

# Use of High-Pressure CO<sub>2</sub> for Concentrating Cr<sup>VI</sup> from Electroplating Wastewater by Mg–Al Layered Double Hydroxide

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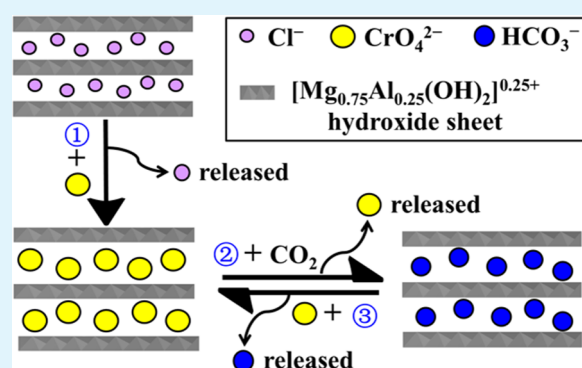
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## Supporting Information

**ABSTRACT:** The desorption of Cr<sup>VI</sup> from Cr<sup>VI</sup>-adsorbed layered double hydroxide (Cr<sup>VI</sup>-LDH) and the recycling of LDH adsorbent are the bottlenecks that limit the practical application of LDH in treating Cr<sup>VI</sup>-containing industrial wastewater. Given the strong affinity of LDH for CO<sub>2</sub>, we studied desorption and enrichment of Cr<sup>VI</sup> from Cr<sup>VI</sup>-LDH as well as recycling of LDH in the presence of high-pressure CO<sub>2</sub>. Results showed that Cr<sup>VI</sup> solution with concentration of 500 mg/L could be enriched more than 20 times in each adsorption–desorption cycle. The regenerated LDH maintained the layer structure and the sheets as revealed by XRD and TEM patterns. FT-IR data showed CO<sub>2</sub> formed HCO<sub>3</sub><sup>−</sup> at high pressure. The transformation from CO<sub>2</sub> to HCO<sub>3</sub><sup>−</sup> followed by the anion-exchange with CrO<sub>4</sub><sup>2−</sup> was the critical factor for Cr<sup>VI</sup> desorption and LDH regeneration. A pilot-scale experiment was carried out with 20 L Cr<sup>VI</sup>-containing electroplating wastewater. The concentration of the desorbed Cr<sup>VI</sup> solution could reach up to 10000 mg/L, which could be used in electroplating after appropriate adjustment. The main advantages of this method are high concentration of Cr<sup>VI</sup>, direct reuse of enriched Cr<sup>VI</sup>, and efficient regeneration of LDH adsorbent. This method showed promises in recycling Cr<sup>VI</sup> and regenerating LDH in treating industrial wastewater.

**KEYWORDS:** chromium(VI), layered double hydroxides (LDHs), electroplating wastewater, CO<sub>2</sub>, recycle, concentration



## INTRODUCTION

Hexavalent chromium (Cr<sup>VI</sup>), which is highly carcinogenic and mutagenic,<sup>1,2</sup> exists widely in the effluents of electroplating, leather tanning, textile, mine tails, and other industries.<sup>3</sup> Especially in the electroplating industry, the concentrations of Cr<sup>VI</sup> in the wastewater sometimes can reach up to hundreds or even thousands of mg/L. Chemical reduction and coprecipitation are the main technologies to dispose Cr<sup>VI</sup> currently.<sup>4</sup> However, these methods produce a large amount of Cr<sup>VI</sup>-containing sludge, and generate comparatively high concentrations of chromium that cannot be reused. Although ion exchange and membrane filtration are favorable for the direct reuse of Cr<sup>VI</sup>, the materials are readily oxidized by Cr<sup>VI</sup>, which limits the practical use of such methods.<sup>5</sup> Therefore, there is an urgent need for the development of a wastewater treatment method, which allows the low concentrations of chromium to be extracted directly from the effluents and further enriched to a higher level for reuse in electroplating and other industries.

Adsorption is an efficient method to remove many harmful substances. The eco-friendly layered double hydroxides (LDHs), with a general formula of [M<sub>1-x</sub><sup>2+</sup>M<sub>x</sub><sup>3+</sup>(OH)<sub>2</sub>]<sup>(A<sup>n-</sup>)<sub>x/n</sub>·yH<sub>2</sub>O</sup>,<sup>6,7</sup> is one of the most promising adsorbents in the removal of highly concentrated toxic anions (such as

CrO<sub>4</sub><sup>2−</sup>, AsO<sub>4</sub><sup>2−</sup>, PO<sub>4</sub><sup>3−</sup>, F<sup>−</sup>), because of their large ionic exchange capacities.<sup>8–10</sup> Adsorptions of Cr<sup>VI</sup> by LDHs have been extensively investigated,<sup>1,11</sup> including the design and preparation of LDHs,<sup>12</sup> the adsorption kinetics and thermodynamics,<sup>13</sup> and the factors affecting the adsorption efficiency.<sup>8,14</sup> In addition, there is also some reports about desorption of Cr<sup>VI</sup>-adsorbed LDH (denoted as Cr<sup>VI</sup>-LDH). For example, the Cr<sup>VI</sup> in the Cr<sup>VI</sup>-LDH sludge can be desorbed in various alkaline solutions (such as NaOH) and salt solutions (NaCl, FeCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, and NaHCO<sub>3</sub>) or a mixture of these solutions via the anion exchange process.<sup>3,15,16</sup> Carbonate is generally considered the best desorbent. Researchers also studied the regeneration of carbonate ions intercalated LDH (named as CO<sub>3</sub><sup>2−</sup>/HCO<sub>3</sub><sup>−</sup>-LDH). A calcination process at around 500 °C followed by reconstruction in water<sup>17</sup> or acid-treatment by inorganic and organic acids has been used to deintercalate CO<sub>3</sub><sup>2−</sup>/HCO<sub>3</sub><sup>−</sup> from CO<sub>3</sub><sup>2−</sup>/HCO<sub>3</sub><sup>−</sup>-LDH.<sup>18</sup> Nevertheless, many drawbacks exist in such regeneration treatments. First, the desorbed chromium is still not concentrated enough.

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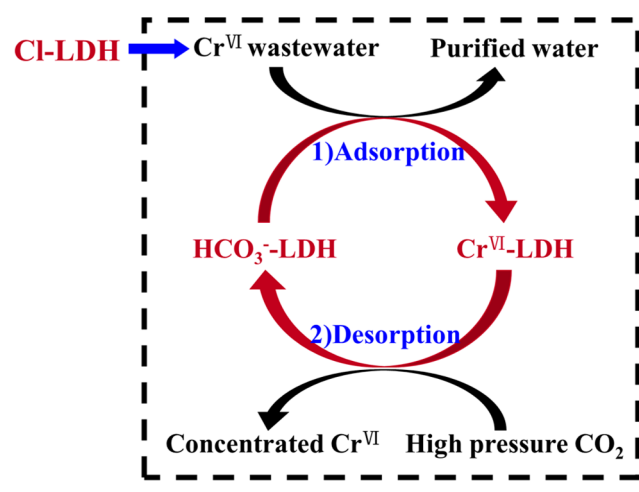
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Second, the heat treatment consumes a large amount of energy and probably modifies the initial surface state and the structure of LDHs. Third, because of the introduction of numerous ionic impurities, the obtained chromium cannot be reused directly. Therefore, to achieve the goals of concentrating  $\text{Cr}^{\text{VI}}$  and regenerating LDHs simultaneously during  $\text{Cr}^{\text{VI}}$ -LDH desorption is the key to decide whether LDHs can be used practically.

LDHs and calcined LDHs are used as excellent  $\text{CO}_2$  sorbents in many reports.<sup>19–22</sup> This illustrates LDHs show high affinity to  $\text{CO}_3^{2-}$  ions as well as  $\text{CO}_2$  and  $\text{HCO}_3^-$  ions. It is also implied that  $\text{CO}_2$  may induce  $\text{Cr}^{\text{VI}}$  desorption from  $\text{Cr}^{\text{VI}}$ -LDH sludge when  $\text{CO}_2$  is introduced into the system. Moreover, the use of  $\text{CO}_2$  gas shows many advantages over the aqueous eluents. Because there is no impurity introduced by  $\text{CO}_2$  desorption, the desorbed chromium can be reused directly. The experimental design for reusing  $\text{Cr}^{\text{VI}}$  in  $\text{Cr}^{\text{VI}}$ -containing wastewater and regenerating LDHs is illustrated in Scheme 1.

**Scheme 1. Proposed Treatment of  $\text{Cr}^{\text{VI}}$ -Containing Wastewater, The Red Circle Represents the Continuous Cycle of  $\text{HCO}_3^-$ -LDH Adsorbent**



The  $\text{Cr}^{\text{VI}}$  in the industrial wastewater is first adsorbed efficiently by Cl-LDH, followed by the introduction of high-pressure  $\text{CO}_2$  into the  $\text{Cr}^{\text{VI}}$ -LDH sludge for  $\text{Cr}^{\text{VI}}$  desorption and enrichment. In the meantime, the  $\text{HCO}_3^-$ -LDH adsorbent is regenerated.

In this study, we investigated the adsorption of  $\text{Cr}^{\text{VI}}$  by LDH, the desorption of  $\text{Cr}^{\text{VI}}$  from  $\text{Cr}^{\text{VI}}$ -LDH sludge by high pressure  $\text{CO}_2$ , the enrichment of  $\text{Cr}^{\text{VI}}$  and the regeneration of LDH adsorbent. The feasibility of this strategy was examined by treating 20 L electroplating wastewater in a pilot-scale experiment. We hope this work could provide a new strategy for the treatment of  $\text{Cr}^{\text{VI}}$ -containing industrial wastewater.

## EXPERIMENTAL METHODS

**Preparation of  $\text{Cr}^{\text{VI}}$ -Containing Water Samples.** The  $\text{Cr}^{\text{VI}}$ -containing water samples were prepared by dissolving appropriate amounts of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ , AR) into distilled water to produce the final concentrations of 100, 500, and 1000 mg/L. All reagents were of analytical grade and used without further purification.

**Preparation of Mg–Al Cl-LDH and Adsorption Experiments of  $\text{Cr}^{\text{VI}}$ .** The Mg–Al Cl-LDH sol (hereafter named as Cl-LDH) was synthesized by a coprecipitation method according to the literature.<sup>3</sup> A mixed solution of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  was prepared by the Mg/Al molar ratio of 3:1. Diluted ammonia (5:1 (v/v)) was then slowly dropped into the mixed solution under continuous stirring. The final pH of the suspension was adjusted to 9.5 with ammonia. The

precipitate was aged for 3 h in the solution at room temperature. The white product was filtered, washed, and dried at 100 °C overnight for tests.

For the adsorption experiments, the white Cl-LDH solid (0.2 g) was added into 50 ml simulated  $\text{Cr}^{\text{VI}}$  solutions of 100, 500, and 1000 mg/L. The final pH of the mixture was adjusted with diluted hydrochloric acid to around 4. The mixture was stirred for 5 h until the LDH reached the adsorption equilibrium. During this process, 1 mL of solution was extracted to determine the concentration of  $\text{Cr}^{\text{VI}}$  at certain intervals. The yellow  $\text{Cr}^{\text{VI}}$ -LDH was then filtered, washed, and dried for further desorption and enrichment treatments. A small amount of this sample was air-dried for XRD, TEM and FT-IR analyses.

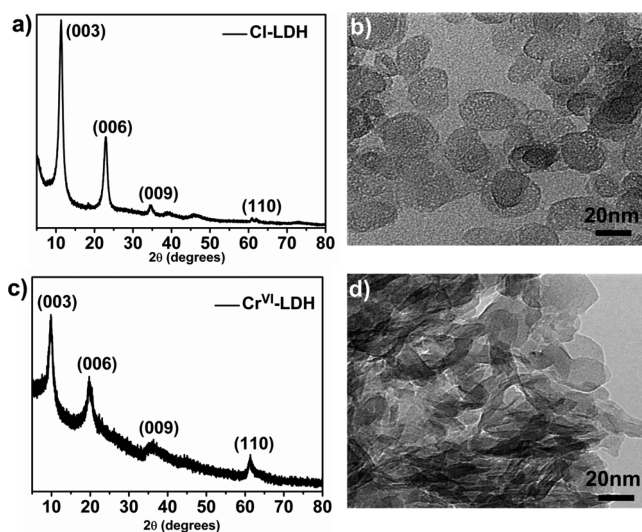
**Desorption and Enrichment of  $\text{Cr}^{\text{VI}}$ .** Dried  $\text{Cr}^{\text{VI}}$ -LDH was mixed with water by the ratio of 1 g of solid per 5 mL of water and then transferred into a cylindrical stainless steel vessel with continuous stirring. The vessel was sealed, with an opening connected to a  $\text{CO}_2$  high pressure bomb. The pressure of the  $\text{CO}_2$  gas was adjusted to 2.5 MPa for  $\text{Cr}^{\text{VI}}$  desorption. After treatment for 14 h, the mixture was separated into a yellow concentrated solution of  $\text{Cr}^{\text{VI}}$  and yellowish LDH precipitate. The concentrated  $\text{Cr}^{\text{VI}}$  solution was centrifuged immediately to avoid the re-adsorption of  $\text{Cr}^{\text{VI}}$  by LDH. The concentrated  $\text{Cr}^{\text{VI}}$  was then analyzed and reused. After four successive  $\text{CO}_2$  treatments, the sediment was washed three times to remove the  $\text{Cr}^{\text{VI}}$  attached on the surface. Finally, a white solid product was obtained. This product was heated at 100 °C to remove residual  $\text{CO}_2$  and reserved for the next adsorption cycle. At the same time, a small amount of this product was collected for residual  $\text{Cr}^{\text{VI}}$  determination, XRD, IR analysis, and TEM study.

**Pilot-Scale Treatment.** 20 L  $\text{Cr}^{\text{VI}}$ -containing electroplating wastewater was used for the pilot-scale experiment. The  $\text{Cr}^{\text{VI}}$  concentration was 1031 mg/L and the pH of the wastewater was about 4. Cl-LDH (320 g) was added into the wastewater under continuous stirring for 5 h. The  $\text{Cr}^{\text{VI}}$  removal efficiency was determined by measuring the  $\text{Cr}^{\text{VI}}$  in the supernatant. The yellow  $\text{Cr}^{\text{VI}}$ -LDH sludge was centrifuged, washed and finally dried. Dried  $\text{Cr}^{\text{VI}}$ -LDH was mixed with water by the ratio of 1 g solid per 5 mL water and then transferred into a cylindrical stainless steel vessel with continuous stirring. The stainless steel vessel was sealed and filled with  $\text{CO}_2$  under the pressure of 2.5 MPa for 14 h. The supernatant containing concentrated  $\text{Cr}^{\text{VI}}$  was then separated for  $\text{Cr}^{\text{VI}}$  determination and reuse. The sediment was rinsed with distilled water 3 times to determine the amount of residual  $\text{Cr}^{\text{VI}}$ .

**Instruments and Characterization.** X-ray diffraction (XRD) data were used to identify the phase composition and structure of LDH. Diffraction data was recorded using a PANalytical Supplementar X'Pert PRO diffractometer with Cu  $K\alpha$  radiation (40 kV, 40 mA). The  $2\theta$  scanning range was from 5° to 80° in a step of 0.016°. The average crystallite size was calculated from the peak broadening using the Scherrer equation. High-resolution transmission electron microscopy (HRTEM) was used to confirm particle size, shape and crystal structure. HRTEM was conducted by a TECNAI F20 at 200 kV. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using KBr pellets in the range of 4000–450  $\text{cm}^{-1}$ . The concentration of  $\text{Cr}^{\text{VI}}$  in the solution was determined by the 1,5-diphenylcarbohydrazide spectrophotometric method (GB 7467 and GB/T 15555.4) using Shimadzu UV-2550 spectrophotometer.

## RESULTS AND DISCUSSION

**Characterization of Mg–Al LDH and Adsorption Behaviors of  $\text{Cr}^{\text{VI}}$ .** The phase composition and crystal structure of the Cl-LDH adsorbent were characterized by XRD, as shown in Figure 1a. The diffraction peaks are symmetrical and sharp, which indicates that Cl-LDH should be a well-crystallized hydrotalcite-like compound belonging to the hexagonal system. Therefore, the sol should have a hydro-talcite-type structure, showing the three characteristic basal reflections due to planes (003), (006), and (009). The



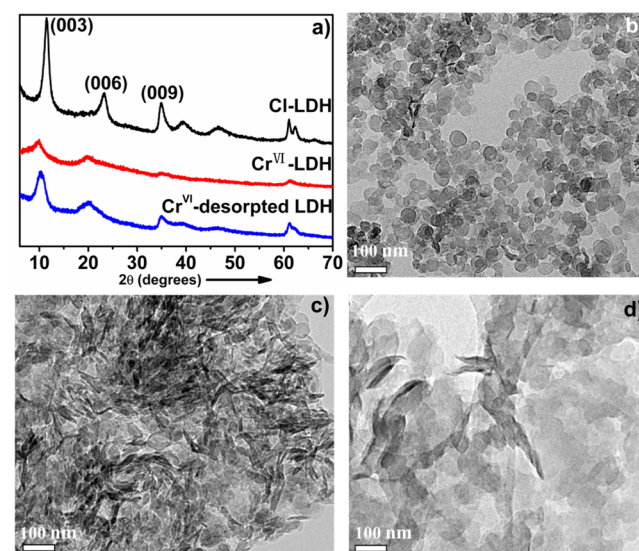
**Figure 1.** XRD patterns and TEM images of Cl-LDH and Cr<sup>VI</sup>-LDH.

interlayer distance is ca. 0.767 nm according to the diffraction by plane (003). Because the width of the brucite-like layer is 0.48 nm,<sup>8</sup> the gallery height should be 0.287 nm. As shown by the TEM images in Figure 1b, the morphology of the Cl-LDH surface is a sheet structure. The Cl-LDH platelets are not uniform with particle sizes in the range of ~20–40 nm. The adsorption behavior of Cl-LDH is shown in Figure S1 in the Supporting Information (SI). It can be observed that the concentration of residual Cr<sup>VI</sup> decreases rapidly in the first 30 min, reaching an adsorption equilibrium after 60 min. This behavior is similar to the results in the literature.<sup>3</sup> The adsorption capacity is about 73 mg/g, which suggests that the Cl-LDH adsorbent should be no less than 6.8 g/L for 500 mg/L Cr<sup>VI</sup> solution to reach the discharge standard.

The reaction of 10 g/L Cl-LDH adsorbent and 500 mg/L Cr<sup>VI</sup> solution resulted in a yellow sediment of Cr<sup>VI</sup>-LDH and a purified aqueous phase (Cr<sup>VI</sup> <0.5 mg/L). In Figure 1c, the diffraction peaks of Cr<sup>VI</sup>-LDH are wider and less intense than that of Cl-LDH, suggesting a lower degree of crystallinity and a less organized stacking arrangement. Meanwhile, the position of the peak for plane (003) is down-shifted to the lower angles in comparison with Cl-LDH. The increase in basal spacing from 0.767 to 0.896 nm indicates larger gallery height and intercalation of Cr<sup>VI</sup> anions by anion exchange. It is further confirmed in the FT-IR spectrum with a new band characteristic of chromate anion at 884 cm<sup>-1</sup>. In the TEM images of Cr<sup>VI</sup>-LDH shown in Figure 1d, the platelets appear to be curved and aggregated. This implies that the intercalated Cr<sup>VI</sup> anions enlarge the gallery height, resulting in the presence of stress and formation of few thinner sheets consequently, which may curve easily.

**Cr<sup>VI</sup> Desorption Studies from Cr<sup>VI</sup>-LDH by CO<sub>2</sub>.** High-pressure CO<sub>2</sub> is introduced to the mixture of dried yellow Cr<sup>VI</sup>-LDH and water for Cr<sup>VI</sup> desorption. The effects of reaction time and pressure on desorption are shown in Figures S2 and S3 in the Supporting Information. The desorption efficiency of Cr<sup>VI</sup> shows a positive correlation with reaction time and CO<sub>2</sub> pressure. Given the results, the optimum pressure and time for desorption are 2.5 MPa and 14 h, respectively. It is calculated that the initial Cr<sup>VI</sup> solution with a concentration of 500 mg/L can be enriched about 22.4 times after desorption. The desorption efficiency of Cr<sup>VI</sup> is about 77%.

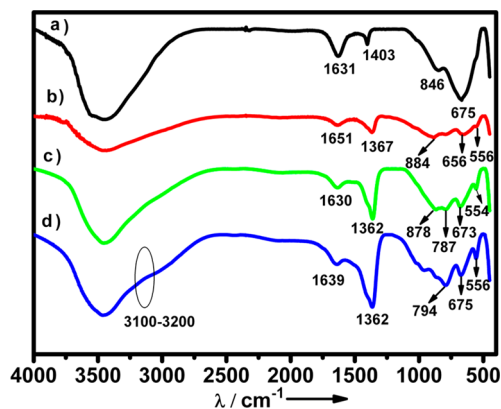
The XRD patterns and TEM images of the desorbed yellowish LDH powder (Cr<sup>VI</sup>-desorbed LDH) are compared to those of the Cl-LDH and Cr<sup>VI</sup>-LDH samples. XRD patterns (Figure 2a) show that LDH keeps the hydroxalite-type layer



**Figure 2.** (a) XRD patterns and TEM images of (b) Cl-LDH, (c) Cr<sup>VI</sup>-LDH, and (d) Cr<sup>VI</sup>-desorbed LDH.

structure after CO<sub>2</sub> treatment. The positions of the diffraction peaks are shifted to the high angles compared to Cr<sup>VI</sup>-LDH. The interlayer distance is ca. 0.812 nm, suggesting the desorption of Cr<sup>VI</sup> from the layer and intercalation of anions with relatively small radius. As shown in the TEM image of Cr<sup>VI</sup>-desorbed LDH (Figure 2d), most of the curved and aggregated platelets change back to platelets with a small part maintaining the curved morphology of Cr<sup>VI</sup>-LDH (Figure 2c). It suggests that the Cr<sup>VI</sup> of Cr<sup>VI</sup>-LDH is probably exchanged with CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> anions in the solution after CO<sub>2</sub> treatment.

In order to explore the state of LDH sample after CO<sub>2</sub> desorption, IR spectrum was further investigated. In Figure 3c, a slight characteristic peak of CO<sub>2</sub> at 673 cm<sup>-1</sup> can be seen, indicating the existence of insignificant amounts of CO<sub>2</sub>. Moreover, the IR spectrum of Cr<sup>VI</sup>-desorbed LDH obtained by Na<sub>2</sub>CO<sub>3</sub> solution immersion (denoted as CO<sub>3</sub><sup>2-</sup>-LDH) was



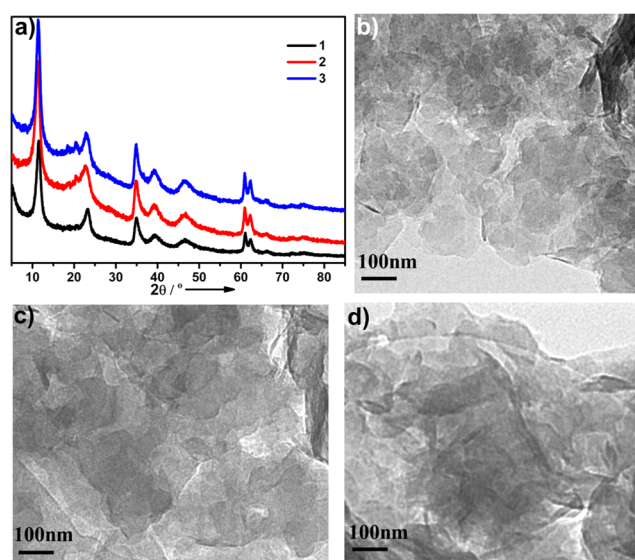
**Figure 3.** FT-IR spectra of (a) Cl-LDH, (b) Cr<sup>VI</sup>-LDH, (c) HCO<sub>3</sub><sup>-</sup>-LDH, and (d) CO<sub>3</sub><sup>2-</sup>-LDH.

also collected and compared. There is no noticeable difference between the samples of  $\text{CO}_2$  desorption and  $\text{Na}_2\text{CO}_3$  solution desorption (Figure 3d). Similar characteristic bands of C–O bond at  $1362\text{ cm}^{-1}$  and  $3100\text{--}3200\text{ cm}^{-1}$  are present in both samples. It should be noted that  $\text{HCO}_3^-$  cannot be well differential from  $\text{CO}_3^{2-}$  by IR analysis. Based on the final acidic pH of 5.4, which stabilizes  $\text{HCO}_3^-$  anions,<sup>23</sup> it is believed that the  $\text{Cr}^{\text{VI}}$ -desorbed LDH should be  $\text{HCO}_3^-$ -LDH. The probable desorption process is proposed as follows. First,  $\text{CO}_2$  reacts with  $\text{H}_2\text{O}$  to form  $\text{HCO}_3^-$  under high pressure.  $\text{HCO}_3^-$  then intercalates into LDH by anion exchange with  $\text{CrO}_4^{2-}$ . Finally, the enriched  $\text{Cr}^{\text{VI}}$  solution is obtained and  $\text{HCO}_3^-$ -LDH simultaneously formed.

As suggested by experiments above,  $\text{HCO}_3^-$  in high concentration formed by high-pressure  $\text{CO}_2$  should be a good desorbent. It can not only desorb  $\text{Cr}^{\text{VI}}$  efficiently, but realize the high concentration of desorbed  $\text{Cr}^{\text{VI}}$ . Because of the desorption equilibrium,  $\text{Cr}^{\text{VI}}$  cannot be desorbed completely in one desorption cycle. When the partially desorbed  $\text{Cr}^{\text{VI}}$ -LDH is reused to absorb  $\text{Cr}^{\text{VI}}$  directly, the ability of re-adsorption decreases significantly (see Table S1 in the Supporting Information). Results show that about 95%  $\text{Cr}^{\text{VI}}$  can be desorbed from the  $\text{Cr}^{\text{VI}}$ -LDH sludge after four successive  $\text{CO}_2$  desorption cycles. The desorbed chromium is enriched to a concentration of above 10 000 mg/L from the initial concentration of 500 mg/L in the first desorption. This corresponds to about 77% desorption efficiency. The enriched chromium solution after appropriate adjustment can be reused in industries. The remaining 23% of the residual chromium can be enriched to a concentration of 5464 mg/L after additional three desorption processes. Thus, the regenerative LDH containing  $\text{HCO}_3^-$  (denoted as  $\text{HCO}_3^-$ -LDH) can be obtained after four desorption processes by  $\text{CO}_2$ .

**Cycling Studies of  $\text{Cr}^{\text{VI}}$  Treatment by LDH and Pilot-Scale Test of Electroplating Wastewater.** The recycling capacity of regenerated  $\text{HCO}_3^-$ -LDH was further studied in this work. The consecutive sorption-regeneration cycles for  $\text{Cr}^{\text{VI}}$  by  $\text{HCO}_3^-$ -LDH were repeated three times according to the above steps. In the XRD patterns (Figure 4a), the regenerated  $\text{HCO}_3^-$ -LDH shows the initial hydroxalcalcite-like layer structure after three sorption-regeneration cycles. From the first to third cycles, almost unchanged morphology of regenerated  $\text{HCO}_3^-$ -LDH can be seen in the TEM images shown in Figure 4b–d. Moreover, Table 1 shows the adsorption capacities of regenerated  $\text{HCO}_3^-$ -LDH adsorbent, the  $\text{Cr}^{\text{VI}}$  desorption efficiency as well as the enrichment multiples after three sorption-regeneration cycles. The adsorption capacities of regenerated  $\text{HCO}_3^-$ -LDH adsorbent are above 70 mg/g (73 mg/g for the initial sample). The  $\text{Cr}^{\text{VI}}$  removal efficiency is constantly at a high level in three continuous cycles of re-adsorption/redesorption. The enrichment multiples of  $\text{Cr}^{\text{VI}}$  desorbed in the first cycle maintain more than 20 times (22.4 times for the first circle) during these processes. In sum, a stable recycling effect of  $\text{HCO}_3^-$ -LDH adsorbent is successfully achieved.

A pilot-scale experiment was conducted on 20 L electroplating wastewater of an initial  $\text{Cr}^{\text{VI}}$  concentration of 1031 mg/L to illustrate the technical feasibility of the proposed strategy. Table S2 in the Supporting Information shows the results of  $\text{Cr}^{\text{VI}}$  removal from electroplating wastewater at a LDH dosage of 16 g/L. It is clear that it can achieve the goals of both desorbing  $\text{Cr}^{\text{VI}}$  from  $\text{Cr}^{\text{VI}}$ -LDH sludge and concentrating the  $\text{Cr}^{\text{VI}}$  solution (10 242 mg/L) by treating the sludge with  $\text{CO}_2$ .



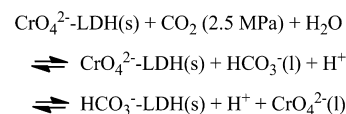
**Figure 4.** (a) XRD patterns of  $\text{HCO}_3^-$ -LDH samples in three repeated cycles, (b–d) TEM images of the reborn  $\text{HCO}_3^-$ -LDH adsorbent in the first, second and third cycles.

**Table 1.  $\text{Cr}^{\text{VI}}$  Desorption Efficiency and the Enrichment Multiples after Desorbing  $\text{Cr}^{\text{VI}}$ -LDH by  $\text{CO}_2$**

	batch no.		
	1	2	3
LDH dosage (g/L)	10	10	10
initial $\text{Cr}^{\text{VI}}$ concentration (mg/L)	500	500	500
desorption ratio (%) after one cycle	77	72	75
desorption ratio (%) after four cycles	95	93	92
adsorption quantity (mg/g) after four desorptions	73	75	71
enrichment multiples	22.4	21.6	21.3

After treatment, the  $\text{Cr}^{\text{VI}}$ -contaminated wastewater meets the wastewater release standard of China ( $\text{Cr}^{\text{VI}} < 0.5\text{ mg/L}$ ). The  $\text{Cr}^{\text{VI}}$  can be desorbed efficiently and enriched 9.9 times. After several successive desorption with  $\text{CO}_2$ , the  $\text{Cr}^{\text{VI}}$ -LDH is almost completely desorbed and formed  $\text{HCO}_3^-$ -LDH which is reused for the next cycle of adsorption/desorption. The uptake capacity of  $\text{HCO}_3^-$ -LDH after three circles does not drop significantly. Meanwhile, the enrichment multiple of desorbed  $\text{Cr}^{\text{VI}}$  solution is still as high as 9.4 after three cycles. Results indicate that both the concentration of  $\text{Cr}^{\text{VI}}$  solution and the regeneration of  $\text{HCO}_3^-$ -LDH adsorbent can be successfully achieved by the desorption strategy of tuning  $\text{CO}_2$  pressure. Therefore, this strategy is highly promising in treating  $\text{Cr}^{\text{VI}}$ -containing industrial effluents.

The following equation sums up the probable mechanism discussed above.



When high-pressure  $\text{CO}_2$  is introduced into the  $\text{CrO}_4^{2-}$ -LDH sludge, the dissolved  $\text{CO}_2$  reacts with  $\text{H}_2\text{O}$  to form  $\text{HCO}_3^-$  solution under acidic condition (pH 5.4). The  $\text{HCO}_3^-$  anion then exchanges  $\text{CrO}_4^{2-}$  from the  $\text{CrO}_4^{2-}$ -LDH layer by an ion-exchange process, yielding the white  $\text{HCO}_3^-$ -LDH solid and an enriched chromium solution. Therefore, a large amount of  $\text{CO}_2$

under high pressure moved the whole reaction to right, leading to the formation of  $\text{HCO}_3^-$ -LDH and de-intercalation of  $\text{Cr}^{\text{VI}}$  continuously. The subsequent removal of high-pressure  $\text{CO}_2$  causes a shift of the chemical equilibrium to the left, resulting in the readsorption of partially desorbed  $\text{Cr}^{\text{VI}}$ . Consequently, the  $\text{CrO}_4^{2-}$ -LDH cannot be completely desorbed in only one treatment. Therefore, after rapid separation of the concentrated  $\text{Cr}^{\text{VI}}$  solution desorbed in the first run, a successive desorption strategy can be adopted to further dispose of the residual  $\text{CrO}_4^{2-}$ -LDH sludge (23% of the total contents). Complete desorption of  $\text{CrO}_4^{2-}$ -LDH can be achieved by breaking the above equilibrium repeated. Besides the general principles of the desorption process discussed here, the desorption may proceed in a more complex way.

Using  $\text{CO}_2$  as the mineralizer of the desorption process is a better strategy for concentrating the desorbed chromium than hydrated eluents. Because hydrated eluents such as alkaline and salt solutions contain a large amount of other cations, the desorbed chromium can neither be concentrated efficiently nor reused directly. Meanwhile, the introduction of gaseous mineralizer  $\text{CO}_2$  does not produce byproducts during desorption, therefore the desorbed chromium can be reused directly. Figure S4 in the Supporting Information summarizes the whole strategy for the  $\text{Cr}^{\text{VI}}$  disposal system by LDH. The  $\text{Cr}^{\text{VI}}$ -containing wastewater is first adsorbed efficiently by Cl-LDH, obtaining the purified water and the  $\text{Cr}^{\text{VI}}$ -LDH sludge. High-pressure  $\text{CO}_2$  (2.5 MPa) is then introduced to the  $\text{Cr}^{\text{VI}}$ -LDH sludge to desorb  $\text{Cr}^{\text{VI}}$ . The enriched  $\text{Cr}^{\text{VI}}$  solution above 10000 mg/L can be reused as an industrial material. A successive  $\text{CO}_2$  desorption strategy can be conducted on the residual  $\text{Cr}^{\text{VI}}$ -LDH. The concentrated  $\text{Cr}^{\text{VI}}$  solution (<10 000 mg/L) is adsorbed again while the regenerated  $\text{HCO}_3^-$ -LDH can be reused. By tuning the  $\text{CO}_2$  pressure, the goals of concentrating the  $\text{Cr}^{\text{VI}}$  solution and regenerating LDH adsorbent may be achieved. Compared with more commonly used carbonate salt immersion method for desorbing the  $\text{Cr}^{\text{VI}}$ -LDH sludge, which usually involves calcination and rehydration or acid-treatment in regenerating the LDH adsorbent, this strategy is more cost-efficient, ecofriendly, facile, and versatile.

In summary, a recycling strategy using high-pressure  $\text{CO}_2$  was proposed for desorption and enrichment of  $\text{Cr}^{\text{VI}}$  from  $\text{Cr}^{\text{VI}}$ -LDH sludge as well as the simultaneous recycling of LDH adsorbent. A transformation from  $\text{CO}_2$  to  $\text{HCO}_3^-$  and subsequent ion exchange with intercalated  $\text{CrO}_4^{2-}$  anions were considered to be the mechanistic steps for  $\text{Cr}^{\text{VI}}$  desorption and LDH regeneration. The feasibility of this strategy was examined both by simulated  $\text{Cr}^{\text{VI}}$  solution and 20 L  $\text{Cr}^{\text{VI}}$ -containing electroplating wastewater. Purified aqueous solution ( $\text{Cr}^{\text{VI}}$  <0.5 mg/L), enriched  $\text{Cr}^{\text{VI}}$  solution (>10000 mg/L), and recycled LDH were simultaneously obtained after  $\text{CO}_2$  treatment. The main advantages of this method are the high concentration of  $\text{Cr}^{\text{VI}}$ , the direct reuse of enriched  $\text{Cr}^{\text{VI}}$  and the efficient regeneration of LDH adsorbent. This work could provide a good example for the highly efficient, economical, and environmentally friendly usage of the LDH adsorbent in the treatment of other highly toxic anionic pollutants.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Adsorption behaviors of  $\text{Cr}^{\text{VI}}$  with different initial concentrations, the effect of factors on desorption efficiency, data in pilot-scale test, and summary of the  $\text{Cr}^{\text{VI}}$  disposal system. This

material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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