Mechanistic Insight of Biochar-layered Double Hydroxide Composite for Efficient Removal of Aqueous Pb(II) and Cu(II)

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Abstract

To explore the heavy metal adsorption mechanisms by biochar-based materials, MgAl-layered double hydroxide (MgAl-LDH) was loaded on a commercial coconut shell biochar (BC) to obtain the composite (BC-LDH) for adsorptive decontamination of Pb(II) and Cu(II) in water. The removal capacities of BC-LDH (294 and 38.6 mg/g) was higher than BC (13.3 and 11.4 mg/g) and LDH (126 and 22.7 mg/g) for aqueous Pb(II) and Cu(II). The pseudo-second-order equation and the Langmuir model could better illustrate the adsorption process, respectively. The interaction mechanisms between BC-LDH and heavy metals were classified as mineral precipitation (Qpre), cation exchange and isomorphic replacement (Qexc), electrostatic attraction (Qele), and surface complexation (Qcom) according to the characterization results. The quantitative analysis indicated that the contributions of the above mechanisms of BC-LDH for Pb(II) and Cu(II) followed the order of Qpre > Qele > Qexc and Qpre > Qexc > Qele, respectively. Compared with BC, the Qpre increased and Qele decreased significantly, certified the combination of BC and LDH provided a kind of viable composite in heavy metal wastewater treatment.

Highlights

- Loading LDH onto biochar increased the removal efficiency for Pb(II) and Cu(II).
- Mechanisms mainly involved precipitation and cation exchange.
- The precipitation contribution of BC-LDH for Pb(II) was 76.26%.
- The contributions of precipitation and ion exchange achieved 89.2% for Cu(II).

1. Introduction

With the rapid progress of the economy, the heavy metal wastewater was discharged increasingly. Heavy metals can be adsorbed and accumulated in plants and animals easily which causes severe toxicity to human organs at a low concentration through food chains (Mohamed Khalith et al., 2021). Therefore, reducing heavy metal pollution is urgent and imperative.

Multitudinous kinds of adsorbents have been developed to capture heavy metals. The biomass can be pyrolyzed to acquire biochar (BC), which created the superiority of low-cost, simple design, and large surface area (Nguyen et al., 2021; Zheng et al., 2021). Besides, layered double hydroxides (LDHs) also have attracted much attention as adsorbents (Zong et al., 2021). The ideal formula of LDH is $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ (El Hassani et al., 2017). The special structure of LDH determines its special properties, such as acid-base (Zhou et al., 2018), chemical composition, structure adjustability (Xie et al., 2019), thermal stability (Ravuru et al., 2019), etc.

The combination of BC and LDH with synergetic effect has exhibited significant improvement in physicochemical properties and adsorption characteristics for pollutants (Chang et al., 2020). The composite material could avoid the limitation of conventional materials in water treatment, like high-cost, low-selectivity, and lower reusable rate. Moreover, the BC, as an ideal support substance, provided wide

reactive areas for metal ions and prevented LDH aggregation (Gholami et al., 2020). In the previous works, the metal ions have been removed by some composites containing BC and LDHs (Wang et al., 2020; Yi et al., 2020). Chen et al. (2018) decorated NiAl-LDH to the porous carbons activated by H_3PO_4 and found the removal capacity of Cr(VI) reached 271.5 mg/g. Xie et al. (2019) synthesized magnetic MgFe-LDH loaded carbon spheres. The maximum adsorption capacities added up to 3.66 mmol/g for Cu(II) and 5.33 mmol/g for Pb(II). Although the results of these studies all indicated that BC-LDH composite material enhanced the adsorption ability of toxic metals, the interaction mechanisms need to be further explored.

Generally, LDHs adsorbed metal ions by the formation of precipitation, complexation with hydroxyl groups, and isomorphism of elements between structure layers (Zhang et al., 2020). BC could remove heavy metals via mineral precipitation, electrostatic attraction, ion exchange, and complexation of functional groups (Wang et al., 2019). Taking Pb(II) adsorbed by BC as an example, the contribution of these four mechanisms was different because the BC was prepared from multiple sources at different temperatures. For the largest contribution, most of the researchers believed that the dominant mechanism was precipitation which accounted for 70.36–89.03% (Wu et al., 2019; Xiao et al., 2020). However, the BC pyrolyzed from wheat straw mainly adsorbed Pb(II) via ion exchange up to 85.12% (Cao et al., 2019). Up to now, the quantitative analysis of heavy metal removal mechanisms is mainly focused on BC materials and there is little research on other materials, such as BC-LDH composite.

In this work, the MgAl-LDH was selected as a typical LDHs to prepare BC-LDH composite to investigate the adsorption mechanisms for aqueous Cu(II) and Pb(II). The qualitative and quantitative interaction mechanisms were performed and discussed in detail. The adsorption isotherm and kinetics were also conducted by batch equilibrium experiments.

2. Materials And Methods

2.1 Synthesis of BC-LDH

The BC powder was bought from Jiangsu Yiqing Activated Carbon Co., LTD, China which was made up of coconut shells carbonized at 900 °C. The other reagents were acquired from Tianjin Damao Reagent Factory.

Solution A contained 1.250 mol/L Mg(II) ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.625 mol/L Al(III) ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and solution B composed of NaOH and Na_2CO_3 (4.125 mol/L OH^- and 1.251 mol/L CO_3^{2-}) were prepared firstly. The coconut shell biochar (3 g) was dispersed in a four-necked flask using distilled water. Then the solution A and solution B were added drop by drop according to the co-precipitation method of LDHs. The pH value was maintained at 10.0 ± 0.1 . After the addition, the mixture was continuously stirred for 12 h and then statically crystallized for another 6 h. The temperature was kept at 60 °C during the preparation process. The precipitate was obtained by centrifuging, washing and desiccating at 80 °C. The MgAl-LDH was also synthesized following the above procedure without BC.

2.2 Batch adsorption experiments

The experiments were implemented in a centrifuge tube containing 50 mg BC-LDH or BC with 20 mL heavy metal solution. The tube was put into a thermostatic oscillator and shaken at 200 rpm and 25 °C. Then the supernatant liquid was obtained by centrifuging at 8000 r/min, filtered through 0.45 µm pore-sized membranes and injected into an atomic flame adsorption spectrometer (AA-7000, Shimadzu, Japan) to get the concentration of heavy metals. The difference value of heavy metals between the initial and equilibrium solutions was applied to calculate the total removal capacity (Q , mg/g). The experiment was conducted three times and the detailed experimental conditions are listed in the figure notes.

2.3 Adsorption mechanistic study

The XRD, XPS, FT-IR, and zeta potential techniques with relevant instruments (Table S1) were applied to characterize BC-LDH material before and after Cu(II) and Pb(II) adsorption. The morphology structure of BC-LDH was detected by SEM with EDS and N_2 adsorption/desorption experiment. The quantitative experiments of different mechanisms were also conducted. The adsorption mechanisms of BC for heavy metals usually involve physical adsorption (Q_{phy}), mineral precipitation (Q_{pre}), cation exchange (Q_{exc}), electrostatic attraction (Q_{ele}) and complexation with functional groups (Q_{com}). Then the contributions of each mechanism were calculated and the specific procedure is listed in Text S1.

3. Results And Discussion

3.1 Properties of BC-LDH

Figure 1a displays the XRD pattern of BC, LDH, and BC-LDH. The main peak in BC at 2θ of 24.00° was observed which was related to the interlayer condensation of carbon. This indicated the amorphous nature of BC (Adorna et al., 2020). The apparent peaks of MgAl-LDH at $2\theta = 11.53^\circ$ (003), 23.40° (006), 34.64° (012), 38.87° (015), 46.03° (018), 60.79° (110), and 62.04° (113) were typical peaks of LDHs (Xu et al., 2021). BC-LDH also showed all the diffraction peaks of MgAl-LDH, indicating that the high purity and good crystal shape of LDH with the combination of BC. However, no obvious diffraction peak of BC was found.

To demonstrate the functional groups of BC-LDH, the materials were analyzed by FT-IR. In Fig. 1b, the broad adsorption bands at 3410 and 1356 cm^{-1} corresponded to the hydroxyl vibrations from the layers or water molecules, respectively (Tang et al., 2018). The peaks existing at $760 - 500\text{ cm}^{-1}$ were assigned to the M–O or O–M–O vibrations (M represents Mg and Al) (Fu et al., 2021). For BC, the carboxyl (–COOH) vibrations occurred weakly at 1702 cm^{-1} . The C–O and C = C vibrations were observed at 1158 and 1576 cm^{-1} , respectively (Xu et al., 2017). To further investigate the functional groups, XPS was used to characterize BC-LDH and BC. The O, as well as C elements, were the basic constituents of BC-LDH and BC (Fig. S1). The C element was rich in BC-LDH and the four main peaks at 282.70, 284.60, 286.10, and 288.34 eV were ascribed to the inorganic carbide, C = C/C–C, C–O–C and O = C–O groups, respectively

(Fig. 1c) (Yu et al., 2019). The deconvolution of O 1s spectra (Fig. 1d) revealed the presence of –OH at 531.81 eV for BC-LDH, H–O–C at 532.81 eV for BC (Swaidan et al., 2021), and another peak at 530.96 eV for BC was C = O group (Kamran and Park, 2020). The main elements of Mg and Al in BC-LDH were also identified. The Al 2p and Mg 1s spectra at 74.45 and 1303.88 eV (Fig. S2) indicated the formation of Al_2O_3 and MgO in BC-LDH (Huang et al., 2018a).

The microstructure and morphology of BC-LDH and BC were shaped by the SEM technique. As reflected in the SEM images, the surface morphology BC was compact and relatively smooth (Fig. 1e). After co-precipitation of MgAl-LDH, the small particles could be seen on the surface of BC-LDH and the surface roughness increased (Fig. 1f). Moreover, the EDS and elemental mapping analysis showed that the Mg, Al, O, and C elements existed and distributed homogeneously on the BC-LDH surface (Fig. S3). The purchased BC had a larger BET surface area of 1195 m^2/g , while BC-LDH had a smaller value of 394.8 m^2/g (Table S2 and Fig. S4). This illustrated that the MgAl-LDH particles may be assembled into the pores of BC during the preparation process and occupied part of the surface area.

3.2 Adsorption isotherm

Figure 2 indicated the isotherms of BC-LDH, BC, and LDH for Pb(II) (a) and Cu(II) (b) were typical isothermal shapes. After hybrid with BC, BC-LDH had increasing adsorption abilities for Cu(II) and Pb(II). The isotherms models of Langmuir and Freundlich (Eq. S5 and S6 in Text S2) were applied to further explore the adsorption mechanisms and the correlation coefficients (R^2) and isothermal parameters were determined (Table 1). The removal process of Cu(II) and Pb(II) by BC-LDH was matched with the Langmuir model well ($R^2 > 0.99$), while that of BC fitted with the Freundlich model well ($R^2 > 0.97$). The q_m values of BC-LDH were 38.6 and 294 mg/g for Cu(II) and Pb(II), respectively, which were larger than other biochar-based or LDH materials (Table 2). Moreover, BC-LDH can be obtained from the commercial biochar via the simple co-precipitation method. This suggested that the composite containing BC and LDH was effective in the wastewater treatment containing heavy metals.

3.3 Adsorption kinetics

Adsorption kinetics are usually applied to assess the reaction rate and the adsorption properties. As shown in Fig. 3, the removal capacity was enhanced significantly along with the increase of time and then tended to equilibrium. For BC-LDH, the adsorption equilibrium time was 100 and 180 min for Cu(II) and Pb(II), respectively, and that of BC and LDH were both 180 and 200 min. The pseudo-first-order (PFO) and pseudo-second-order (PSO) models (Eq. S7 and S8 in Text S2) were employed to depict the adsorption kinetic data. The R^2 values of PSO were entirely greater than that of PFO (Table 3). This indicated that it was preferable for PSO to explain the adsorption behaviors. Therefore, the adsorption of Pb(II) and Cu(II) onto the active sites of BC-LDH and BC were chemical reactions mainly involving ion exchange, surface complexation, and precipitation according to the hypothesis of PSO (Ho and McKay, 1998).

3.4 Adsorption mechanisms

To clarify the interaction mechanisms between BC-LDH and heavy metals, a series of characterizations were performed and discussed in detail. Despite no apparent changes were observed in the FT-IR spectra of BC-LDH after heavy metal adsorption (Fig. S5), the differences were obviously occurred in the XPS spectra and XRD patterns before and after adsorption and applied to elucidate the interaction mechanisms qualitatively. The quantitative analysis of each mechanism was also conducted.

3.4.1 Mineral precipitation

Biochar can release anions, such as OH^- , SO_4^{2-} , CO_3^{2-} , and PO_4^{3-} . The previous reports have testified the precipitation between the heavy metals and anions (Bandara et al. 2020) or surface groups of LDH materials (Li et al., 2021). Figure 4a illustrated that all the characteristic XRD peaks of BC-LDH after Cu(II) and Pb(II) loading were not shifted. This indicated the structure of BC-LDH was not destroyed during the adsorption process. After adsorption of Pb(II), BC-LDH had some distinctly characteristic peaks. The new peaks were attributed to the $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ based on the PDF card of 13-0131 (Zhang et al., 2020). Nonetheless, there was unapparent changes in the XRD pattern of BC-LDH adsorbed Cu(II). Coincidentally, Zhang et al. (2021) also did not detect the typical XRD peaks of Cu(II) after adsorbing onto cow manure biochar. To further explore the mineral precipitation mechanisms, the XPS survey spectra were used (Fig. S6). It could be seen that Cu 2p and Pb 4f spectra were distinctly presented in BC-LDH after adsorption. As shown in Fig. 4b, the three new peaks were discovered in the spectrum of Cu 2p. The binding energy at 953.82 eV was Cu $2p_{1/2}$, which meant the emergence of $\text{Cu}(\text{OH})_2$ (Huang et al., 2018b). Furthermore, the Pb $4f_{5/2}$ was also observed at the binding energy at 143.06 eV corresponding to the Pb(II) oxidation state such as $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (Cheng et al., 2020).

The above XRD and XPS analysis indicated that the precipitation was involved in the adsorption mechanisms of BC-LDH (Fig. 4a, b) and BC (Fig. 4c, d). Moreover, the contribution ratio to the total removal amount of BC-LDH reached 76.26% for Pb(II) and 45.0% for Cu(II) according to the quantitative analysis (Fig. 5). This suggested that the mineral precipitation dominated the removal performance of BC-LDH. As for BC, the contribution ratios were 65.55% and 16.14%, respectively. Compared with BC, the increased contribution of precipitation of BC-LDH may be due to the loading of MgAl-LDH on BC.

3.4.2 Cation exchange and isomorphic replacement

Cation exchange is critical to the adsorption mechanism of BC for heavy metals and it can occur between the aqueous metal cations and the cations released from biochar materials. In this work, the concentrations of Na(I), Ca(II), Mg(II), and K(I) in the aqueous solutions all increased after adsorption by BC-LDH (Table S3), which explained the occurrence of ion exchange.

The isomorphic substitution is one of the characteristics of LDH materials. The XPS data were used to calculate the atomic ratio of Mg/Al of BC-LDH. With the procedure of isomorphic substitution of Mg element with aqueous Cu(II) or Pb(II), the molar ratio of Mg/Al of BC-LDH reduced from 1.94 to 1.62 and

1.83, respectively. The replacement of LDH layer element was interconnected with the characteristics of aqueous metal ions, such as ionic charge and radius (Huang et al., 2018a). In the case of MgAl-LDH, this reaction will occur more easily when the ionic radius of metal is closer to Mg (0.066 nm). In consequence, Pb (0.12 nm) is more difficult to undergo isomorphic substitutions than Cu (0.072 nm) (Ravuru et al., 2019).

As shown in Fig. 5, the cation exchange and isomorphic replacement was another key mechanism of Cu(II) adsorption by BC-LDH and BC. The contributions were 44.18% and 45.87%. Moreover, the Q_{exc} of BC for Cu(II) was 4.89 mg/g and that of BC-LDH increased to 13.03 mg/g, suggesting the isomorphic replacement contributed to these mechanisms. By contrast, the contributions of Q_{exc} for Pb(II) adsorption by BC-LDH and BC were only 9.95% and 3.35%, respectively.

3.4.3 Electrostatic attraction

The surface charge of adsorbent is the vital factor impacting the removal performance of functional material for aqueous metals (Ahmed et al., 2021). The negative charge of material can easily remove metal cations through electrostatic attraction and the zeta potential values link with the surface charge. For BC, the negative zeta potentials at the pH range of 3–12 decreased after heavy metal adsorption (Fig. 6a), demonstrating the important role of electrostatic attraction during the adsorption process. The quantitative analysis also identified this and the electrostatic attraction effect accounted for 29.82% (Pb(II)) and 28.52% (Cu(II)). After loading of MgAl-LDH, the surface charge of BC-LDH changed from negative to positive (Fig. 6b). Then the contribution of electrostatic attraction decreased sharply (accounted for 12.46% and 7.67%) and the amounts were only 19.7 and 2.26 mg/g for Pb(II) and Cu(II), respectively.

3.4.4 Complexation with functional groups

In general, the oxygen-containing functional groups (OFGs) of BC could chelate with heavy metals in aqueous solution and it showed great significance in removing contaminants from water. However, the contribution of the complexation is usually lower than that of precipitation (Li et al., 2018; Zhang et al. 2021). The XPS methods and quantitative analysis in this work also confirmed this. After adsorbing, the areas of C 1s spectra of BC-LDH and BC changed significantly (Fig. 7). The O = C–O ratio decreased by 8.79% and 3.00% while the C–O–C ratio decreased by 7.20% and 4.24% (Table S4), demonstrating the role of the complexation of Pb(II) and Cu(II) with OFGs. The contributions of the complexation were only 1.01% for Pb(II) and 3.08% for Cu(II). Then the ability of complexation with OFGs of BC-LDH for heavy metals was weak. Moreover, the contributions of physical adsorption were also lower than 0.5% and could be ignored.

To sum up, the adsorption mechanisms of Pb(II) and Cu(II) onto BC-LDH and BC included mineral precipitation, complexation with OFGs, ion exchange and isomorphic replacement, and electrostatic attraction based on the characterization analysis results. The quantitative analysis of the above mechanisms indicated that the key mechanisms were precipitation, ion exchange, and electrostatic effect. As the results, the contributions of BC-LDH followed the sequence of Q_{pre} (76.26%) > Q_{le}

(12.46%) > Qexc (9.95%) for Pb(II) and Qpre (45.0%) > Qexc (44.18%) > Qele (7.67%) for Cu(II). As for BC, the orders of mechanistic contributions were Qpre (65.55%) > Qele (29.82%) > Qexc (3.35%) for Pb(II) and Qexc (45.87%) > Qele (28.52%) > Qpre (16.14%) for Cu(II).

4. Conclusion

In this work, the biochar from commercial coconut shell was combined with MgAl-LDH to improve the adsorption capability for aqueous heavy metals and to investigate the intercalation mechanisms qualitatively and quantitatively. After loading MgAl-LDH, BC-LDH had all the typical XRD patterns of LDHs and the specific surface area decreased from 1195 to 394.8 m²/g. Moreover, the maximum adsorption ability of BC-LDH was significantly improved compared to BC and LDH. The adsorption data can be described by the pseudo-second-order kinetic equation and the Langmuir isothermal model. Among the mechanisms of Pb(II) and Cu(II) adsorption by BC-LDH, the precipitation reaction was dominated and the contributions were 76.26% for Pb(II) and 45.0% for Cu(II). The cation exchange and isomorphic replacement was another main mechanism of Cu(II) and the contribution was 44.18%. The electrostatic attraction and surface complexation was also involved in the adsorption process. However, the contributions of surface complexation and physical adsorption were less than 3.1%. Compared with BC, the higher adsorption capacity of BC-LDH for Pb(II) and Cu(II) and the increased precipitation contribution certified that the combination of BC and LDH can provide a viable candidate material for heavy metals removal.

Declarations

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Authors' contributions

Xinyue Su: investigation, conceptualization, methodology, formal analysis, writing -original draft; Yan Chen: conceptualization, methodology, writing-review & editing; Yanfei Li: conceptualization, methodology, formal analysis; Jing Li: investigation, methodology; Wen Song: methodology; Xuguang Li: formal analysis, writing-review & editing; Lianguo Yan: conceptualization, resources, supervision, writing-review & editing, project administration, funding acquisition.

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Declarations

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Consent to participate Not applicable

Consent for publication Not applicable

Conflict of interest The authors declare no competing interests.

References

Adorna J, Borines M, Dang VD, Doong RA (2020) Coconut shell derived activated biochar-manganese dioxide nanocomposites for high performance capacitive deionization. *Desalination* 492: 114602.

Ahmed W, Mehmood S, Nunez-Delgado A, Ali S Qaswar M, Shakoar A, Mahmood M, Chen DY (2021) Enhanced adsorption of aqueous Pb(II) by modified biochar produced through pyrolysis of watermelon seeds. *Sci Total Environ* 784: 147136.

Bandara T, Xu J, Potter ID, Franks A, Chathurika JBAJ, Tang C (2020) Mechanisms for the removal of Cd(II) and Cu(II) from aqueous solution and mine water by biochars derived from agricultural wastes. *Chemosphere* 254: 126745.

Cao Y, Xiao W, Shen G, Ji G, Zhang Y, Gao C, Han L (2019) Carbonization and ball milling on the enhancement of Pb(II) adsorption by wheat straw: Competitive effects of ion exchange and precipitation. *Bioresour Technol* 273: 70-76.

Chang H, Hu R, Zou Y, Quan X, Zhong N, Zhao S, Sun Y (2020) Highly efficient reverse osmosis concentrate remediation by microalgae for biolipid production assisted with electrooxidation. *Water Res* 174: 115642.

Chen S, Huang Y, Han X, Wu Z, Lai C, Wang J, Deng Q, Zeng Z, Deng S (2018) Simultaneous and efficient removal of Cr(VI) and methyl orange on LDHs decorated porous carbons. *Chem Eng J* 352: 306-315.

Cheng Y, Hou P, Pan H, Shi H, Kang P (2020) Selective electrocatalytic reduction of carbon dioxide to oxalate by lead tin oxides with low overpotential. *Appl Catal B: Environ* 272: 118954.

El Hassani K, Beakou BH, Kalnina D, Oukani E, Anouar A (2017) Effect of morphological properties of layered double hydroxides on adsorption of azo dye Methyl Orange: A comparative study. *Appl Clay Sci* 140: 124-131.

Fu D, Kurniawan TA, Avtar R, Xu P, Othman MHD (2021) Recovering heavy metals from electroplating wastewater and their conversion into Zn₂Cr-layered double hydroxide (LDH) for pyrophosphate removal from industrial wastewater. *Chemosphere* 271: 129861.

- Gholami P, Khataee A, Soltani RDC, Dinpazhoh L, Bhatnagar A (2020) Photocatalytic degradation of gemifloxacin antibiotic using Zn-Co-LDH@biochar nanocomposite. *J Hazard Mater* 382: 121070.
- Gonzalez MA, Pavlovic I, Barriga C (2015) Cu(II), Pb(II) and Cd(II) sorption on different layered double hydroxides. A kinetic and thermodynamic study and competing factors. *Chem Eng J* 269: 221-228.
- Ho YS, McKay G (1998) A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Saf and Environ Prot* 76(4): 332-340.
- Huang QQ, Chen Y, Yu HQ, Yan LG, Zhang JH, Wang B, Du, B, Xing LT (2018a) Magnetic graphene oxide/MgAl-layered double hydroxide nanocomposite: One-pot solvothermal synthesis, adsorption performance and mechanisms for Pb^{2+} , Cd^{2+} , and Cu^{2+} . *Chem Eng J* 341: 1-9.
- Huang ZJ, Huang ZY, Feng LJ, Luo XW, Wu PX, Cui LH, Mao XY (2018b) Modified cellulose by polyethyleneimine and ethylenediamine with induced Cu(II) and Pb(II) adsorption potentialities. *Carbohydr Polym* 202: 470-478.
- Ippolito JA, Strawn DG, Scheckel KG, Novak JM, Ahmedna M, Niandou MAS (2012) Macroscopic and molecular investigations of copper sorption by a steam-activated biochar. *J Environ Qual* 41: 1150-1156.
- Kamran U, Park SJ (2020) MnO_2 -decorated biochar composites of coconut shell and rice husk: An efficient lithium ions adsorption-desorption performance in aqueous media. *Chemosphere* 260: 127500.
- Li Y, Bi HY, Liang YQ, Mao XM, Li H (2021) Synthesis of novel magnetic rhamnolipid-activated layered double hydroxides nanocomposite for simultaneous adsorption of Cu(II) and m-cresol from aqueous solution, *Powder Technol* 386: 350-360.
- Li Y, Liu X, Zhang P, Wang X, Cao Y, Han L (2018) Qualitative and quantitative correlation of physicochemical characteristics and lead sorption behaviors of crop residue-derived chars. *Bioresour Technol* 270: 545-553.
- Mohamed Khalith SB, Rishabb Anirud R, Ramalingam R, Karuppannan SK, Dowlath MJH, Pandion K, Ravindran B, WoongChang S, Ovi D, Arasu MV, Ignacimuthu S, Al-Dhabi NA, Chandrasekaran M, Arunachalam KD (2021) Synthesis and characterization of magnetite carbon nanocomposite from agro waste as chromium adsorbent for effluent treatment. *Environ Res* 202: 111669.
- Nguyen DLT, Binh QA, Nguyen XC, Huyen Nguyen TT, Vo QN, Nguyen TD, Phuong Tran TC, Hang Nguyen TA, Kim SY, Nguyen TP, Bae J, Kim IT, Van Le Q (2021) Metal salt-modified biochars derived from agro-waste for effective congo red dye removal. *Environ Res* 200: 111492.
- Ravuru SS, Jana A, De S (2019) Synthesis of NiAl-layered double hydroxide with nitrate intercalation: Application in cyanide removal from steel industry effluent. *J Hazard Mater* 373: 791-800.

- Swaidan A, Barras A, Addad A, Tahon JF, Toufaily J, Hamieh T, Szunerits S, Boukherroub R (2021) Colorimetric sensing of dopamine in beef meat using copper sulfide encapsulated within bovine serum albumin functionalized with copper phosphate ($\text{CuS-BSA-Cu}_3(\text{PO}_4)_2$) nanoparticles. *J Colloid Interface Sci* 582: 732-740.
- Tang J, Mu B, Zong L, Wang A (2018) One-step synthesis of magnetic attapulgite/carbon supported NiFe-LDHs by hydrothermal process of spent bleaching earth for pollutants removal. *J Cleaner Prod* 172: 673-685.
- Wang H, Wang S, Chen Z, Zhou X, Wang J, Chen Z (2020) Engineered biochar with anisotropic layered double hydroxide nanosheets to simultaneously and efficiently capture Pb^{2+} and CrO_4^{2-} from electroplating wastewater. *Bioresour Technol* 306: 123118.
- Wang L, Wang Y, Ma F, Tankpa V, Bai S, Guo X, Wang X (2019) Mechanisms and reutilization of modified biochar used for removal of heavy metals from wastewater: A review. *Sci Total Environ* 668: 1298-1309.
- Wu J, Wang T, Zhang Y, Pan WP (2019) The distribution of Pb(II)/Cd(II) adsorption mechanisms on biochars from aqueous solution: Considering the increased oxygen functional groups by HCl treatment. *Bioresour Technol* 291: 121859.
- Xiao J, Hu R, Chen G (2020) Micro-nano-engineered nitrogenous bone biochar developed with a ball-milling technique for high-efficiency removal of aquatic Cd(II), Cu(II) and Pb(II). *J Hazard Mater* 387: 121980.
- Xie Y, Yuan X, Wu Z, Zeng G, Jiang L, Peng X, Li H (2019) Adsorption behavior and mechanism of Mg/Fe layered double hydroxide with Fe_3O_4 -carbon spheres on the removal of Pb(II) and Cu(II). *J Colloid Interface Sci* 536: 440-455.
- Xu H, Zhu S, Xia M, Wang F (2021) Rapid and efficient removal of diclofenac sodium from aqueous solution via ternary core-shell CS@PANI@LDH composite: Experimental and adsorption mechanism study. *J Hazard Mater* 402: 123815.
- Xu Y, Li J, Huang W (2017) Porous graphene oxide prepared on nickel foam by electrophoretic deposition and thermal reduction as high-performance supercapacitor electrodes. *Materials* 10(8): 936-953.
- Yi Y, Huang Z, Lu B, Xian J, Tsang EP, Cheng W, Fang J, Fang Z (2020) Magnetic biochar for environmental remediation: A review. *Bioresour Technol* 298: 122468.
- Yu S, Wei D, Shi L, Ai Y, Zhang P, Wang X (2019) Three-dimensional graphene/titanium dioxide composite for enhanced U(VI) capture: Insights from batch experiments, XPS spectroscopy and DFT calculation. *Environ Pollut* 251: 975-983.

Zhang P, Zhang X, Yuan X, Xie R, Han L (2021) Characteristics, adsorption behaviors, Cu(II) adsorption mechanisms by cow manure biochar derived at various pyrolysis temperatures. *Bioresour Technol* 331: 125013.

Zhang X, Yan L, Li J, Yu H (2020) Adsorption of heavy metals by l-cysteine intercalated layered double hydroxide: Kinetic, isothermal and mechanistic studies. *J Colloid Interface Sci* 562: 149-158.

Zheng C, Yang Z, Si M, Zhu F, Yang W, Zhao F, Shi Y (2021) Application of biochars in the remediation of chromium contamination: Fabrication, mechanisms, and interfering species. *J Hazard Mater* 407: 124376.

Zhou H, Jiang Z, Wei S (2018) A new hydrotalcite-like absorbent FeMnMg-LDH and its adsorption capacity for Pb²⁺ ions in water. *Appl Clay Sci* 153: 29-37.

Zong P, Shao M, Cao D, Xu X, Wang S, Zhang H (2021) Synthesis of potential Ca-Mg-Al layered double hydroxides coated graphene oxide composites for simultaneous uptake of europium and fulvic acid from wastewater systems. *Environ Res* 196: 110375.

Tables

Table 1. Adsorption isothermal parameters of Cu(II) and Pb(II) by BC-LDH, BC and LDH.

Material	Model	Parameters	Pb(II)	Cu(II)
BC-LDH	Langmuir	q_m (mg/g)	294	38.6
		b (L/mg)	0.827	0.661
		R^2	0.999	0.999
	Freundlich	k_f	113	14.1
		$1/n$	0.156	0.198
		R^2	0.748	0.623
BC	Langmuir	q_m (mg/g)	13.3	11.4
		b (L/mg)	0.386	0.467
		R^2	0.481	0.695
	Freundlich	k_f	8.61	1.72
		$1/n$	0.439	0.788
		R^2	0.978	0.995
LDH	Langmuir	q_m (mg/g)	126	22.7
		b (L/mg)	0.145	0.253
		R^2	0.991	0.998
	Freundlich	k_f	11.2	3.34
		$1/n$	0.397	0.313
		R^2	0.578	0.698

Table 2. Comparison of adsorption capacity of different adsorbents towards Cu(II) and Pb(II).

Adsorbent	q_c (mg/g)		Reference
	Cu(II)	Pb(II)	
BC-LDH	38.6	294	This work
Magnetic graphene oxide/LDH	23.0	192	Huang et al., 2018a
LDH-Cl	36	108	Gonzalez et al., 2015
Wheat straw biochar		164.2	Li et al., 2018
Rice husk biochar		73.5	Li et al., 2018
Steam-activated biochar	42.3		Ippolito et al., 2012

Table 3. Adsorption kinetics parameters of Cu(II) and Pb(II) by BC-LDH, BC and LDH.

Material	Model	Parameters	Pb(II)	Cu(II)
BC-LDH	Pseudo-first-order	q_e (mg/g)	23.96	3.99
		k_1 (1/min)	0.0048	0.0059
		R^2	0.599	0.821
	Pseudo-second-order	q_e (mg/g)	162	30.1
		k_2 (mg·min/g)	0.0121	0.0139
		R^2	0.999	0.999
BC	Pseudo-first-order	q_e (mg/g)	51.86	2.49
		k_1 (1/min)	0.003	0.004
		R^2	0.544	0.558
	Pseudo-second-order	q_e (mg/g)	114	10.9
		k_2 (mg·min/g)	0.0131	0.054
		R^2	0.974	0.998
LDH	Pseudo-first-order	q_e (mg/g)	41.5	6.46
		k_1 (1/min)	0.006	0.005
		R^2	0.570	0.795
	Pseudo-second-order	q_e (mg/g)	125	15.45
		k_2 (mg·min/g)	0.024	0.028
		R^2	0.999	0.998

Figures

Figure 1

XRD patterns (a) and FTIR spectra (b) of materials, XPS spectra C 1s (c) and O 1s (d), and SEM images of BC (e) and BC-LDH (f).

Figure 2

Adsorption isotherms of BC-LDH, BC and LDH for Pb(II) (a) and Cu(II) (b). ($m = 0.05$ g, pH = 5.0 for Cu(II) and 5.69 for Pb(II), $C_0 = 5 - 500$ mg/L for Cu(II) and 100 - 2000 mg/L for Pb(II), $t = 300$ min).

Figure 3

Adsorption kinetics of BC-LDH, BC and LDH for Pb(II) (a) and Cu(II) (b). ($m = 0.05$ g, pH = 5.0 for Cu(II) and 5.69 for Pb(II), $C_0 = 100$ mg/L for Cu(II) and 400 mg/L for Pb(II), $t = 5 - 600$ min).

Figure 4

XRD patterns of BC-LDH (a) and BC (c) before and after heavy metal adsorption, and XPS spectra of Cu 2p and Pb 4f in BC-LDH (b) and BC (d).

Figure 5

Capacities and contribution ratios of the adsorption mechanisms of BC-LDH and BC for Pb(II) (a) and Cu(II) (b).

Figure 6

Zeta potentials of BC (a) and BC-LDH (b) before and after adsorption of Cu(II) and Pb(II).

Figure 7

XPS spectra of C 1s in BC-LDH (a) and BC (b) before and after the adsorption of Cu(II) and Pb(II).

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