Removal of hexavalent chromium from aqueous solution by calcined Zn/Al-LDHs

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ABSTRACT

In this study, Zn/Al-layered double hydroxides (Zn/Al-LDHs) were synthesized by a co-precipitation method and characterized with X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy. Then the hexavalent chromium Cr(VI) adsorption experiments on calcined Zn/Al-LDHs were carried out to analyze the effects of pH, temperature, adsorption time, initial Cr(VI) concentration and adsorbent dosage on the removal of Cr(VI) from aqueous solutions. The maximum adsorption capacity for Cr(VI) on calcined Zn/Al-LDHs under optimal conditions was found to be over 120 mg/g. The kinetic and isotherm of Cr(VI) adsorption on calcined Zn/Al-LDHs can be described with the pseudo-second-order kinetic model and Langmuir isotherm, respectively.

Key words | adsorption, chromium, isotherms, kinetics, layered double hydroxides

INTRODUCTION

Chromium is a highly toxic pollutant generated from many industrial processes such as electroplating, leather tanning, textile industries, metal finishing and chromate preparation (Gupta et al. 2011). It is considered by the International Agency for Research on Cancer to be a powerful carcinogenic agent that modifies the DNA transcription process, causing important chromosome aberrations (Benoit 1976; Rengaraj et al. 2001). Moreover, chromium ions hardly degrade into harmless end products (Khezami & Capart 2005). Therefore, the chromium ions in industrial wastewaters would endanger public health and the environment if they were discharged without adequate treatment. Generally, the effluent from the above-mentioned industries may contain chromium at concentration ranging from dozens to hundreds of milligrams per litre, whereas the National Institute for Occupational Safety and Health recommends that the level of chromium in industrial wastewater should be reduced to less than 0.1 mg/L (Pérez-Candela et al. 1995; Khezami & Capart 2005).

Chromium exists in trivalent and hexavalent forms in aqueous systems. The trivalent chromium (Cr(III)) is a trace metal nutrient for humans, but hexavalent chromium (Cr(VI)) is toxic, carcinogenic and mutagenic in nature (Rojas et al. 2005; Garg et al. 2007). Several approaches such as reduction and precipitation (Chang 2003), adsorption (Mathew et al. 2015), ion exchange (Dąbrowski et al. 2004), biological degradation (Cheung & Gu 2007), extraction (Chakraborty et al. 2005), ultrafiltration (Aroua et al. 2007), reverse osmosis (Padilla & Tavani 1999) and electrochemical methods (Rana et al. 2004) are available for removing chromium from effluents. Of these methods, adsorption is regarded as one of the most promising technologies because of its cost-effectiveness, versatility and operability (Álvarez-Ayuso & Nugteren 2005). The key is to develop innovative adsorbents with high chromium adsorption capacity and fast process kinetics.

Layered double hydroxides (LDHs), also known as lamellar compounds, feature with a general formula \([M_1^{2+} \cdot xM_2^{3+} (OH)_2]^{x+} (A^{n-})_{x/n} \cdot mH_2O\) consisting of octahedral brucite-like host layers \((M^{2+}/M^{3+})\): divalent and trivalent metal cations; \(x = 0.2-0.33\), charge-balancing anions \((A^{n-})\), and interlayer water molecules (Ma et al. 2007; Zhang et al. 2014). Because LDHs can offer a large interlayer surface to host diverse anionic species and have the additional advantage of being potentially easily recyclable, they are attracting current research interest for the removal of heavy metals ions in effluents (Wang et al. 2006; Dadwah et al. 2009; Türk & Alp 2014).

Although there are several reports concerning the preparation and properties of Zn/Al-LDHs, the applications of calcined Zn/Al-LDHs (C-Zn/Al-LDHs) for Cr(VI) removal...
are limited. The objective of this study is to investigate the performance of C-Zn/Al-LDHs in removing Cr(VI) from water. The parameters that influence adsorption, such as initial Cr(VI) concentration, absorbent dose, pH value, adsorption time and temperature, were investigated.

MATERIALS AND METHODS

Materials

Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, NaOH, HNO₃ and Na₂CO₃ were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All reagents were analytically pure and used as raw materials without further purification. Deionized water was used throughout the experimental processes.

Preparation of Zn/Al-LDHs

Zn(NO₃)₂ solution (1.5 M, 100 mL) and Al(NO₃)₃ solution (1 M, 50 mL) were mixed together to form solution A. NaOH (1 M, 150 mL) and Na₂CO₃ (0.5 M, 150 mL) were mixed together to form solution B. Solution A and B were added into a 1,000 mL flask drop by drop at room temperature (25°C) under mechanical stirring (300 rpm), and the pH value of the reaction mixture was controlled to a constant value (7, 8, 9, 10, 11 or 12) by the dropping speed of solution B. Then the reaction mixture was crystallized at 70°C for 48 h to obtain a precipitate. Afterwards, the precipitate was filtrated, washed with deionized water and dried at 80°C for 48 h to obtain Zn/Al-LDHs. Then Zn/Al-LDHs were calcined at 400°C for 4 h to obtain C-Zn/Al-LDHs.

Characterization

Powder X-ray diffraction (XRD) patterns of the Zn/Al-LDHs were collected using a Bruker D8 Advanced XRD diffractometer at Cu Kα radiation and a fixed power source (40 kV and 40 mA, λ = 0.15406 Å). Fourier transform infrared (FTIR) spectra were recorded in the range of 4,000–400 cm⁻¹ at a 2 cm⁻¹ resolution on a Bruker EQUINOX55 spectrometer using KBr pellet technique. A scanning electron microscope (SEM) (FEI Quanta250) was used to study the surface morphology of Zn/Al-LDHs.

Adsorption experiments

Cr(VI) stock solution was prepared by dissolving potassium chromate (K₂Cr₂O₇) in pure water. The working solution for all experiments was freshly prepared from the stock solution. Batch sorption experiments were carried out in a series of conical flasks (250 mL). A given dose of an adsorbent was added to 100 mL Cr(VI) solution with a given concentration and pH value in a thermostatic water bath/shaker at shaking rate of 200 rpm. HNO₃ (0.1 M) and NaOH (0.1 M) were used to adjust the pH value of working solution. The pH value of the solution was measured with a pH meter (SPSIC PHS-25) using a combined glass electrode. Chromium concentration in the supernatant was determined by an INESA 4510F atomic absorption spectrophotometer according to a standard method (American Public Health Association 2012). The adsorption time between adsorbents and the solution was 80 min, which was considered as the adsorption time of adsorption equilibrium status, and then the solid material was separated by centrifugation. All assays were carried out in triplicate and only mean values are presented. The adsorption capacity (qt, mg/g) at adsorption time t and equilibrium adsorption capacity (qe, mg/g) of Cr(VI) on C-Zn/Al-LDHs were determined using the following equations:

\[ q_t = \frac{(c_0 - c_t)}{m} V \]  

\[ q_e = \frac{(c_0 - c_e)}{m} V \]

where \( c_0 \), \( c_t \), and \( c_e \) (mg/L) are the concentration of Cr(VI) in solution at initial, adsorption time \( t \) and adsorption equilibrium status, respectively; \( m \) (mg) is the dosage of C-Zn/Al-LDHs, and \( V \) (L) is the volume of solution.

RESULTS AND DISCUSSION

Characterization of Zn/Al-LDHs

XRD patterns of Zn/Al-LDHs synthesized at various pH values ranging from 7 to 12 are depicted in Figure 1. All samples show two obvious diffraction peaks around 11.6 and 23.4° corresponding to the basal reflections of LDHs from (003) and (006) planes, respectively. It is observed that the intensities of diffraction peaks from (003) and (006) planes in the XRD pattern of the Zn/Al-LDHs synthesized at pH = 9 are stronger than those synthesized at other pH values, indicating that the Zn/Al-LDHs with high degree of crystallinity and layered structure can be synthesized at pH = 9. Moreover, the XRD patterns of the
Zn/Al-LDHs synthesized at pH > 9 show an impure peak around 20°. In this work, the Zn/Al-LDHs synthesized at pH = 9 were calcined at 400°C for the Cr(VI) adsorption experiments.

The FTIR spectrum of the Zn/Al-LDHs synthesized at pH = 9 is shown in Figure 2. The broad and strong band in the range 3,600–3,200 cm⁻¹ centered at 3,444 cm⁻¹ is attributed to the O-H stretching vibration of surface and interlayer water molecules (Cavani et al. 1991). The broad shoulder band around 3,070 cm⁻¹ is ascribed to the hydrogen bonds between water and carbonate anions in the interlayer galleries (Trujillano et al. 2005). The band observed near 1,617 cm⁻¹ is originated from the bending vibration of interlayer water molecules (Sahu et al. 2013). The narrow band at 1,365 cm⁻¹ is due to the asymmetric stretching vibration of the interlayer carbonate anions (Benselka-Hadj Abdelkader et al. 2011). The bands in the low-frequency region are ascribed to the deformation vibration of HO-Zn-Al-OH at 428 cm⁻¹, and the stretching vibrations of Al-OH at 783 and 553 cm⁻¹, and Zn-OH at 617 cm⁻¹ (Feng et al. 2006).

The morphology of LDHs may affect their physicochemical properties and further practical applications. A SEM image of the Zn/Al-LDHs synthesized at pH = 9 is exhibited in Figure 3. A large amount of micro-particles with approximate hexagon shape disorderly intermeshed with each other, which is consistent with previous studies (Ogawa & Asai 2000).

**Effects of adsorption conditions on Cr(VI) removal**

pH value is one of the most important parameters while assessing the adsorption capacity of an adsorbent for removing metal ions from aqueous solution (Garg et al. 2007). Adsorption experiments were carried out in the pH range of 1 to 9 keeping other parameters constant (chromium concentration = 100 mg/L, adsorption time = 80 min, adsorbent dose = 1 mg/mL, temperature = 60°C). Figure 4(a) shows that the amount of Cr(VI) adsorbed by C-Zn/Al-LDHs increases firstly with increasing pH, and reaches the maximum of 76.85 mg/g at around pH 3, then decreases with further increasing of pH value. This finding indicates that pH value has a strong effect on the removal of Cr(VI). Rao et al. (2002) found that the favorable effect of low pH can be attribute to the neutralization of negative charges on the surface of the adsorbents by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions (HCrO₄⁻) and their subsequent adsorption. However, the competition adsorption of excess OH⁻ ions with HCrO₄⁻ occurs at high pH value. Additionally, calcined LDHs containing vaporizable anions possess a ‘structural memory effect’, so that calcined LDHs can be reconstructed to the

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**Figure 1** XRD patterns of the Zn/Al-LDHs synthesized at different pH values: (a) pH 7; (b) pH 8; (c) pH 9; (d) pH 10; (e) pH 11; (f) pH 12.

**Figure 2** FTIR spectrum of the Zn/Al-LDHs synthesized at pH = 9.

**Figure 3** SEM image of the Zn/Al-LDHs synthesized at pH = 9.
original LDHs structure with water and the anions in aqueous solution (Wong & Buchheit 2004). Therefore, C-Zn/Al-LDHs were possibly rebuilt to the initial layered structure by the ‘structural memory effect’ under the acidic condition, and the released Zn$^{2+}$ and Al$^{3+}$ from Zn/Al-LDHs easily aggregate with OH$^{-}$/CO$_3^{2-}$ in solution, promoting the adsorption of chromium (Novillo et al. 2014). Maximum adsorption capacity was observed at pH = 3 and hence it was taken as the optimal pH value for further adsorption experiments.

The effect of temperature on the Cr(VI) adsorption by the C-Zn/Al-LDHs was examined at the temperature range of 10 to 90 °C keeping other parameters constant (chromium concentration = 100 mg/L, adsorption time = 80 min, adsorbent dose = 1 mg/mL, pH = 3). It can be seen in Figure 4(b) that the maximum of chromium adsorption occurs at 25 °C. It was reported that the temperature has two main effects on the adsorption process (Khezami & Capart 2005). On the one hand, the increase of temperature decreases the solution viscosity and increases the diffusion rate of the adsorbate molecules across the external boundary layer and internal pores. On the other hand, the increase of temperature decreases the equilibrium adsorption capacity of the adsorbent for a particular adsorbate.

Adsorption experiments were conducted by varying the adsorption time from 20 to 140 min keeping other parameters constant (chromium concentration = 100 mg/L, temperature = 25 °C, absorbent dose = 1 mg/mL, pH = 3). As exhibited in Figure 4(c), the adsorption amount of chromium on the C-Zn/Al-LDHs increases with increasing adsorption time, and reaches the adsorption equilibrium at ca. 80 min, indicating that highly effective adsorption of chromium could be obtained over a relatively short period. Therefore, an 80 min adsorption time was used for further experiments.

The adsorption experiments of Cr(VI) on the C-Zn/Al-LDHs were studied at different adsorbent dose range of 0.2 to 1.6 mg/mL keeping other parameters constant (chromium concentration = 100 mg/L, temperature = 25 °C, pH = 3, adsorption time = 80 min). The results show that the adsorption amount of chromium on C-Zn/Al-LDHs increases from 79.25 to 109.65 mg/g with the adsorbent dose increasing from 0.2 to 0.6 mg/mL (Figure 4(d)), which may be due to the increase of adsorbent surface area and adsorption sites (Garg et al. 2004). However, the adsorption capacity of chromium significantly decreases with further increase in the adsorbent dosage, probably due to the overlap of adsorption sites resulting from overcrowding of adsorbent particles (Namasivayam et al. 1998).

The adsorption experiments were performed by varying chromium concentration from 20 to 140 mg/L keeping other parameters constant (adsorbent dose = 0.6 mg/mL, pH = 3, temperature = 25 °C, adsorption time = 80 min). As shown in Figure 4(e), the adsorption capacity of chromium on the C-Zn/Al-LDHs increases from 29.63 and 120.83 mg/g with the increase of Cr(VI) concentration from 20 to 100 mg/L, then has a little decrease with the further increase of Cr(VI) concentration.

Adsorption performance of Cr(VI) on the C-Zn/Al-LDHs and other adsorbents reported in the literature are given in Table 1. The results show that the C-Zn/Al-LDHs have an acceptably high adsorption capacity for the removal
of Cr(VI), indicating the C-Zn/Al-LDHs have a good application potential for the removal of Cr(IV) from wastewater.

**Adsorption kinetics and isotherms**

The pseudo-first-order (Equation (3)) and pseudo-second-order (Equation (4)) kinetics equations were used to explain the adsorption mechanism and characteristics of adsorbent (Khezami & Capart 2005; Türk & Alp 2014).

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

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

where \(k_1\) and \(k_2\) are the rate constants of the pseudo-first-order and the pseudo-second-order kinetics, respectively.

The data shown in Figure 4(c) were used to analyse the rate of adsorption using pseudo-first-order and pseudo-second-order kinetic models. As shown in Figure 5(a), the correlation coefficient for the pseudo-first-order model is low \((R^2 < 0.55)\), implying that the pseudo-first-order model is not suitable to depict the adsorption kinetics of Cr (VI) on the C-Zn/Al-LDHs. The kinetic parameters of the pseudo-second-order model were determined from the linear plot of \(t/q_t\) against \(t\) (Figure 5(b)). High correlation coefficient \((R^2 > 0.99)\) indicates that the adsorption kinetics of Cr(VI) on the C-Zn/Al-LDHs can be described by the pseudo-second-order model. The calculated value of \(q_e\) also agreed very well with the experimental value.

Adsorption is a physicochemical process that involves mass transfer of a solute from liquid phase to adsorbent. An adsorption isotherm describes how adsorbate interacts with adsorbent in an adsorption system. Two classical

**Table 1** Cr(VI) adsorption capacities of various adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>pH value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Zn/Al-LDHs</td>
<td>120.8</td>
<td>3</td>
<td>This work</td>
</tr>
<tr>
<td>Sawdust</td>
<td>3.6</td>
<td>3.5</td>
<td>Baral et al. (2006)</td>
</tr>
<tr>
<td>Spent activated clay</td>
<td>5.0</td>
<td>2</td>
<td>Weng et al. (2008)</td>
</tr>
<tr>
<td>Modified bentonite</td>
<td>19.8</td>
<td>3-4</td>
<td>Zhang et al. (2013)</td>
</tr>
<tr>
<td>Ceria nanoparticles</td>
<td>26.8</td>
<td>7.4</td>
<td>Di et al. (2006)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>52.2</td>
<td>3</td>
<td>Selvi et al. (2003)</td>
</tr>
</tbody>
</table>

**Figure 5** The pseudo-first-order (a) and the pseudo-second-order (b) adsorption kinetics of chromium adsorption on the C-Zn/Al-LDHs.

**Figure 6** Linear plots of Langmuir (a) and Freundlich (b) isotherms of Cr(VI) adsorption on the C-Zn/Al-LDHs.
adsorption models, Langmuir and Freundlich isotherms, have been widely used to describe the adsorption equilibrium. Equations (5) and (6) were used to determine Langmuir and Freundlich isotherm’s parameters, respectively (Khezami & Capart 2005; Türk & Alp 2014).

\[
\frac{1}{q_e} = \frac{1}{bQ} + \frac{1}{Q}
\]

(5)

\[
\ln q_e = \ln k_f + \frac{1}{n} \ln c_e
\]

(6)

where \( Q \) (mg/g) is saturated monolayer adsorption capacity, and \( b \) is Langmuir constant (L/mg). The slope and intercept of the linear plot of \( 1/q_e \) versus \( 1/c_e \) are the values of \( b \) and \( Q \), respectively. The constants \( k_f \) and \( n \) of the Freundlich model are related to the strength of the adsorptive bond and the bond distribution. The linear plot of \( \ln q_e \) versus \( \ln c_e \) gives a slope of \( 1/n \) and intercept of \( \ln k_f \).

The adsorption isotherm of Cr(VI) on the C-Zn/Al-LDHs is shown in Figure 4(e). Figure 6(a) and (b) show the linear plots of Langmuir and Freundlich isotherms for the adsorption of Cr(VI) on the C-Zn/Al-LDHs, respectively. The Langmuir parameters \( Q \) and \( b \) were found to be 136.99 mg/g and 0.13 L/mg, respectively, with high correlation \( R^2 \) (0.99), while the linear plot of the Freundlich isotherm has a low correlation coefficient \( R^2 < 0.76 \), implying that the adsorption isotherm of Cr(VI) on the C-Zn/Al-LDHs is consistent with the Langmuir model.

**CONCLUSIONS**

Zn/Al-LDHs with high degree of crystallinity and layered structure were synthesized by a co-precipitation method, and then C-Zn/Al-LDHs were used to remove Cr(VI) from aqueous solution. The adsorption of Cr(VI) on the C-Zn/Al-LDHs is rapid during the initial periods and reaches the adsorption equilibrium at ca. 80 min. The maximum adsorption capacity of Cr(VI) on the C-Zn/Al-LDHs is over 120 mg/g. The kinetic and isotherm of the adsorption of Cr(VI) on the C-Zn/Al-LDHs can be suitably described by the pseudo-second-order kinetics and Langmuir isotherm models, respectively. The findings demonstrate that C-Zn/Al-LDHs have a good application potential for the removal of Cr(VI) from aqueous solutions.

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