Effect of Preparation Methods on the Adsorption of Glyphosate by Calcined Ca–Al Hydrotalcite

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ABSTRACT: Calcined Ca–Al hydrotalcites were prepared by the clean method (Ca-LDO-1) and traditional co-precipitation method (Ca-LDO-2), respectively. The effect of the preparation method on the adsorption of glyphosate by calcined Ca–Al hydrotalcites was investigated. The adsorbents were also characterized by X-ray diffraction (XRD), thermogravimetric (TG) analysis, inductively coupled plasma optical emission spectroscopy (ICP-OES), and low-temperature N₂ adsorption–desorption, respectively. Compared with Ca-LDO-2, Ca-LDO-1 had higher specific surface area and pore volume, which caused it to show better adsorption performance and reusability for the adsorbing of glyphosate. In addition, the kinetics and thermodynamics of the adsorption of glyphosate by Ca-LDO-1 were studied. The results showed that it was more consistent with the pseudo-second-order kinetic equation and Langmuir isotherm equation.

INTRODUCTION

Glyphosate is a kind of herbicide with high efficiency and broad-spectrum nonselectivity, which is widely used in agricultural and nonagricultural fields. However, glyphosate can affect the ecological environment in the process of production and use. For example, the long-term use of glyphosate can cause the accumulation of glyphosate derivatives in the human body toxins and also cause the loss of nutrients in the soil, soil hardening, and water pollution. The removal of glyphosate in water mainly includes the chemical method, biological method, membrane separation method, and adsorption method. Among the above methods, the adsorption method has the advantages of simple process, convenient operation, high removal efficiency, and less secondary pollution. The selection of adsorption material is the key factor affecting the adsorption efficiency. The adsorbents for glyphosate removal include zeolite, activated carbon, kaolin, metal organic framework materials, and hydrotalcite and its calcined product.

Hydrotalcite (LDH) materials have a special layered structure, memory effect, and interlayer anion exchangeability. They are widely used in the adsorption of heavy metal ions,9–12 organic dyes,13–15 phosphate ions, halogen ions, and pesticides in wastewater.16–19 Li et al. discussed the effect of intercalation ions on the adsorption of glyphosate by Mg–Al LDH. The results showed that Mg–Al LDH with Cl⁻ as the intercalation ion has the best adsorption property. And the adsorption mechanism of Mg–Al LDH for glyphosate includes both surface adsorption and intercalation ion exchange. Subsequently, Khenifet al. reported the adsorption of glyphosate by Ni–Al LDH intercalated with NO₃⁻. They also found that the adsorption of glyphosate by LDH included two stages: glyphosate attaching to the surface of LDH and entering into the interlayer of LDH through intercalation ion exchange.19 Compared with LDH, calcined LDH has a higher specific surface area, which makes it show better adsorption performance. Cai et al. found that the maximum adsorption capacity of calcined Zn–Al–Ti LDH is more than three times that of Zn–Al–Ti LDH.20 However, the above LDH and its calcined product were prepared by co-precipitation from soluble metal salts and alkali. A large amount of wastewater with a high concentration of salt would be produced in the production process. In addition, LDH intercalated with NO₃⁻ or Cl⁻ was prepared under isolation air, resulting in the production and regeneration of such LDHs more complex. Therefore, it is still important to develop a clean, simple, and low-cost preparation method for LDH with high-efficiency adsorption performance.

Among the hydrotalcite-like materials, Ca–Al LDH intercalated with CO₃²⁻ has the lowest production cost, which is more suitable for large-scale application as an adsorbent in the adsorption field.21–26 Herein, Ca–Al LDH was prepared by the clean method under isolation air, resulting in the higher specific surface area and pore volume, which makes it show better adsorption performance. In addition, the kinetics and thermodynamics of the adsorption of glyphosate by Ca-LDO-1 were studied. The results showed that it was more consistent with the pseudo-second-order kinetic equation and Langmuir isotherm equation.
intercalated with CO$_3^{2-}$ was cleanly prepared from Ca(OH)$_2$, Al(OH)$_3$, and CO$_2$, and its calcined product was applied to the adsorption of glyphosate. The effects of preparation methods on the adsorption of glyphosate by calcined Ca–Al LDH were investigated. Compared with calcined Ca–Al LDH prepared by the traditional co-precipitation method, calcined Ca–Al LDH prepared by the clean method showed better adsorption performance for glyphosate. In addition, the calcined Ca–Al LDH can be reused after simple calcination for the adsorption of glyphosate. It provides an alternative method for the large-scale application of LDH in the adsorption field.

**RESULTS AND DISCUSSION**

**Material Characterization and Analysis.** The Ca–Al LDH was characterized by XRD, as shown in Figure 1a. The XRD patterns of Ca-LDH-1 and Ca-LDH-2 showed characteristic diffraction peaks at 12 and 24°, respectively, indicating that they both have the typical LDH structure. The intensity of the characteristic diffraction peak of Ca-LDH-1 was obviously higher than that of Ca-LDH-2, which indicated that Ca-LDH-1 prepared by the clean method has better crystallinity and more complete crystal structure. The peaks at 2θ angles of 29 and 36° belonged to the characteristic diffraction peak of impure CaCO$_3$, which indicated that there is a small amount of CaCO$_3$ impurity in those Ca–Al LDH samples.

Figure 1b showed the XRD spectra of calcined Ca–Al LDH. The characteristic diffraction peaks of Ca-LDH-1 and Ca-LDH-2 at 12 and 24° disappeared after roasting over 300 °C for 2 h, indicating that their layered structure was destroyed. The peaks of Ca-LDO-1 and Ca-LDO-2 at 2θ angles of 18, 23, 29, 34, 39, and 49° belonged to the characteristic diffraction peaks of Ca–Al composite oxide and CaO, respectively. The Ca–Al composite oxide was obtained by calcination of Ca–Al LDH, while CaO was mainly obtained by decomposition of CaCO$_3$. The above results showed that both Ca-LDH-1 and Ca-LDH-2 can be transformed from layered hydrotalcite structure to mixed oxide by roasting. In addition, the diffraction peak intensity of Ca-LDO-1 increased with increasing calcination temperature from 300 to 500 °C, indicating that the crystal structure tends to be complete. However, the diffraction peak intensity of Ca-LDO-1 decreased with further increasing calcination temperature to 600 °C. When the calcination temperature reached 700 °C, the structure of Ca-LDO-1 changed obviously due to the collapse of pore structure, which was similar to the results reported in the literature.$^{10,20}$

The thermogravimetric (TG) curves of Ca-LDH-1 and Ca-LDH-2 were shown in Figure 2. The TG curve of Ca-LDH-1 showed a mass loss in the temperature range of 110–200 °C and 200–500 °C, respectively. The mass loss at 110–200 °C was attributed to the removal of surface adsorbed water and crystal water of Ca-LDH-1 (8.5% mass loss), and the mass loss at 200–500 °C was caused by the dehydroxylation in the crystal lattice and decomposition of interlamellar carbonate anions (10.7% mass loss).$^{20}$ The TG curve of Ca-LDH-2 showed mass loss in the temperature range of 50–200 °C and 200–460 °C, respectively. The mass loss at 50–200 °C was attributed to the removal of surface adsorbed water and crystal water by Ca-LDH-2 (9.2% mass loss), and the mass loss at 200–460 °C was caused by the dehydroxylation and decomposition of carbonate anions (13.9% mass loss).$^{20}$ In addition, the mass loss percentages of Ca-LDH-1 and Ca-LDH-2 were not the same in the two temperature ranges, which further indicated that their compositions and structures are different.

To explore the composition and structure differences between Ca-LDO-1 and Ca-LDO-2, the actual Ca/Al molar ratio was determined by ICP-OES. The specific surface area,
pore size, and pore volume were characterized by the low-temperature N$_2$ adsorption–desorption method, and the results were shown in Table 1. The actual Ca/Al molar ratio (3.96) of Ca-LDO-1 prepared by the clean method was close to that in the raw material (4.0), but the actual Ca/Al molar ratio (4.13) of Ca-LDO-2 was higher than that in the raw material (4.0). Part of Al$^3+$ was dissolved in the strong alkaline environment of the co-precipitation system rather than precipitated. In addition, the specific surface area ($S_{BET}$) of Ca-LDO-1 (14.377 m$^2$/g) was more than 4 times that of Ca-LDO-2 (3.441 m$^2$/g), which was similar to the result reported by previous literature.\textsuperscript{27} The average pore sizes of Ca-LDO-1 and Ca-LDO-2 were 3.804 and 3.053 nm, respectively. However, the pore volume of Ca-LDO-1 (0.061 cm$^3$/g) was more than 7 times that of Ca-LDO-2 (0.008 cm$^3$/g). In conclusion, Ca-LDO-1 had relatively higher specific surface area and pore volume, which made it more suitable to be used as an adsorbent. In addition, the effect of calcination temperature on the $S_{BET}$ of Ca-LDO-1 was also investigated. As shown in Figure 3, the $S_{BET}$ of Ca-LDO-1 increased slightly with increasing calcination temperature from 300 to 500 °C. However, the $S_{BET}$ of Ca-LDO-1 decreased with further increasing calcination temperature to 700 °C, which might be caused by the collapse of the pore structure.

### Table 1. Composition and Structure of Calcined Ca–Al LDH

| adsorbent | Ca/Al molar ratio$^a$ | $S_{BET}$ (m$^2$/g) | pore size (nm) | pore volume (cm$^3$/g) |
|-----------|------------------------|----------------------|----------------|----------------------|
| Ca-LDO-1  | 3.96                   | 14.377               | 3.804          | 0.061                |
| Ca-LDO-2  | 4.13                   | 3.441                | 3.053          | 0.008                |

$^a$Detected by ICP-OES.

\[\text{Figure 3. Effect of calcination temperature on the } S_{BET} \text{ of Ca-LDO-1.}\]

mg/g adsorption capacity using Ca-LDO-1 instead of Ca-LDH-1. A 55.8% adsorption percentage was obtained with 19.9 mg/g adsorption capacity using Ca-LDO-2 as the adsorbent. It was worth noting that the adsorption percentage of Ca-LDO-1 is significantly higher than that of Ca-LDO-2. It was well known that the $S_{BET}$ and pore volume of an adsorbent are the key factors affecting its adsorption performance.\textsuperscript{8–19} According to the characterization results of low-temperature $N_2$ adsorption and desorption (Table 1), the $S_{BET}$ and pore volume of Ca-LDO-1 were significantly higher than those of Ca-LDO-2, which might be one of the reasons for its better adsorption performance. In addition, the surface basicity of the adsorbent had an effect on its adsorption performance of glyphosate since glyphosate is a kind of acidic compound. As shown by previous literature, the surface alkali density of Ca-LDO-1 was higher than that of Ca-LDO-2, which was another reason for the better adsorption of Ca-LDO-1.\textsuperscript{17–29} Compared with the co-precipitation process of Ca-LDO-2, the clean preparation process of Ca-LDO-1 had the advantages of no wastewater discharge and lower production cost.\textsuperscript{27}

In addition, the reusability of Ca-LDO-1 was also investigated. As the results showed in Figure 4, the adsorption of Ca-LDO-1 decreased only slightly in the fifth run, indicating that it has good reusability for the adsorption of glyphosate. According to the results in the literature, the calcined LDH prepared by roasting LDH at 500 °C has a special structural memory effect.\textsuperscript{15} Calcined LDH could recover to the original layered structure of LDH in the aqueous solution. And the glyphosate was mainly adsorbed on the surface or between the layers of Ca-LDO-1. After adsorbing glyphosate, Ca-LDO-1 was calcined again at 500 °C to remove glyphosate and used in the next run of adsorption experiments.

#### Effect of Ca/Al Molar Ratio on the Adsorption of Glyphosate by Calcined Ca–Al Hydrotalcite.

According to the results in the literature, the molar ratio of metal ions is one of the key factors affecting the adsorption performance of calcined LDH.\textsuperscript{10,15} Therefore, the effect of Ca/Al molar ratio on the adsorption of glyphosate by calcined Ca–Al LDH prepared by the clean method was investigated under the condition of keeping other preparation conditions unchanged. As shown in Figure 5, the adsorption percentage increased from 83.7 to 96.8% with increasing Ca/Al molar ratio from 1:1 to 4:1. However, the adsorption percentage decreased to 87.2% with further increasing Ca/Al molar ratio to 5:1. According to previous literature, the molar ratio of metal ion has a significant effect on the composition, specific surface area, and pore structure of calcined LDH, which leads to the difference of

\[\text{Figure 4. Effect of adsorbent on the adsorption of glyphosate.}\]
adsorption performance. The above results showed that the optimum Ca/Al molar ratio is 4:1.

Effect of Calcination Temperature on the Adsorption of Glyphosate by Calcined Ca−Al Hydroxalite. Calcination temperature is also one of the key factors affecting the adsorption performance of calcined LDH. Therefore, the effect of calcination temperature on the adsorption of glyphosate by calcined Ca−Al LDH was investigated in the range of 300 to 700 °C. To enlarge the performance gap of the adsorbent, the dosage of the adsorbent was reduced from 1.4 g/L to 1.0 g/L with other adsorption conditions unchanged. As the results showed in Figure 6, the adsorption of glyphosate by calcined Ca−Al LDH first decreased and then increased with rising calcination temperature from 300 to 500 °C. And the adsorption percentage decreased rapidly with further rising calcination temperature to 700 °C. According to the literature and the results of XRD characterization, the layered structure of LDH had been partially destroyed, but the stable porous mixed metal oxide structure had not been formed with rising calcination temperature from 300 to 400 °C. Therefore, the adsorption performance of calcined Ca−Al LDH decreased. When the calcination temperature reached 500 °C, the carbonate and hydroxyl between the layers of LDH were completely removed, forming a stable porous composite metal oxide structure with a relatively higher $S_{BET}$, which improved the adsorption performance. However, a high calcination temperature will lead to structural collapse and lower $S_{BET}$ (Figure 3), resulting in the decrease of adsorption percentage. In addition, the calcined Ca−Al LDH roasting at high temperature loses its structure memory effect and cannot be reduced to the layered structure, which may be another reason for its low adsorption performance. Therefore, the optimum roasting temperature is 500 °C.

Adsorption Kinetics. Figure 7 showed the adsorption kinetic curve of glyphosate on Ca-LDO-1. The process of glyphosate adsorption on Ca-LDO-1 was fitted by the pseudo-first-order kinetic model (1), pseudo-second-order kinetic model, (2) and diffusion model in particles (3), respectively. The corresponding fitting equation was as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - kt$$  \hspace{1cm} (1)

$$\frac{t}{Q_t} = \frac{1}{k_1 Q_e^2} + \frac{t}{Q_e}$$  \hspace{1cm} (2)

$$Q_t = k_3 t^{1/2} + C$$  \hspace{1cm} (3)

where $Q_e$ and $Q_t$ are the adsorption capacity (mg g$^{-1}$) at adsorption equilibrium and $t$ (min); $K_1$ (min$^{-1}$) and $K_3$ (g mg$^{-1}$ min$^{-1/2}$) are the pseudo-first-order kinetic adsorption percentage constant and the pseudo-second-order kinetic adsorption constant, respectively; $K_1$ (mg g$^{-1}$ min$^{-1}$) is the intraparticle diffusion rate constant; and $C$ is the constant related to the thickness of the reaction boundary layer.

The fitted rate constant and correlation coefficient ($R^2$) were shown in Figure 7, Table 2, and Table 3. As shown by the fitting results, the correlation coefficient of pseudo-second-order kinetics ($R^2 = 0.9895$) was higher than that of pseudo-first-order kinetics ($R^2 = 0.9449$). And the theoretical equilibrium adsorption capacity obtained by pseudo-second-order kinetics was closer to the actual experimental value (Table 2). It indicated that the adsorption process of glyphosate by Ca-LDO-1 followed the pseudo-second-order kinetics, and there were physical adsorption and chemical adsorption in the adsorption process, which were consistent with the results of glyphosate adsorption by LDH reported by previous literature. As shown in Table 3, the intraparticle diffusion process could be divided into three stages. In the first two stages, the $K$ value was larger and the adsorption process was faster. In the third stage, the $K$ value was smaller and the adsorption process was slower. When the adsorption tended to equilibrium, the $C$ value was not 0, which indicated that the adsorption of glyphosate by Ca-LDO-1 is affected by the diffusion in the particles.

Adsorption Thermodynamics. Figure 8 showed the adsorption isotherms of glyphosate by Ca-LDO-1 at different initial concentrations, which were fitted by Langmuir (4) and Freundlich isotherms (5), respectively. The corresponding fitting equations were as follows:

$$\frac{\rho_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{\rho}{Q_m}$$  \hspace{1cm} (4)

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln \rho$$  \hspace{1cm} (5)
where \( \rho_e \) is the mass concentration of glyphosate (mg L\(^{-1}\)) at adsorption equilibrium; \( Q_e \) is the adsorption capacity of CaLDO for glyphosate at adsorption equilibrium (mg g\(^{-1}\)); \( Q_m \) is the theoretical maximum adsorption capacity of Ca-LDO-1 for glyphosate (mg g\(^{-1}\)); \( K_L \) is the Langmuir constant (L g\(^{-1}\)); \( K_F \) is the Freundlich constant (mg\(^{1-n}\) L\(^n\) g\(^{-1}\)); and \( n \) is the adsorption strength constant.

The fitting results of adsorption thermodynamics were shown in Figure 8 and Table 4. The correlation coefficient fitted by the Langmuir isotherm equation was bigger than that of the Freundlich isotherm equation, indicating that the Langmuir isotherm equation can better describe the adsorption process of glyphosate on Ca-LDO-1. The above results showed that the adsorption of glyphosate by Ca-LDO-1 is a monolayer adsorption, which is consistent with the results reported in the literature.\(^{18,19}\)

The thermodynamic parameters at the experimental temperature were calculated. The corresponding equation was as follows:

\[
\Delta G = \Delta H - T \Delta S 
\]  
(6)

\[
\ln K_d = \frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]  
(7)

Table 2. Pseudo-first-order and Pseudo-second-order Kinetic Parameters of Glyphosate Adsorption by Ca-LDO-1

| \( Q_{exp} \) (mg g\(^{-1}\)) | \( \rho_0 \) (mg L\(^{-1}\)) | \( K_1 \) (min\(^{-1}\)) | \( Q_{cal} \) (mg g\(^{-1}\)) | \( R^2 \) |
|---|---|---|---|---|
| 41 | 50 | 0.0234 | 27.3660 | 0.9449 |

Table 3. Particle Diffusion Model Fitting Parameters of Glyphosate Adsorption by Ca-LDO-1

| \( \rho_0 \) (mg L\(^{-1}\)) | \( K_{i1} \) (mg g\(^{-1}\)·min\(^{-1/2}\)) | \( C_{i1} \) | \( R^2 \) | \( K_{i2} \) (mg g\(^{-1}\)·min\(^{-1/2}\)) | \( C_{i2} \) | \( R^2 \) | \( K_{i3} \) (mg g\(^{-1}\)·min\(^{-1/2}\)) | \( C_{i3} \) | \( R^2 \) |
|---|---|---|---|---|---|---|---|---|---|
| 50 | 6.252 | -9.132 | 0.9894 | 2.3645 | 16.729 | 0.9746 | 0.3688 | 35.316 | 0.8453 |

Figure 7. Kinetic curve of glyphosate adsorption by Ca-LDO-1 (a), pseudo-first-order kinetic model (b), pseudo-second order-kinetic model (c), and diffusion model in particles (d).
adsorption (J mol⁻¹) is the absolute temperature (K); $T$ is the absolute temperature (K); $\Delta S$ is the entropy change of adsorption (J mol⁻¹ K⁻¹); $\Delta H$ is the enthalpy change of adsorption (kJ mol⁻¹); $\Delta G$ is the Gibbs free energy change of adsorption (kJ mol⁻¹). $R$ is the ideal gas constant (8.314 J mol⁻¹ K⁻¹); $K_d$ is the distribution coefficient; $\rho_a$ and $\rho_e$ are the mass concentration of dye adsorbed by the adsorbent and the equilibrium mass concentration of dye in the solution (mg L⁻¹), respectively.

As the results showed in Table 5, $\Delta H > 0$ indicated that the adsorption of glyphosate on Ca-LDO-1 is an endothermic process, which is consistent with the experimental results. $\Delta G < 0$ and decreased with the increase of temperature, indicating that the adsorption process is spontaneous and the increase of temperature is conducive to the adsorption reaction. $\Delta S > 0$ indicated that the disorder degree increases in the adsorption process, which is conducive to the adsorption reaction and increases the adsorption randomness of the solid–liquid interface.

### CONCLUSIONS

Compared with Ca-LDO-2 prepared by the traditional co-precipitation method, Ca-LDO-1 prepared by the clean method had higher $S_{BET}$ and pore volume, which caused it to show better performance for the adsorption of glyphosate. The preparation process of Ca-LDO-1 had the advantages of no wastewater discharge and lower production cost. Under the condition of 50 mg/L initial concentration and 1.4 g/L adsorbent dosage, the adsorption percentage of glyphosate by Ca-LDO-1 reached 96.8% with 41 mg/g adsorption capacity. In addition, Ca-LDO-1 could be reused by simple calcination. The results of adsorption kinetics and thermodynamics showed that the adsorption of glyphosate by Ca-LDO-1 follows the pseudo-second-order kinetic equation and Langmuir isotherm equation. The adsorption process was a monolayer adsorption and endothermic.

### EXPERIMENTAL

Preparation of Calcined Ca–Al LDH. The clean method of calcined Ca–Al LDH was similar to the process reported in the literature. Ca(OH)₂ (0.16 mol, 12.48 g) and Al(OH)₃ (0.04 mol, 5.16 g) were added into a three-port flask with 120 mL of water, stirred, and heated to 85 °C. CO₂ was added to the reaction system by bubbling within 20 min, and the reaction was continuously stirred for 40 min. After that, the reactant was crystallized in an oven at 70 °C for 19 h. After filtration, drying, and grinding, Ca–Al LDH (labeled as Ca-LDH-1) was obtained. Finally, calcined Ca–Al LDH (labeled as Ca-LDO-1) was obtained by roasting Ca-LDH-1 at 500 °C for 2 h and crushing through 200 mesh sieve.

The co-precipitation method of calcined Ca–Al LDH was similar to the process reported in the literature. CaCl₂ (0.16 mol, 18.5 g) was added into 80 mL of H₂O to prepare the salt solution; NaOH (0.06 mol, 2.5 g), NaAlO₂ (0.04 mol, 5.16 g), and Na₂CO₃ (0.02 mol, 2.12 g) were added into 80 mL of H₂O to prepare the alkali solution. Under the condition of continuous stirring, the salt solution and alkali solution were simultaneously dropped into a three-neck flask with 40 mL of H₂O at 85 °C through a peristaltic pump with 3.0 mL/min pumping rate. The reaction was kept at 85 °C for another 40 min with stirring and then crystallized at 70 °C for 19 h. After filtration, drying, and grinding, Ca–Al LDH (labeled as Ca-LDH-2) was obtained. Finally, calcined Ca–Al LDH (labeled...
as Ca-LDO-2) was obtained by roasting Ca-LDO-2 at 500 °C for 2 h and crushing through 200 mesh sieve.

**Characterization of Calcined Ca–Al LDH.** The crystal structures of Ca–Al LDH and calcined Ca–Al LDH were characterized by X-ray diffraction (XRD, DX-2700, Haoyuan instrument, China). The continuous scanning mode of Cu Kα ray (λ = 0.154056 nm) was used. The scanning range of 2θ was from 10 to 90°, and the scanning speed was 0.02°/s. The tube voltage was 30 kV, and the tube current was 40 mA.

The specific surface area, pore size, and pore volume of calcined Ca–Al LDH were measured by the low-temperature N₂ adsorption–desorption method (AutosORB-iQ, Quantachrome, USA). The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) formula, and the pore size and volume were calculated by the Barrett–Joyner–Halenda (BJH) formula.

Calcined Ca–Al LDH was also characterized by the thermogravimetric analysis (HCT-I, Heven Instrument, China). The test temperature was programmed from room temperature to 650 °C with a heating rate of 10 °C/min. The composition of calcined Ca–Al LDH was tested by ICP-OES (PerkinElmer 8300, USA) after the sample was dissolved in HNO₃.

**Adsorption Performance of Calcined Ca–Al LDH.** Glycophosate (0.0527 g) was dissolved in water. And it was added into a 1000 mL volumetric flask to prepare a 50 mg/L glycophosate solution. The adsorbent (0.14 g) and 100 mL of the glycophosate solution (50 mg/L) were added into a 150 mL conical flask. The conical flask was placed in a constant temperature shaking box for shaking adsorption (30 °C, 220 rpm). After shaking for 1 h, the adsorbent was removed by filtration. Then, 4 mL of 50% H₂SO₄ 2 mL of 250 g/L KBr solution, and 4 mL of 14 g/L NaNO₃ solution were successively added to the filtrate. After shaking and standing for 30 min, the ultraviolet spectrophotometer (λ = 243 nm) was used for detection.

The adsorbed Ca-LDO-1 was dried and calcined at 500 °C for 2 h and then used in the next batch of adsorption experiments to investigate the reusability of Ca-LDO-1.

**REFERENCES**

(1) Pereira, H. A.; Hernandes, P. R. T.; Netto, M. S.; Reske, G. D.; Viecoli, V.; Oliveira, L. F. S.; Dotto, G. L. Adsorbents for glyphosate removal in contaminated waters: a review. *Environ. Chem. Lett.* 2021, 19, 1525–1543.

(2) Duan, C.; Zhang, Y.; Li, J.; Kang, L.; Xie, Y.; Qiao, W.; Zhu, C.; Luo, H. Rapid Room-Temperature Preparation of Hierarchically Porous Metal-Organic Frameworks for Efficient Uranium Removal from Aqueous Solutions. *Nanomaterials* 2020, 10, 1539–1552.

(3) Paéz, M. R.; Ochoa-Muñoz, Y.; Rodriguez-Páez, J. E. Efficient removal of a glyphosate-based herbicide from water using ZnO nanoparticles (ZnO-NPs). *Bioscat. Agric. Biotechnol.* 2019, 22, 101434–101447.

(4) Ren, Z.; Dong, Y.; Liu, Y. Enhanced Glyphosate Removal by Montmorillonite in the Presence of Fe(III). *Ind. Eng. Chem. Res.* 2014, 53, 14485–14492.

(5) Park, H.; May, A.; Portilla, L.; Dietrich, H.; Münch, F.; Rejeck, T.; Sarcletti, M.; Banspal, I.; Zahn, D.; Halik, M. Magnetite nanoparticles as efficient materials for removal of glyphosate from water. *Nature Sustainability* 2020, 3, 129–135.

(6) Jia, D.; Liu, M.; Xia, J.; Li, C. Effective removal of aqueous glyphosate using CuFe₂O₄@biochar derived from phragmites. *J. Chem. Technol. Biotechnol.* 2020, 95, 196–204.

(7) Chubar, N.; Gilmour, R.; Gerda, V.; Mičušk, M.; Omastova, M.; Heister, K.; Man, P.; Fraissard, J.; Zaitsev, V. Layered double hydroxides as the next generation inorganic anion exchangers: Synthetic methods versus applicability. *Adv. Colloid Interface Sci.* 2017, 245, 62–80.

(8) Gu, P.; Zhang, S.; Li, X.; Wang, X.; Wen, T.; Jehan, R.; Alsaeedi, A.; Hayat, T.; Wang, X. Recent advances in layered double hydroxide-based nanomaterials for the removal of radionuclides from aqueous solution. *Environ. Pollut.* 2018, 240, 493–505.

(9) Xu, S.-d.; Li, D.; Guo, X.-y.; Yan, W.; Gao, J. Selenium(VI) removal from caustic solution by synthetic Ca-Al-Ci layered double hydroxides. *Trans. Nonferrous Met. Soc. China* 2019, 29, 1763–1775.

(10) Hu, Y.; Wang, X.; Zou, Y.; Wen, T.; Wang, X.; Alsaeedi, A.; Hayat, T.; Wang, X. Superior sorption capacities of Ca-Ti and Ca-Al bimetallic oxides for U(VI) from aqueous solutions. *Chem. Eng. J.* 2017, 316, 419–428.

(11) Liapain, M.; Zhu, J.; Xu, Y.; Sun, L.; Zhu, R. Fabrication of layered double hydroxide/carbon nanomaterial for heavy metals removal. *Appl. Clay Sci.* 2020, 199, 105867–105879.

(12) Dias, A. C.; Fontes, M. P. F. Arsenic(V) removal from water using hydrotalcites as adsorbents: A critical review. *Appl. Clay Sci.* 2020, 191, 10615–10626.

(13) Mandal, S.; Kalaivanan, S.; Mandal, A. B. Polyethylene glycol-modified layered double hydroxides: synthesis, characterization, and study on adsorption characteristics for removal of acid orange II from aqueous solution. *ACS Omega* 2019, 4, 3745–3754.

(14) Cui, J.; Wei, C.; Zhang, M.; Zhu, J.; Li, F.; Du, X.; Chen, L.; Li, C. 2D to 3D controllable synthesis of three Zn-Co-LDHs for rapid adsorption of MO by TEA-assisted hydrothermal method. *Appl. Surf. Sci.* 2020, 534, 147564–147575.

(15) Zhang, H.; Chen, H.; Azat, S.; Mansurov, Z. A.; Liu, X.; Wang, J.; Su, X.; Wu, R. L. Super adsorption capability of rhombic dodecahedral Ca-Al layered double oxides for Congo red removal. *J. Alloys Compd.* 2018, 768, 572–581.

(16) Qi, L.; Liu, K.; Wang, R.; Li, J.; Zhang, Y.; Chen, L. Removal of chlorine ions from desulfurization wastewater by modified fly ash hydrotalcite. *ACS Omega* 2020, 5, 31665–31672.

(17) Chen, S.; Xu, Y.; Tang, Y.; Chen, W.; Chen, S.; Hu, L.; Boulon, G. Pretreatment by recyclable Fe₂O₃@Mg/Al-CO₃-LDH magnetic nano-adsorbent to dephosphorize for the determination of trace F and Cl in phosphorus-rich solutions. *RSC Adv.* 2020, 10, 44361–44372.

(18) Li, F.; Wang, Y.; Yang, Q.; Evans, D. G.; Forano, C.; Duan, X. Study on adsorption of glyphosate (N-phosphonomethyl glycine) pesticide on MgAl-layered double hydroxides in aqueous solution. *J. Hazard. Mater.* 2005, 125, 89–95.
(19) Khenififi, A.; Derriche, Z.; Mousty, C.; Prévot, V.; Forano, C. Adsorption of Glyphosate and Glufosinate by Ni$_2$AlNO$_3$ layered double hydroxide. *Appl. Clay Sci.* **2010**, *47*, 362−371.

(20) Cai, Y.; Ma, Y.; Feng, J.; Zhu, M.; Wang, X.; Lv, Z.; Fang, M.; Tan, X.; Wang, X. Insight into the performance and mechanism of low-cost phytic acid modified Zn-Al-Ti LMO for U(VI) removal. *Chem. Eng. J.* **2020**, *402*, 125510−125519.

(21) Milagres, J. L.; Bellato, C. R.; Vieira, R. S.; Ferreira, S. O.; Reis, C. Preparation and evaluation of the Ca-Al layered double hydroxide for removal of copper(II), nickel(II), zinc(II), chromium(VI) and phosphate from aqueous solutions. *J. Environ. Chem. Eng.* **2017**, *5*, 5469−5480.

(22) Wei, L.; Zietzschmann, F.; Rietveld, L. C.; Halem, D. Fluoride removal by Ca-Al-CO$_3$ layered double hydroxides at environmentally-relevant concentrations. *Chemosphere* **2020**, *243*, 125307−125315.

(23) Xu, Y.; Ding, Y.; Wang, J.; Zhu, M.; Yang, M.; Qian, G.; Sun, Y. In-situ synthesis of calcium aluminum layered double hydroxides for advanced treatment of leachate biochemical tail water. *Sci. Total Environ.* **2020**, *701*, 134891−134899.

(24) Li, D.; Yan, W.; Guo, X.; Tian, Q.; Xu, Z.; Zhu, L. Removal of selenium from caustic solution by adsorption with Ca-Al layered double hydroxides. *Hydrometallurgy* **2020**, *191*, 105231−105239.

(25) Lesbani, A.; Asri, F.; Palapa, N. R.; Taher, T.; Rachmat, A. Efficient removal of methylene blue by adsorption using composite based Ca/Al layered double hydroxide-biochar. *Global NEST J.* **2020**, *22*, 250−257.

(26) Zhang, S.; Yu, F.; He, W.; Zheng, D.; Cui, H.; Lv, L.; Tang, W.; Han, N. Experimental investigation of chloride uptake performances of hydrocalumite-like Ca-Al LDHs with different microstructures. *Appl. Sci.* **2020**, *10*, 3760−3775.

(27) Zhou, X.; Zhang, C. Effect of preparation method on the catalytic property of calcined Ca−Al hydrotalcite for the synthesis of ethyl methyl carbonate. *ACS Omega* **2021**, *6*, 5056−5060.

(28) Wan, D.; Liu, H.; Liu, R.; Qu, J.; Li, S.; Zhang, J. Adsorption of nitrate and nitrite from aqueous solution onto calcined (Mg−Al) hydrotalcite of different Mg/Al ratio. *Chem. Eng. J.* **2012**, *195-196*, 241−247.

(29) Han, S. J.; Bang, Y.; Kwon, H. J.; Lee, H. C.; Hiremath, V.; Song, I. K.; Seo, J. G. Elevated temperature CO$_2$ capture on nanostructured MgO-Al,O$_3$ aerogel: Effect of Mg/Al molar ratio. *Chem. Eng. J.* **2014**, *242*, 357−363.