Research Article

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Preparation of composite soybean straw-based materials by LDHs modifying as a solid sorbent for removal of Pb(II) from water samples

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Abstract: In this study, the nanocomposites from biomass (soybean straw) and layered double hydroxides (LDHs), denoted as B/LDHs, were fabricated using the mechanical-hydrothermal method. The obtained B/LDHs nanocomposites were characterized by TEM, SEM, FT-IR, and N₂ adsorption-desorption techniques. Adsorption of the heavy-metal ions Pb(II) on the B/LDHs was determined at 25°C and pH 6.0 using a batch technique. The experimental results demonstrated that biomass contributed to the sorption process. The pseudo-second-order, Langmuir, and Freundlich models well fitted the sorption process, indicating chemisorption and monolayer adsorption were the main adsorption mechanisms. Meanwhile, it is found that there is an obvious effect of adsorbent concentration in the studied adsorption system. In comparison with soybean straw and Mg–Al LDHs, the B/LDHs nanocomposites exhibit significantly enhanced sorption capacities. It is evident from this study that the construction of B/LDHs nanocomposites is an effective strategy for improving the sorption capacity of LDHs, and the modified LDH-based adsorbent shows a good potential in the removal of heavy metals from water. More importantly, it solves the problem of a large number of agricultural waste disposals. And, it achieved the goal of a win-win situation.

Keywords: layered double hydroxide, soybean straw, nanocomposite, adsorption, heavy-metal

1 Introduction

Biomass [1–5] refers to all kinds of organisms produced by photosynthesis through the use of atmosphere, water, and land. Its advantages are renewable, low pollution, and wide distribution. Representative biomass includes crops, crop waste (wheat straw, corn cob, soybean stalk, orange peel, coconut shell, rice husk, etc.), wood, wood waste, and animal waste. Straw, as a kind of agricultural waste, is produced in large quantities every year. At present, its use is still at a very inefficient level in China. It is of great strategic significance to pay attention to the development and utilization of renewable biomass resources in the face of rapid resource consumption and environmental degradation.

Layered double hydroxides (LDHs) [6–10] are commonly used adsorbents. And, its chemical composition is as follows: $[M_{(1-x)}^{II}M_x^{III}(\text{OH})_2]^{x+}[A_{x/m}^{n-}]^{x-} \cdot m\text{H}_2\text{O}$, where M^{II} and M^{III} refer to divalent and trivalent metal cations, respectively; A stands for the interlayer anion; x is for per mole of LDHs M^{III} moles; and m is the number of moles of crystal water in the middle layer per mole LDHs. LDHs have a lamellar crystal structure, and the lamellar plates are positively charged with exchangeable anions. Different types of metal ions (M^{II} and M^{III}) and interlayer anions (Aⁿ⁻) lead to different LDHs properties. Therefore, LDHs are a kind of new inorganic lamellar materials. It has broad application prospects in the fields of catalyst, adsorbent, ion exchange agent, combustion promoter, pesticide slow-release preparation, and liquid flowtype regulator, especially in the fields of pharmaceutical transport carrier and sewage treatment, etc.

In recent years, the pollution of global freshwater resources is one of the main environmental problems faced by human beings. In particular, heavy metal ions have aroused widespread concern. With the rapid development of petrochemical, printing, dyeing, textile, plastic, leather, food, and other industries, industrial wastewater containing heavy metal ions are discharged into soil and

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water in large quantities, which seriously threatens the living space of human beings. To ensure the supply of freshwater resources, reducing water pollution or the treatment and recycling of polluted water resources are paid more and more attention by various countries.

At present, there are ion-exchange [8], membrane filtration [11], chemical precipitation [12], biological methods [13], and adsorption [14–21] to treat heavy metals and organic dyes in industrial wastewater. Among these treatment methods, the adsorption method has its place with the advantages of good treatment effect, simple operation, and good selectivity, especially in the field of heavy metal pollution, and organic pollution wastewater with strong pollution, low concentration, and difficult to be effectively treated by other treatment methods [14,15,18,22]. The commonly used adsorbents are activated carbon [23,24], polymers [25], graphene-based nanomaterials [26–28], some industrial wastes [29,30], etc., but most of these adsorbents are of high price and low adsorption capacity. It is imperative to develop new highly effective adsorbents.

Recently, the synthesis of biomass/LDH materials from LDH and biomass provides a win-win strategy. There are two main reasons for explaining the rationale of adding LDH to straw: first, cellulose contained in soybean straw can provide substrate for LDH growth. Second, lignin contained in soybean straw has abundant hydroxyl, methoxy, and carbonyl groups on its surface, which forms hydrogen bond with hydroxyl groups and water molecules on and between LDH laminates. Therefore, combining biomass with synthetic materials is oftentimes quite advantageous [31]. It not only solves the problem of a large number of agricultural waste treatments but also has a certain breakthrough in the preparation of new adsorbent. Due to its particle stability, pore characteristics, and surface activity, more and more attention has been paid to these kind of materials [32–35]. For example, Wang et al. [32] found that the maximum As(V) sorption capacity of Ni/Fe-LDHs-biochar composites was 4.38 mg/g, which was approximately three times as large as the mechanical mixture of Ni/Fe-LDHs and biochar. Xue et al. [33] reported that the biochar/MgFe-LDHs composite has a strong sorption ability to nitrate with the maximum adsorption capacity of 24.8 mg/g. Wan et al. [34] indicated that the biochar/MgAl-LDHs composite containing 40% MgAl-LDHs exhibited the highest phosphate removal rate with >95%. Huang et al. [35] examined that the BC@EDTA-LDHs' nano-adsorbent was used to remove Cr(VI) with the maximum adsorption capacity of 38 mg/g. However, the above biomass materials are calcined or lye washed before being used for adsorption. Calcining brings a series of problems, such as adsorption capacity decreases, greenhouse effect, and air pollution.

More importantly, the pretreatment of biomass will consume more resources. To achieve the full utilization of resources and environmental protection, we used un-calcined or un-lye washing biomass to obtain a new adsorbent.

The objectives of this study were as follows: (1) to synthesize the compounds of Biomass (soybean straw)/MgAl-LDHs (B/LDHs) using the mechanical-hydrothermal method [36]; (2) to analyze the properties of B/LDHs using various characterization methods; and (3) to study the adsorption performance of B/LDHs for heavy metal ions Pb(II).

2 Experimental

2.1 Materials

Al(OH)₃, Pb(NO₃)₂, NaNO₃, and HNO₃ were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Mg(OH)₂ was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. All chemicals were of analytical grade and used as received. Soybean straw was from local agricultural waste. Soybean straw was cleaned and dried. Then, it was crushed to obtain the powder. At last, the powder was passed through a 100-mesh sieve and standby. Water was purified with a Direct-Pure UP water purification system (Rephile, China).

2.2 Preparation of B/LHDs nanocomposites

The B/LHDs nanocomposites were prepared by the mechanical-hydrothermal method in our previous studies [36]. Different from previous studies, soybean straw (1.0 g) powder was added in the first step. After a series of reaction treatments, it finally obtained the B/LDHs' nanocomposite sample. This sample was abbreviated as 10% B/LDHs (see supporting information for specific preparation).

Under the same conditions, the 50% B/LDHs and the Mg–Al LDHs without the soybean straw were prepared.

2.3 Characterization

Under the conditions of 10 kV acceleration voltage and gold spraying, the morphology of the samples were analyzed using a JSM-6700F scanning electron microscopy (SEM, JEOL, Japan) and a JEM-2100 transmission electron

microscopy (TEM, JEOL, Japan). Fourier transform infrared spectra (FTIR) (Nicolet 5700 Spectrometer, USA) of adsorbents were recorded under the conditions that the resolution is better than 0.09 cm^{-1} , the wavenumber accuracy is 0.01 cm^{-1} , and the quick scanning speed is 65 times/second. FTIR of adsorbents was recorded in the range of $4,000\text{--}400\text{ cm}^{-1}$. The samples were pressed with KBr pellets. The N_2 adsorption-desorption isotherms were determined using an Autosorb IQ-MP system (Quantachrome Instruments, USA), and the test samples were degassed at 120°C for 5 h under vacuum before measurement. The specific surface area (A_s) and pore volume (V_p) of the samples were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

2.4 Adsorption experiments

The heavy metal ion Pb(II) was used as the target to test the adsorption capacity of B/LDHs. The sorption experiments were conducted under a batch of equilibration techniques at a temperature of 25.0°C , solubilizing Pb(II) solutions at different concentrations ranging $0\text{--}500\text{ mg/L}$ in water containing 0.010 M of NaNO_3 to get $\text{Pb(NO}_3)_2$ solutions. NaNO_3 was applied as a maintainer for the constant ionic strength of the solutions. With the use of 0.1 M HNO_3 and NaOH solutions, the pH values of the Pb(II) solutions were adjusted to 6.0. The mass-given adsorbent sample with 25 mL of the pollutant solutions was blended in polyethylene centrifuge tubes. The centrifuge tubes were allowed to swing in a thermostatic water bath vessel (Jiangsu Medical Instrument Factory, China) at a temperature of $25.0 \pm 0.2^\circ\text{C}$ for 24 h, and then, the supernatant solution was filtered through a $0.45\text{ }\mu\text{m}$ membrane. The residual pollutant concentrations in the filtrates were measured using the AAS-3600 flame atomic absorption spectrometry (Shanghai Metash Instruments Co., Ltd., China) for Pb(II) .

The sorption amount (Γ_t) was determined by the difference between the initial and the residual concentrations of Pb(II) :

$$\Gamma_t = (C_0 - C_t)/C_s, \quad (1)$$

where Γ_t (mg/g) is the sorption amount at time t , C_0 (mg/L) and C_t (mg/L) are the initial and the remaining concentrations at time t , respectively, and C_s (g/L) is the sorbent dosage.

Sorption kinetic tests showed that $t = 10\text{ h}$ was required to reach equilibrium. To ensure sorption equilibrium, $t = 24\text{ h}$ was selected in the equilibrium sorption tests.

The adsorption capacity and the removal rates (E_R) in this study were calculated as follows:

$$\Gamma_e = (C_0 - C_e)/C_s \quad (2)$$

$$E_R (\%) = (C_0 - C_e)/C_0 \times 100\% \quad (3)$$

where the C_e refers to the equalized one and Γ_e indicates the equilibrium adsorption capacity.

The tests shall be conducted three times, and the final values were taken as the average of overall measurements, with a relative error of less than 5%.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Characterizations

Figure 1 shows the SEM and TEM images of the 50% B/LDHs, 10% B/LDHs, Mg–Al LDHs, and soybean straw samples. The B/LDHs samples featured irregular flaky particles (Figure 1a–d). Furthermore, with the decrease of soybean straw contents, a large number of flake structures could be observed growing on the soybean straw (Figure 1c and d). In addition, hexagonal crystals, typical of LDHs, were observed, and the lateral size of the LDH crystals was $\sim 200\text{ nm}$, which has been reported in our previous studies [36]. Furthermore, the soybean straw showed irregular block structures.

Figure 2 shows the FT-IR spectra of 50% B/LDHs, 10% B/LDHs, Mg–Al LDHs (LDHs), and soybean straw (B) samples. In the spectrum of soybean straw (B), the bands at $3,464$ and $1,620\text{ cm}^{-1}$ were attributed to the hydroxyl group and water deformations, the band at $2,880\text{ cm}^{-1}$ arose from the characteristic peak of methylene on the molecular chain of total cellulose, and $1,080\text{ cm}^{-1}$ arose from the stretching vibration peak of C–H on total cellulose. In the spectrum of the LDH sample, the strong broad band centered at approximately $3,700\text{ cm}^{-1}$ was assigned to the O–H stretching modes of the hydroxyl groups in the LDH layers and the interlayer water, and another band corresponding to water deformation was recorded at approximately $1,620\text{ cm}^{-1}$; the band at $1,362$ was attributed to the ν_3 vibrations of CO_3^{2-} , indicating the presence of CO_3^{2-} in the LDH phase [27]; the other peaks from $\sim 1,000$ to 400 cm^{-1} were attributed to the stretching and bending of the Mg–O and Al–O lattice. The characteristic absorption peaks of LDHs and B

Figure 1: (a, c, e, and g) SEM and (b, d, f, and h) TEM images of (a and b) 50% B/LDHs, (c and d) 10% B/LDHs, (e and f) Mg–Al LDHs, and (g and h) soybean straw.

appear at 3,700 and 1,080, respectively, in the B/LDHs samples, indicating that LDHs were successfully loaded

on the soybean straw surface. These results were consistent with the results of TEM and SEM.

Figure 2: FT-IR spectra of 50% B/LDHs, 10% B/LDHs, Mg–Al LDHs (LDHs), and soybean straw (B).

The N_2 adsorption–desorption isotherms of the 50% B/LDHs, 10% B/LDHs, Mg–Al LDHs (LDHs), and soybean straw (B) samples (Figure 3) showed a type IV adsorption isotherm with a type H3 hysteresis loops when P/P_0 ratio was greater than ~ 0.4 [37], which was manifested as fractured pores formed by the accumulation of flap-like particles. The A_s , V_p , and average pore size (D_p) of the samples are listed in Table 1. With the increase of soybean straw contents, A_s and pore data (D_p , V_p) of the B/LDHs samples decreased significantly. In addition, the mesoporous structure of D_p of ~ 3.4 – 9.3 nm remained in the nanocomposites, which is conducive to its application as an adsorbent.

3.2 Removal performance of B/LDHs composites for Pb(II)

3.2.1 Effects of pH

The pH value of the solution is one of the important parameters affecting the adsorption process. Under the

Figure 3: N_2 adsorption–desorption isotherms of 50% B/LDHs, 10% B/LDHs, Mg–Al LDHs (LDHs), and soybean straw (B).

Table 1: Specific surface area (A_s) and pore data (D_p , V_p) of B, B/LDHs, and LDHs samples

Sample	A_s (m^2/g)	D_p (nm)	V_p (cm^3/g)
B	6.508	3.416	0.008
50% B/LDHs	9.726	3.828	0.037
10% B/LDHs	39.93	3.815	0.169
LDHs	62.95	9.324	0.342

conditions of $C_0 = 50$ mg/L, $C_s = 1.0$ g/L, $C_{NaNO_3} = 0.010$ M, and 25°C , the effects of pH on the adsorption of Pb(II) by B, LDHs, and 50% B/LDHs were studied (Figure 4), respectively. As the pH value of 4–10, Γ_e and E_R for Pb(II) increased, similar results are reported in the literature [27]. In addition, the removal of Pb(II) under high pH (above 8.5) can be attributed to the precipitation of Pb(II) hydroxides [38].

3.2.2 Adsorption kinetics and removal efficiency

First, B/LDHs adsorption kinetics test for Pb(II) ($C_0 = 100$ mg/L, pH = 6.0) was performed to evaluate the contact time required for adsorption equilibrium, where the sorbent dosage (C_s) was 1.0 g/L, the concentration of $NaNO_3$ (C_{NaNO_3}) was 0.010 M, and the temperature was 25°C . The results showed that the adsorption capacity increased significantly in the first 3 h and then increased slowly until reaching equilibrium (Figure S1(a) in the supporting information). It took about 12 h to reach equilibrium. The contact time of 24 h was to choose the decision Γ_e ensures adsorption equilibrium. In addition, it is found that the sorption kinetic processes could be described by the pseudo-second-order kinetic model (Figure S1(b) in the supporting information).

Figure 4: Effects of pH on the removal efficiency of B, LDHs, and 50% B/LDHs for Pb(II). $C_0 = 50$ mg/L, $C_s = 1.0$ g/L, $C_{NaNO_3} = 0.010$ M, and 25°C .

Under the conditions of $C_s = 1.0$ g/L, $C_{\text{NaNO}_3} = 0.010$ M, and 25°C , the removal rates of Pb(II) ($C_0 = 30$ mg/L, pH = 6.0) on the B, B/LDHs, and LDHs samples from aqueous solutions were determined, as shown in Figure 5. The E_R values of the B and LDHs were 43.7 and 59.8%, respectively. The E_R value of the 10% B/LDHs was 47.9%, which was close to the B sample. This may be due to the small specific surface area of the 10% B/LDH composites. However, the E_R value of the 50% B/LDHs was 97.3%. Although the specific surface area of 50% B/LDH composites was relatively small, its adsorption capacity is large. This indicates that a large amount of soybean straw powder provides an adequate growth site for LDHs. However, if the soybean straw content exceeds 50%, the adsorption amount decreases again, the reason is not clear at present. The above results indicate that the goal of “treating waste with waste” could be achieved. Under the same conditions, the E_R values of the B/LDHs were 98.9% when Pb(II) concentration was very low at $C_0 = 0.25$ mg/L. The residual Pb(II) after adsorption was ~ 2.75 $\mu\text{g/L}$, which was lower than the World Health Organization standard for drinking water quality (10 $\mu\text{g/L}$ for Pb(II)) [38]. These results indicate the potential of the 50% B/LDHs composites as the sorbents for wastewater and drinking water treatments.

To evaluate the recyclability of 50% B/LDHs composite materials, the recovery tests were carried out under the conditions of $C_s = 1.0$ g/L, $C_{\text{NaNO}_3} = 0.010$ M, and 25°C , in which Pb(II) $C_0 = 50$ mg/L and pH = 6.0. The desorption efficiency (E_D) of adsorbing Pb(II) from 50% B/LDHs was determined. The results showed that the E_D values of Pb(II) were about 95.6% in the hydrochloric acid solution with pH = 4.0. Therefore, the hydrochloric acid solution with pH = 4.0 was used as the eluent for the recovery test. After 4 cycles, the E_R values of Pb(II) decreased by only less than 8% (Figure S2 in the supporting information).

Figure 5: Removal rates of Pb(II) on B, B/LDHs and LDHs samples. ($C_0 = 50$ mg/L, pH = 6.0). $C_s = 1.0$ g/L, 25°C , and $C_{\text{NaNO}_3} = 0.010$ M.

These results indicate that the 50% B/LDH composites have a good recyclability for removing heavy-metal pollutants from wastewater.

3.2.3 Sorption isotherm

To evaluate the adsorption capacity of B, B/LDHs, and LDHs samples to Pb(II), the adsorption isotherm was determined at $C_s = 1$ g/L, $C_{\text{NaNO}_3} = 0.010$ M, pH = 6.0 for Pb(II), and 25°C , as shown in Figure 6.

Adsorption isotherms are usually described by Langmuir or Freundlich isotherms. Langmuir model can be expressed as follows:

$$\Gamma_e = \frac{K_L \Gamma_m C_e}{1 + K_L C_e} \quad (4)$$

or in a linear form as

$$\frac{C_e}{\Gamma_e} = \frac{C_e}{\Gamma_m} + \frac{1}{K_L \Gamma_m} \quad (5)$$

The Freundlich model can be expressed in a non-linear form as

$$\Gamma_e = K_F C_e^{n_F} \quad (6)$$

or in a linear form as

$$\lg \Gamma_e = \lg K_F + n_F \lg C_e. \quad (7)$$

In these equations, the maximum sorption amount is Γ_m , the Langmuir equilibrium constant is K_L , and the Freundlich constants are K_F and n_F .

The linear and nonlinear regression Langmuir and Freundlich isotherms were used to fit the adsorption data of different composites. The nonlinear model diagram is

Figure 6: Sorption isotherms of Pb(II) on B, B/LDHs, and LDHs samples. $C_s = 1.0$ g/L, $C_{\text{NaNO}_3} = 0.010$ M, 25°C , pH 6.0. The dots represent experimental data, the solid lines represent Langmuir model fits, and the dashed lines represent Freundlich model fits.

Table 2: Nonlinear-fit data of model parameters for Pb(II) sorption on B, LDHs, and B/LDHs samples

Sample	Langmuir isotherm			Freundlich isotherm		
	Γ_m (mg/g)	$K_L \times 10^{-2}$ (L/mg)	R^2	K_F ($L^{n_F} \text{mg}^{1-n_F}/\text{g}$)	n_F	R^2
B	40.8	4.66	0.999	15.1	0.161	0.993
LDHs	60.3	3.96	0.955	16.7	0.211	0.987
10% B/LDHs	68.3	2.44	0.997	13.3	0.264	0.968
50% B/LDHs	78.6	143	0.927	50.0	0.0776	0.979

Figure 7: Sorption isotherms of Pb(II) on 50% B/LDHs at different sorbent dosages. $C_{\text{NaNO}_3} = 0.010$ M, 25°C , pH 6.0. The dots represent experimental data, the solid lines represent Langmuir model fits, and the dashed lines represent Freundlich model fits.

consistent with the experimental data (Figure 6), and the linear model diagram is a straight line (Figure S3 in the supporting information). The best values of the model parameters, Γ_m , K_L , K_F , n_F , and the correlation coefficient (R^2), are listed in Table 2 (and Table S1 in the supporting information). The correlation coefficient (R^2) of each model fitting curve was high, indicating that both Langmuir and Freundlich models could well describe the adsorption isotherms of different composites. In addition, the optimal fitting values of model parameters using nonlinear regression and linear regression are very similar. Furthermore, it can be seen from Table 2, Γ_m values

increase with the increase of the content of B. This is due to the availability of more adsorption sites (or functional groups) from straw lignin and LDH nurturing substrate effect of straw cellulose. It is worth noting that the Γ_m value of 50% B/LDHs increased by 15% over 10% B/LDHs composites. From the point of view of saving resources, it is necessary to replace hydroxides with a large amount of soybean straw.

3.2.4 Effect of sorbent dosage

The amount of adsorbent used (C_s) in adsorption test is an important factor affecting the adsorption capacity of solid adsorbent in aqueous solutions [39,40]. It is of great theoretical and practical significance to study the effect of C_s on adsorption properties. Taking 50% B/LDHs as an example, the adsorption isotherm of Pb(II) at different C_s values was measured. Using the 50% B/LDHs as an example, the sorption isotherms for Pb(II) at different C_s values were measured under the conditions of $C_{\text{NaNO}_3} = 0.010$ M, pH = 6.0, and 25°C , as shown in Figure 7. The adsorption isotherm decreased significantly with the increase of C_s . The C_s dependence of adsorption isotherms is a well-known solid (or adsorbent concentration) effect (C_s effect) [41,42].

Langmuir and Freundlich isotherms were used for nonlinear and linear regression to fit adsorption data under different C_s values. The nonlinear model diagram was consistent with the experimental data (Figure 7), and

Table 3: Nonlinear fit data of model parameters for Pb(II) sorption on 50% B/LDHs at different C_s

C_s (g/L)	Langmuir isotherm			Freundlich isotherm		
	Γ_m (mg/g)	K_L (L/mg)	R^2	K_F ($L^{n_F} \text{mg}^{1-n_F}/\text{g}$)	n_F	R^2
1.00	78.6	1.43	0.927	50.0	0.0776	0.979
2.00	61.2	0.698	0.889	26.0	0.149	0.989
4.00	43.8	0.0283	0.933	16.0	0.190	0.790
8.00	31.2	1.92	0.981	16.9	0.129	0.851

the linear model diagram was a straight line (Figure S4 in the supporting information). The best values of the model parameters, Γ_m , K_L , K_F , n_F , and R^2 , are listed in Table 3 (and Table S2 in the supporting information). The high R^2 values of various model fitting curves indicated that the Langmuir and Freundlich models fully described the adsorption isotherms of any given C_s value. In addition, the optimal fitting values of model parameters using non-linear regression and linear regression are very similar. Furthermore, it can be seen from Table 3 that the Γ_m values decreased with increasing C_s . In fact, all Langmuir and Freundlich parameters change with the change of C_s . Similar results have been reported in the literature. The C_s -dependence of the model parameters violates the predictions of the Langmuir and Freundlich models.

4 Conclusion

The B/LDHs nanocomposites were successfully fabricated using a mechanical-hydrothermal route. The so-obtained nanocomposites were efficient adsorbents to remove heavy metal ions. The experimental results demonstrated that biomass was donated in the sorption process. The pseudo-second-order, Langmuir and Freundlich models well fitted the sorption process, indicating chemisorption and monolayer adsorption were the main adsorption mechanisms. Meanwhile, it is found that there is an obvious effect of adsorbent concentration in the studied adsorption system. Since biomass was from local agricultural waste, the use of biomass as a carrier for LDHs was environmentally friendly. The B/LDHs nanocomposites are potential sorbents for wastewater treatment. Furthermore, the synthesis of biomass/LDHs materials from LDHs and biomass provides a win-win strategy.

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have read and agreed to the published version of the manuscript.

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