Fabrication and Characterization of Novel ZnAl-Layered Double Hydroxide for the Superadsorption of Organic Contaminants from Wastewater

Anyu Li, Hua Deng,* Chenghui Ye, and Yanhong Jiang

ABSTRACT: An imidazole ester skeleton (zeolitic imidazolate framework (ZIF)) was grown on the surface of a ZnAl-layered double hydroxide (ZnAl-LDH) material to form a porous composite (ZIF-ZnAl-LDH). To understand the adsorption characteristics of the two materials, the effects of pH, adsorption time, and adsorption concentration on the adsorption of Congo red (CR) solution were investigated comprehensively. In addition, ZnAl-LDH and ZIF-ZnAl-LDH were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), Brunauer−Emmett−Teller (BET), and X-ray photoelectron spectroscopy (XPS). The results clearly showed that ZnAl-LDH had a lamellar structure with a diameter of approximately 200−500 nm and ZIF-ZnAl-LDH had a regular three-dimensional hexagonal structure. The kinetics and thermodynamics of the CR adsorption by ZnAl-LDH and ZIF-ZnAl-LDH can be described using pseudo-second-order (PSO) and Langmuir models, respectively. The highest value of adsorption capacity obtained from the Langmuir equation was equal to 625.00 and 909.09 mg/g for these two compounds, respectively. The values of the standard Gibbs free energy ($\Delta G^\circ$), entropy ($\Delta S^\circ$), and enthalpy ($\Delta H^\circ$) obtained for these adsorption processes prove that the adsorption of CR by ZnAl-LDH and ZIF-ZnAl-LDH is a spontaneous endothermic process. Furthermore, through the analysis of the characterization results, it is concluded that the adsorption mechanisms of ZnAl-LDH and ZIF-ZnAl-LDH on CR are mainly dominated by electrostatic action, functional group action, surface pore adsorption, and anion exchange.

1. INTRODUCTION

Rapid development of the global economy has caused significant environmental pollution, especially in water reservoirs contaminated by wastewater rich in ammonia and phosphorus, heavy metals with high persistence and mobility, and electroplating- and dye-related chemicals, which affect human survival and health. A significant amount of dye is used in China, and the textile industry has developed in recent years. Furthermore, China’s dye output accounts for more than 60% of the world’s total output; therefore, the harm caused by dye wastewater is severe. Congo red (CR) wastewater is a common type of dye wastewater. CR is a typical benzidine direct azo dye that can produce more toxic aromatic amines under anaerobic conditions. Thus, it is very important to study the adsorption of CR wastewater for wastewater treatment. At present, commonly used dye wastewater treatment methods include membrane separation, oxidation, photocatalytic degradation, and adsorption. Adsorption is a well-established treatment method and offers simple operation and low energy consumption. Traditional adsorption materials include zeolite, activated carbon, and biochar. However, due to the poor adsorption effect of traditional adsorption materials on CR, their development is limited. Thus, at present, research on adsorbents with better adsorption effects is popular. Layered bimetallic hydroxide is a new material with electrification, anion exchangeability, and rich hydroxyl functional groups and can be represented by $\{M_{1-x}^{2+}M_x^{3+}(OH)_{2}\}^{2+}(A^{m-})_{y/e}\gamma H_2O$. Because the anions...
in the interlayer (such as NO$_3^−$, and Cl$^−$) can be exchanged with other anions and have the flexibility to change to other bimetallic types, they have been studied by researchers. Deng et al.\textsuperscript{18} can effectively remove CR from wastewater using sodium dodecyl sulfate (sDS) intercalation and acrylamide (AM) to fix layered double hydroxide (LDH). The adsorption capacity of AM/SDS-LDH toward CR is 1427.98 mg/g. This large value is mostly attributed to the high surface area of this material. Zhang et al.\textsuperscript{19} prepared and synthesized MgAl–CO$_3^−$ layered double hydroxide. The adsorption process for CR conforms to pseudo-second-order (PSO) and the Langmuir models, and the theoretical adsorption capacity can reach 934.43 mg/g. Zhang et al.\textsuperscript{20} synthesized CaAl-LDHs for the adsorption of CR wastewater. Research shows that the adsorption process mainly includes anion exchange and hydrogen bonding with oxygen or nitrogen. Similar to other adsorbents, the adsorption of CR by CaAl-LDHs also follows the Langmuir model and PSO. Zeng et al.\textsuperscript{21} synthesized CoFeNi-LDH using the coprecipitation method for the adsorption treatment of CR and rhodamine B (RhB). The synthesized three-metal layered double hydroxide has good stability and catalytic activity.

In this work, ZnAl-LDH and zeolitic imidazolate framework (ZIF)-ZnAl-LDH are prepared using the coprecipitation method, which is relatively simple, low in cost, and operable. To study the adsorption mechanism of CR, the adsorption kinetics and adsorption isotherm of the two materials were studied. At the same time, a series of characterizations such as Fourier transform infrared (FTIR), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Brunauer–Emmett–Teller (BET) were used to study the performance and mechanism of the CR removal from wastewater aqueous solution.

2. RESULTS AND DISCUSSION

2.1. LDH Surface Structure Analysis. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) micrographs of ZnAl-LDH clearly demonstrated regular lamellar structures with crystalline sizes in the 200–500 nm range (see Figure 1a). The particle sizes of ZnAl-LDH obtained in this work were somewhat larger than those of the samples synthesized by Zhan et al.\textsuperscript{22} and Li et al.\textsuperscript{23} As seen from the SEM and HRTEM images in Figure 1b, after the addition of 2-methylimidazole and sodium formate and heating in a water bath, the lamellar structure began to form a three-dimensional structure (hexagonal body), and the surface of the material became rougher.

2.2. XRD Analyses. Figure 2a,b shows the XRD patterns of ZnAl-LDH and ZIF-ZnAl-LDH, respectively, with characteristic diffraction peaks at 2θ = 10.78/11.99, 24.36/24.40, 34.50/34.25, and 62.77/62.85° corresponding to the (003), (006), (009), and (010) crystal planes, respectively. The results show that the synthesized ZnAl-LDH and ZIF-ZnAl-LDH have obvious hydrotalcite characteristics, and no other excess peaks are found, further indicating that the synthesized products have high purity.\textsuperscript{24}

2.3. FTIR Analyses. Figure 3 shows an FTIR spectrum, and the surface functional group absorption peaks observed for ZnAl-LDH and ZIF-ZnAl-LDH are –OH (3454 and 3448 cm$^{-1}$, respectively)\textsuperscript{25,26} and –C$=$C (1628 and 1604 cm$^{-1}$, respectively).\textsuperscript{27} Upon the addition of 2-methylimido to ZIF-ZnAl-LDH, new peaks appeared at 1421, 1307, and 1144 cm$^{-1}$, corresponding to –NH$_2$ bonds formed by the 2-methylimido moiety.

2.4. XPS Analyses. The XPS of ZnAl-LDH and ZIF-ZnAl-LDH showed peaks at 1021.63 and 1044.63 eV (see Figure 4), indicating that Zn exists on the surface.\textsuperscript{28} The peak intensity of ZIF-ZnAl-LDH was lower than that of ZnAl-LDH, which is most likely because the Zn ions are surrounded by the 2-methylimidido moiety and because the chemical environment around the Zn has changed. ZnAl-LDH and ZIF-ZnAl-LDH give rise to a signal peak at 73.80 eV, indicating the presence of ZnAl-LDH and ZIF-ZnAl-LDH are –OH (3454 and 3448 cm$^{-1}$, respectively)\textsuperscript{25,26} and –C$=$C (1628 and 1604 cm$^{-1}$, respectively).\textsuperscript{27} Upon the addition of 2-methylimidido to ZIF-ZnAl-LDH, new peaks appeared at 1421, 1307, and 1144 cm$^{-1}$, corresponding to –NH$_2$ bonds formed by the 2-methylimidido moiety.

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Al. In contrast to the above results related to the Zn\textsuperscript{2+} signal intensity, the signal intensity of the Al peak for ZIF-ZnAl-LDH is higher than that of the peak for ZnAl-LDH, confirming that Zn\textsuperscript{2+} is the metal center of LDH.\textsuperscript{29}

**2.5. Specific Surface Area Analyses.** The surface area and porosity of ZIF-ZnAl-LDH and ZnAl-LDH were obtained using nitrogen adsorption−desorption curves (see Figure 5 and Table 1). Both ZIF-ZnAl-LDH and ZnAl-LDH showed type IV N\textsubscript{2} adsorption isotherms with an H\textsubscript{3} hysteresis loop. The surface area, pore volume, and average diameters of ZIF-ZnAl-LDH and ZnAl-LDH were 20.92 and 10.18 m\textsuperscript{2}/g, 0.0043 and 0.0029 cm\textsuperscript{3}/g, and 4.31 and 3.92 nm, respectively (see Table 1). Thus, the surface and porosity characteristic values of ZIF-ZnAl-LDH were larger than those of ZnAl-LDH. In fact, the surface area of ZIF-ZnAl-LDH was 2 times larger than that of ZnAl-LDH, very likely because of the presence of 2-methylimidazole, which increased the surface roughness. Both of these factors are beneficial for CR adsorption, which agrees with the conclusions presented by Zhou et al.\textsuperscript{30}

**2.6. Effect of pH on Adsorption.** CR is an anionic dye, and the pH of the solution greatly affects the adsorption. Generally, when the pH of the solution is below the p\textsubscript{H\text{PZC}}, the surface of the material is positively charged, which is beneficial for anionic dye absorption due to static electricity. In contrast, when the pH of the solution is above p\textsubscript{H\text{PZC}}, the surface of the material is negatively charged, which produces a repulsive force on anionic dyes and is not conducive to adsorption.\textsuperscript{31} Diagrams of the adsorption amount with pH and \(\zeta\)-potential are shown in Figure 6. The p\textsubscript{H\text{PZC}} values of ZIF-ZnAl-LDH and ZnAl-LDH were equal to 10.25 and 8.75, respectively. For ZIF-ZnAl-LDH, the pH is in the range from 1 to 8. The adsorption capacity increased as the pH increased, mainly due to the enhancement of adsorption caused by the electrostatic effect, with the highest adsorption capacity of 240.8 mg/g (at pH = 8). However, at pH > 8, even if the pH of the solution is still below p\textsubscript{H\text{PZC}}, the adsorption capacity decreases, mainly due to the increased hydroxide content of the solution, which produces strong competitive adsorption with CR, resulting in a decrease in adsorption capacity.\textsuperscript{32} Similarly, ZnAl-LDH has a similar trend, reaching a maximum adsorption capacity of 209.49 mg/g at pH = 7. However, ZnAl-LDH decreased at pH
very likely because the surface area and pH<sub>PC</sub> values for ZnAl-LDH were below those for ZIF-ZnAl-LDH.

2.7. Analysis of the Adsorption Kinetics. In the field of adsorption, adsorption kinetics is a very important research parameter. It is an important index of adsorption time and process design that determines the adsorption rate of adsorbents to adsorbents and can be used to calculate the adsorption rate of adsorbents. Figure 7 shows the adsorption kinetics of ZIF-ZnAl-LDH and ZnAl-LDH on CR. Both materials demonstrated a fast adsorption stage from 0 to 240 min (see Figure 7a), and the adsorption amount changed slightly from 240 to 1440 min, indicating that the adsorption equilibrium was basically reached. To further elaborate on the adsorption process, we use PFO, PSO, and intraparticle diffusion (IPD) to fit and analyze the adsorption data, as shown in the following formulas

\[ Q_e = \frac{(C_0 - C_e) \times V}{m} \]  

(1)

\[ Q_t = Q_e \left[ 1 - \exp\left( -\frac{K_1}{2.303}t \right) \right] \]  

(2)

\[ \frac{t}{Q_t} = \frac{1}{K_2Q_e^2} + \frac{t}{Q_e} \]  

(3)

\[ Q_t = K_3^{1/2} + C \]  

(4)

Here, \( Q_0 \), \( Q_e \), and \( Q_m \) are the adsorption capacity, saturated adsorption capacity, and theoretical maximum adsorption capacity (mg/g) at time \( t \), respectively; \( C_0 \) and \( C_e \) are the initial concentration and the equilibrium concentration after adsorption of CR (mg/L), respectively; \( K_1 \) (g/(mg-min)), \( K_2 \) (g/(mg)), and \( K_3 \) (mg/(g·min<sup>0.5</sup>)) represent the PFO constants, PSO constants, and IPD constants, respectively; and \( t \) (min) and \( C \) (mg/g) represent the adsorption time and the thickness of the boundary layer, respectively.

The model parameters obtained by fitting the adsorption of CR by ZIF-ZnAl-LDH and ZnAl-LDH using three adsorption kinetic equations are shown in Table 2. The CR amounts adsorbed by ZIF-ZnAl-LDH and ZnAl-LDH fitted by the PFO model were 278.97 and 97.13 mg/g, respectively (see Table 2), which are below the experimentally obtained values (equal to 233.8 mg/g for ZIF-ZnAl-LDH and 193.10 mg/g for ZnAl-LDH). This discrepancy is very likely because of the low values of the corresponding correlation coefficients of the fitting (0.3530 and 0.6740, respectively). The PSO model can fit the adsorption process of CR, and the theoretical equilibrium adsorption amounts of ZIF-ZnAl-LDH and ZnAl-LDH are 232.56 and 192.31 mg/g, respectively. These values are very close to the actual equilibrium adsorption amounts, indicating that the adsorption process of CR by ZIF-ZnAl-LDH and ZnAl-LDH conforms to the PSO model, and the adsorption process is mainly chemical adsorption. At the same time, IPD has a good fit in sections, as shown in Figure 7c. The results show that the adsorption of CR by ZIF-ZnAl-LDH and ZnAl-LDH can be divided into three stages: fast adsorption, slow adsorption, and adsorption approaching equilibrium. At the same time, the IPD fitting line did not pass through the origin, indicating that there are other processes (liquid film diffusion and surface adsorption) that dominate the adsorption. By comparing the values of \( C_1 \), \( C_2 \), and \( C_3 \) in Table 2, we found that both ZIF-ZnAl-LDH and ZnAl-LDH follow the rule \( C_1 < C_2 < C_3 \) which shows that the influence of the boundary layer on the adsorption of the three stages increases one by one.

2.8. Analysis of the Adsorption Isotherm. The adsorption isotherms of ZIF-ZnAl-LDH and ZnAl-LDH for CR are seen in Figure 8. The amount of CR adsorbed by both materials increased as the CR concentration increased. At low CR concentrations, the adsorption capacity increased rapidly but then gradually slowed as the CR content increased further. At low CR concentrations, sufficient amounts of functional
groups and adsorption sites exist on the adsorbent surface, which allows for fast absorption. As the CR concentration in the solution increases, an increasing number of functional groups on the adsorbents become consumed and occupied. At the same time, the competition of the CR molecules for adsorption sites increases, which is favorable for achieving equilibrium. To further analyze the adsorption characteristics of ZIF-ZnAl-LDH and ZnAl-LDH on CR, the experimental results were fitted using the Langmuir and Freundlich models, as shown below

\[ Q_e = \frac{Q_m C_0}{(K_L + C_e)} \]  

\[ Q_e = K_F C_e^{1/n} \]  

Here, \( Q_e \) and \( Q_m \) are the saturated adsorption and theoretical maximum adsorption capacities (in mg/g), respectively; \( C_e \) is the initial CR concentration (in mg/L); and \( K_L \) and \( K_F \) are the Langmuir constant (L/mg) and the Freundlich constant ((L/mg)\(^{1/n}\)), respectively.

The Langmuir equation can be used to further calculate the separation factor \( R_L \) of the adsorption reaction; while comparing the adsorption capacity, the partition coefficient (PC) of the adsorbent is also calculated to explain the true adsorption capacity of CR for different adsorbents

\[ R_L = \frac{1}{1 + C_0 K_L} \]  

\[ PC = \frac{Q_e}{C_0 W} \]  

\( R_L \) is a dimensionless parameter separation factor, which is used to further describe the adsorption performance of the adsorbent. When \( R_L = 0 \), \( 0 < R_L < 1 \), and \( R_L = 1 \), the adsorption is irreversible, the adsorption process is beneficial, and the adsorption process is linear, respectively. \( Q \) is the adsorption capacity (mg/g); \( C_0 \) is the initial concentration (mg/L); and \( W \) is the removal rate (%).

Using the data of adsorption isotherms, the thermodynamic parameters of the two materials, as well as the temperature effect on the CR adsorption by ZIF-ZnAl-LDH and ZnAl-LDH, can be obtained. The thermodynamic parameters, such as Gibbs free energy (\( \Delta G^\circ \), kJ/mol), enthalpy (\( \Delta H^\circ \), kJ/mol), and entropy (\( \Delta S^\circ \), kJ/(mol·K)), can be calculated using the Langmuir constant \( K_L \). In the end, it is more accurate to explain whether the adsorption process is an adsorption reaction or an exothermic reaction using the following formulas

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

\[ \ln(pK_L) = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]  

where \( T \) is the temperature in K; \( R \) is the gas constant (please note that the meaning of \( R \) is different from the front dimensionless parameter separation factor \( R_L \)) and equal to 8.314 J/(mol·K); \( \rho \) is the density of water at standard temperature and equal to \( 10^3 \) mg/L; and \( K_L \) is the Langmuir model parameter.

At temperatures of 298, 308, and 318 K, two isothermal adsorption models were used to fit the CR adsorption data of ZIF-ZnAl-LDH and ZnAl-LDH, as seen in Table 3. For both materials, the \( R^2 \) values of the Langmuir model and the Freundlich model are higher than 0.9, but the \( R^2 \) of the Langmuir model is slightly higher than that of the Freundlich model, as shown in Table 3, indicating that ZIF-ZnAl-LDH

| Sample       | Adsorption Kinetics Parameters of ZIF-ZnAl-LDH and ZnAl-LDH for CR |
|--------------|---------------------------------------------------------------|
|              | ZIF-ZnAl-LDH | ZnAl-LDH |
|              | Q (mg/g)      | Kd1 (g/(mg·min)) | R2 | Q (mg/g)      | Kd1 (g/(mg·min)) | R2 |
|              | 278.97        | 2.0 × 10⁻⁴      | 0.3530 | 120.12       | 16.4340          | 0.9486 |
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The units of \( K_d \) are "mg/(g·min)".
and ZnAl-LDH adsorbed on CR mainly form a single molecular layer; however, physical and chemical adsorptions of multiple molecular layers still occur. The calculated $R_1$ is listed in Table 3. It can be found that the $R_1$ ranges of both materials are 0–1, indicating that the adsorption process for CR is effective. The same time, it can be found from Table 3 that the $K_L$ and $R_F$ values of ZIF-ZnAl-LDH and ZnAl-LDH have very obvious characteristics. First, as the adsorption temperatures of the materials increase, the $K_L$ and $R_F$ values also increase. Thus, an increase in temperature increases the adsorption capacity for CR. Second, at the same temperature, the $R_1$ and $K_L$ values of ZIF-ZnAl-LDH are always higher than those of ZnAl-LDH, which indicates that ZIF-ZnAl-LDH loaded with 2-methylimidazole improves the adsorption capacity of CR, which is one of the reasons why ZIF-ZnAl-LDH has a better cycling performance than ZnAl-LDH. The thermodynamic parameters are shown in Table 4. As the temperature of the two materials increased, the value of $\Delta G^\circ$ gradually decreased, indicating that the increase in temperature was conducive to adsorption. At the same time, the values of $\Delta H^\circ$ and $\Delta S^\circ$ were greater than 0, indicating that the adsorption process of CR by ZIF-ZnAl-LDH and ZnAl-LDH is an endothermic reaction. The further shows that an increase in temperature will promote adsorption. The theoretical maximum adsorption capacities of ZnAl-LDH and ZIF-ZnAl-LDH for CR calculated by the Langmuir model are 625.00 and 909.09 mg/g, respectively. Compared with the adsorption capacity obtained in the pH analysis, the adsorption capacity obtained by the Langmuir model is more representative of the adsorption performance of the materials. PC can be used to represent the true adsorption performance of the adsorbent, and compared with the adsorption capacity of LDH/layered double oxide (LDO) for CR reported in recent years, that of the adsorbent in this study shows a higher partition coefficient and adsorption performance compared with the adsorption capacity of LDH/layered double oxide (LDO) for CR reported in recent years, that of the adsorbent in this study shows a higher partition coefficient and adsorption performance compared with the adsorption capacity of LDH/layered double oxide (LDO) for CR reported in recent years, that of the adsorbent in this study shows a higher partition coefficient and adsorption performance.

### Table 3. Adsorption Isotherm Parameters of ZnAl-LDH and ZIF-ZnAl-LDH for CR

| adsorption thermodynamics | $T$ (K) | $Q_e$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $R_L$ | $1/n$ | $K_F$ ((L/mg)$^{1/n}$) | $R^2$ |
|---------------------------|--------|--------------|--------------|-------|-------|-------|------------------------|-------|
| ZnAl-LDH                  | 298    | 526.32       | 0.0489       | 0.9888| 0.0329–0.8035| 0.4319 | 1.3799 | 0.9676 |
|                           | 308    | 588.24       | 0.0651       | 0.9920| 0.0250–0.7544| 0.3089 | 1.5324 | 0.9777 |
|                           | 318    | 625.00       | 0.0975       | 0.9916| 0.0168–0.6722| 0.2455 | 1.6200 | 0.9710 |
| ZIF-ZnAl-LDH              | 298    | 714.29       | 0.3788       | 0.9996| 0.0043–0.3455| 0.2275 | 1.7065 | 0.9138 |
|                           | 308    | 833.33       | 0.5714       | 0.9994| 0.0027–0.2593| 0.1742 | 1.7691 | 0.9210 |
|                           | 318    | 909.09       | 2.2222       | 0.9999| 0.0007–0.0826| 0.1543 | 1.8188 | 0.9185 |

### Table 4. Thermodynamic Parameters of ZnAl-LDH and ZIF-ZnAl-LDH Adsorption of CR

| samples                  | $\Delta G^\circ$ (kJ/mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (kJ/(mol*K)) |
|--------------------------|---------------------------|---------------------------|-------------------------------|
| ZnAl-LDH                 | 298 K                      | 26.75                     | 28.38                         |
|                          | 308 K                      | 33.84                     | 38.64                         |
|                          | 318 K                      | 38.64                     | 43.72                         |
| ZIF-ZnAl-LDH             | 298 K                      | 31.82                     | 33.94                         |
|                          | 308 K                      | 33.94                     | 38.37                         |
|                          | 318 K                      | 38.64                     | 43.72                         |

### Table 5. $Q_{max}$ Comparison of CR from Different LDH/LDO Adsorbents

| LDH/LDO adsorbent         | $Q_{max}$ (mg/g) | reference | PC (mg/(g·μm)) |
|---------------------------|------------------|-----------|----------------|
| Fe$_3$O$_4$/MgAl-LDH composite | 289.00         | 43        | 1.16           |
| Mg–Fe–CO$_3$–LDH          | 143.27          | 46        | 2.60           |
| C/MnCuAl-LDO              | 454.55          | 47        | 3.49           |
| NiFe-LDH                  | 205.00          | 48        | 2.41           |
| NiFe-LDO                  | 330.00          |           | 4.40           |
| ZIF-ZnAl-LDH              | 909.09          | this work | 4.71           |

2.9. Study on the Cyclic Adsorption of Materials. The recyclability of adsorbents is of great significance for industrial production. To obtain a reusable adsorbent, sodium hydroxide is used to carry out adsorption–desorption experiments on ZnAl-LDH and ZnAl-LDH (see Figure 9). When both materials adsorb CR for the first time, the removal rates reach 98.01% and 76.99%, respectively, and gradually decrease as the usage time increases, while the removal rates of CR can still reach 67.11% after ZIF-ZnAl-LDH is recycled four times, indicating that ZIF-ZnAl-LDH has a better cycling performance than ZnAl-LDH. At the same time, the increase in cyclicity leads to a decrease in CR adsorption, which is attributed to the consumption or damage of the functional groups and adsorption sites on the surface of the adsorption material.
2.1.0. Analysis of Possible Adsorption Mechanisms.

To reveal the adsorption mechanism of the material on CR, FTIR and XRD data before and after the adsorption of CR on the material were analyzed, as shown in Figure 10. As shown in Figure 10a, −OH in ZnAl-LDH moves from a high wavenumber (3454 cm\(^{-1}\)) to a low wavenumber (3450 cm\(^{-1}\)), and the waveform becomes wider, which shows that −OH participates in the CR adsorption and follows the same rule as ZIF-ZnAl-LDH.\(^{51}\) ZIF-ZnAl-LDH without adsorption has an obvious −NH\(_2\) peak (see Section 2.3 for the specific analysis). After CR is adsorbed, the −NH\(_2\) peak basically disappears, further indicating that the functional group participates in the adsorption process of CR. ZnAl-LDH and ZIF-ZnAl-LDH show new peaks at wavenumbers of 1116 and 1146 cm\(^{-1}\), respectively, which belong to the S=O peak, indicating that CR may be adsorbed on the surface of the material through electrostatic action.\(^{20}\) Figure 10b shows the XRD patterns of the two materials. After the adsorption of CR, some crystal peaks of the two materials collapsed, especially that of ZIF-ZnAl-LDH, and all crystal peaks at 10–30\(^{\circ}\) disappeared. The disappearance of the crystallization peak indicates that the material has changed from a crystalline state to an amorphous state, which can indicate that the chemical action is the main reaction process in the adsorption of CR by the two materials. Based on a summary of Sections 2.1–2.8, the adsorption mechanism of CR by the two new materials was analyzed, the adsorption mechanism diagram was drawn, and the following adsorption mechanisms were proposed. First, the adsorption of CR by the two materials was mainly chemical adsorption, and CR was adsorbed or fixed to the surface of the materials through the action of functional groups. Second, the two materials have positive charges and are adsorbed through electrostatic interaction with −SO\(_3\) between CR molecules. Finally, surface adsorption and anion exchange are also possible processes of CR adsorption.

3. CONCLUSIONS

ZIF-ZnAl-LDH materials were synthesized by a coprecipitation method, and ZnAl-LDH was wrapped with 2-methylimidine. The XRD, XPS, FTIR, and other characterization results of the two materials show that both materials have obvious bimetallic layered structures, but ZIF-ZnAl-LDH has a higher crystallinity and more abundant functional groups on its surface. By fitting the CR adsorption data of ZnAl-LDH and ZIF-ZnAl-LDH, it was concluded that the data for both materials conform to the PSO and Langmuir models. The highest adsorption capacity of ZIF-ZnAl-LDH (909.09 mg/g) to CR is higher than that of ZnAl-LDH (625.00 mg/g), possibly due to the superior surface structure of ZIF-ZnAl-LDH. The mechanism result shows that electrostatic interaction, anion exchange, functional group interaction, and surface adsorption play an important role in the adsorption
process of CR. Through recycling experiments, it is proven that, after four cycles of adsorption, the removal rates of CR by ZnAl-LDH and ZIF-ZnAl-LDH are still 57.78% and 67.11%, respectively. Compared with ZnAl-LDH, the synthesized ZIF-ZnAl-LDH has a very good adsorption capacity for experiments with dye wastewater, which is of great significance for the practical application of the adsorbent in the future; thus, ZIF-ZnAl-LDH has good application prospects as an anionic dye adsorption material.

4. MATERIALS AND METHODS

4.1. Preparation of Materials. Zinc/aluminum LDH was prepared by coprecipitation. First, 80 mL of 0.1 M Zn\textsuperscript{2+} solution and 20 mL of a 0.05 M Al\textsuperscript{3+} solution were mixed in deionized water to obtain a solution with a total metal ion concentration of 0.15 mol/L. A 2 M NaOH solution was then slowly added under vigorous stirring until a pH of approximately 7.5 was obtained. After storing the solution at 60 °C for 24 h, the white precipitate was centrifuged, rinsed several times with water, and dried at 70 °C for 48 h. The obtained sample was marked as ZnAl-LDH.

To prepare ZIF-ZnAl-LDH, 1.50 g of 2-methylimidazole (C\textsubscript{4}H\textsubscript{4}N\textsubscript{2}) and 0.80 g of sodium formate were added to 120 mL of methanol and stirred until full dissolution was achieved, after which 0.72 g of dry ZnAl-LDH was added. The resulting slurry was stirred at 60 °C for 5 h. The precipitate was centrifuged, rinsed three times with methanol, and dried at 60 °C.

4.2. Characterization of Materials. SEM (SIGMA 500, Germany) was used to observe the microstructure of the samples. HRTEM (JEM2100F, Japan) was used to observe the grain boundary structure and the layered structure. XRD (Shimadzu XRD-6100, Japan) was used to analyze the crystallographic information of the samples. Fourier transform infrared (FTIR) spectroscopy (Thermo Scientific Nicolet iS50) was used to identify the functional groups in the sample. XPS (Thermo Fisher 250Xi) was used to analyze the surface elements (C, O, Zn, Al) of the biochar semiquantitatively and in terms of valence.

4.3. Adsorption Kinetics and Thermodynamics Studies. The effect of the contact time (0, 5, 10, 20, 40, 60, 80, 100, 120, 240, 960, and 1440 min) between LDH and CR on the adsorption of LDH was studied. First, 20 mg of ZnAl-LDH and ZnAl-LDH were added separately to 50 mL of solutions of 100 mg/L CR and oscillated at 25 °C and 150 rpm. PFO, PSO, and IPD were used for fitting; the samples were removed at designated times. The effects of different initial concentrations (5, 10, 20, 40, 60, 80, 100, 120, 150, 200, 250, 300, 400, 500, and 600 mg/L) on adsorption were studied. Then, 20 mg of ZnAl-LDH and ZnAl-LDH were added to 50 mL of CR solutions with different concentrations. The samples were removed after mixing at three temperatures (25, 35, and 45 °C) for 1440 min, the concentration of CR in the filtrate was measured by a 722 spectrophotometer, and the Langmuir model and Freundlich model were used for fitting, as shown below. Then, 20 mg of ZnAl-LDH and ZnAl-LDH samples (three parallel samples per pH) were weighed and added to 50 mL of a 100 mg/L CR solution. The pH of the solution was then adjusted to 2, 3, 4, 5, 6, 7, 8, 9, and 10 using appropriate concentrations of sodium hydroxide and hydrochloric acid. The solutions were agitated continuously at 25 °C and 150 rpm for 1440 min, removed, filtered with 0.22 μm microporous membrane, and used to determine the residual CR concentration in the filtrate with a 722 spectrophotometer.

4.4. Adsorption–Desorption Study. First, 20 mg of ZnAl-LDH and ZIF-ZnAl-LDH samples were weighed and added to 50 mL of a 100 mg/L CR solution. The solution was shaken at 25 °C for 1440 min, filtered, and dried for later use. The two samples were immersed in a 0.1 mol/L sodium hydroxide solution, magnetically stirred for 24 h and then filtered, dried, and saved for later use. Then, the two materials after the first desorption were used to continue to adsorb CR under the same conditions, and four consecutive adsorption–desorption experiments were performed to obtain a series of regular patterns between the number of cycles and the amount of adsorption.

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Notes

The authors declare no competing financial interest.

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