydroxide. Russ. J. Inorg. Chem. 31, 651–653.

Poeppelmeier, K.R., Hwu, S.-J., 1987. Synthesis of lithium dialuminate by salt imbibition. Inorg. Chem. 26, 3297–3302.

Saalfeld, H., Wedde, M., 1974. Refinement of the crystal structure of gibbsite, Al(OH)3. Z. Kristallogr. 139, 129–135.

Sposito, G., 1984. The Surface Chemistry of Soils. Oxiford University Press, New York.

Tarasov, K.A., Isupov, V.P., Chupakhina, l.E., O'Hare, D., 2004. A time resolved, *in-situ* X-ray diffraction study of the de-intercalation of anions and lithium cations from $[LiAl_2(OH)_6]_nX{\cdot}qH_2O$ ($X=Cl^-$, Br^-, NO_3^-, SO_4^{2-}). J. Mater. Chem. 14, 1443–1447.

US-EPA, 2003. National Primary Drinking Water Standards, EPA 816-F-03-016, Washington D.C.

Wang, S.L., Johnston, C.T., 2000. Assignment of the structural OH stretching bands of gibbsite. Am. Mineral. 85, 739–744.

You, Y., Vance, G.F., Zhao, H., 2001. Selenium adsorption on Mg–Al and Zn–Al layered double hydroxides. Appl. Clay Sci. 20, 13–25.