ABSTRACT

Mg-Al layered double hydroxides (LDHs) adsorbent was synthesized in situ on γ-Al₂O₃ for the removal of Cr(VI) from aqueous solution. The material was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy, Raman spectroscopy, scanning electronic microscopy and thermogravimetry and differential thermal analysis. Compared to the LDHs powder, the calcined LDHs sorbent prepared in situ on γ-Al₂O₃ had higher specific surface area and was easy to recover and reuse. The adsorptive capacity for removing Cr(VI) from aqueous solution was resulting from the memory effect of LDHs based on the XRD results. Both the pseudo-second-order kinetic model and the Langmuir model fit the experimental data well. Furthermore, the adsorbent exhibits excellent sorption–regeneration performances.

Key words | chromium, in situ, layered double hydroxides, removal

INTRODUCTION

Chromium (Cr) can exist in six oxidation states, but in the environment the predominant ones are trivalent Cr(III) and hexavalent Cr(VI). Cr(III) naturally occurs in nature and is an essential micronutrient for humans. Cr(VI) is the most toxic form, being carcinogenic and mutagenic to living organisms, and is often present in industrial effluents of metal finishing, leather tanning, chemical engineering, etc. (Miretzky & Cirelli 2013). At present, the amount of Cr(VI) in industrial wastewater exceeds the maximum allowable limit allowed by the European Union (European Union 1998). Recently, some treatment methods, including chemical precipitation, flotation, reduction, ion exchange, electrodialysis, solvent extraction, biosorption, membrane separation and adsorption have been developed for the removal heavy mental ions (such as chromium, arsenate, antimony, cadmium) and other pollutants from aqueous solution (Goswamee et al. 1998; Goh et al. 2008, 2010; Owlad et al. 2009; Lee et al. 2013; Mukherjee et al. 2013). Among these methods, adsorption technology has been considered an attractive method for the removal of Cr(VI) from aqueous solutions due to its low cost, simplicity, rapidness, lack of toxicity constraints, low energy consumption, high efficiency and possible regeneration (Fan et al. 2012). The existing research of the sorbents for the removal of Cr(VI) is often focused on activated carbon, agricultural and industrial wastes (such as hazelnut shell, sawdust, blast-furnace slag, fly ash), etc. (Owlad et al. 2009; Miretzky & Cirelli 2010). Unfortunately, these sorbents usually trap Cr(VI) ions by nonspecific electrostatic interaction and thus display little specific adsorption affinity to Cr(VI) ions. So, it is necessary to develop new sorbents for removal of Cr(VI) ions from aqueous solution. Layered double hydroxides (LDHs) with high anion exchange capacity and large surface area have shown high efficiency in contaminant removal comparing the above-mentioned adsorbents (Goh et al. 2008; Gan et al. 2011; King et al. 2012; Lee et al. 2013). LDHs also known as hydrotalcite-like compounds are a class of anionic clays whose structures are based on brucite-like layers. Layered double hydroxides have the general formula \[\text{M}^\text{II}_1\text{M}^\text{III}_x(\text{OH})_{2x}\text{A}^{2-}\text{H}_2\text{O},\] whereby M\(^{\text{II}}\) and M\(^{\text{III}}\)
are divalent and trivalent metal cations respectively, and A represents the intercalated anion (Arizaga et al. 2007; Goh et al. 2008; Cursinoa et al. 2013). Recently, LDHs have attracted intensive attention because of their potential application in removal of Cr(VI) from aqueous solution. For example, the design and preparation of LDHs, the factors affecting the adsorption efficiency and the adsorption kinetics, and the thermodynamics have been extensively investigated (Goswamee et al. 1998; Lazaridis & Asouhidou 2003; Álvarez-Ayuso & Nugteren 2005; Goh et al. 2008; Lee et al. 2013). Moreover, more studies focus on the calcined LDHs compound, which expresses high adsorptive capacity for Cr(VI) and was found to be a better adsorbent (Lazaridis & Asouhidou 2003; Álvarez-Ayuso & Nugteren 2005). However, all of these powder sorbents tend to aggregate and become hard to separate from residual solution. Therefore, the combination of Fe3O4 nanoparticle and LDHs has been developed recently to enhance separation and re-dispersion performance of LDHs in aqueous solution (Chen et al. 2012). Even so, in this way the adhesion between LDHs and Fe3O4 is still weak. So, the method of preparation of LDHs by in situ growth has shown its potential in improvement of adhesion, mechanical stability and large specific surface. Not only is the substrate the source of MIII but also the LDHs film grows directly on the substrate (such as γ-Al2O3, anodic aluminum oxide). Thus the case of in situ growth exhibits good adhesion and mechanical stability because of the presence of chemical bonding between the substrate and LDHs (Guo et al. 2009).

The objectives of this work are to: (1) prepare MgAl-LDHs by the in situ growth process of LDHs film on the surface of γ-alumina oxide (denoted as LDHs/γ-Al2O3) and calcine it for a novel Cr(VI) sorbent; (2) characterize the structural characteristics of the sorbents by X-ray diffraction (XRD), Fourier transmission infrared (FT-IR) spectroscopy, Raman spectroscopy, scanning electron microscopy, thermogravimetric analysis and N2 adsorption–desorption; (3) investigate the adsorption, desorption, kinetic and thermodynamic behaviors of Cr(VI) on the sorbents using batch equilibration method.

**METHODS**

**Reagents and standard solutions**

γ-Al2O3 (40–60 mesh) was obtained from Aladdin (Shanghai, China). Mg(NO3)2·6H2O, urea, potassium dichromate, ethanol, hydrochloric acid, nitric acid, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Stock solution of 1,000 mg L⁻¹ Cr(VI) in deionized water was prepared from potassium dichromate. The working solutions were prepared by series dilution of the stock solution immediately prior to their use. The solution was prepared weekly and stored in a refrigerator. All reagents used were of the highest available purity and of at least analytical grade. Millipore ultrapure water was used throughout this work.

**Preparation of MgAl-CO3-LDHs/γ-Al2O3**

The MgAl-CO3-LDHs/γ-Al2O3 (denoted as LDHs/γ-Al2O3) was synthesized by the method of urea hydrolysis reported by Zhang et al. (2005). Typically, γ-Al2O3 was calcined in air at 550 °C for 4 h, and γ-Al2O3 was used as both the substrate and the sole source of aluminum. In brief, Mg(NO3)2·6H2O and urea (molar ratio of 1:3) were dissolved in deionized water to give a solution with Mg2⁺ concentration of 1 mol L⁻¹. Then 0.15 g calcined γ-Al2O3 was impregnated in 25 mL above-mentioned solution under vacuum for 1 h. After the residual solution was removed, the white particles were transferred into an autoclave and heated at 120 °C for 12 h to obtain the MgAl-CO3-LDHs crystals grown on the surface of the γ-Al2O3. Finally, the product was taken out, rinsed with water, and dried at ambient temperature. The MgAl-CO3-LDHs was also prepared by a standard co-precipitation method (Li et al. 2015).

**Preparation of calcined LDHs/γ-Al2O3**

One part LDHs/γ-Al2O3 was calcined in air at 500 °C for 4 h to obtain magnesium aluminum oxide/γ-Al2O3 (denoted as LDO/γ-Al2O3).

**Characterization**

XRD patterns of the samples were collected using a Bruker D8 Advance XRD diffractometer at Cu Kα radiation and a fixed power source (40 kV and 40 mA, λ = 1.5406 Å). FT-IR spectra were recorded in the range 400–4,000 cm⁻¹ on a Nicolet NEXUS 470 FT-IR spectrophotometer using KBr pellet technique. Raman spectra were recorded at ambient temperature with a Thermo Fisher confocal laser micro Raman spectrometer DXR780 with a laser power of 1 mW. Thermogravimetry and differential thermal analysis (TG-DTA) curves were obtained on a NETZSCH STA 449C instrument in the temperature range of 30–800 °C with a
heating rate of 10 °C min⁻¹ in N₂. The specific surface area and pore-size distribution were evaluated using the nitrogen adsorption method (Quantachrome Autosorb 1-C). A field emission scanning electron microscope (FE-SEM) (Hitachi S-4800) was used to study the surface morphology of sample. The Cr(VI) concentration was measured momentarily using a UV-Vis spectrophotometer (Shimadzu UV2550).

**Batch experiments**

The adsorption of Cr(VI) was conducted in batch experiments. It was carried out by stirring 0.05 g of sorbent with 25 mL of Cr(VI) solution containing the different concentrations in the range from 10 to 190 mg L⁻¹ at ambient temperatures, different pH (1–11), and different contact time (5–240 min). Different initial concentration of Cr(VI) solution was prepared by proper dilution from stock 1,000 mg L⁻¹ Cr(VI) standard, and pH of the solution was monitored by adding 0.1 mol L⁻¹ of HCl solution or 0.1 mol L⁻¹ of NaOH solution as required. After adsorption, the suspensions were centrifugally separated and then filtered with a 0.45 μm microfiltration membrane. The concentration of Cr(VI) in the filtrate was diluted to appropriate concentrations, and then analyzed by a UV-Vis spectrophotometer. The adsorption capacity of Cr(VI) can be obtained from equilibrium data according to the following equation (Fan et al., 2014a, 2014b):

\[ Q = \frac{(C_i - C_f)V}{1,000W} \]

where \( Q \) represents the adsorption capacity (mg g⁻¹); \( C_i \) and \( C_f \) are the initial and final concentrations of Cr(VI) (mg L⁻¹), respectively. \( V \) is the volume of the solution (mL). \( W \) is the weight of sorbent (g). Unless stated all the laboratory measurements were performed in triplicate and the averages of the results are presented in this study. In all above batch experiments, the mixtures were magnetically stirred at a constant rate of 150 rpm at 25 °C. The samples were centrifuged at 4,800 rpm for 5 minutes and then filtered with a 0.45 μm pore size cellulose filter membrane to remove any undissolved particles before analysis.

**Desorption and regeneration experiments**

Desorption experiments were conducted to investigate the reusability and regeneration potential of the sorbent. The same sorbent was used in consecutive adsorption–desorption regeneration cycles. One gram of the sorbent was soaked in 50 mL of 0.1 mol L⁻¹ Na₂CO₃ solution for 3 h, filtered, washed with deionized water to eliminate the excess of Na₂CO₃, and calcined at 400 °C for 2 h before being reused in a new adsorption–desorption cycle. The desorption ratio of Cr(VI) from the sorbents was calculated as follows (Fan et al. 2014a, 2014b):

\[ \text{Desorption ratio (％)} = \frac{\text{amount of metal ion desorbed into solution}}{\text{amount of metal ion adsorbed on the sorbents}} \times 100 \]  

\[ \text{Recovery ratio of the sorbents for Cr(VI) was calculated as follows:} \]

\[ \text{Recovery ratio (％)} = \frac{\text{amount of metal ion desorbed in the second cycle}}{\text{amount of metal ion desorbed in the first cycle}} \times 100 \]  

**RESULTS AND DISCUSSION**

**Characteristics of LDHs sorbents**

In this work, LDHs/γ-Al₂O₃ was synthesized with three different Mg ion concentrations. As we can see, in Figure 1, the two diffraction peaks at 11.7° and 23.5° are attributed to (003) and (006) characteristic diffraction peaks of the LDHs (JCPDS No. 89-0460), respectively, showing the formation of...

![Figure 1](https://iwaponline.com/wst/article-pdf/75/6/1466/454998/wst075061466.pdf)
of the layer structure of MgAl\textsubscript{2}CO\textsubscript{3}\textcdot\text{H}_2\text{O}. According to Bragg's equation, the basal spacing d\textsubscript{003} can be calculated and the value is 0.75 nm, which is consistent with that reported in the literature for CO\textsubscript{3}\textsuperscript{2−} intercalated MgAl-LDHs. Because the characteristic peaks were different, the brucite could not be synthesized (JCPDS No. 86-0441).

The XRD patterns of LDHs/γ-Al\textsubscript{2}O\textsubscript{3} with Mg ion concentration of 1 M and 0.5 mol L\textsuperscript{-1} present all of the characteristic peaks of LDHs, but with 0.1 mol L\textsuperscript{-1} only the strongest diffraction peak of (003) could be detected. Moreover, the intensity of LDHs diffraction peak increases as the Mg ion concentration increases. To obtain better chromium removal, 1 mol L\textsuperscript{-1} Mg\textsuperscript{2+} solution was adopted to synthesize LDHs/γ-Al\textsubscript{2}O\textsubscript{3} and used after further processing. Figure 2 shows the XRD patterns of γ-Al\textsubscript{2}O\textsubscript{3} substrate (d), LDHs/γ-Al\textsubscript{2}O\textsubscript{3} (a), calcined LDHs/γ-Al\textsubscript{2}O\textsubscript{3} (denoted as LDO/γ-Al\textsubscript{2}O\textsubscript{3}), and LDO/γ-Al\textsubscript{2}O\textsubscript{3} after Cr(VI) adsorption (denoted as Cr-LDH/γ-Al\textsubscript{2}O\textsubscript{3}). These samples all present the typical characteristic peaks of γ-Al\textsubscript{2}O\textsubscript{3} substrate (JCPDS No. 29-0063). Because the rehydration of the LDO was carried in air atmosphere, besides dichromate intercalated LDHs the product of rehydration could include LDH\textcdot\text{CO}_3\text{H}_2O phase. In Figure 2(b), only the weak and broad diffraction peak of (003) could be detected. As shown in Figure 2(c), after being calcined, the LDHs characteristic peaks of LDHs/γ-Al\textsubscript{2}O\textsubscript{3} disappeared. However, the LDO/γ-Al\textsubscript{2}O\textsubscript{3} shows typical LDHs characteristic peaks after Cr(VI) adsorption from solution. The changes of XRD patterns also show the calcined LDHs could be able to regenerate the layered structure when they are exposed to water and anions. Water could be absorbed to reform the hydroxyl layers, and Cr(VI) anions and water are incorporated into the interlayer galleries. So the adsorption of Cr(VI) with LDO/γ-Al\textsubscript{2}O\textsubscript{3} could be derived from the conversion of the mixed metal oxides into LDHs, which has been variously referred to as reconstruction, rehydration or the ‘calcination–rehydration process’, ‘structural memory effect’ or simply ‘memory effect’ (Sasaki et al. 2005).

Typical images of LDHs/γ-Al\textsubscript{2}O\textsubscript{3}, Cr-LDH/γ-Al\textsubscript{2}O\textsubscript{3}, LDO/γ-Al\textsubscript{2}O\textsubscript{3} and γ-Al\textsubscript{2}O\textsubscript{3} are shown in Figure 3. It can be seen that the LDHs/γ-Al\textsubscript{2}O\textsubscript{3} surface consists of a platelet-like structure (Figure 3(a)). Owing to calcination, the platelet-like structure on the γ-Al\textsubscript{2}O\textsubscript{3} substrate disappears (Figure 3(c)), but reforms after adsorption of Cr(VI) (Figure 3(b)). So the FE-SEM images also showed good agreement with XRD results.

The FT-IR spectra of γ-Al\textsubscript{2}O\textsubscript{3}, LDO/γ-Al\textsubscript{2}O\textsubscript{3}, Cr-LDH/γ-Al\textsubscript{2}O\textsubscript{3} and LDHs/γ-Al\textsubscript{2}O\textsubscript{3} are shown in Figure 4. In Figure 4, the peaks at about 1,383 cm\textsuperscript{-1} were assigned to stretching vibration of carbonate. As we can see, the peaks from carbonate decrease clearly. The broad band around 860 cm\textsuperscript{-1} and a broad complex band around 554 cm\textsuperscript{-1} are attributed to the OH stretching vibration and Al-O stretching vibration. The spectra of LDO/γ-Al\textsubscript{2}O\textsubscript{3} and Cr-LDH/γ-Al\textsubscript{2}O\textsubscript{3} showed no significant differences with respect to the original LDHs/γ-Al\textsubscript{2}O\textsubscript{3} except for the decrease of carbonate band intensity. Figure 5 shows the Raman spectra of γ-Al\textsubscript{2}O\textsubscript{3}, LDO/γ-Al\textsubscript{2}O\textsubscript{3}, Cr-LDH/γ-Al\textsubscript{2}O\textsubscript{3} and LDHs/γ-Al\textsubscript{2}O\textsubscript{3}. As we can see, only the bands at about 551 cm\textsuperscript{-1} were found in γ-Al\textsubscript{2}O\textsubscript{3}, LDO/γ-Al\textsubscript{2}O\textsubscript{3}, and LDHs/γ-Al\textsubscript{2}O\textsubscript{3}. However, the Raman spectra of Cr-LDH/γ-Al\textsubscript{2}O\textsubscript{3} clearly showed intense bands at 334 and 842 cm\textsuperscript{-1}, which are assigned to the v\textsubscript{1} symmetric stretching vibration and v\textsubscript{4} bending vibration of CrO\textsubscript{4} (Frost et al. 2005).

The Brunauer–Emmett–Teller surface area and pore diameter of γ-Al\textsubscript{2}O\textsubscript{3}, LDHs/γ-Al\textsubscript{2}O\textsubscript{3}, LDO/γ-Al\textsubscript{2}O\textsubscript{3} and LDHs powder are listed in Table 1. In Table 1, the surface area of the LDO/γ-Al\textsubscript{2}O\textsubscript{3} is compared with the values for other samples. The comparison indicates that with γ-Al\textsubscript{2}O\textsubscript{3} as substrate, the surface area of LDHs increases from 48.72 to 120.02 m\textsuperscript{2} g\textsuperscript{-1}, and it reaches to 138.29 m\textsuperscript{2} g\textsuperscript{-1} after 500 °C calcination.

**Adsorption kinetics**

The dynamics of the adsorption process in terms of the order and the rate constant can be evaluated by using the kinetic adsorption data. The adsorption process of Cr(VI) on LDO/γ-Al\textsubscript{2}O\textsubscript{3} sorbents from an aqueous solution can be explained by using kinetic models and examining the
rate-controlling mechanism of the adsorption process. According to literature, several models (e.g. pseudo-first-order and pseudo-second-order kinetic models) can be used to express the kinetics of the adsorption process (Lagergren 1898; Ho & McKay 1999). Pseudo-first-order kinetics is one of the most used models to describe adsorption from aqueous solution by a solid sorbent. The linear form of the pseudo-first-order rate expression is

\[
\log(q_e - q_t) = \log \left( \frac{q_e}{k_1 t} \right) - \frac{k_1 t}{2.303}
\]

(4)

where \(k_1\) (min\(^{-1}\)) is the rate constant of the pseudo-first-order adsorption; \(q_e\) and \(q_t\) (mg g\(^{-1}\)) are the adsorption capacities at
equilibrium and at time $t$ (min), respectively. The rate constants $k_1$, $q_e$ and correlation coefficients $r^2$ were calculated using the slope and intercept of plots of $\log(q_e - q_t)$ versus $t$ and are presented in Table 2. Figure S10(a) (Supplementary Information, available with the online version of this paper) indicates that the plots of $\log(q_e - q_t)$ versus $t$ for the Cr(VI) ions did not converge well and give straight lines ($r^2 = 0.985$), which indicated that the pseudo-first-order equation was inappropriate to describe the adsorption process of the Cr(VI) ions on the LDO/γ-Al2O3 sorbent. The pseudo-second-order model is based on the assumption that the rate limiting step might be chemical biosorption, involving valence forces through sharing or exchange of electrons between adsorbate and sorbent. The pseudo-second-order rate expression is linearly expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where $k_2$ (g mg$^{-1}$ min$^{-1}$) is the rate constant of the pseudo-second-order adsorption. The linear plots of $t/q_t$ versus $t$ were plotted. The slopes and intercepts of these curves were used to determine the pseudo-second-order constants $k_2$, $q_e$ and correlation coefficient $r^2$. Calculated kinetic parameters are presented in Table 2. The results showed that the pseudo-second-order equation fitted well to the data with correlation coefficient $>0.99$ and straight line (Figure S10(b), Supplementary Information, available with the online version of this paper). It is clear from Table 2 that the calculated value (22.36 mg g$^{-1}$) of adsorption capacity for Cr(VI) ions on the LDO/γ-Al2O3 sorbent at equilibrium from the slope of the pseudo-second-order plot was in good agreement with the experimental value of adsorption capacity. These findings proved the suitability of the pseudo-second-order rate equation for the description of the Cr(VI) ions adsorption on the LDO/γ-Al2O3 sorbent from aqueous solution.

### Adsorption isotherms

Adsorption isotherms are mathematical models and the adsorption capacity is illustrated at different aqueous equilibrium concentrations. The sorption isotherms of Cr(VI) on the LDO/γ-Al2O3 is shown in Figure S12 (Supplementary Information, available with the online version of this paper). It is important to get an accurate equilibrium relationship between the solid- and liquid-phase concentrations of Cr (VI) ions. In the present study, the equilibrium models of Langmuir and Freundlich are analyzed to investigate the suitable adsorption isotherm. The Langmuir equation is based on the assumption of a structurally homogeneous sorbent where all adsorption sites are identical and energetically equivalent. The Langmuir adsorption isotherm applied to equilibrium adsorption assumes monolayer adsorption onto a surface with a finite number of identical sites (Langmuir 1918). The linear expression of the Langmuir adsorption isotherm can be described as Equation (6)

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} b} + \frac{C_e}{q_{\text{max}}}$$

(6)

where $q_e$ is the amount of adsorbed metals in the sorbent (mg g$^{-1}$), $C_e$ is the equilibrium ion concentration of metal ions in solution (mg L$^{-1}$), $b$ (L mg$^{-1}$) is the equilibrium constant related to the adsorption energy, and $q_{\text{max}}$ is the maximum adsorption capacity (mg g$^{-1}$). A linear plot was obtained when $C_e/q_e$ was plotted against $C_e$ over the entire concentration range of investigated metal ions. The Freundlich adsorption isotherm is an empirical equation to describe heterogeneous systems (Freundlich 1906). The linear equation of the Freundlich adsorption isotherm can be represented by Equation (7)

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$$

(7)

where $K_F$ and $n$ are the Freundlich constants; $C_e$ is the equilibrium concentration of metal ion in solution (mg L$^{-1}$). According to Equation (7), the values of $K_F$ and $n$ can be determined experimentally by plotting $\log q_e$ versus $\log C_e$.

### Table 1 | The structural properties of the γ-Al2O3 and adsorbents

<table>
<thead>
<tr>
<th>Structural property</th>
<th>LDHs/γ-Al2O3</th>
<th>LDO/γ-Al2O3</th>
<th>γ-Al2O3 powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m$^2$ g$^{-1}$)</td>
<td>120.02</td>
<td>138.29</td>
<td>95.31</td>
</tr>
<tr>
<td>Pore diameter (nm)</td>
<td>8.2</td>
<td>8.1</td>
<td>12.6</td>
</tr>
</tbody>
</table>

### Table 2 | Comparison between adsorption kinetic parameters of pseudo-first-order and pseudo-second-order models

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Rate constant (k) (g mg$^{-1}$ min$^{-1}$)</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>Correlation coefficient ($r^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>0.0237</td>
<td>18.94</td>
<td>0.985</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>0.00154</td>
<td>22.36</td>
<td>0.995</td>
</tr>
</tbody>
</table>
was obtained as 20.04 mg g\(^{-1}\). The Langmuir constant, \(b\), which denotes adsorption energy, was found to be 0.205 L mg\(^{-1}\) g\(^{-1}\). The high value of correlation coefficient \((r^2 = 0.998)\) and a good agreement between the experimental data and isotherm parameters indicated the experimental data fitted well with the Langmuir isotherms. The values of \(K_F\) and \(n\) are 7.39 and 4.77, respectively. It was found that the correlation coefficient obtained from the Freundlich isotherm model for the sorbent is 0.954 which is lower than that for the Langmuir isotherm model as given in Table 3. These results indicated that the equilibrium data are not fitted well with the Freundlich isotherm model. Comparing the results obtained from the different adsorption isotherms, Langmuir and Freundlich, it was concluded that the adsorption of the Cr(VI) ions on the LDO/\(\gamma\)-Al\(_2\)O\(_3\) sorbent from aqueous solution fitted well with the Langmuir isotherm, which indicates the monomolecular adsorption of Cr(VI) ions onto the sorbent.

Regeneration

Regeneration of any exhausted sorbents is an important factor in the adsorption process for improving the process economics. Desorption of Cr(VI) from the LDO/\(\gamma\)-Al\(_2\)O\(_3\) was carried out in a Na\(_2\)CO\(_3\) solution to evaluate the regeneration behavior of the adsorbent (Fan et al. 2014a, 2014b).

The regenerative adsorbent was calcined at 500 °C before reusing for removal of Cr(VI) from aqueous solution. It was found that the desorption ratio of Cr(VI) from the LDO/\(\gamma\)-Al\(_2\)O\(_3\) sorbent was about 98% under stirring for 3 h. The same sample of the LDO/\(\gamma\)-Al\(_2\)O\(_3\) sorbent was used for the adsorption–desorption cycle of Cr(VI) from solutions. After eight adsorption–desorption cycles, the adsorption capacity for Cr(VI) was not significantly decreased and recovery ratio of the LDO/\(\gamma\)-Al\(_2\)O\(_3\) sorbent for Cr(VI) was found to be about 80%, see Figure 6. These results indicated that the LDO/\(\gamma\)-Al\(_2\)O\(_3\) sorbent had a good regeneration ability for Cr(VI) ion.

CONCLUSIONS

In this study, we have demonstrated a simple approach for the synthesis of calcined LDHs in situ on \(\gamma\)-Al\(_2\)O\(_3\), which exhibits a high dispersion of LDHs nanoplatelets and strong adhesion to the substrate. The Cr(VI) adsorption mechanism was considered to be the memory effect of LDHs. The adsorbent shows a superior sorption capability for Cr(VI) owing to its high specific surface area. It was also found that the adsorbent had fast adsorption kinetics and can be used several times. The Langmuir isotherm represented the equilibrium data better than Freundlich isotherms. The equilibrium data fitted very well to the pseudo-second-order equation compared to the pseudo-first-order kinetics model. It is expected that the calcined LDHs/\(\gamma\)-Al\(_2\)O\(_3\) can be potentially used as an efficient and recyclable adsorbent in removal of Cr(VI) ions from aqueous solutions.

ACKNOWLEDGEMENTS

The project was supported by Program for Liaoning Excellent Talents in University (grant no. LJJQ2014042), China Postdoctoral Science Foundation (grant no. 2015M571343) and General Project of Liaoning Provincial Department of Education (grant no. L2015361).

The adsorption–desorption isotherms, pore size distributions, TG-DTA curves of adsorbents and other further information can be found in the Supplementary Information (available with the online version of this paper).

REFERENCES


