Rapid and effective removal of Cr(VI) from aqueous solution using exfoliated LDH nanosheets

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Abstract

Direct exfoliation of lactate-intercalated [MgAl-NO₃]-LDH nanocomposites (LCT-LDH) into single-layer LDH nanosheets in water media, termed LDHNSs, to enlarge the overall surface area and adsorption rate. The LDHNSs were then used as adsorbents to remove Cr(VI) from aqueous solution by batch adsorption method. Adsorption experiments considered the effects of various factors such as pH, dosage, contact time, and temperature on Cr(VI) removal efficiency. The morphology, texture, and surface properties of the [MgAl-NO₃]-LDH, LCT-LDH, LDHNSs, and Cr-LDHNSs were characterized by HRTEM, AFM, XRD, FT-IR, XPS, elemental analyzer and zeta potential analyzer. It was found that the optimum pH for Cr(VI) maximum removal efficiency onto LDHNSs was pH 6.0. Adsorption data were found to be better fitted by the Langmuir isotherm, and the maximum adsorption capacity of LDHNSs for Cr(VI) was 125.97 mg/g at 308K. The adsorption of Cr(VI) onto LDHNSs was rapid, and the contact time required to reach complete adsorption equilibrium within 8 min. Thermodynamic analysis showed that the adsorption process was endothermic, spontaneous, and physical in nature, involving weak interactions such as electrostatic attraction, ion-exchange, and hydrogen bonding between the Cr(VI) species and the binding sites on the LDHNSs.

Keywords: Layered double hydroxides; Exfoliation; Adsorption; Chromium; Nanosheets

1. Introduction

Heavy metal pollution is mainly caused by the indiscriminate disposal of wastewater from different chemical engineering processes, including alloys and steel manufacturing, electroplating, leather tanning, metal finishing, oxidative dyeing, and pigments synthesis[1,2]. There is increasing demand for rapid and effective methods to remove heavy metal because heavy metal pollution is a hazardous threat to environment and human health. Among various heavy metals, chromium gives rise to harmful effects on ecosystems and human beings because of its highly toxicity, carcinogenicity and mutagenicity, and thus chromium has become an important environment concern[3, 4]. In aqueous systems, chromium (Cr) usually exists in two stable oxidation states: Cr(III) and Cr(VI), which exhibit very different toxicity, solubility and mobility[5, 6]. Cr(III) has less toxicity and is an essential micronutrient for normal glucose metabolism at low concentrations. Cr(VI) is of particular importance due to its great toxicity, which is reported to be five hundred times more toxic than the Cr(III)[5, 6]. Therefore, it is imperative to develop rapid and effective approaches for Cr(VI) removal from wastewater before being discharged into the aquatic environments.

Different techniques are available: electrochemical oxidation, bioremediation, chemical coagulation, membrane technologies, ion-exchange, adsorption, etc. The adsorption has been proved to be a most economical and efficiency technology for the removal of Cr(VI) from aqueous solution[6,7]. For this purpose, a number of adsorbents have been investigated for Cr(VI) removal, including activated carbon[8],

chitosan[9], metal oxide[10], and nanosize zero-valent iron[11]. However, these adsorbents display a number of disadvantages such as complicated synthetic procedures, low adsorption efficiency, and slow adsorption rate, which may hinder their practical applications. All of these disadvantages have promoted the development of new adsorbents for Cr(VI) removal, which display rapid adsorption rate and high adsorption capacity, especially for dealing with Cr(VI) pollution accidents.

Layered double hydroxides (LDHs), a class of hydrotalcite-like layered compounds that can be described by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[(A^{m-})_{x/m}]^{x-} \cdot nH_2O$. LDHs consist of positively charged hydrotalcite-like host layers and charge-balanced interlayer inorganic anions as well as water molecules. While the charge-balanced interlayer inorganic anions and water molecules can exchange with other inorganic or organic anions[12, 13]. The salient features of the LDHs, including ion-exchange capability, unique layered nanostructure, and high structural charge density, all contribute to their considerable potential for application as selective adsorbents[12-14]. In our previously study, we used aluminum magnesium mixed hydroxide (AMH) sol as an adsorbent to adsorb Cr(VI)[14]. The amount of Cr(VI) adsorbed onto AMH was higher than that previously reported. However, it took 30 min to reach adsorption saturation at an initial Cr(VI) concentration of 20 mg/L. This behavior can be attributed to the layers of the LDHs that usually stack together due to Coulomb forces and hydrogen bonds between the layers and the interlayer anions. The Cr(VI) species can ion-exchange and intercalate

116 into the interlayer regions of the LDHs. However, diffusion, penetration, and
117 transportation of Cr(VI) species from the host layers to the inner surfaces are limited
118 by the stacked layers. In other words, the stacked LDH layers is unfavorable for the
119 adsorption of contaminants. The most effective method to overcome this problem may
120 be the exfoliation of LDHs into single-layer nanosheets[15]. LDH layers in the bulky
121 form are layer-by-layer stacking as a result of Coulomb forces and hydrogen bonds,
122 thereby inhibiting the release of LDH layers in aqueous solution. Recently, liquid
123 exfoliation of LDHs into single-layer nanosheets has attracted much attention mainly
124 because of their applications as building blocks for making new designed
125 nanomaterials[16-19]. However, exfoliation is difficult for LDHs. The high charge
126 density of the layers and the high anion content lead to strong electrostatic interactions
127 between the layers and hydrophilic groups[16-19]. At the same time, the combination
128 of interlayer anions and solvents are also key factors. Before exfoliation, therefore,
129 LDH interlayer space is typically modified with carboxylates, amino acids, and
130 anionic surfactants, for example, to achieve desirable interlayer distance and
131 hydrophobic environment[16-20]. The theory rests on organic anions intercalating
132 into the interlayer space of LDHs, causing an expansion of the interlayer spacing. This
133 may weaken the interactions between the host layers and the interlayer anions as well
134 as water molecules, and consequently the exfoliation of LDHs into single-layer
135 nanosheets is easily achieved[16-18,21]. The exfoliation of LDHs into single-layer
136 nanosheets results in materials with the same chemical compositions but drastically
137 enhanced nanosheets surface activity, increases the available surface area, and reduces

diffusion resistance, and consequently improves adsorption rate. Moreover, exfoliated host layers, which are positively charged and have a thickness of 1-2 nm, may cause electrostatically-driven interfacial assembly and then restack in the presence of water[22]. A number of related studies have focused on methods of exfoliating LDHs into single-layer LDH nanosheets[23] and application of LDH nanosheets in catalysts[24], polymer/nanocomposites[25] and core/shell multifunctional materials[26]. However, most of these LDHs exfoliations were carried out in organic solvents that can be considered as new pollutants, limiting the application of exfoliated LDHs in water treatment. To the best of the authors' knowledge, only a few studies have focused on applying the exfoliation of LDHs in water.

The objectives of this study were to exfoliate the LDHs into single-layer LDH nanosheets (defined as LDHNSs) in water and used as adsorbent. Cr(VI) was selected as the model adsorbate to investigate the adsorption behavior of heavy metals onto LDHNSs. To prove the mechanism of the adsorption, the morphology, texture, and surface properties of [MgAl-NO₃]-LDH, LCT-LDH, and LDHNSs before and after adsorption of Cr(VI) species were characterized by various characterization techniques including, high-resolution electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, Fourier transformed infrared spectra, and element and zeta potential analysis. The effects of pH, dosage, contact time, and temperature on the removal of Cr(VI) were investigated. Adsorption isotherms and kinetic data were obtained. Thermodynamic parameters were also determined. In addition, interactions between Cr(VI) and LDHNSs species were

discussed in details.

2. Experimental section

2.1. Materials

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and NaOH (analytically pure) were supplied by Sinopharm Chemical Reagent Co., Ltd. Lactate (analytically pure) was obtained from Medicine Group (Shanghai, China). All of these chemicals were used as received without further purification.

2.2. Preparation of [MgAl-NO₃]-LDH

The [MgAl-NO₃]-LDH precursor was prepared by following a standard co-precipitation method from metal nitrates[14,21]. A 2M NaOH aqueous solution was added to 2000mL of a mixed aqueous solution containing 0.75 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Mg/Al molar ratio = 3:1). Temperature (25 °C) and pH (10 ± 0.2) were kept constant with stirring during the addition of NaOH solution to the mixed solution, and then precipitates formed when the suspensions were aged for 1 h at 25 °C. The precipitates were then filtered and washed six times with distilled water in a filter, and the filter cake was heated to 80 °C for 6 h in an oven to convert the filter cake into [MgAl-NO₃]-LDH sol.

2.3. Anion exchange and exfoliation

The lactate-intercalated LDH nanocomposite (LCT-LDH) was prepared in a three-neck flask (equipped with a reflux condenser) under a nitrogen atmosphere. A 2.5M lactate solution was added to the [MgAl-NO₃]-LDH sol (1:1, v/v) and allowed to react for 24 h at 30 °C. The suspension was reflux condensed with vigorous stirring

Table 1. Comparison of different adsorbents for chromium [Cr(VI)] removal from aqueous solution.

Adsorbents	Chromate	Model used to calculated adsorption capacities	Adsorption capacity (mg/g)	pH; temp.(°C)	Reference
Alumium magnesium mixed hydroxide (AMH)	Cr(VI)	Langmuir	112.00	pH 4;40	[14]
Maghemite nanoparticles	Cr(VI)	Freundlich	19.20	pH 2-3;25	[37]
Bagasse fly ash	Cr(VI)	Langmuir	4.35	pH 5;30	[51]
Clay	Cr(VI)	Langmuir	13.90	pH 6;25	[52]
LDHNSs	Cr(VI)	Langmuir	125.97	pH 6;35	This work

during this time.

The nanocomposite (0.5 g) was mixed with 100 mL of ultra-pure water in a conical flask, which was tightly capped after purging with nitrogen gas. Then, the mixture was refluxed under vigorous agitation until a translucent colloidal suspension was produced, showing that the LCT-LDH was exfoliated into single-layer LDH nanosheets (defined as LDHNSs). The content of LDHNSs in the colloidal suspension was estimated to be 5 mg/mL.

2.4. Characterization

The morphology and size of the pristine [MgAl-NO₃]-LDH, LCT-LDH, LDHNSs, and Cr-LDHNSs were characterized by a JEM-2100 high-resolution transmission electron microscope (HRTEM, JEOL, Japan). The surface images and height profiles of the samples were determined by a MultiMode 8 atomic force microscope (AFM, Bruker, USA). The crystal structures of the samples were identified by a D/Max-rB powder diffractometer (XRD, Rigaku, Japan) using a Cu-K α radiation source in the 2θ range of 2°-70° with a scanning rate of 2°/min. Any resulting chemical bond and surface functional group changes of the samples were determined by a Perkin-Elmer 100 Fourier transform infrared spectrometer (FT-IR, Perkin-Elmer, USA) using the KBr pellet technique, and scanned from 500 to 4000 cm⁻¹ with a 4 cm⁻¹ spectral resolution. The actual elemental content was analyzed by a ICAP-9000 inductively-coupled plasma spectrometer (ICP, Thermo Jarrell Ash IRIS, USA). Both the elemental composition and chemical binding energy of LDHNSs before and after the adsorption of Cr(VI) were measured by an AXIS-Ultra X-ray

photoelectron spectroscope (XPS, Kratos, USA) using a monochromatic Al K α source, operating at 150 W (10 mA, 15 KV) and at 45° to the surface of samples. Narrow scanned XPS spectra were also used to obtain information about the chemical state of chromium. The zeta potentials of samples in a KNO₃ solution (0.001 M) were determined by a ZetaPALS zeta potential analyzer (Brookhaven, New York, USA), with results presented as the average value of three parallel measurements.

2.5. Adsorption experiments

A Cr(VI) stock solution was prepared by dissolving 1000 mg of potassium chromate in 1L of deionized water (Cr(VI) = 1000 mg/L). The stabilized LDHNSs were tested in batch experiments for the adsorption of Cr(VI) in aqueous solution. These batch experiments were carried out at 308 K in Erlenmeyer flasks. The adsorption of Cr(VI) on the LDHNSs was first tested at different pH values (2.0-10.0) for probing the dependence of Cr(VI) adsorption on solution pH. The pH was adjusted to the desired values with 0.1 M HNO₃ or 0.1 M NaOH using a pH meter (PB-10, Sartorius, Germany). The suspension was allowed to stand for 2 h at room temperature and the pH of the suspension was adjusted during this period if necessary. Batch adsorption experiments were performed by mixing 0.10 g of LDHNSs with 50 mL of varying Cr(VI) concentrations (20-200 mg/L) in a set of 100mL Erlenmeyer flasks until adsorption equilibrium were reached. The mixtures were then shaken on a thermostated shaker (SHZ-82, Jintan, China) at 150 rpm and at different temperatures. After a given contact time for adsorption, the mixtures were centrifuged at 5000 rpm for 15 min (LG10-2.4A centrifuge, Jingli, China). The concentration of Cr(VI) in the

supernatant was analyzed with a UV-visible spectrophotometer (1601, Shimadzu, Japan) at $\lambda_{\max} = 540$ nm.

3. Results and discussion

3.1. Characterization

HRTEM was used to determine the morphology and size of [MgAl-NO₃]-LDH, LCT-LDH, and LDHNSs before and after the adsorption of Cr(VI) from aqueous solution. Figure 1 (a) shows that the [MgAl-NO₃]-LDH precursor was composed of small, crystalline, laminated hexagonal platelets with an average size in the range of 20-50 nm. Compared to the original [MgAl-NO₃]-LDH, the LCT-LDH nanocomposites were slightly larger with an average particle size in the range of 50-80 nm and, at the same time, remained the hexagonal platelets form (Fig. 1(b)). When large-sized lactate molecules intercalated into interlayer regions, the aliphatic tails of lactate molecules are elongated and present a certain degree of interdigitation, which consequently weakens the interlayer attractive force through the destructure of the hydrogen bonding network. The size of LCT-LDH then increases. Figure 1(c) shows that the LDHNSs were predominantly single-layer nanosheets, and had a mean lateral size of tens of nanometers, they appeared smooth and well-defined in disk form. From the HRTEM image of the Cr-LDHNSs (Fig. 1(d)), it can be seen that Cr(VI) was firmly adsorbed on the surface of LDHNSs. This can be attributed to electrostatic interactions and hydrogen bonds between the LDHNSs and the Cr(VI) species. At the same time, LDH nanosheets can restack due to the surface-attached Cr(VI) species, which leads to effective aggregation.

XRD is one of the techniques employed to gain insight into crystalline structure [27]. The XRD pattern of the [MgAl-NO₃]-LDH shown in Fig. 2A indicated that the as-prepared [MgAl-NO₃]-LDH precursor had a layered structure with an interlayer spacing of 0.78 nm. The thickness of the [MgAl-NO₃]-LDH sheets was approximately 0.48 nm, so that the gallery height was 0.30 nm. However, the material was very poorly crystallized because the diffraction peaks were broad and asymmetric[28]. When the lactate molecules intercalated into the interlayer spacing of the [MgAl-NO₃]-LDH precursor, the XRD pattern of LCT-LDH indicated that the interlayer spacing increased to 1.74 nm. The interlayer spacing of 1.74 nm indicates a tilted trimolecular layer arrangement of the intercalated lactate molecules in the galleries. The computed interlayer spacing for a tilted trimolecular layer, considering the length of an all-trans lactate size as 0.46 nm, a tile angle of ~58°, and the thickness of the MgAl-LDH layer as 0.48 nm was 1.65 nm as compared to the X-ray measured value of 1.74 nm. The XRD pattern of LDHNSs exhibited a clear difference between LDHNSs and [MgAl-NO₃]-LDH as well as LCT-LDH nanocomposite. The layered structure of LDH was destroyed by exfoliating. After adsorption of Cr(VI) onto LDHNSs, the XRD pattern of Cr-LDHNSs was different from LDHNSs, which indicates that the Cr-LDHNSs tended to restack and return to a layered structure. Figure 2B shows that the crystal structure of the LCT-LDH was generated by separately creating the structure of the inorganic LDH host and the organic lactate guest, and then putting them together[29]. This inorganic-organic hybrid system was built by electrostatic attraction, hydrogen bonds, and van der Waals forces.

AFM was used to characterize the surface shape and the number of layers of samples. AFM images and height profiles of the [MgAl-NO₃]-LDH, LCT-LDH, LDHNSs, and Cr-LDHNSs are shown in Fig. 3(a)-(d). Figure 3(a) shows that the [MgAl-NO₃]-LDH had pseudo hexagonal shape with an average thickness of ~ 7.8-8.2 nm, corresponding to 9 stacked single layers, due to van der Waal forces between the layers[19, 25]. Compared to [MgAl-NO₃]-LDH, LCT-LDH remains pseudo hexagonal shape. However, the thickness of the layers increased to ~ 11.5-12 nm (Fig. 3(b)). This indicates that the intercalation of lactate molecules could enlarge interlayer distance and weaken interactions between the layers[19]. Figure 3(c) shows that the LDHNSs had disk shape with an average thickness of ~ 1-2 nm, corresponding to 2 stacked single layers. This indicates that the [MgAl-NO₃]-LDH was exfoliated into LDH nanosheets. When Cr(VI) species adsorbed on the surface of LDHNSs, they could form Cr-LDHNSs complex. Figure 3(d) suggests that the Cr-LDHNSs complex remained disk shape with an average thickness of ~ 16.2-17.5 nm. This reveals that the LDH nanosheets restacked together because of hydrogen bonding between the Cr(VI) species and the hydroxyl groups of the LDHNSs.

FT-IR analysis is an effective method for characterization of [MgAl-NO₃]-LDH, LCT-LCD, LDHNSs, and Cr-LDHNSs. It can be also used to identify the presence of anions in the interlayer regions. Furthermore, information about the functional groups and their bonds can be obtained[27-30]. Spectra of the samples in the range of 500-4000 cm⁻¹ are shown in Fig. 4. In all spectra, a strong and broad adsorption band was observed at 3424-3471 cm⁻¹, but the band characteristic of free OH was not found,

292 indicating that all OH groups were hydrogen-bonded[31-33]. Additionally, a strong
 293 adsorption band can be observed at 610-658 cm^{-1} in all sample spectra, which can be
 294 attributed to the metal-oxygen (M-O) bending vibration[32,34]. In the spectrum of
 295 $[\text{MgAl-NO}_3]\text{-LDH}$ (Fig. 4(a)), an adsorption band appeared at 1634 cm^{-1} , which can
 296 be attributed to the $\delta(\text{H-OH})$ vibration mode[31]. The 1200-1500 cm^{-1} region
 297 corresponds to the interlayer anions, and thus the adsorption band obtained at 1388
 298 cm^{-1} can be assigned to nitrate ions[34]. The FT-IR spectrum for the LCT-LDH (Fig.
 299 4(b)) was significantly different from that of $[\text{MgAl-NO}_3]\text{-LDH}$. The adsorption peaks
 300 at 2976 and 2935 cm^{-1} can be attributed to the stretching vibrations of $-\text{CH}_2-$ or $-\text{CH}-$
 301 groups[31,32]. The peaks at 1605, 1361, and 1125 cm^{-1} were attributed to C=O ,
 302 C-O-C , and C-O stretching vibrations, respectively[21,31-34]. Based on these data,
 303 organic molecules were effectively intercalated into the interlayer galleries of
 304 $[\text{MgAl-NO}_3]\text{-LDH}$. Compared to LCT-LDH, the spectrum exhibited some changes
 305 after LCT-LDH was exfoliated into single-layer LDH nanosheets (Fig. 4(c)), the
 306 essential characteristic bands shifted and the nanostructure varied. After the
 307 adsorption of Cr(VI) , the characteristic stretching vibration of the OH bond shifted to
 308 a lower wavenumber (from 3452 cm^{-1} to 3424 cm^{-1}) and the intensity slightly
 309 weakened. On the other hand, compared with LDHNSs, the C=O , C-O-C , and M-O
 310 bonds shifted to higher wavenumbers and the $-\text{CH}_2-$ or $-\text{CH}-$ groups as well as C-O
 311 bonds disappeared. However, the spectrum exhibited a new adsorption band at 885
 312 cm^{-1} due to the $\nu(\text{Cr-O})$ stretching vibration associated with Cr adsorbed on the
 313 LDHNSs[35]. According to a related study, the characteristic band of the $\nu(\text{Cr-O})$

mode for free chromate was recorded at 890 cm^{-1} [35]. This slight shift of the Cr-O band toward the lower wavenumber (from 890 cm^{-1} to 885 cm^{-1}) indicates that the HCrO_4^- and CrO_4^{2-} ions were exchanged with the interlayer lactate anions in solution, and the stretching vibration of the free chromate was stronger than that of the Cr-O bond in Cr-LDHNSs[14].

Hydrotalcite-like compounds have a general formula:

It is possible to synthesize a series of hydrotalcite-like compounds with different stoichiometries. Generally, x has a value varying from 0.17 to 0.33 and the CO_3^{2-} , NO_3^- , and Cl^- ions are the most common interlayer anions[28]. The nature of the M^{2+} , M^{3+} , and $\text{M}^{2+}/\text{M}^{3+}$ molar ratios, ionic radius of metal ions, A^{m-} , and the values of x in the LDHs are influenced by the chemical compositions and colloidal properties of the LDHs. If the bivalent cation is Mg^{2+} and the trivalent cation has an ionic radius similar to that of Mg^{2+} , LDHs can be easily formed. At the same time, if the trivalent cation is Al^{3+} , the Al^{3+} ions in the hydrotalcite-like layer remain distant from one another, due to electrostatic repulsion between the positive charges[28,29]. The chemical elements and basic properties of $[\text{MgAl-NO}_3]\text{-LDH}$ and LCT-LDH were analyzed by ICP (Table S1, Supporting Information). Experimental results confirmed that their actual constitutions were close to the theoretical ratio of the components and belong to typical hydrotalcite-like structures.

XPS analysis provided information on the chemical state of the LDHNSs before and after the adsorption of Cr(VI)[36]. For total soluble chromate, which includes

Cr(VI) and Cr(III), Cr(III) was generated from Cr(VI) reduction which was also determined. Figure 5 (a) and (b) show the typical wide scan XPS spectra of LDHNSs before and after the adsorption of Cr(VI). The wide scan XPS spectra of LDHNSs not only exhibited the O 1s peak (531.7 eV) and C 1s peak (283.9 eV), but also displayed two peaks at 74.9, and 50.1 eV which can be attributed to Al 2p and Mg 2p, respectively. The peak of O 1s was assigned to chemically or physically adsorbed water[36,37], and the peak of C 1s was attributed to residual lactate in the sample. Compared to LDHNSs, the wide scan XPS spectra of Cr-LDHNSs show that almost all peaks, such as O 1s, C 1s, Al 2p, and Mg 2p, remained in the same position. However, the intensities of these peaks significantly decreased, indicating that the surface active groups of LDNSs strongly reacted with Cr(VI), which weakened the binding energy. Moreover, a new peak at about 582.4 eV was observed in Fig. 5(b), corresponding to Cr 2p. This indicates that the adsorption of Cr(VI) onto LDHNSs. In addition, the narrow scan of Cr 2p XPS spectra is shown in Fig. 5(c). Figure 5(c) suggests that the Cr ($2p_{3/2}$) and Cr ($2p_{1/2}$) peaks appeared at 577.9 and 587.2 eV respectively, both of which can be attributed to Cr(VI)[37]. Moreover, it can be seen that a weak redox reaction occurred during the adsorption process, which shows that a very small amount of Cr(VI) was reduced to Cr(III) by residual lactate in the system. Thus, it can be concluded that the adsorption of Cr onto LDHNSs was mainly the Cr(VI) species rather than the Cr(III) species.

3.2. Cr(VI) removal studies

3.2.1. Effect of pH

The pH of the system is a key factor for the adsorption of heavy metals from aqueous solution. It has a strong influence on the chemical potential of the adsorbent surface and the ionic state of the Cr(VI) species[38]. Cr(VI) species removal by LDHNSs was measured in batch experiments with pH values from 2.0 to 10.0 at an initial Cr(VI) concentration of 100 mg/L. As shown in Fig. 6(a), the removal efficiency was greatly dependent on the pH with the maximum removal efficiency achieved at pH = 6.0. The removal efficiency of Cr(VI) from aqueous solution initially increased with increasing pH, and then gradually reached a plateau. It is obvious that pH determines the quantity of Cr(VI) removed as well as provides a favorable surface charge for the adsorption. The variation in removal efficiency of Cr(VI) at different pH values may be attributed to the affinity of LDHNSs for the different species of Cr existing in the studied pH range[38]. At pH 2.0-6.0, various forms of chromium ions such as HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ co-exist in the solution. At pH>7.0, the predominant ionic species of chromium was CrO_4^{2-} (Fig. 6(b)). Based on the calculation diagram, the Cr(VI) species existed mainly as HCrO_4^- and CrO_4^{2-} at pH 6.0. The high positive charge density on the LDH nanosheets at pH 6.0 (Fig. S1, Supporting Information). Therefore, negatively charged HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and CrO_4^{2-} ions were readily adsorbed on the positively charged LDHNSs due to electrostatic attraction. At pH 2.0-4.0, the Cr(VI) species existed mostly as HCrO_4^- and thus lower Cr(VI) removal efficiency was expected because of electrostatic attraction between

the Cr(VI) species and the LDHNSs decreased with decreasing pH. Moreover, the adsorbent might dissolve at lower pH values, reducing the availability of adsorption sites. Based on these reasons, the removal efficiency of Cr(VI) by LDHNSs decreased at lower pH values.

The equilibrium pH increased with an increase in the initial pH, it remained nearly constant in the pH range of 5.0-8.0. Based on the maximum removal efficiency and equilibrium pH, a pH of 6.0 was selected for further experiments.

3.2.2. Effect of adsorbent dosage

The effect of the dosage on the removal efficiency of Cr(VI) by LDHNSs at pH 6.0 is shown in Fig. S2(Supporting Information). The initial Cr(VI) concentration ranged from 20 to 200 mg/L and the adsorbent dosage ranged from 0.5 to 3.0 mg/L. The results indicate that the Cr(VI) removal efficiency by LDHNSs gradually increased, and then reached a plateau with increasing dosage. This phenomenon is partly because of the abundant reactive sites on the adsorbent surfaces and the high concentration gradient of solutes between the bulk solution and the solid-liquid interface. The positive charge density on the surface of adsorbent increased with increasing dosage, and consequently more readily attracted HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and CrO_4^{2-} ions[39].

Exfoliation means that the layered structures were destroyed and interactions (e.g., electrostatic attraction, hydrogen bonding, and van der Waals forces) between the host layers and the interlayer anions were weakened. The single-layer LDH nanosheets should enhance the accessibility of active sites as the Cr(VI) species

adsorb on the surface of LDHNSs, and thus the adsorption capacity of the LDHNSs for Cr(VI) species significantly increased with increasing adsorbent dosage. With further adsorption, the Cr(VI) species will be formed a monolayer on the surface of LDHNSs, which exhibits a little inhibiting action on Cr(VI) adsorption by occupying reactive sites[40]. On the other hand, the exfoliated LDH nanosheets may restack and form a three-dimensional network structure, which reduces the diffusion rate and accessibility of the Cr(VI) species from the host layers to the inner surfaces. Therefore, the adsorption capacity of Cr(VI) species onto LDHNSs reached a constant level with further increasing dosage.

3.2.3. Effect of contact time and initial concentration

Figure 7 shows the effect of contact time on Cr(VI) adsorption capacity at different initial concentrations ranging from 10 to 200 mg/L. It was obvious that the adsorption rate of Cr(VI) onto LDHNSs was very rapid and the adsorption reached completely equilibrium within 8 min with no significant difference for different initial Cr(VI) concentrations. The rapid adsorption rate was related to the colloidal properties of the LDHNSs. On the one hand, the single-layer LDHNSs were well dispersed in aqueous solution and less diffusion resistance were produced because of single-layer structure and relatively high surface area. On the other hand, due to large amount of available active sites on the LDHNSs, the active sites were not fully occupied by the Cr(VI) species. These features led to rapid contact between the Cr(VI) species and the active sites on the surface of LDHNSs. Indeed, many researchers have evaluated the ability of LDHs to remove chromate from aqueous

solution by adsorption and ion-exchange[12,41-43]. Adsorption of Cr(VI) onto carbonate-containing LDHs are effective, it required 30 min to reach equilibrium at the lowest concentration of 57 mg/L. When the Cr(VI) concentration is higher than 200 mg/L, the adsorption process is completed after 24 h[12]. Calcined hydrotalcite can enhance Cr(VI) adsorption efficiency due to its porous structure and larger surface area, however it still required more than 4 h to reach adsorption equilibrium in the concentration range of 10-200 mg/L[43].. While the adsorption of Cr(VI) by chloride-containing LDHs to reach saturated state, the adsorption time required 7 days[42]. These behaviors can be attributed to the typical layered structures and octahedral units of LDHs. The Mg^{2+} or Al^{3+} octahedral units can form infinite sheets by sharing edges. These sheets are stacked together due to electrostatic attraction, hydrogen bonds, and van der Waal forces between the sheets[44]. This great inhibits the diffusion, penetration, and transportation of the Cr(VI) species from the external surfaces to the internal surfaces. Therefore, the time to reach Cr(VI) adsorption equilibrium is longer using LDHs.

3.2.4. Adsorption isotherms

The adsorption equilibrium is important in describing adsorption behavior. The parameters derived from the representative models provide important information about the adsorption mechanisms[45, 46]. In this study, the classic Langmuir[47] and Freundlich[48] isotherms were used to examine the relationship between the amount of the Cr(VI) adsorbed and the equilibrium concentration in solution at constant temperature and pH. The adsorption isotherms obtained for the adsorption of Cr(VI)

species on the LDHNSs at 308 K and pH 6.0 are shown in Fig. 8.

Langmuir isotherm

The Langmuir isotherm assumes that adsorption occurs on homogeneous adsorbent surfaces, meaning that when a surface site is occupied by an adsorbate molecule, further adsorption cannot occur at this site[47]. The Langmuir isotherm model can be expressed by the following relationship:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e (mg/g) is the amount of Cr(VI) adsorbed on the adsorbent, q_m (mg/g) is the maximum adsorption capacity, C_e (mg/L) is the Cr(VI) concentration in the equilibrium solution, and K_L is the Langmuir constant related to the adsorption energy[47, 49, 50].

Freundlich isotherm

The Freundlich isotherm assumes that adsorption occurs on heterogeneous adsorbent surfaces[41]. The Freundlich isotherm model can be described by the following relationship:

$$q_e = K_F C_e^{1/n} \quad (2)$$

where K_F (L/mg) and n are Freundlich constants related to the capacity and intensity of adsorption[41].

The parameters for the two isotherms obtained from the experimental data are listed in Table S2 (Supporting Information). According to the experimental data, the Langmuir isotherm model fits better than the Freundlich isotherm model. The maximum adsorption capacity of LDHNSs for Cr(VI) was 125.97 mg/g at 308 K.

Comparisons of various adsorbents for the adsorption of the Cr(VI) species are listed in Table 1, the results indicate a higher adsorption capacity of the LDHNSs for Cr(VI) species[14, 37, 51, 52]. This is because the removal of Cr(VI) species by LDHNSs involves a combination of electrostatic attraction, ion-exchange, and hydrogen bonding.

3.2.5. Adsorption kinetics

Adsorption kinetics of Cr(VI) onto LDHNSs is one of the most important parameters for determining the adsorption mechanism and investigating the adsorption efficiency[53, 54]. In this study, two kinetic models, pseudo-first-order and pseudo-second-order models were applied to test the experimental data and predict the adsorption kinetics.

The pseudo-first-orderkinetic model[53] is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_e (mg/g) and q_t (mg/g) are the amount of Cr(VI) adsorbed by LDHNSs at equilibrium and time t (min), respectively. k_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order adsorption[53]. k_1 and q_e are determined from the slope and intercept of the plot of $\ln(q_e - q_t)$ versus t , respectively.

The pseudo-second-order kinetic model[55] is expressed as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption ($\text{g/mg} \cdot \text{min}$). The values of k_2 and q_e are obtained from the slope and intercept of the plot of t/q_t versus t , respectively.

The calculated kinetic parameters with the correlation coefficients are given in Table S3(Supporting Information). The calculated $q_{e,cal}$ values obtained from the pseudo-first-order kinetic model do not give reasonable values, which are too low compared with the experimental $q_{e,exp}$ values. This finding indicates that the adsorption process of Cr(VI) onto LDHNSs does not fit to the pseudo-first-order model in this case. However, the results present an ideal follow the pseudo-second-order kinetic model, with $R^2>0.9999$. A good agreement with this adsorption model is confirmed by the similar data of calculated $q_{e,cal}$ and the experimental data $q_{e,exp}$ for all cases. The rate constant k_2 decreased with increasing Cr(VI) concentration.

3.2.6. Adsorption thermodynamics

Activation energy

The activation energy, E_a , was determined using the Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (5)$$

where E_a is the activation energy (KJ/mol), A is the Arrhenius factor, R is the gas constant (8.314 J/(mol·K)), and T is the adsorption temperature (K)[50]. By plotting $\ln k_2$ versus $1/T$, E_a was obtained from the slope of the linear plot, and k_2 was the pseudo-second-order rate constant. The E_a value obtained was 0.072 KJ/mol for Cr(VI) by LDHNSs. The magnitude of E_a provides information about the nature of the adsorption process, for example, whether it is physical or chemical. For physical adsorption, the values of E_a are usually below 40 KJ/mol, because physisorption is weak[56]. Higher values of E_a suggest chemisorption and involve forces that are

much stronger than those involved in physisorption[57].The positive E_a value is an indicator of an energy barrier in the adsorption process. The calculated E_a value was found to be lower than 40 KJ/mol indicating that the adsorption process of Cr(VI) onto LDHNSs was physisorption (Table S4).

Thermodynamic parameters

The thermodynamic parameters include Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), may give a better understanding of the impact of temperature on the adsorption process. The parameters were calculated on the basis of the following equations[49]:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

where $K_d = q_e/C_e$, is the distribution coefficient, q_e and C_e are the equilibrium concentration of Cr(VI) on the adsorbent (mg/L) and in solution (mg/L), respectively, R is the gas constant (8.314 J/mol·K), and T is the temperature (K).

The data of ΔG^0 , ΔH^0 , and ΔS^0 for the adsorption of Cr(VI) species onto LDHNSs at different temperatures are given in Table S4 (Supporting Information). The negative values of ΔG^0 indicate that the adsorption process is spontaneous and thermodynamically feasible. In addition, an increase in the negative values of ΔG^0 at higher temperatures means that adsorption was less favorable at lower temperatures. The enthalpy change (ΔH^0) for the adsorption of Cr(VI) onto LDHNSs was positive, meaning that the adsorption process was endothermic. As the Cr(VI) species adsorbed on the surface of LDHNSs, LDH nanosheets tended to restack together because of the

interactions between the Cr(VI) species and the hydroxyl groups of the LDHNSs, and consequently significant variations in the adsorbent structure. Thus, it results in a positive value of ΔS^0 .

3.2.7. Adsorption mechanism

According to the experimental results, possible mechanisms were proposed and discussed as followed: (a) electrostatic attraction between the exfoliated LDH nanosheets and the oppositely charged Cr species, (b) the intercalation of lactate molecules within the galleries of [MgAl-NO₃]-LDH may act as reducers for partial reduction of Cr(VI) to Cr(III), and thus ion-exchange occurs between the organic anions and the Cr(VI)/Cr(III) species, and (c) hydrogen bonding between the Cr(VI)/Cr(III) species and the hydroxyl groups of the LDHNSs.

4. Conclusions

The [MgAl-NO₃]-LDH precursor used in this study was synthesized by the co-precipitation method in keeping a Mg/Al molar ratio of 3:1. Lactate molecules intercalated into the interlayer space of the [MgAl-NO₃]-LDH to form inorganic-organic nanocomposite, and then the lactate-intercalated inorganic-organic nanocomposite was exfoliated into single-layer LDH nanosheets in water to form stable translucent colloidal solution, which denoted as LDHNSs and used as adsorbents to remove Cr(VI) from aqueous solution. The present study concerning the adsorption rate and adsorption capacity of LDHNSs, indicate great potential for Cr(VI) removal from aqueous solution. The adsorption of Cr(VI) onto LDHNSs to reach completely equilibrium within 8 min. The adsorption data followed the Langmuir

isotherm model. The maximum adsorption capacity of LDHNSs for Cr(VI) was found to be 125.97 mg/g at 308K. Thermodynamic analysis indicate that the adsorption process was endothermic, spontaneous, and physical in nature, involving weak interactions, such as electrostatic attraction, ion-exchange, and hydrogen bonding between the Cr(VI) species and the binding sites on the LDH nanosheets. This study is important for designing LDH-based adsorbents, which show a rapid adsorption rate as well as high adsorption efficiency for the removal of Cr(VI) species from aqueous solution.

Acknowledgements

This work was supported by the National Science Foundation of China (nos. 51178253 and 21677087). Thanks to Dr. Edward C. Mignot, Shandong University and Dr. Maria Nash from sciencedocs for the linguistic advice.

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Fig. 1. HRTEM images of (a) [MgAl-NO₃]-LDH, (b) LCT-LDH, (c) LDHNSs, and (d) after adsorption of Cr(VI) onto LDHNSs.

Fig. 2. A: X-ray diffraction patterns of (a) [MgAl-NO₃]-LDH, (b) LCT-LDH, (c) LDHNSs, and (d) Cr-LDHNSs.
 B: Schematic structure illustration of lactate molecules intercalated into interlayer regions of [MgAl-NO₃]-LDH.

Fig. 3. AFM images and height profiles of (a) [MgAl-NO₃]-LDH, (b) LCT-LDH, (c) LDHNSs, and (d) Cr-LDHNSs.

Fig. 4. FT-IR spectra of (a) [MgAl-NO₃]-LDH, (b) LCT-LDH, (c) LDHNSs, and (d) after adsorption of Cr(VI) onto LDHNSs.

Fig. 5. XPS spectra of (a) LDHNSs, (b) LDHNSs after reacting with 100 mg/L of Cr(VI) for 10 min at pH 6.0, and (c) narrow scan XPS spectra of Cr 2p.

(a)

(b)

Fig. 6. Effect of initial pH on the removal efficiency of Cr(VI) onto LDHNSs and equilibrium pH (initial Cr(VI) concentration = 100 mg/L, LDHNSs dosage = 2.0 g/L, contact time = 10 min at 308 K) (a), and the speciation diagram of Cr(VI) calculated at T = 308 K and initial Cr(VI) concentration = 100 mg/L (b).

Fig. 7. Effect of contact time on the adsorption capacities of Cr(VI) onto LDHNSs at different initial Cr(VI) concentrations (LDHNSs dosage = 2.0 g/L, pH = 6.0 at 308 K).

Fig. 8. Comparison of different isotherms for the adsorption of Cr(VI) onto LDHNSs at 308 K.