Facile Fabrication of ZnMgAl/LDH/Algae Composites as a Potential Adsorbent for Cr(VI) Ions from Water: Fabrication and Equilibrium Studies

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ABSTRACT: In order to improve the adsorption capacity of natural layered double hydroxyl (LDH) materials, the natural organic sources such as algae containing hydroxyl groups, amino groups, peptide connections, and alginate structures were used to improve LDH for the preparation of ZnMgAl LDH-algae composites (LDH-A_x). The structure of prepared composites was established and characterized via various techniques such as scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. The LDH-A2 sample displayed the highest efficiency for Cr(VI) removal, which reached to 99% at the optimum conditions. The prepared composite LDH-A2 showed high stability and reusability (91.7%) after five cycles. The kinetic studies revealed that the Cr uptake by LDH-A1 is described as pseudo-first order, while the case of LDH-A2 is described as pseudo-second order. This study reported that the easily synthesized LDH-A_x has an interesting environmental approval process to eliminate Cr ions from aqueous media quickly and effectively.

1. INTRODUCTION

The freshwater resources are the most important natural factor for the humanity and the recent civilization. The incessant contamination of them by the industrial and the agricultural drainage wastewater represents a critical challenge for the safety of the humanity.1,2 The water and the environmental agencies, in addition to the interested researchers, developed several advanced technologies to monitor and remove the present water pollutants.3,4 The universally identified toxic pollutants in water supplies are the synthetic dyes, heavy metals, pesticides, phosphates, pharmaceutical residuals, ammonium, and other dissolved chemicals.5−7

Hexavalent chromium ions (Cr(VI)) were categorized from the toxic heavy metals, which were investigated as potentially toxic and very poisonous pollutants. It can increase the risk of cancer throughout the digestive system, nephropathy, and gastro-intestinal ulceration.8,9 The concentrations of 200 and 5 μg/L of Cr(VI) were determined as the concentration levels accepted in wastewater treatment and tap water, respectively.10

Chemical precipitation methods, biological methods, ion-exchange purification, adsorption, and membrane filtration were applied as promising techniques in the metal ion elimination.11,12 Decontamination of Cr(VI) by innovative species of adsorbents that are of low cost and high affinity was endorsed strongly in the later years.13,14 Additionally, continuous efforts have been introduced to develop new generation of the hybrid materials that are of simple preparation methods, low cost precursor, and high adsorption properties.15,16

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Layered double hydroxides (LDH) have been researched in wastewater management applications as encouraging adsorption materials.\cite{17-21} Eshaq et al. reported the removal of Cr(VI) using MgZnAl LDH and calcined one. The results showed that the calcined MgZnAl LDH exhibited higher removal than the uncalcined one through the anion exchange mechanism.\cite{22} Goswamee et al. investigated the adsorption of Cr(VI) by Mg–Al, Ni–Al, and Zn–Cr LDH.\cite{21}

The incredibly large potential of materials such as sorbents is mainly attributed to their large specific surface area, large interparticle anion exchange capacity, tunable interior structure, relatively inexpensive cost, and low-toxicity properties.\cite{17,22} Layered double hydroxides consist of brucites such as a layered structure consisting of a positively charged metal-hydroxide layer with intercalated anions and molecules of water.\cite{23,24} The general formula \([M^{2+} \cdot (1-x) M^{3+} x (OH)_2] [\text{An}^{-}] x/n \cdot zH_2O\) describes the molecular structure of the LDHs, where \(M^{2+}\) could be common (Mg\(^{2+}\), Zn\(^{2+}\), or Ni\(^{2+}\)), and \(M^{3+}\) could be common (Ga\(^{3+}\), Al\(^{3+}\), or Fe\(^{3+}\)).\cite{25,26} The inorganic anion or organic anion compensating non-framework charge (NO\(_3\)\(^-,\) Cl\(^-,\) SO\(_4\)\(^{2-}\), RCO\(_2\)\(^-)\) is identified as A\(^{-}\); \(x\) is usually about 0.2–0.33.\cite{27} Thus, several types of layered double hydroxides of versatile metal ions were prepared and used as a sorbent for various types of wastewater pollutants.\cite{25,28}

In a particular period, marine algae are commonly used as a green and sustainable adsorbent in the water management sectors. This was related to its significance as available mineral resources and renewable, high bio-sorption capacities, low cost, high surface area, and high binding affinities.\cite{29}

However, the algae were thoroughly examined as adsorbent substances, but surprisingly no recent research reported on exploiting the algae as a substrate for LDH, producing a novel hybrid structure of promising adsorption potentiality. From the examined algae as bio-sorbents, Sargassum sp. algae were strongly suggested for their large adsorption ability, which was linked to its richness by large binding sites.\cite{30}

Therefore, this study aims to study the adsorption properties of the ZnMgAl LDH/algae composite for Cr(VI) adsorption as a novel product to enhance the adsorption capacity. The effect of different parameters such as the contact time, initial chromium concentration, pH of the solution, and the catalyst weight on Cr(VI) removal was investigated. Also, the mechanisms were investigated based on different theoretical kinetic and isotherm models, either the traditional models or the advanced models based on the statistical theoretical theory.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Carriers. The XRD diffraction patterns of LDH materials are shown in Figure 1. The XRD of LDH samples as shown in Figure 1 illustrated the diffraction peaks at \(2\theta\) of 11.6, 23.28, 34.77, 39.27, 46.76, 62.02, and 66.02\(^\circ\), which are attributed to the 003, 006, 012, 015, 018, 113, and 116 diffraction peaks, respectively, and that all donated peaks were of hydrotalcite materials. The peaks were observed as straight and symmetrical, completely proving that highly pure LDH catalyst samples had already been obtained successfully. The strength of the characteristic peaks of LDH to LDH-A1 and LDH-A2 was gradually decreased, suggesting a change in the prepared samples’ crystallinity and gradual diminishment of the hydrotalcite framework. Moreover, the peak located at \(2\theta = 11.6^\circ\) (003) was shifted to a lower angle, which indicates an increase in the \(d\)-spacing of the LDH layers due to the incorporation of algae particles between the LDH layers. The crystallinity of LDH-A1 and LDH-A2 was decreased by the addition of a certain quantity of algae regarding suppressed hydrotalcite structure formation or induced collapse of the hydrotalcite structure.

The FTIR spectra of the synthesized samples are illustrated in Figure 2. The prepared composites were strongly established with FTIR analysis. Throughout the spectrum, they actually have the same functional group on the material surface. The broad peak centered at 3460 cm\(^{-1}\) belonged to the stretching of the hydroxyl (OH) group of the interparticle water molecules and the existence of alginic arrangement as the main constituent of algae.\cite{31} The absorption peaks located at 1367 and 644 cm\(^{-1}\) have belonged to the stretching vibration (SV) of the carbonate molecule. The sharp peak assigned at 446 cm\(^{-1}\) was associated with the SV of metal hydroxyl bonding. The two peaks at 2967 and 2931 cm\(^{-1}\) were attributed to the SV of CH aliphatic of algae, which started to appear in the LDH-A1 and LDH-A2 samples.\cite{32} The intensities of peaks located at 3464, 1367, 774, 525, and 446 cm\(^{-1}\) were decreased gradually in the case of LDH-A1 and LDH-A2, respectively, due to involving the algae particles in the LDH layers.

Figure 1. XRD pattern of the prepared ZnMgAl LDH, LDH-A1, and LDH-A2.

Figure 2. FTIR spectra of the prepared composites ZnMgAl LDH, LDH-A1, and LDH-A2.
SEM of various prepared samples is shown in Figure 3. The LDH surface morphology of the prepared materials with different algae concentrations was evidently different. The LDH sample species showed a bulk shape. The LDH material showed aggregated flakes, while in the case of LDH-A1, it showed aggregated nanoparticles, but in the case of LDH-A2, it showed flakes like aggregates. The EDX analysis of the LDH-A1 sample reflected its composition from 10.71% C, 63.3% O, 10.2% Mg, 7.81% Al, to 8.7% Zn. The LDH-A2 sample was composed of 20.6% C, 60.84% O, 6.81% Mg, 6.08% Al, and 5.87% Zn. The increase in the carbon content was related to the increase in the ratio of the admixed algae.

Such morphological features were associated with changes in the porosity properties and the surface area. The area and the pore diameter of the synthetic ZnMgAl-LDH are 30.6 m²/g and 11.8 nm, respectively. The admixing between the algae structure and the layers of ZnMgAl-LDH caused noticeable increment in the surface area to 33.4 and 39.3 m²/g for LDH-A1 and LDH-A2, respectively. This might be related to the nature of the algae surface as their irregular surface of numerous micro- to nano-nudes, which can increase the surface area. On the other hand, the pore diameter shows remarkable declination to 8.5 and 5.4 nm for LDH-A1 and LDH-A2, respectively, which might be related to the expected intercalation of their structure within the interlayers of LD filling some of the open spaces.

2.2. Adsorption Results. 2.2.1. Effect of the Solution pH.

The pH values of the treated solution have a vital effect in controlling the uptake capacities as the surficial charges and the speciation of chromium ions. The presence of hexavalent chromium Cr(VI) was described in three forms, and all of them are anionic species including HCrO₄⁻, Cr₂O₇²⁻, and CrO₄²⁻. The superiority of each form varies depending on the pH of the solution medium and the concentration of dissolved Cr ion.33 The Cr₂O₇²⁻ and HCrO₄ species were identified as the prevalent equilibrium species within the pH range of 2–6 and appeared as anionic species of the chromate ions at the alkaline solutions.38 The regular increases in the investigated pH cause a noticeable reduction in the uptake capacities of the LDH-A1 and LDH-A2 for Cr(VI), and the greatest values were accomplished at pH 2 (42.4 mg/g for LDH-A1 and 64.3 mg/g for LDH-A2) (Figure 4). Therefore, it was revealed that acidic levels are recommended for Cr(VI) reduction. This could be explained by the composite saturation with negatively charged (OH⁻) hydroxyl-free radicals with the further enlargement in pH far above 6, which causes considerable attraction–repulsion.34 This is supported by the value of the pH(ZPC) as it is of valuable significances in understanding the dominant charges on the surface of the adsorbents.35 The measured pH(ZPC) value of LDH-A1 and LDH-A2 are pH 4.8 and 5.2, respectively, which reflected the enrichment of the composite surface in the negative charges during the adsorption of Cr(VI) ions at the pH values higher than these values.

2.2.2. Contact Time and the Kinetic Studies. 2.2.2.1. Influence of the Contact Time. The two forms of the LDH/algae composite validated uptake curves similar to those reported in the literature for the adsorption with different contact intervals (Figure 5a). The representative data are of two different uptake stages. The initiation of the processes was dominated by Cr(VI) adsorption rates (first stage), and this was followed by noticeable nearly fixed rates, which were detected from the plateau parts of the curves (second stage) (Figure 5a). The first stages covered the time range from 30 to 540 min for both LDH-A1 and LDH-A2. This behavior revealed the enrichment of the LDH/algae composites with numerous receptor sites starting with the experiments. The consistent occupation of the LDH/algae receptor sites by the Cr(VI) ions with expanding the experiment time caused reduction in the capacities of LDH/algae composites and their uptake rates for Cr(VI) ions until the stage of the complete saturation. Therefore, the equilibrium time for both LDH-A1 and LDH-A2 is 540 min with equilibrium uptake capacities of 50 and 70.5 mg/g, respectively. Additionally, such results validated an enhancement in the efficiency of the synthetic composite by increasing the ration of the interlayered algae.

2.2.2.2. Kinetic Study. Evaluation of LDH-A1 and LDH-A2 adsorption behaviors considering the criteria of intra-particle diffusion model revealed different types of Cr(VI) uptake mechanisms by them, which is not limited by the diffusion of the ions only (Figure 5b).30 The segments that appeared in the curves were related essentially to three different mechanisms. For the first segment, it was observed at the starting of the experiments and validated abrupt Cr(VI) uptake processes by the surficial receptors of the LDH-A1 and LDH-A2 composites,36 and this mechanism appeared as the essential one. The second segment represented an assistant adsorption mechanism and appeared after certain intervals with the full occupation of the LDH-A1 and LDH-A2 surficial receptors.
Generally, the effective mechanism during this stage is the layered adsorption processes that took place with very weak impact for the diffused Cr(VI) ions. The third segment that was detected after the equilibration is a strong indication of the presence of Cr(VI) as thick layers over LDH-A1 and LDH-A2. Additionally, the essential mechanisms during this stage are the inter-ionic attraction and/or molecular association mechanisms.37

The determination coefficient ($R^2$) displayed strong agreement between the Cr(VI) uptake behaviors of LDH-A1 and LDH-A2 and the suggestions of both the pseudo-first order and pseudo-second order model (Figure 5c,d and Table.1). For LDH-A1, the kinetic studies showed preference to be described according to the theoretical hypothesis of the pseudo-first order model, which is supported also by the obtained theoretical equilibrium capacity (71.37 mg/g), which is closer to the experimental values than the obtained value form the pseudo-second order model. The uptake reactions using LDH-A2 showed slightly noticeable partialities for the pseudo-second order model as compared to the pseudo-First order kinetic model (Table 1 and Figure 5 c,d). This manifested Cr(VI) physisorption by LDH-A1 and chemisorption reaction for LDH-A2. The reported excellent fitness for the Cr(VI) adsorption using LDH-A1 and chemisorption reaction for LDH-A2. The reported excellent fitness for the Cr(VI) adsorption using LDH-A1 and LDH-A2 with both kinetic models demonstrated complex adsorption mechanisms that include different chemical and physical effects, which will be investigated deeply in further equilibrium and thermodynamic studies. The expected chemisorption mechanisms might involve internal diffusion and complexation in addition to the electron sharing and exchange.38,39

2.2.3. Cr(VI) Concentration and the Equilibrium Behavior.
2.2.3.1. Cr(VI) Concentration. This parameter is of valuable impact in identifying the maximum uptake capacities of LDH-A1 and LDH-A2 for Cr (VI) in addition to the mechanisms. The capacities of LDH-A1 and LDH-A2 are of consistent intensification with addressing the higher Cr(VI) concentrations (Figure 6a). It is a normal behavior for the common escalation in the driving forces of Cr(VI) ions with increasing their concentrations. The increment in LDH-A1 and LDH-A2 capacities was detected until the Cr(VI) concentration of 175

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Table 1. Estimated Theoretical Parameters of the Studied Kinetic and Equilibrium Models

| model               | parameters       | LDH-A1       | LDH-A2       |
|---------------------|------------------|--------------|--------------|
| pseudo-first order  | $K_1$ (min$^{-1}$) | 0.0068       | 0.0082       |
|                     | $q_e$(cal) (mg/g) | 71.37        | 112.75       |
|                     | $R^2$            | 0.97         | 0.93         |
| pseudo-second order | $K_2$ (mg/min)   | $4.8 \times 10^{-5}$ | $4.57 \times 10^{-5}$ |
|                     | $q_e$(cal) (mg/g) | 66.7         | 94.96        |
|                     | $R^2$            | 0.96         | 0.98         |
| Langmuir            | $q_m$ (mg/g)     | 93.9         | 161.9        |
|                     | $b$ (L/mg)       | 0.02         | 0.33         |
|                     | $R^2$            | 0.98         | 0.95         |
|                     | $X^2$            | 1.4          | 4.2          |
|                     | $R_L$            | 0.16−0.5     | 0.012−0.06   |
| Freundlich          | $1/n$            | 0.754        | 0.668        |
|                     | $k_F$            | 95.4         | 140.8        |
|                     | $R^2$            | 0.98         | 0.96         |
|                     | $X^2$            | 1.7          | 2.1          |
| D-R model           | $\beta$ (mol$^2$/kJ$^2$) | 0.256       | 0.0287       |
|                     | $q_m$ (mg/g)     | 85.9         | 104.25       |
|                     | $R^2$            | 0.92         | 0.75         |
|                     | $E$ (kJ/mol)     | 1.39         | 4.17         |
mg/L, which is the equilibrium concentration (Figure 6a). The experimentally reported LDH-A1 and LDH-A2 maximum capacities for Cr(VI) are 87 and 110.7 mg/g, respectively (Figure 6a). This revealed the effective upgrading in the capacities of uptake of LDH for Cr(VI) by the combination between it and the used algae and with increasing the ratio of the intercalated algae.

2.2.3.2. Equilibrium Modeling. The fitting values were estimated considering both the determination coefficients ($R^2$) and the chi square ($X^2$) for the nonlinear fitting with Freundlich and Langmuir models (Table 1 and Figure 6b,c). The Cr(VI) uptake by LDH-A1 is in better agreement with the Langmuir model than the Freundlich model (Table 1). However, the adsorption of Cr(VI) by LDH-A2 is in better agreement with the Freundlich model considering the values of the fitting parameters (Table 1). This is the declared monolayer uptake form for LDH-A1 by its homogeneous active sites. For LDH-A2, the uptake of Cr(VI) is of heterogeneous and multilayer properties (Table 1). The theoretically estimated parameters from the Langmuir model demonstrated a theoretical $q_{\text{max}}$ of 93.9 and 161.92 mg/g for LDH-A1 and LDH-A2, respectively (Table 1). Based on the fitting process with the Dubinin–Radushkevich model (D-R), the expected Cr(VI) $q_{\text{max}}$ are 85.9 104.25 mg/g for LDH-A1 and LDH-A2, respectively (Table 1 and Figure 6d). Moreover, the Gaussian energies of LDH-A1 and LDH-A2 are 1.39 and 4.17 kJ/mol, respectively which are characteristic values for the physisorption reactions.36

Figure 6. (A) Uptake of Cr(VI) at different initial concentrations. (B) fitting of the results with the Langmuir model, (C) fitting of the results with the Freundlich model, and (D) fitting of the results with the Dubinin–Radushkevich model.

Figure 7. (A) Temperature effect on the Cr(VI) uptake. (B) Linear fitting with the Van’t Hof equation.
as an effective factor in the Cr(VI) uptake reactions was evaluated within a range of 25–50 °C (Figure 7a). LDH-A1 and LDH-A2 showed a decrease in the Cr(VI) adsorbed quantities at the studied high temperatures (Figure 7a). This confirmed exothermic adsorption properties, and the general data validated the suitability of LDH-A1 and LDH-A2 to be applied in different conditions.

2.2.4.2. Thermodynamic Studies. The LDH-A1 and LDH-A2 thermodynamic properties were examined based on the essential thermodynamic parameters as the Gibbs free energy (ΔG°), the enthalpy (ΔH°), and the entropy (ΔS°). The ΔG° value was calculated from eq 1, while the ΔH° and ΔS° values were presented as estimated parameters from the fitting relation with the Van’t Hoff equation (eq 2) (Figure 7b and Table 2).

\[ \Delta G^\circ = -RT \ln(K_c) \]  
(1)

\[ \ln(K_c) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \]  
(2)

Table 2. Theoretical Values of the Thermodynamic Parameters

| thermodynamic parameters | reaction temperature | LDH-A1 | LDH-A2 |
|--------------------------|----------------------|--------|--------|
| ΔG° (kJ mol⁻¹)            | 298.15               | -18.25 | -20.11 |
|                          | 303.15               | -17.75 | -19.77 |
|                          | 308.15               | -17.55 | -19.60 |
|                          | 313.15               | -17.13 | -19.50 |
|                          | 318.15               | -17.13 | -19.58 |
|                          | 323.15               | -6.36  | -7.275 |
| ΔH° (kJ mol⁻¹)            |                      | -31.92 | -26.03 |
| ΔS° (J K⁻¹ mol⁻¹)         |                      | -46.45 | -20.43 |

The free energies of LDH-A1 and LDH-A2 are of negative signs, validating spontaneous uptake properties (Table 2). Additionally, the favorability of their reactions can be enhanced at the high-temperature conditions. The negative enthalpy values signified exothermic properties for LDH-A1 and LDH-A2 (Table 2). Moreover, the negative entropy for them emphasized the systematic decrease in the randomness in their uptake reactions for Cr(VI) (Table 2).

2.2.5. Effect of Adsorbents Dosages. The predicted improvement in the Cr(VI) removal percentages using higher masses of LDH-A1 and LDH-A2 was appraised, and the results are declared by Figure 4. The observed Cr(VI) removal percentages using LDH/algae (1) increased by 29.2, 45.8, 60.5, 74.2, and 84.6% with increasing the LDH-A1 masses by 0.02, 0.04, 0.06, 0.08, and 1 g, respectively (Figure 8). For the LDH-A2 composite, the percentages upgraded to 48.3, 66.2, 84.6, 94.8, and 98.7% (Figure 8). This was related to the expected increase in the numbers of exposed receptors sites and the total surface area.

2.2.6. Reusability. The reusability of LDH-A1 and LDH-A2 was conducted using 0.1 g of each for 70 min at a certain concentration of 50 mg/L, volume of 100 mL, pH of 4, and temperature of 30 °C. The used LDH-A1 and LDH-A2 powders after each reusing test were washed extensively, dried at 60 °C for about 8 h, and reapplied again in a new test. Both LDH-A1 and LDH-A2 are of significant reusability considering the performed five cycles (Figure 9). The determined Cr(VI) removal percentages by LDH-A1 are 84.6, 84.1, 83.2, 80.4, and 77.6% for the five cycles (Figure 9). For the LDH-A2, the achieved percentages in the investigated cycles are 98.7, 98.4, 96.3, 94.4, and 91.7% in order (Figure 9).

2.2.7. Adsorption Mechanism. The adsorption mechanism can be discussed based on the nature of the adsorbent as a hybrid material from algae and ZnMgAl LDH. For the algae structure, the adsorption occurred two methods (1) by the electrostatic attractions between the Cr(VI) ions and the charged functional groups on the surface of the used algae and (2) by formation of complexation or hydrogen bonds with the functional groups especially the nitrogen-bearing functional groups (Figure 10). For the LDH component, the uptake of the Cr(VI) ions involved several mechanisms as follows: (1) the electrostatic attraction between the dissolved ions and the charged functional groups of ZnMgAl LDH, (2) the ion exchange process with the interlayer ions of ZnMgAl LDH, and (3) the formation of complexation or hydrogen bonding with active groups of LDH especially the hydroxyl groups (Figure 10).

2.2.8. Comparison Study. The synthetic ZnMgAl LDH/algae composites (LDH-A1 and LDH-A2) were compared with other adsorbents in the literature considering the achieved maximum uptake capacities (Table 3). The composites are of higher capacities than several adsorbents including natural diatomite and other types of its base composites with MCM-14 and magnetite in addition to other materials such as polyaniline, carbon nanotubes, Ca−Al LDH, kaolinite/iron oxide composite, and biochars (Table 3).
3. CONCLUSIONS

We present a convenient strategy to fabricate a ZnMgAl LDH/algae composite by a precipitation method. The as-prepared composites exhibited the same crystallinity and functional groups with closed morphology. The Cr(VI) removal capacity was influenced under different pH solutions. Moreover, the adsorption of Cr(VI) by LDH-A2 is of better fitness with the Freundlich model. The LDH-A2 composite exposed high adsorption capacity and a maximum removal of approximately 100%. The prepared composites transmitted high stability and reusability after five cycles that achieved 91% removal.

4. EXPERIMENTAL WORK

4.1. Materials. The seaweed Sargassum sp. algae were used as a carrier for the synthetic LDH and collected from the northern coast of Egypt. Magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, 98%), NaOH pellets (98%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), aluminum nitrate nonahydrate (Al₉(NO₃)₁₉·9H₂O, 98%), and potassium hydroxide (98%) were used in the synthesis of the catalyst. All the incorporated chemicals were delivered by Sigma Aldrich Company and of the laboratory specifications.

4.2. Preparation of ZnMgAl LDH/Algae Composite (LDH/Aₓ). An aqueous solution (A) containing the dissolved nitrate precursors of zinc (1.63 g), magnesium (9.75 g), and aluminum (5.44 g) in 120 mL of distilled water (DW) was prepared. The second alkaline solution B was prepared by dissolving potassium carbonate (9.1 g) and potassium hydroxide (8.61 g) in 200 mL of DW. The third solution C was prepared via the dispersion of a certain amount of algae (0, 0.75, and 1.5 g of milled algae) in 120 mL of DW. Solutions A and B were added simultaneously to solution C under vigorous mechanical stirring. The pH was adjusted by nitric acid (HNO₃) and 0.1 M ammonium nitrate to be 9.5. The obtained precipitate was adjusted at 80 °C under mechanical stirring for 18 h. The product was transferred to a centrifuge and washed with hot distilled water and ethyl alcohol several times to remove the excess of ions. The white precipitate was dried in a vacuum oven under 80 °C for 18 h to obtain various samples donated as LDH, LDH-A1, and LDH-A2, respectively.

4.3. Characterization Techniques. The changes in the present crystalline phases and the lattice properties were identified considering the XRD patterns of the products, which were obtained by a PANalytical (Empyrean). The external morphological feature was evaluated using a high-resolution scanning electron microscope (Gemini, Zeiss-Ultra 55). The changes in the chemical properties and the surface functional groups were evaluated using an FTIR-FT Raman spectrometer (Vertex 70).

4.4. Adsorption Experiments. The adsorption affinity of algae/LDH for Cr(VI) ions was assessed using ICP, respectively. The experiment was repeated three times, and the used results are the average values with standard deviations lower than 3.6% for Cr(VI) ions.

4.4.1. Effect of pH. The assessment of the pH effect on the affinity of algae/LDH for the Cr(VI) ions was followed from pH 2 to 8. The experimental affecting factors were considered at 0.06 g as the algae/LDH mass, 100 mL as volumes, and 50 mg/L as the addressed concentration at 30 °C as the temperature, and 240 min as the contact period.

4.4.2. Effect of the Test Time Interval and Kinetic Behavior. The impacts of the experiment time periods and the kinetic behaviors were followed from 5 to 780 min after adjusting the experimental factors at 0.06 g as the algae/LDH mass, 100 mL as the inspected volumes, 50 mg/L as the tested concentration, 30 °C as the temperature, and 240 min as the contact period.

Table 3. Comparison Study between the Synthetic LDH/Algae Composites and Other Adsorbents in the Literature

| adsorbents                  | qₑₓₘᵡ (mg/g) | references |
|----------------------------|-------------|------------|
| diatomite/magnetite        | 69.16       | 42         |
| diatomite                  | 24.9        | 43         |
| kaolinite crusted by iron oxide | 76.62     | 44         |
| diatomite/MCM-41           | 70.87       | 45         |
| oxidized SWCNTs            | 44.64       | 46         |
| Ca–Al LDH                  | 104.8       | 47         |
| carbonaceous adsorbents    | 56.5        | 48         |
| modified magnetic chitosan | 51.8        | 49         |
| FeOOH/AIOOH/MWCNTs         | 60.6        | 50         |
| zinc–biochar               | 102.6       | 51         |
| MWCNTs/Fe₃O₄               | 76.92       | 52         |
| polyaniline                | 59.17       | 53         |
| 3D hierarchical GO-NiFe LDH| 53.6        | 54         |
| LDH-A1                     | 93.9        | this study |
| LDH-A2                     | 161.9       | this study |

Figure 10. Predicted uptake mechanism of Cr(VI) by LDH-A1 and LDH-A2.

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| modified magnetic chitosan | 51.8        | 49         |
| FeOOH/AIOOH/MWCNTs         | 60.6        | 50         |
| zinc–biochar               | 102.6       | 51         |
| MWCNTs/Fe₃O₄               | 76.92       | 52         |
| polyaniline                | 59.17       | 53         |
| 3D hierarchical GO-NiFe LDH| 53.6        | 54         |
| LDH-A1                     | 93.9        | this study |
| LDH-A2                     | 161.9       | this study |
4.4.3. Effect of Algae/LDH Mass. The potential enhancement in the Cr(VI) elimination efficiency by inducing the Algae/LDH masses was investigated from 0.04 to 0.1 g at fixed values for the experimental parameter at 100 mL for the volumes, 50 mg/L for the concentrations, 780 min for the time, 30 °C for the temperature, and pH 4.

4.4.4. Equilibrium Studies. The effect of increasing the initial concentrations of the studied contaminants on the uptake capacity and the equilibrium behaviors was addressed for different concentrations with the range from 50 to 250 mg/L. The other affecting factors were fixed at 0.06 g as the composite mass, 100 mL of polluted solution volumes, pH 4, 30 °C, and 780 min as the studied time interval. The equilibrium behaviors were evaluated based on the results of the linear regression fitting with different theoretical isotherm models including Langmuir, Freundlich, and Dubinin–Radushkevich models, and their representative equations are listed in Table 1.

4.4.5. Thermodynamic Studies. The thermodynamics of the algae/LDH adsorption system for Cr(VI) was studied considering the reaction temperature from 298 to 333 K. The other affecting factors were fixed at 0.06 g as the mass, 100 mL of polluted solution volumes, 50 mg/L as contaminants concentrations, and 240 min as the studied time interval.

ASSOCIATED CONTENT

1. Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04842.

Representative equations of the studied kinetic and isotherm models and their parameters (PDF)

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This article was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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