Preparation and Adsorption Properties of Soybean Dreg/Hydrocalumite Composites

Bei Tang, Guanping Peng, Deyi Luo, and Xi Zhou*

ABSTRACT: The application of biomass-based composites in the field of adsorption has attracted extensive attention. Herein, soybean dreg/hydrocalumite composites were prepared by in situ self-assembly from soybean dregs and applied to the adsorption of Congo Red (CR). The composites were characterized by scanning electron microscopy, X-ray diffraction, Fourier infrared spectroscopy, and N2 physical adsorption–desorption. The results showed that the adsorption property of soybean dregs/hydrocalumite for CR was better than that of soybean dregs or hydrocalumite. Effects of preparation and adsorption conditions on the adsorption of CR by soybean dregs/hydrocalumite were also investigated. The removal rate of soybean dregs/hydrocalumite (30%BD-LDH) prepared under the optimized conditions reached 97.4% with a 486.8 mg·g\(^{-1}\) adsorption capacity. Also, the adsorption capacity of 30%BD-LDH was about 2.4 times and 3.0 times that of hydrocalumite and soybean dregs, respectively. In addition, the adsorption process of CR by 30%BD-LDH was more in line with the pseudo-second-order kinetic and Langmuir isothermal models.

INTRODUCTION

Soybean dreg were the main byproducts of the soybean product processing industry, with an annual output of more than 20 million tons. The soybean dreg was easy to decay and difficult to preserve since it contained a lot of protein and water. Except for a small part was used in the area of animal feeds, food production, and functional component extraction, most of the soybean dregs are discarded or burned, resulting in waste resources and environmental pollution.\(^1\) Therefore, the resource utilization of soybean dregs had become a key technical problem to be solved in this area.

The soybean dreg could be used as a cheap adsorption material since it contains rich oxygen-containing functional groups and has a loose and porous structure.\(^2\)\(^−4\) However, the specific surface area of the soybean dreg is small; therefore, its adsorption performance needs to be further improved. According to the previous literature, the main methods to improve the adsorption properties of biomass adsorbents included modification, carbonization, and preparation of composites.\(^5\)\(^−14\) Recently, combined with the advantages of biomass organic adsorption materials and traditional inorganic adsorption materials, the organic/inorganic composite adsorbents had attracted much attention.\(^15\)\(^−32\) For example, Abu-Danso et al. found that the maximum adsorption capacities of clay/cellulose composites for Pb (II) and Cd (II) reach 389.78 and 115.96 mg·g\(^{-1}\), respectively.\(^16\) Mirjavadi et al. reported that the magnetic zeolite/cellulose nanofibers showed high adsorption capacity for the removal rate of Zn\(^{2+}\).\(^17\) Olu-
and full of folds and pores, which was conducive to the adsorption of CR. Typical layered regular hexagonal crystals could be seen from Figure 1c,d, indicating that as-synthesized LDH4 had a typical hydrotalcite-like layered structure. Hydrocalumite flakes were stacked and aggregated in different sizes, mainly between 1 and 2 μm. Compared with hydrocalumite, the surface morphology and structure of 30%BD-LDH4 changed remarkably, as shown in Figure 1e,f. Hydrocalumite crystals grown on the cellulose skeleton of BD were distributed in a petal shape, resulting in the good dispersion of hydrocalumite crystals. In addition, the size of 30%BD-LDH4 was smaller than that of BD. The reason might be that BD was hydrolyzed under strong alkaline preparation conditions during the preparation of 30%BD-LDH4, which reduced the polymerization degree of BD.19

BD, LDH4, and 30%BD-LDH4 were characterized by X-ray diffraction (XRD), and the results are shown in Figure 2. In the XRD spectrum of BD, the wide and low diffraction peak at 22° was the diffraction peak of cellulose in BD.8,10 The characteristic diffraction peaks of hydrocalumite appeared at 11.3, 23.0, 31.1, 38.9, and 47.5° in the XRD spectrum of LDH4 and 30%BD-LDH4. The strong peaks at 11.3 and 23.0° were (003) and (006) crystal plane diffraction of hydrocalumite, which was a typical double-layer structure.9,21 However, the peak strength of 30%BD-LDH4 was weaker than that of LDH4 at the corresponding angle, indicating that the crystallinity of 30%BD-LDH4 was relatively low. The diffraction peaks at 29.4, 36.0, 39.4, 47.5, and 48.5° indicate that there was a small amount of impurity CaCO₃ in LDH4 and 30%BD-LDH4. In addition, the cellulose diffraction peak was not observed in the XRD spectrum of 30%BD-LDH4, indicating that BD was wrapped by hydrocalumite flakes, which was consistent with the SEM characterization results (Figure 1).27

The functional groups of BD, LDH4, and 30%BD-LDH4 were determined by Fourier transform infrared (FT-IR) spectroscopy. As shown in Figure 3, the spectrum peaks of BD at 3295 and 2914 cm⁻¹ were assigned to the stretching
vibration of $\text{−OH}$ and $\text{C−H}$, respectively. The peaks at 1738, 1631, and 1534 cm$^{-1}$ were related to the stretching vibration of $\text{C=O}$ and $\text{C=C}$, respectively. The strong peak at 1037 cm$^{-1}$ was attributed to the stretching vibration of $\text{C−O}$ and $\text{C−O}$. As shown by the results, BD had hydroxyl, carboxyl, and other oxygen-containing functional groups, which could provide more active sites for CR adsorption. The absorption peaks at 3642 and 3585 cm$^{-1}$ in the spectrum of LDH were attributed to the stretching vibration of Ca$^{2+}$- and Al$^{3+}$-bonded OH on the laminate. Also, the peaks at 1357−1476 and 873 cm$^{-1}$ were caused by the stretching vibration of CO$_3^{2−}$. In addition, the characteristic absorption peaks of BD and hydrocalumite were found in the FT-IR spectrum of 30% BD-LDH4, indicating that BD was successfully introduced into the composite.

The specific surface area ($S_{\text{BET}}$), pore size distribution, and pore volume of adsorbents were detected by N$_2$ physical adsorption−desorption, and the results are shown in Figure 4 and Table 1. The $S_{\text{BET}}$ of 30%BD-LDH4 (17.106 m$^2$·g$^{-1}$) was about 10.3 times and 3.4 times that of BD (1.657 m$^2$·g$^{-1}$) and LDH4 (4.983 m$^2$·g$^{-1}$), respectively. The BJH average pore sizes of BD, LDH4, and 30%BD-LDH4 were 3.395, 4.306, and 32.524 nm, respectively. Also, the pore volumes of BD, LDH4, and 30%BD-LDH4 were 0.005, 0.026, and 0.106 cm$^3$·g$^{-1}$, respectively. The above results showed that the pore diameter and pore volume of 30%BD-LDH4 were also much larger than those of BD and LDH4. According to the literature, the growth of hydrocalumite crystals on the BD surface was limited with a smaller size and uniform dispersion. The spherical network structure formed by the coating of BD with hydrocalumite flakes not only increased the $S_{\text{BET}}$ of 30%BD-LDH4 but also created much new pores with a large size. Generally, the large pore size of the adsorbent was conducive to the entry of macromolecules such as CR. Also, the high pore volume was conducive to the improvement of adsorption capacity. In addition, the $S_{\text{BET}}$, pore size, and pore volume of 30%BD-LDH4 after adsorption of CR were much lower than those of the fresh sample. The reason might be that the surface and pores of 30%BD-LDH4 were filled with adsorbed CR.

### Evaluation of Adsorption Properties

#### Effect of Adsorbents on the Adsorption of CR

The adsorption properties of BD, LDH4, and 30%BD-LDH4 for CR were investigated under the conditions of an 800 mg·L$^{-1}$ CR initial concentration, a 1 g·L$^{-1}$ adsorbent dosage, 30 °C, and 2 h, and the results are shown in Figure 5. The removal rate was 24.4% with a 195.6 mg·g$^{-1}$ adsorption capacity using BD as an adsorbent. The adsorption performance of LDH4 was slightly better than that of BD. The removal rate was 29.8% with a 238.5 mg·g$^{-1}$ adsorption capacity in the presence of LDH4. However, the removal rate was quickly increased to 72.8% with a 582.7 mg·g$^{-1}$ adsorption capacity by replacing the adsorbent with the 30%BD-LDH4 composite. The results showed that the adsorption property of 30%BD-LDH4 for CR was significantly better than that of single BD and LDH4. According to the characterization results of N$_2$ physical adsorption−desorption (Table 1), the $S_{\text{BET}}$, pore size, and pore volume of 30%BD-LDH4 were much higher than those of BD and LDH4.
BD and LDH4, which might be one of the reasons for the better adsorption performance of 30%BD-LDH4.

In addition, the effects of BD dosage on the adsorption of CR by soybean dreg/hydrocalumite composites were also investigated. When the amount of BD increased from 20% (based on the total mass of the composite) to 30%, the adsorption removal rate of CR increased from 66.7 to 72.8%, and the adsorption capacity increased from 533.8 to 582.7 mg·g⁻¹. However, the adsorption removal rate of CR decreased from 72.8 to 44.3% with the further increase of the BD dosage to 50%. Also, the adsorption capacity also decreased from 582.7 to 354.0 mg·g⁻¹. These results showed that proper addition of BD was conducive to the improvement of the adsorption performance of soybean dreg/hydrocalumite composites, but excessive addition of BD would reduce the adsorption capacity. The reusability of 30%BD-LDH4 was also investigated. The results showed that the adsorption capacity of reused 30%BD-LDH4 for the third run was slightly lower than that of fresh 30%BD-LDH4. It might be caused by the incomplete desorption of CR.

Effects of Preparation and Adsorption Conditions on the Adsorption of CR by Soybean Dregs/Hydrocalumite. The ratio of raw materials has a remarkable influence on the structure and crystal growth of hydrotalcite-like materials. The effects of Ca/Al molar ratio on the adsorption of CR by soybean dreg/hydrocalumite composites were investigated under the conditions of an 800 mg·L⁻¹ CR initial concentration, a 1 g·L⁻¹ adsorbent dosage, 30 °C, and 2 h. As shown in Figure 6a, the adsorption capacity of soybean dregs/hydrocalumite increased from 58.7 to 582.7 mg·g⁻¹ with increasing Ca/Al molar ratio of raw materials from 1:1 to 4:1. However, the adsorption capacity of soybean dregs/hydrocalumite decreased to 541.6 mg·g⁻¹ with the further increase of Ca/Al molar ratio to 5:1. Therefore, the optimum Ca/Al molar ratio of soybean dregs/hydrocalumite was 4:1.

The effect of CR initial concentration on the adsorption of CR by 30%BD-LDH4 was also investigated in the range of 600–1200 mg·L⁻¹ under the conditions of a 1 g·L⁻¹ adsorbent dosage, 30 °C, and 2 h. As shown by the results in Figure 6b, the adsorption capacity of 30%BD-LDH4 for CR increased from 538.0 to 621.4 mg·g⁻¹ with the increase of the initial concentration of CR from 600 to 1200 mg·L⁻¹. However, the removal rate decreased from 89.7 to 51.8%. It was consistent with the expected results. The contact probability between CR and the adsorbent was improved with increasing CR initial concentration. In addition, the greater the concentration difference between CR and the adsorbent, the stronger the mass-transfer driving force, resulting the improvement of adsorption capacity. However, the adsorption sites provided by the adsorbent were fixed. The increase of CR initial concentration would lead to the decrease of removal rate.

The adsorbent dosage had a significant effect on the adsorption efficiency. The effect of 30%BD-LDH4 dosage on the adsorption of CR was investigated under the conditions of an 800 mg·L⁻¹ CR initial concentration, 30 °C, and 2 h, and the results are shown in Figure 6c. When the 30%BD-LDH4...
dosage increased from 1 to 2.4 g·L⁻¹, the adsorption capacity of 30%BD-LDH4 decreased from 582.7 to 329.4 mg·g⁻¹, but the CR removal rate increased from 72.8 to 98.8%.

In addition, the effect of adsorption time on the adsorption of CR by 30%BD-LDH4 was also investigated under the conditions of an 800 mg·L⁻¹ CR initial concentration, a 1.6 g·L⁻¹ 30%BD-LDH4 dosage, and 30 °C. As shown in Figure 6d, the adsorption capacity and removal rate increased with prolonging adsorption time. When the adsorption time was extended from 5 to 180 min, the adsorption capacity increased rapidly from 311.5 to 486.8 mg·g⁻¹, and the removal rate of CR increased quickly from 62.3 to 97.4%. However, the adsorption capacity and removal rate did not change significantly with further prolonging of the adsorption time to 540 min.

**Adsorption Kinetics.** In order to further study the adsorption rate and adsorption mechanism of CR by 30%BD-LDH4, the pseudo-first-order kinetic model (1), pseudo-second-order kinetic model (2), and intra-particle diffusion model (3) were selected to analyze the adsorption process. The formula of each model was as follows:

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1 t
\]

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

| Qₑ₀ (mg·g⁻¹) | ρ₀ (mg·L⁻¹) | k₁ (min⁻¹) | Qₑ (mg·g⁻¹) | R² | k₂ (g·mg⁻¹·min⁻¹) | Qₑ (mg·g⁻¹) | R² |
|--------------|-------------|-------------|-------------|----|------------------|-------------|----|
| 432          | 700         | 0.0126      | 61.1        | 0.944 | 0.0018          | 435         | 0.999 |
| 494          | 800         | 0.0103      | 88.4        | 0.888 | 0.0004          | 500         | 1.00 |
| 547          | 900         | 0.0108      | 156         | 0.980 | 0.0003          | 556         | 0.999 |

Figure 7. Pseudo-first-order kinetic model (a), pseudo-second-order kinetic model (b), and intra-particle diffusion model (c) of CR adsorption by 30%BD-LDH4.
Table 3. Particle Diffusion Model Fitting Parameters of CR Adsorption by 30%BD-LDH4

| T/K    | ρ0 (mg·L⁻¹) | Kt (mg·g⁻¹·min⁻¹) | Ct | R²   | ρ0 (mg·g⁻¹·min⁻¹) | Kt (mg·g⁻¹·min⁻¹) | Ct | R²   | ρ0 (mg·g⁻¹·min⁻¹) | Kt (mg·g⁻¹·min⁻¹) | Ct | R²   |
|--------|-------------|-------------------|----|------|------------------|-------------------|----|------|------------------|-------------------|----|------|
| 293    | 700         | 23.9              | 254| 0.972| 700              | 2.63              | 397| 0.993| 700              | 0.248             | 428| 0.891|
| 303    | 800         | 29.9              | 254| 0.964| 800              | 7.42              | 396| 1.00 | 800              | 0.605             | 481| 0.972|
| 313    | 900         | 31.3              | 258| 0.979| 900              | 12.7              | 376| 0.997| 900              | 1.333             | 521| 0.850|

Figure 8. Langmuir adsorption isotherm (a) and Freundlich adsorption isotherm (b).

Table 4. Langmuir and Freundlich Isotherm Parameters for Adsorption of CR by 30%BD-LDH4

| T/K    | Qm/(mg·g⁻¹) | QL/(mg·g⁻¹) | K1/(L·g⁻¹) | R²   | n   | Kf/(mg⁻¹·L·g⁻¹) | R²   |
|--------|-------------|-------------|------------|------|-----|-----------------|------|
| 293    | 775         | 0.0292      | 833        | 0.984| 310 | 6.71           | 0.862|
| 303    | 650         | 0.0711      | 667        | 0.999| 445 | 16.9           | 0.943|
| 313    | 584         | 0.0904      | 588        | 0.999| 444 | 24.3           | 0.843|

where Qₑ and Qₑ are the adsorption capacity (mg·g⁻¹) at adsorption equilibrium and t (min), respectively; K₁ (min⁻¹), K₂ (g·mg⁻¹·min⁻¹), and K₃ (mg·g⁻¹·min⁻¹) are the rate constants of the pseudo-first-order kinetic model, pseudo-second-order kinetic model, and intra-particle diffusion model, respectively. Cₛ is the constant related to the thickness of the reaction boundary layer.

The kinetic model and fitting parameters of CR adsorption by 30%BD-LDH4 are shown in Figure 7 and Tables 2 and 3. As shown by the results, the correlation coefficient of the pseudo-second-order kinetic model (R² > 0.999) was higher than that of the pseudo-first-order kinetic model (R² > 0.888). Also, the calculated theoretical adsorption capacity (Qₑ) obtained by the pseudo-second-order kinetic model was closer to the experimental adsorption capacity (Qₑexp). The results showed that the adsorption process of CR by 30%BD-LDH4 followed the pseudo-second-order kinetic model. As shown by the results in Table 3, the adsorption process of CR by 30% BD-LDH4 was divided into three different stages. The straight line in the first stage did not pass through the origin, indicating that internal diffusion was not the only rate control step in the adsorption process. In the whole adsorption process, liquid film diffusion and internal diffusion were dominant. The C value increased with the progressive adsorption stage and the increase of CR concentration, indicating that the boundary layer effect increased. The C value of each stage was not 0, indicating that the adsorption process was controlled by a variety of diffusion mechanisms.

Adsorption Thermodynamics. The maximum adsorption capacity of the adsorbent and the interaction behavior could be predicted by the adsorption isotherm model. Therefore, the Langmuir isotherm model (4) and Freundlich isotherm model (5) were selected to analyze the adsorption of CR by 30%BD-LDH4. The corresponding fitting equations were as follows:

\[
Q_e = k_1 t^{0.5} + C_s \tag{3}
\]

where Qₑ and Qₑ are the adsorption capacity (mg·g⁻¹) at adsorption equilibrium and t (min), respectively; K₁ (min⁻¹), K₂ (g·mg⁻¹·min⁻¹), and K₃ (mg·g⁻¹·min⁻¹) are the rate constants of the pseudo-first-order kinetic model, pseudo-second-order kinetic model, and intra-particle diffusion model, respectively. Cₛ is the constant related to the thickness of the reaction boundary layer.

\[
\frac{\rho_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{\rho_e}{Q_m} \tag{4}
\]

\[
\ln Q_e = \ln K_f + \frac{1}{n} \ln \rho_e \tag{5}
\]

where ρₑ is the concentration of CR (mg·L⁻¹) at adsorption equilibrium; Qₑ is the equilibrium adsorption capacity of 30% BD-LDH4 for CR (mg·g⁻¹); Qₑ is the theoretical maximum adsorption capacity of 30%BD-LDH4 for CR (mg·g⁻¹); and K₁, K₂, and n are the constants of Langmuir, Freundlich, and adsorption strength, respectively.

The isotherms and fitting parameters of adsorption thermodynamics are shown in Figure 8 and Table 4. The correlation coefficient fitted by the Langmuir isotherm model (R² > 0.984) was higher than that of the Freundlich isotherm model (R² > 0.843). It indicated that the Langmuir isotherm model could better fit the adsorption process of CR by 30%
BD-LDH4. The theoretical adsorption capacity calculated by the Langmuir isothermal model was closer to the actual adsorption capacity, indicating that the adsorption of CR by 30%BD-LDH4 was monolayer adsorption. The theoretical maximum adsorption capacity decreased with the increase of temperature, indicating that the increase of temperature was not conducive to the adsorption.36 In addition, the \( n \) values of the Freundlich isotherm model were higher than 1, indicating that CR was favorable to be adsorbed on 30%BD-LDH4.

The thermodynamic parameters Gibbs free energy change (\( \Delta G, \text{kJ} \cdot \text{mol}^{-1} \)), standard enthalpy change (\( \Delta H, \text{kJ} \cdot \text{mol}^{-1} \)), and standard entropy change (\( \Delta S, \text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \)) in the process of CR adsorption by 30%BD-LDH4 were analyzed to understand the spontaneity and feasibility of the adsorption process. The calculation equations were as follows:

\[
\Delta G = -RT \ln K_d \\
\ln K_d = \frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]

where \( T \) is the absolute temperature (K), \( R \) is the ideal gas constant (8.314 J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}), and \( K_d \) is the distribution coefficient.

The thermodynamic parameters of CR adsorption by 30%BD-LDH4 are shown in Table 5. The value of \( \Delta G \) was negative, indicating the spontaneity and feasibility of the adsorption process. The value of \( \Delta G \) increased with the increase of temperature, meaning that a low temperature was conducive to the adsorption of CR by 30%BD-LDH4. The value of \( \Delta H \) was negative, meaning that the adsorption process was exothermic. The value of \( \Delta S \) was negative, indicating that the randomness of the solid–liquid interface in the adsorption process was reduced.

**Comparison of Adsorption Properties.** For comparison, the adsorption performance of 30%BD-LDH4 for CR was compared with those of other similar adsorption materials reported by the previous literature12–14,36–39 and the results are shown in Table 6. The \( Q_m \) of these reported adsorbents for CR was in the range of 79.6–541.8 mg g\(^{-1}\), which was lower than that of 30%BD-LDH4 (666.7 mg g\(^{-1}\)). The above results showed that the adsorption performance of 30%BD-LDH4 for CR was better than that of similar adsorption materials reported by the previous literature. In addition, 30%BD-LDH4 also had the advantages of cheap raw materials, simple preparation methods, environmental protection, and safety. Therefore, 30%BD-LDH4 had good application potential in the field of wastewater adsorption treatment.

**Adsorption Mechanism.** In order to analyze the possible adsorption mechanism of 30%BD-LDH4 for CR, the 30%BD-LDH4 samples before and after saturated adsorption of CR were characterized by XRD and FT-IR, respectively. As shown by the XRD results in Figure 9, the peak intensity of 30%BD-LDH4 was decreased after adsorption of CR, which might be caused by the interaction between CR molecules and the 30% BD-LDH4 surface.37 The FT-IR results are shown in Figure 10. After 30%BD-LDH4 adsorbed CR, new peaks appeared at 1044, 1175, and 1226 cm\(^{-1}\), which were caused by the stretching vibration of \( \text{SO}_3^- \) of the sulfonic acid group in the CR molecule. It indicated that CR was adsorbed on the surface of 30%BD-LDH4.37 The peaks at 422 and 528 cm\(^{-1}\) corresponding to the lattice vibration of metal ions are significantly weakened, indicating that metal ions on the laminate adsorb CR molecules through electrostatic attraction.36 The –OH peaks at 3515 and 3670 cm\(^{-1}\) basically disappeared, indicating that the –OH on the surface of 30% BD-LDH4 can form hydrogen bonds with N–H or N=N in CR molecules and participate in the adsorption process.40 Therefore, the adsorption of CR by 30%BD-LDH4 might rely on electrostatic attraction and hydrogen bonding.

**Table 5. Adsorption Thermodynamic Parameters of CR by 30%BD-LDH4**

| T/K | \( \Delta G/(\text{kJ} \cdot \text{mol}^{-1}) \) | \( \Delta H/(\text{kJ} \cdot \text{mol}^{-1}) \) | \( \Delta S/(\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \) |
|-----|---------------------------------|---------------------------------|---------------------------------|
| 293 | -11.4                           |                                 |                                 |
| 303 | -8.79                           | -89.1                           | -0.265                          |
| 313 | -6.14                           |                                 |                                 |

indicating the feasibility and spontaneity of the adsorption process. The value of \( \Delta G \) increased with the increase of temperature, indicating that the increase of temperature was not conducive to the adsorption of CR by 30%BD-LDH4. The value of \( \Delta H \) was negative, indicating that the adsorption process was exothermic. The value of \( \Delta S \) was negative, indicating that the randomness of the solid–liquid interface in the adsorption process was reduced.

**Comparison of Adsorption Properties.** For comparison, the adsorption performance of 30%BD-LDH4 for CR was compared with those of other similar adsorption materials reported by the previous literature12–14,36–39 and the results are shown in Table 6. The \( Q_m \) of these reported adsorbents for CR was in the range of 79.6–541.8 mg g\(^{-1}\), which was lower than that of 30%BD-LDH4 (666.7 mg g\(^{-1}\)). The above results showed that the adsorption performance of 30%BD-LDH4 for CR was better than that of similar adsorption materials reported by the previous literature. In addition, 30%BD-LDH4 also had the advantages of cheap raw materials, simple preparation methods, environmental protection, and safety. Therefore, 30%BD-LDH4 had good application potential in the field of wastewater adsorption treatment.

**Adsorption Mechanism.** In order to analyze the possible adsorption mechanism of 30%BD-LDH4 for CR, the 30%BD-LDH4 samples before and after saturated adsorption of CR were characterized by XRD and FT-IR, respectively. As shown by the XRD results in Figure 9, the peak intensity of 30%BD-LDH4 was decreased after adsorption of CR, which might be caused by the interaction between CR molecules and the 30% BD-LDH4 surface.37 The FT-IR results are shown in Figure 10. After 30%BD-LDH4 adsorbed CR, new peaks appeared at 1044, 1175, and 1226 cm\(^{-1}\), which were caused by the stretching vibration of \( \text{SO}_3^- \) of the sulfonic acid group in the CR molecule. It indicated that CR was adsorbed on the surface of 30%BD-LDH4.37 The peaks at 422 and 528 cm\(^{-1}\) corresponding to the lattice vibration of metal ions are significantly weakened, indicating that metal ions on the laminate adsorb CR molecules through electrostatic attraction.36 The –OH peaks at 3515 and 3670 cm\(^{-1}\) basically disappeared, indicating that the –OH on the surface of 30% BD-LDH4 can form hydrogen bonds with N–H or N=N in CR molecules and participate in the adsorption process.40 Therefore, the adsorption of CR by 30%BD-LDH4 might rely on electrostatic attraction and hydrogen bonding.

**Table 6. Adsorption Properties of 30%BD-LDH4 and Other Materials**

| adsorbent          | temperature/°C | \( Q_m/\text{mg g}^{-1} \) | references | year |
|--------------------|----------------|--------------------------|------------|------|
| Chit/AILP-Kao      | 30             | 104.6                    | 12         | 2021 |
| CNF-Fe(0)@FeS      | 25             | 111.1                    | 13         | 2020 |
| Cel-TAS            | 30             | 541.8                    | 14         | 2019 |
| Al(OH)\(_2\)/CuMn-Al-LDH | 30            | 136.99                   | 36         | 2019 |
| MNP@NiFe LDH       |                | 79.6                     | 37         | 2021 |
| NiAl LDH           | 25             | 120.5                    | 38         | 2017 |
| IL-LDH             | 20             | 303.03                   | 39         | 2019 |
| 30%BD-LDH4         | 30             | 666.7                    | present study | 2021 |
**CONCLUSIONS**

Compared with a single soybean dreg and hydrocalumite, the soybean dreg/hydrocalumite composite had a higher specific surface area, pore diameter, and pore volume, which made it perform better adsorption for CR. The amount of the soybean residue, the molar ratio of Ca/Al, the initial concentration of CR, adsorbent dosage, and adsorption time had significant effects on the adsorption property of soybean dregs/hydrocalumite for CR. Among the investigated soybean dreg/hydrocalumite composites, 30%BD-LDH showed the best adsorption property. Under the optimized conditions, the adsorption removal rate of CR by 30%BD-LDH could reach 97.4% with a 486.8 mg g⁻¹ adsorption capacity. The adsorption process of CR by 30%BD-LDH was more in line with the pseudo-second-order kinetic and Langmuir isothermal adsorption process of CR by 30%BD-LDH. The theoretical maximum adsorption capacity reached 97.4% with a 486.8 mg g⁻¹ adsorption removal rate of CR by 30%BD-LDH could reach 97.4% with a 486.8 mg g⁻¹ adsorption capacity. The adsorption process of CR by 30%BD-LDH was more in line with the pseudo-second-order kinetic and Langmuir isothermal models. The theoretical maximum adsorption capacity reached 666.7 mg g⁻¹ at 303 K, which was higher than that of similar adsorption materials reported in the literature. The results provide a feasible new method for the development of high-efficiency biomass composite adsorbents and the high-value utilization of soybean dregs.

**EXPERIMENTAL SECTION**

**Preparation of Adsorbents.** Pretreatment of soybean dreg was as follows: The fresh soybean dreg was washed with water until the filtrate was clear, then immersed in 95% ethanol solution for 3 h, and washed with 95% ethanol solution three times. After drying at 80 °C for 2 h, the solid material was crushed and passed through a 200 mesh sample sieve to obtain the product (marked as BD). Preparation of soybean dreg/hydrocalumite composites was as follows: BD (3.00 g) was added into a three-neck flask containing 80 mL of distilled water to prepare the soybean dreg homogenate. CaCl₂ (18.50 g) was added into 120 mL of water to prepare solution A. NaAlO₂ (3.28 g), Na₂CO₃ (3.20 g), and NaOH (2.40 g) were added into 120 mL of water to prepare solution B. Under the conditions of stirring at 80 °C, solutions A and B were simultaneously dropped into the three-neck flask containing the soybean dreg homogenate through a peristaltic pump with 2.0 mL/min. The reaction was carried out at 80 °C for 2 h and then crystallized at 80 °C for 17 h. After filtration, washing, drying, grinding, and crushing through a 200 mesh sieve to obtain the soybean dreg/hydrocalumite composite, the composite was marked as xBD-LDH, where x was the percentage of added BD in the total mass of the composite and y was the molar ratio of Ca/Al in the raw material.

The preparation method of hydrocalumite was similar to the preparation process of soybean dreg/hydrocalumite composites in the absence of soybean dregs.

**Characterization of Adsorbents.** The surface morphology of the absorbent was detected by SEM (Sigma 300, Zeiss, Germany) with a 3 kV acceleration voltage. The crystal structure of the absorbent was characterized by powder XRD (DX-2700BH, Haoyuan instrument, China) using the continuous scanning mode of the Cu Kα ray (λ = 0.154056 nm). The scanning range of 2θ ranged from 10 to 80°. The functional groups of the absorbent were analyzed by FT-IR (Nicolet iS5, Thermo Fisher, USA) in the range of 400 – 4000 cm⁻¹. The physical structure of the absorbent was tested by the N₂ adsorption–desorption method (Autosorb-iQ, Quantachrome, USA). The specific surface area (Sₐ) was calculated by the Brunauer–Emmett–Teller equation, and the pore size and volume were calculated by the Barrett–Joyner–Halenda equation.

**Adsorption Performance of Adsorbents.** CR was dissolved into 200 mL of distilled water, and then, the volume was fixed with a 1000 mL volumetric flask to prepare CR solutions with different concentrations in the range of 600–1200 mg L⁻¹. Typically, 50 mL of 800 mg L⁻¹ CR solution was transferred into a 250 mL conical flask. After adding 0.050 g of 30%BD-LDH₄, the mixture was sealed and placed in a desktop constant temperature oscillator with rotation (220 rpm) at 30 °C for 2 h. After centrifugation, the solid was filtered out using a 0.22 μm filter membrane. The absorbance of the filtrate was determined by spectrophotometry (λ = 498 nm), and the residual adsorption concentration was calculated by substituting the standard curve equation y = 0.0178x + 0.0078 (R² = 0.9999). The removal rate (η) and adsorption capacity (Q) of the adsorbent were calculated by eqs 8 and 9, respectively,

$$\eta = \frac{\rho_0 - \rho}{\rho_0} \times 100\% \tag{8}$$

$$Q = \frac{\rho_0 - \rho}{m} \times V \tag{9}$$

where ρ₀ and ρ are the concentrations of CR in the solution before and after adsorption, respectively, mg L⁻¹; m is the mass of the absorbent, g; and V is the volume of CR solution, L.

**AUTHOR INFORMATION**

**Corresponding Author**

Xi Zhou – Department of Food and Chemical Engineering, Shaoyang University, Shaoyang, Hunan 422000, P. R. China; orcid.org/0000-0002-6736-7160; Email: z_zhouxi@163.com

**Authors**

Bei Tang – Department of Food and Chemical Engineering, Shaoyang University, Shaoyang, Hunan 422000, P. R. China

Guanping Peng – Department of Food and Chemical Engineering, Shaoyang University, Shaoyang, Hunan 422000, P. R. China
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04460

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was funded by the Scientific Research Fund of Hunan Provincial Education Department of China (19A4444) and the Science and Innovation Project of Graduate Students in Shaoyang University of China (CX2019ST012).

REFERENCES
(1) Nguyen, T. A. H.; Ngo, H. H.; Guo, W. S.; Nguyen, T. V.; Zhang, J.; Liang, S.; Chen, S. S.; Nguyen, N. C. A comparative study on different metal loaded soybean milk by-product ‘okara’ for biosorption of phosphorus from aqueous solution. Bioresour. Technol. 2014, 169, 291–298.
(2) Nguyen, T. A. H.; Ngo, H. H.; Guo, W. S.; Pham, T. Q.; Li, F. M.; Nguyen, T. V.; Bu, X. T. Adsorption of phosphate from aqueous solutions and sewage using zirconium loaded okara (ZLO): fixed-bed column study. Sci. Total Environ. 2015, 523, 40–49.
(3) Gao, J.; Si, C.; He, Y. Application of soybean residue (okara) as a low-cost adsorbent for reactive dye removal from aqueous solution. Desalin. Water Treat. 2015, 53, 2266–2277.
(4) Li, Y.; Li, Y.; Zang, H.; Chen, L.; Meng, Z.; Li, H.; Ci, L.; Du, Q.; Wang, D.; Wang, C.; Li, H.; Xia, Y. ZnCl2-activated carbon from soybean dregs as a high efficiency adsorbent for cationic dye removal: isotherm, kinetic, and thermodynamic studies. Environ. Technol. 2020, 41, 2013–2023.
(5) Cai, S.; Zhang, Q.; Wang, Z.; Hua, S.; Ding, D.; Cai, T.; Zhang, R. Pyrrolic N-rich biochar without exogenous nitrogen doping as a functional material for bisphenol A removal: Performance and mechanism. Appl. Catal., B 2021, 291, 120093.
(6) 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.
(7) Marthy, T. P. K.; Gowrishankar, B. S.; Chandraprabha, M. N.; Krishna, R. H. Solution combustion synthesis of calcium aluminate nanocomposite using coffee husk extract as green fuel and its application in adsorptive amputation of anionic dyes. Mater. Res. Express 2020, 7, 035503.
(8) Wang, X.; Zhou, W.; Wang, C.; Chen, Z. Cotton fiber supported layered double hydroxides for the highly efficient adsorption of anionic organic pollutants in water. New J. Chem. 2018, 42, 9463–9471.
(9) Qi, L.; Liu, K.; Wang, R.; Li, J.; Zhang, Y.; Chen, L. Removal of chlorine ions from desulfiturization wastewater by modified by ash hydroxolate. ACS Omega 2020, 5, 31665–31672.
(10) Hu, F.; Wang, M.; Peng, X.; Qiu, F.; Zhang, T.; Dai, H.; Liu, Z.; Cao, Z. High-efficient adsorption of phosphates from water by hierarchical CuAl/biomass carbon fiber layered double hydroxide. Colloids Surf., A 2018, 555, 314–323.
(11) Yang, C.; Wang, L.; Yu, Y.; Wu, P.; Wang, F.; Liu, S.; Luo, X. Highly efficient removal of amoxicillin from water by Mg-Al layered double hydroxide/cellulose nanocomposite beads synthesized through in-situ coprecipitation method. Int. J. Biol. Macromol. 2020, 149, 93–100.
(12) Ahmad, R.; Ansari, K. Comparative study for adsorption of Congo red and methylene blue dye on chitosan modified hybrid nanocomposite. Process Biochem. 2021, 108, 90–102.
(13) Sankaramakrishnan, N.; Singh, N.; Srivastava, I. Hierarchical nano Fe (0)@ FeS doped cellulose nanofibres derived from agrowaste—Potential biocatalysts for treatment of organic dyes. Int. J. Biol. Macromol. 2020, 151, 713–722.
(14) Laureano-Anzaldo, C. M.; Haro-Mares, N. B.; Meza-Contreras, J. C.; Robledo-Ortiz, J. R.; Manríquez-González, R. Chemical modification of cellulose with zwitterion moieties used in the uptake of red Congo dye from aqueous media. Cellulose 2019, 26, 9207–9227.
(15) Ji, J.; Xie, W. Removal of aflatoxin B1 from contaminated peanut oils using magnetic attapulgite. Food Chem. 2021, 339, 128072.
(16) Abu-Danso, E.; Peräniemi, S.; Leiviskä, T.; Kim, T.; Tripathi, K. M.; Bhattachar, A. Synthesis of clay-cellulose biocomposite for the removal of toxic metal ions from aqueous medium. J. Hazard Mater. 2020, 381, 120871.
(17) Mirjavadi, E. S.; Tehrani, R. M.; Khadir, A. Effective adsorption of zinc on magnetic nanocomposite of Fe3O4/zelite/cellulose nanofibers: kinetic, equilibrium, and thermodynamic study. Environ. Sci. Pollut. Res. 2019, 26, 33478–33493.
(18) Ohu-Owuolabi, B. I.; Alabi, A. H.; Diagbaya, P. N.; Unaonah, E. I.; Düring, R.-A. Adsorptive removal of 2,4,6-trichlorophenol in aqueous solution using calcined kaolinite-biomass composites. J. Environ. Manage. 2017, 192, 94–99.
(19) Belgacem, C.; Tarres, Q.; Espinach, F. X.; Mutjé, P.; Boufi, S.; Delgado-Aguilar, M. High-yield lignocellulosic fibers from date palm biomass as reinforcement in polypropylene composites: Effect of fiber treatment on composite properties. Polymers 2020, 12, 1423.
(20) Abd-El-Raoof, F.; Tawfik, A.; Komarneni, S.; Ahmed, S. E. Hydrotalcite and hydrocalumite as resources from waste materials of concrete aggregate and Al-dross by microwave-hydrothermal process. Constr. Build. Mater. 2019, 207, 10–16.
(21) Zhang, T.; Zhao, B. C.; Chen, Q. Y.; Peng, X.; Yang, D.; Qiu, F. Layered double hydroxide functionalized biomass carbon fiber for highly efficient and recyclable fluoride adsorption. Appl. Biol. Chem. 2019, 62, 12.
(22) Sobhana, S. S. L.; Bogati, D. R.; Reza, M.; Gustafsson, J.; Fardin, P. Cellulose bioteemplates for layered double hydroxides networks. Microporous Mesoporous Mater. 2016, 225, 66–73.
(23) Zubair, M.; Jarrah, N.; Khalid, A.; Manzar, M. S.; Kazeem, T. S.; Al-Harthi, M. A. Starch-NiFe-layered double hydroxide composites: Efficient removal of methyl orange from aqueous phase. J. Mol. Liq. 2018, 249, 254–264.
(24) Duan, S.; Ma, W.; Cheng, Z.; Zong, P.; Sha, X.; Meng, F. Preparation of modified Mg/Al layered double hydroxide in saccharide system and its application to remove As(V) from glucose solution. Colloids Surf., A 2016, 490, 250–257.
(25) Domínguez, M.; Pérez-Bernal, M. E.; Ruano-Casero, R. J.; Barriga, C.; Rives, V.; Ferreira, R. A. S.; Carlos, L. D.; Rocha, J. Multilayered white-light luminescence in lanthanide-doped hydrocalumite and mayenite. Chem. Mater. 2011, 23, 1993–2004.
(26) Gévers, B. R.; Labuschagne, F. J. W. J. Green synthesis of hydrocalumite (CaAl-OH-LDH) from Ca(OH)2 and Al(OH)3 and the parameters that influence its formation and speciation. Crystals 2020, 10, 672–698.
(27) Bessaies, H.; Iftekhar, S.; Asif, M. B.; Kherriji, J.; Necibi, C.; Sillanpää, M.; Hamrouni, B. Characterization and physicochemical aspects of novel cellulose-based layered double hydroxide nanocomposite for removal of antimy and fluoride from aqueous solution. J. Environ. Sci. 2021, 102, 301–315.
(28) Cui, M.; Li, Y.; Sun, Y.; Wang, H.; Li, M.; Li, L.; Xu, W. Study on adsorption performance of MgO/Calcium alginic composite for congo red in wastewater. J. Polym. Environ. 2021, 5, 1–11.
(29) Guo, R.; Jiao, T.; Li, R.; Chen, Y.; Guo, W.; Zhang, L.; Zhou, J.; Zhang, Q.; Peng, Q. Sandwiched Fe3O4/carboxylate graphene oxide nanostructures constructed by layer-by-layer assembly for highly efficient and magnetically recyclable dye removal. ACS Sustainable Chem. Eng. 2018, 6, 1279–1288.
(30) Huang, X.; Wang, R.; Jiao, T.; Zhou, G.; Zhan, F.; Yin, J.; Zhang, L.; Zhou, J.; Peng, Q. Facile preparation of hierarchical AgNP-loaded MXene/Fe3O4/Polymer nanocomposites by electrosprinning with
enhanced catalytic performance for wastewater treatment. *ACS Omega* 2019, 4, 1897–1906.

31) Zhao, H.; Wang, R.; Deng, H.; Zhang, L.; Gao, L.; Zhang, L.; Jiao, T. Facile preparation of self-assembled chitosan-based POSS-CNTs-CS composite as highly efficient dye absorbent for wastewater treatment. *ACS Omega* 2021, 6, 294–300.

32) Ge, L.; Yin, J.; Yan, D.; Hong, W.; Jiao, T. Construction of nanocrystalline cellulose-based composite fiber films with excellent porosity performances via an electrospinning strategy. *ACS Omega* 2021, 6, 4958–4967.

33) Sheshdeh, R. K.; Khosravi-Nikou, M. R.; BadiiLimaee, K. N. Y. Adsorption of Acid Blue 92 dye on modified diatomite by nickel oxide nanoparticles in aqueous solutions. *Prog. Color, Color. Coat.* 2012, 5, 101–116.

34) Moghadam, R. M.; Khosravi-Nikou, M. R.; Anvaripour, B. Equilibrium, kinetics and thermodynamics studies on adsorptive removal of cobalt ions from wastewater using MIL-100(Fe). *Int. J. Sustain. Eng.* 2019, 12, 131–140.

35) Hajilari, M.; Shariati, A.; Khosravi-Nikou, M. Equilibrium adsorption of bioethanol from aqueous solution by synthesized silicalite adsorbents: experimental and modeling. *Adsorption* 2019, 25, 13–31.

36) Eniola, J. O.; Kumar, R.; Al-Rashdi, A. A.; Ansari, M. O.; Barakat, M. A. Fabrication of novel Al(OH)₃/CuMnAl-layered double hydroxide for detoxification of organic contaminants from aqueous solution. *ACS Omega* 2019, 4, 18268–18278.

37) Taher, T.; Putra, R.; Palapa, N. R.; Lesbani, A. Preparation of magnetite-nanoparticle-decorated NiFe layered double hydroxide and its adsorption performance for congo red dye removal. *Chem. Phys. Lett.* 2021, 777, 138712–138717.

38) Bharali, D.; Deka, R. C. Adsorptive removal of congo red from aqueous solution by sonochemically synthesized NiAl layered double hydroxide. *J. Environ. Chem. Eng.* 2017, 5, 2056–2067.

39) Lyu, H.; Ling, Y.; Fan, J.; Chen, Y.; Yu, Y.; Xie, Z. Preparation of ionic liquid-functionalized layered double hydroxide via thiol-ene click chemistry for highly efficient removal of azo dyes during broad pH range. *J. Clean. Prod.* 2019, 211, 1026–1033.

40) Li, N.; Chang, Z.; Dang, H.; Zhan, Y.; Lou, J.; Wang, S.; Attique, S.; Li, W.; Zhou, H.; Sun, C. Deep eutectic solvents assisted synthesis of MgAl layered double hydroxide with enhanced adsorption toward anionic dyes. *Colloids Surf., A* 2020, 591, 124507.