Water–n-BuOH solvothermal synthesis of ZnAl– LDHs with different morphologies and its calcined product in efficient dyes removal

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Abstract:

In this study, water–n-BuOH mixed solvents were used to synthesize the ZnAl-layered double hydroxides (ZnAl-LDHs) *via* hydrothermal method. The XRD, FT-IR, SEM, ICP and CHN analyses revealed that the type of intercalated anions, the layer Zn/Al ratios, and morphologies of the LDHs depended on the ratio of $V(\text{water})/V(\text{n-BuOH})$ in the mixed solvents. When the ratio of $V(\text{water})/V(\text{n-BuOH})$ is 3 or 0.3, the as-prepared LDHs had 3D “silk flowers” (ZnAl-LDH-3) or “Sedimentary rock” morphology (ZnAl-LDH-0.3). Adsorption properties of dyes on calcined LDHs were studied. Compared with ZnAl-LDO-0.3 and ZnAl-LDO-w (calcined from the LDHs obtained in pure water), ZnAl-LDO-3 showed much better adsorption efficiency for anionic dyes thanks to its much larger BET-specific surface area. The sorption kinetics for dyes was appropriately described by the pseudo-second-order model and sorption isotherms can be fitted more satisfactorily by the Langmuir model. With the increasing concentrations of dyes from 10 mg/L to 400 mg/L, the maximum absorption capacities of ZnAl-LDO-3 were 1540 mg/g (2.21 mmol/g) for congo red, 1153 mg/g (3.52 mmol/g) for methyl orange and 390 mg/g (0.63 mmol/g) for active red (X-3B), respectively. The adsorption dyes onto the external surface is still the main mechanism for LDO adsorbents. The ZnAl-LDO-3 was a potential adsorbent for dyeing wastewater treatment.

Keywords: layered double hydroxides; Morphologies; Water–n-BuOH solvent; removal of dyes; adsorption mechanism

1. Introduction

A wide variety of dyes are widespread used in printing and dyeing, cosmetics, pesticides, medicine and other industries, which are released into the water system during producing and using. Most of these dyes are extremely stable and difficult to natural degradation after entering the water system, which results in serious environmental pollution due to their carcinogenicity and toxicity [1]. So, the removal of these dyes from natural water sources and industrial wastewater becomes a crucial issue. Various treatment technologies, such as electrochemistry [2], ion-exchange [3-6], membrane filtration [7-9], flocculation [10], photocatalytic degradation [11-15] and adsorption [16-21] have been used for dye-contaminated wastewater. Among them, adsorption is the most popular and effective due to its attractive advantages such as low cost, fast and strong operability. Many adsorbents had been designed for removing dyes, such as activated carbon [22], fly ash [23], nature clays [24] and transition metal oxides [19, 25]. However, it is still important to develop economically adsorbents with larger adsorption capacity and high removal efficiency.

Layered double hydroxides (LDHs), which are consist of positively-charged metal hydroxide layers and counter-anions in the interlayer, are anion-exchanging lamellar materials [26-30]. Their calcined products, namely layered double oxides (LDO), normally with much higher surface areas than those of LDHs, have good structural memory effect [31]. Thanks to anion-exchangeability of LDHs and unique memory effect of LDOs, the LDHs and their calcined products have been used as adsorbents to manage wastewater polluted by dyes, such as congo red (CR) [18, 32], methyl orange (MO) [33-35], and Acid yellow [36].

As far as we know, the morphology and size have significant influence on adsorption property of LDHs [37, 38], so the control synthesis of LDHs with various morphologies and sizes has attracted the attention of researchers[39]. To date, several morphologies of LDHs appeared. For example, LDH hollow spheres [40] were synthesized using template method. Sphere-like LDH particles were synthesized by hydrothermal treatment [34], and the adsorption capacity of its calcined products for methyl orange had reached 248.3 mg/g. Using a facile isoelectric point (IEP) method, nano-sized spherical [41] were obtained with CO₂ capture capacity of 0.83 mmol/g. Hollow LDH nanowires [42] were synthesized through an addition of hydrazine, and the adsorption capacity of methyl orange was 210 mg/g. Alcohols, as an organic additive, often are widely used to obtain materials with special morphology and size. For example, using ethanol as additive, pyramid-SnO₂[43], nanostructure α -Fe₂O₃[44], ZnSnO₃ hollow microspheres [45], Bi₂WO₆ hollow nano-spheres [46] and thin plate-like MgAl-LDH [18] were prepared. Using ethylene glycol as additive, BaCO₃ dumbbells [47], Fe/CNTs magnetic carbon nanotubes [48], NiO nanoflowers [49] and YF₃ nanocrystals [50] were synthesized. n-BuOH is also a kind of alcohol, and can also adjust the morphology and size of the materials [51, 52], but it is slightly soluble in water, so there are a few reports about using n-BuOH as additive to control morphology and size. As we know, the synthesized LDHs using n-BuOH as additive has not yet been reported.

In the present work, using water–n-BuOH mixed solvents, three kinds of ZnAl–LDHs with different morphologies and sizes were synthesized by the hydrothermal method. Interestingly, the type of anions, which intercalated into LDH interlayer to balance the charge, depended on the ratio of water/n-BuOH in the solvent. The adsorption properties of the calcined products (LDOs)

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4 were investigated in detail. The adsorption kinetics, adsorption isotherms and adsorption
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6 mechanism were also studied.
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10 **2. Experimental**

11 **2.1. Reagents and Materials**

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14 The $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, n-BuOH, urea, CR, MO and RR(X-3B) were in
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16 analytical grade and used without purification.
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20 **2.2. Preparation of Samples**

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22 A series of samples were synthesized in water, water–n-BuOH mixed solvent and pure n-
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24 BuOH by the hydrothermal method. The synthesis process in detail was as follows: 0.5950 g (2
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26 mmol) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.3751 g (1 mmol) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.4201 g (7 mmol) urea were
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28 dissolved in 200 mL distilled water in a flask. The mixed solution was heated to boiling under
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30 continuous magnetic stirring for 24 h. The obtained solids were collected by filtration, washed
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32 with a large amount of water, and subsequently dried at 70 °C for 3 h. The product was
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34 designated as ZnAl–LDH–w. Using the above method, ZnAl–LDHs were synthesized in water–
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36 n-BuOH mixed solvent, and the volume ratios of water/n-BuOH were 3 and 0.3, respectively.
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38 The obtained samples were designated as ZnAl–LDH–3 and ZnAl–LDH–0.3. The as-synthesized
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40 ZnAl–LDHs were calcined at 400 °C for 4 h to produce the layered double oxide (LDO), and
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42 denoted ZnAl–LDO–w, ZnAl–LDO–3, and ZnAl–LDO–0.3, respectively. In pure n-BuOH, the
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44 yellowish sample were obtained and designated as ZnO–BuOH.
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51 **2.3. Adsorption experiments**

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53 Sorption experiments were conducted as follows: At room temperature, 0.010 g adsorbents
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55 were added to 100 mL simulated dye wastewater (concentration ranging from 10 to 300 mg/L for
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57 MO and RR, but from 10 to 400 mg/L for CR) under magnetic stirring for specific time period.
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After adsorption, the suspensions were separated by centrifugation at 10 000 rpm. The concentration of residual dyes was analyzed by UV–vis spectroscopy.

The adsorption capacity q_t (1) and q_e (2), removal efficiency E% (3) and distribution coefficient K_d (4) is given from the following relations:

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (1)$$

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (2)$$

$$E\% = 100 \times \frac{c_0 - c_e}{c_0} \quad (3)$$

where C_0 was the initial concentration of dyes in solution (ppm), C_t was the concentration of dyes at time t of adsorption (ppm), C_e was the equilibrium concentration (ppm), q_t was the amount adsorbed per gram of adsorbent at time t (min), q_e was the equilibrium sorption capacity (mg/g), m was the mass of adsorbent (g), and V was the volume of solution (L).

2.4 Characterization Technique

The morphologies and structures of the samples were characterized with scanning electron microscopy (SEM, JSM-7001F), fourier-transform infrared (FT-IR, Bruker TENSOR 27) transmission electron microscopy (TEM, JEM-2100), and X-ray diffractometer (Bruker, Advanced D8).

The surface area of LDO samples were measured by the BET-specific surface area method. The samples were out-gassed at 200 °C for 4 h. The isotherms using the nitrogen adsorption/desorption were measured on the ASAP 2420 instrument.

For determining the composition of ZnAl–LDH samples, ICP-AES (concentrated HNO_3 solution was used to dissolve the solids beforehand for doing the ICP, ELAN9000) and CHN analyses (VARIO EL III) were conducted.

3. Results and discussions

3.1. Characterization of ZnAl-LDHs.

The XRD patterns of the ZnAl-LDH-w, ZnAl-LDH-3, ZnAl-LDH-0.3 precursors and their calcined products are displayed Fig. 1. Using pure water as solvent, CO₃-LDH was successfully synthesized, with the basal spacing (d_{basal}) of 0.76 nm (Fig. 1a), the same as reported in the literature (JCPDS: 48-1023) [53]. When using mixture of water/n-BuOH as the solvent, a series of strong ($00l$) reflections characteristics of a layered phase were observed (Fig. 1b-c). When the ratio of $V(\text{water})/V(\text{n-BuOH})$ is 3 (more water, less n-BuOH), the basal spacing (d_{basal}) of ZnAl-LDH-3 is 0.76 nm (Fig. 1b) the same as that of CO₃-LDH (Fig. 1a), for which the 1364 cm⁻¹ in the FT-IR spectra (Fig. 2b) verified the presence of the CO₃²⁻ anions. Interestingly enough, under the condition with less water and more n-BuOH, the ratio of $V(\text{water})/V(\text{n-BuOH})$ of 0.3, the d_{basal} of 0.89 nm (Fig. 1c) appeared, corresponding to the NO₃-LDH and the IR band at 1380 cm⁻¹ for free NO₃⁻ was observed (Fig. 2c), meaning NO₃⁻ anions had intercalated into interlayer[54]. When 0.050 g ZnAl-LDH-0.3 was added to 50 cm³ formamide with stirring, a translucent colloidal suspension showing a Tyndall light scattering (Fig. S1) was obtained, the same as reported in the literature for swollen NO₃-LDH in formamide[55]. The results of elemental analysis also confirmed the presence of NO₃⁻ anions (N%= 2.90%) (Table 1). After the LDHs were calcined at 400 °C for 4 h, the ($00l$) reflections disappeared, and at the same time the diffraction peaks of Zn-Al oxides appeared at the 2θ range of ~ 30–40° (Fig. 1d-f), indicating the formation of LDO[56]. In the corresponding FT-IR spectra (Fig. 2d), the bands at 1363 cm⁻¹ and 1380 cm⁻¹ disappeared, meaning that the interlayer anions were removed. The structures of the yellowish sample obtained in pure n-BuOH were also characterized with XRD (Fig. S2). The diffraction peaks of the sample can be indexed to ZnO (JCPDS: 36-1451) instead of LDH[57].

Based on ICP and CHN analysis results, the chemical formulas of ZnAl-LDHs were determined in Table 1. The molar ratio of Zn/Al is 1.9 in ZnAl-LDH-w obtained in pure water solvent. However, the Zn/Al molar ratios in the layers obtained in the water/n-BuOH mixture were significantly reduced to be 1.7 and 1.5, respectively, suggesting that the positive charge of metal plate increased [58, 59].

Fig. 3a-c shows the SEM images of the as-synthesized ZnAl-LDHs. The ZnAl-LDH-w (Fig.3a) is hexagonal platelets with a size of $\sim 7\ \mu\text{m}$ across the hexagonal surface. Using the water-n-BuOH mixed solvent with the ratio of $V(\text{water})/V(\text{n-BuOH})$ at 3, the ZnAl-LDH-3 (Fig.3b) has a 3D “silk flowers” shape, and clearly its plate-like form with 10~20 nm thick is much thinner than that of ZnAl-LDH-w (Fig.3a). Its TEM image also shows that the 3D “silk flowers” morphology is composed of thin hexagonal plate layers (Fig.3e). When the ratio of $V(\text{water})/V(\text{n-BuOH})$ is 0.3, the as-synthesized ZnAl-LDH-0.3 (Fig.3c) shows “Sedimentary rock” shape with a size of $\sim 2\ \mu\text{m}$ across the hexagonal surface and a thickness of $\sim 1\ \mu\text{m}$. TEM image also show its micrometer size (Fig. 3f). The formation of three different morphologies may be related to the different crystal growth interfaces. The 3D “silk flowers” shaped LDH particles grow on the interface between liquid-liquid interfaces[60, 61] (water and BuOH) (Fig. S3a), and “sedimentary rock” shaped LDH particles grow on the solid-liquid interface[62] (Fig. S3b), but hexagonal platelets LDH particles grow in pure water. On the basis of these results, it can be concluded that the morphology and particle size of the LDHs can be tuned by the ratios of $V(\text{water})/V(\text{n-BuOH})$. As Fig. 3g-i showed, when LDHs precursors were calcined to be LDOs, the morphologies were well retained for ZnAl-LDH-w and ZnAl-LDH-3 precursors, but thin sheets in the edge were curled for ZnAl-LDH-0.3.

N_2 adsorption-desorption curves of ZnAl-LDOs for surface area analysis were shown in Fig. 4. In all the cases, the typical IV isotherms with H3-type hysteresis loop ($P/P_0=0.4-0.8$) were observed, implying the mesopore size distribution[63]. The BET analysis results of LDO adsorbents were listed in Table 2. The BET-specific surface area of ZnAl-LDO-3 and ZnAl-LDO-0.3 are up to about $100\text{ m}^2/\text{g}$, and much larger than ZnAl-LDO-w ($20.1\text{ m}^2/\text{g}$), probably because of the thinner lamella and smaller sizes of the as-synthesized LDHs via using water/n-BuOH mixtures as solvents.

3.2 Adsorption properties of ZnAl-LDO sorbent materials

The adsorption of different LDO to dyes was investigated. The 0.010 g LDO was dispersed into 100 mL solutions of dyes (100 mg/L) for 6 h under stirring at room temperature. The comparison of the removal rates of different LDOs for three anion dyes were given in Fig. 5. It is very obviously that ZnAl-LDO-3 and ZnAl-LDO-0.3 obtained in water/n-BuOH mixed solvent have much higher removal efficiency than ZnAl-LDO-w obtained in pure water, mainly because their BET-specific surface area is much larger than the BET-specific surface area of ZnAl-LDO-w. Compared with ZnAl-LDO-0.3, ZnAl-LDO-3 with slightly larger BET-specific surface area showed a better adsorption efficiency for anion dyes. According to the above results, a detailed investigation of the adsorption behavior for anion dyes by the ZnAl-LDO-3 was carried out.

3.3 Adsorption Kinetics and isotherm

Fig. 7(A) shows the effect of contact time on the removal efficiency of dyes by ZnAl-LDO-3. It can be seen that, the adsorption velocity is very fast in the first 10 min for all the systems, but is relatively flat after it, with a slight increase in the removal efficiency. Obviously, the

adsorption reaches equilibrium within 30 min for all the systems, and no significant change is observed thereafter. However, the removal efficiency and adsorption capacities of ZnAl-LDO-3 for different anion dyes are different, and the order follows CR>MO>RR. Based on the molecular structures of the three kinds of dyes shown in Fig. 6, SO₃⁻ groups of RR(X-3B) molecules, located in the β position of naphthalene ring, have larger steric hindrance than SO₃⁻ groups of the MO and CR molecules, so the adsorption capacities for RR(X-3B) molecules are much lower than CR and MO molecules. Attributed to CR with more negative charges and larger molecular structure, the adsorption capacities for CR are higher than for MO. The removal efficiency of CR, MO and RR(X-3B) are 91.3%, 67.4% and 25.6 % in 360 min, respectively, and the adsorption capacities are 913 mg/g, 674 mg/g and 256 mg/g, respectively.

Kinetic studies are very important for exploring the adsorption mechanism and possible adsorption processes[64]. Two kinetics models, pseudo-first-order and pseudo-second-order model, are chosen for the description of the sorption process for three kinds of anionic dyes[65].

The two kinetic rate equations can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_t (mg/g) is the adsorption capacity at time t , and q_e (mg/g) is the equilibrium adsorption capacity at equilibrium time. Both k_1 (min⁻¹) and k_2 (g/mg⁻¹·min⁻¹) are the rate constants of pseudo-first-order and pseudo-second-order models. The k_1 value could be estimated by plotting $\ln(q_e - q_t)$ against t and the k_2 value by plotting t/q_t against t . All the

kinetic parameters were summarized in Table 3. Moreover, the linear relationship of t/q_t versus t is presented in Fig. 7(B).

Using pseudo-second-order model, the correlation coefficient ($R^2 > 0.999$) is higher than that of pseudo-first-order, and its calculated sorption capacity ($q_{e,cal}$) (Table 3) is closed to the experimental value ($q_{e,exp}$). Therefore, the sorption kinetic models were well-fitted with the pseudo-second-order model, suggesting that chemical reaction/chemisorption is assumed to be the rate-controlling step[66].

Fig. 8 indicates isothermic curves in adsorption of dyes. The max adsorption capacities are 1540 mg/g (2.21 mmol/g) of CR, 1153 mg/g (3.52 mmol/g) of MO and 390 mg/g (0.63 mmol/g) of RR(X-3B), respectively. Langmuir and Freundlich isotherms models are used to simulate the adsorption of dyes on ZnAl-LDO-3. The two isotherms are described as:

$$\frac{c_e}{q_e} = \frac{c_e}{q_{max}} + \frac{1}{q_{max} K_L} \quad (7)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (8)$$

where q_e (mg/g) is the equilibrium adsorption capacity of dyes adsorbed by the ZnAl-LDO-3, c_e (mg/L) is the concentration of dyes at equilibrium, q_{max} (mg/g) is the theoretical maximum monolayer sorption capacity, K_L (L/mg) is the Langmuir sorption constant, K_F (L/g) is the Freundlich constant, and $1/n$ is the adsorption intensity. The parameters of the Langmuir and Freundlich isotherms are listed in Table 4. The q_{max} (mg/g) obtained from Langmuir isotherms model are 1515 mg/g of CR, 1190 mg/g of MO and 341 mg/g of RR(X-3B), respectively, which are closer to the experimental results. Furthermore, the adsorption processes of dyes on ZnAl-LDO-3 fit much better the Langmuir isotherms model, with a higher correlation coefficient

($R^2 > 0.96$) than the Freundlich isotherms model, which suggests a monolayer adsorption of anion dyes on the ZnAl-LDO-3[67]. The linear relationship of c_e/q_e versus c_e is presented in Fig. 9.

3.4 Adsorption mechanism

The adsorption mechanisms of ZnAl-LDO-3 for dyes were also detailed investigated. Fig. 10 (a-c and a'-c') shows the XRD patterns of the ZnAl-LDO-3 after adsorption of dyes. It is observed clearly that the layered structure can be restored after the adsorption of each dye but the existing forms of dyes into interlayer are different. After adsorption of CR and MO with one-dimensional linear, the basal spacing, d_{003} , are about 3.0 nm and 2.4 nm respectively (Fig. 10a-b). Based on the thickness of the LDH layer of 0.48 nm[68], the gallery heights of the restored LDHs can be calculated as ~ 2.52 nm ($3.0 - 0.48$) for CR and 1.92 nm ($2.4 - 0.48$) for MO, close to the lengths of CR (2.45 nm) and MO (1.6 nm) (Fig. 10d-e), which indicate that CR and MO molecules are “standing” between in the interlayers of LDHs. In exactly the same way, it can be determined that RR(X-3B) molecules “lie flat” between layers (Fig. 10c). FT-IR spectra of adsorbents after adsorption of dyes were given in Fig. S4. The characteristic bands of $-\text{SO}_3^-$ are observed at the 1100–1200 cm^{-1} region[69], but with small shift compared with free dyes, meaning that the interaction between dyes and the layer. The band assigned to S–O bond is also observed at about 1044 cm^{-1} . In a word, some dyes may be absorbed into the interlayer of LDHs through electrostatic attraction.

For calcined products of LDHs, there are usually two ways to remove dyes from solution: (a) adsorption dyes into interlayer through reconstruct the LDH structure[70], and (b) adsorption dyes onto the external surface[71]. It is meaningful to investigate the contribution of each adsorption way. In case of adsorption of CR, the maximum adsorption capacity of the (a) way can be reckoned based on charge balance using the following formula:

$$q_E(CR) = \frac{(Al\% \times m_s \times Mr_{(CR)} / Mr_{(Al)})}{m_s} \times 1000$$

Where $q_E(CR)$ (mg/g) are the adsorption capacity of the (1) way. Mr (g/mol) is molar mass, m_s is the mass of adsorbents and $Al\%$ is Al mass percent (15.8%, ICP-AES). The $q_E(CR)$ is about 41 mg/g, and the maximum $q_{e, exp}(CR)$ is 1540 mg/g (Table 4), so the maximum contribution of (a) way is just only 2.7%. In fact, (b) way is still the main mechanism for LDO adsorbents.

4. Conclusions

In summary, using water–n-BuOH mixed solvent, ZnAl–LDHs with different morphologies and sizes were synthesized. When the ratio of $V(\text{water})/V(\text{n-BuOH})$ is 3 (more water, less n-BuOH), the as-synthesized ZnAl–LDH–3 had 3D “silk flowers” morphology with CO_3^{2-} anion intercalating into LDH interlayer. When the ratio of $V(\text{water})/V(\text{n-BuOH})$ is 0.3 (less water, more n-BuOH), the ZnAl–LDH–0.3 had “Sedimentary rock” morphology with NO_3^- anion into LDH interlayer. Compared with ZnAl–LDO–0.3 and ZnAl–LDO–w (obtained in pure water solvent), ZnAl–LDO–3 showed much better adsorption efficiency for anion dyes because of its much larger BET-specific surface area. Its sorption kinetics for dyes was appropriately described by the pseudo–second–order model and sorption isotherms can be fitted more satisfactorily by the Langmuir model. The maximum absorption capacity of ZnAl–LDO–3 is 1540 mg/g (2.21 mmol/g) for CR, 1153 mg/g (3.52 mmol/g) for MO and 390 mg/g (0.63 mmol/g) of RR(X-3B), respectively. The adsorption way of dyes onto the external surface is the main mechanism for LDO adsorbents. The ZnAl–LDO–3 was a potential adsorbent for dyeing wastewater treatment.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at

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Tables and Table Captions:

Table1. ICP and CHN Analysis Results and Chemical Formula of ZnAl-LDHs

Sample	wt %, found (calcd)					Zn/Al	chemical formula
	Zn	Al	C	H	N		
ZnAl-LDH-w	41.37 (40.75)	8.88 (8.72)	1.87 (1.94)	2.88 (2.85)		1.9	$[\text{Zn}_{0.66}\text{Al}_{0.34}(\text{OH})_2][(\text{CO}_3)_{0.17} \cdot 0.5\text{H}_2\text{O}]$
ZnAl-LDH-3	37.45 (36.60)	9.38 (9.09)	2.14 (2.02)	3.37 (3.37)		1.7	$[\text{Zn}_{0.63}\text{Al}_{0.38}(\text{OH})_2][(\text{CO}_3)_{0.19} \cdot 0.9\text{H}_2\text{O}]$
ZnAl-LDH-0.3	33.04 (32.29)	9.18 (8.79)	0.64 (0.68)	3.33 (3.26)	2.90 (2.96)	1.5	$[\text{Zn}_{0.60}\text{Al}_{0.40}(\text{OH})_2][(\text{CO}_3)_{0.07} (\text{NO}_3)_{0.26} \cdot \text{H}_2\text{O}]$

Table 2. Summary of BET-specific surface area analysis results of LDO Adsorbents

Adsorbents	BET surface area	Pore volume	Average pore diameter
	(m ² /g)	(cm ³ /g)	(nm)
ZnAl-LDO-w	20.1	0.039	7.7
ZnAl-LDO-3	104.0	0.10	3.9
ZnAl-LDO-0.3	93.5	0.095	4.1

Table 3. Kinetic Parameters for the Adsorption of anion dyes onto ZnAl-LDO-3 Adsorbent

	qe,exp (mg/g)	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		qe,cal	k ₁ (1/min)	R ²	qe,cal	k ₂	R ²
		(mg/g)			(mg/g)	(g/(mg min))	
CR	913	112	0.011	0.953	909	0.0011	0.999
MO	674	62.2	0.066	0.929	667	0.0015	1.000
RR	256	19.4	0.316	0.933	333	0.0030	0.999

Table 4. Parameters of the Langmuir and Freundlich Isotherms for the Sorption of anion dyes onto ZnAl-LDO-3 Adsorbent.

adsorbate	Langmuir equation				Freundlich equation		
	q _{exp} (mg/g)	q _m (mg/g)	K _L (L/mg)	R ²	n	K _F (L/mg)	R ²
MO	1153	1190	0.068	0.96	2.5	171.4	0.90
RR	390	341	0.040	0.98	2.5	41.5	0.92
CR	1540	1515	0.083	0.98	3.0	275.4	0.84

Figure Captions:

Fig. 1 XRD patterns of (a) the ZnAl-LDH-w, (b) ZnAl-LDH-3, (c) ZnAl-LDH-0.3, and their calcined products (d) ZnAl-LDO-w, (e) ZnAl-LDO-3, (f) ZnAl-LDO-0.3.

Fig. 2 FT-IR spectra of (a) the ZnAl-LDH-w, (b) ZnAl-LDH-3, (c) ZnAl-LDH-0.3, and calcined product (d) ZnAl-LDO-3.

Fig. 3 SEM and TEM images of (a, d) the ZnAl-LDH-w, (b, e) ZnAl-LDH-3, (c, f) ZnAl-LDH-0.3, and SEM images of calcined products (g) ZnAl-LDO-w, (h) ZnAl-LDO-3, (i) ZnAl-LDO-0.3

Fig. 4 N₂ adsorption-desorption isotherms for LDOs adsorbents

Fig. 5 The comparison of the removal rate of different LDOs for three anion dyes.

Fig. 6 The molecular structures of anion dyes.

Fig. 7 (A) Effects of contact time on removal efficiency of ZnAl-LDO-3 for anion dyes at an initial concentration of 100 mg/L and (B) Pseudo-second-order kinetic plots for the sorption of anion dyes by the ZnAl-LDO-3 adsorbents.

Fig. 8 Adsorption curve of dyes with an initial concentration increasing from 10 mg/L to 400 mg/L. q_e is the equilibrium sorption capacity (mg/g), and C_0 is the initial concentration of dyes in solution (mg/L).

Fig. 9 The linear relationship of c_e/q_e versus c_e .

Fig. 10 XRD patterns of the ZnAl-LDO-3 adsorbent after adsorption (a and a') after adsorbed CR, (b and b') after adsorbed MO, (c and c') after adsorbed RR and molecular size of dyes (d) CR, (e) MO and (f) RR.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Graphical Abstract