Cu(II) and Cd(II) Removal from Aqueous Solution with LDH@GO-NH₂ and LDH@GO-SH: Kinetics and Probable Mechanism

Wei Liao

Sichuan University

Di Bao

Sichuan University

Huiqiang Li (✉ lhq_scu@163.com)

Sichuan University <https://orcid.org/0000-0002-9008-3596>

Ping Yang

Sichuan University

Research Article

Keywords: Adsorption capacities, Amino-group, Thiol-group, Characterization, Heavy metals, Adsorption mechanism

Posted Date: April 29th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-157072/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on July 28th, 2021. See the published version at <https://doi.org/10.1007/s11356-021-15558-y>.

Cu(II) and Cd(II) Removal from Aqueous Solution with LDH@GO-NH₂ and LDH@GO-SH: Kinetics and Probable Mechanism

Wei Liao, Di Bao, Hui-qiang Li*, Ping Yang

College of Architecture and Environment, Sichuan University, Chengdu 610065, China.

E-mail: Lwei0314@163.com, baodi33@126.com, lhq_scu@163.com, yping63@163.com

Tel. +8618200288011, +8618225600405, +8618980668020, +8618602804508

* Author to whom correspondence should be addressed; E-mail: lhq_scu@163.com Tel.

+8618980668020

Abstract:

Two novel adsorbents of thiol- and amino-functionalized GO grafted onto LDH (LDH@GO-NH₂ and LDH@GO-SH) were synthesized and contrasted for adsorption properties for Cu(II) and Cd(II). Characterization experiments illustrated that thiol group (-SH) and amino group (-NH₂) were existed onto LDH@GO-NH₂ and LDH@GO-SH. Adsorption isotherm results showed that the adsorption processes were satisfactorily fitted by both Langmuir and Freundlich models. The maximum adsorption capacity of Cd(II) on LDH@GO-SH at 308 K was 102.77 mg/g, which was about triple that of LDH@GO-NH₂. The enhancement in adsorption capacity was due to the cooperative effect of LDH and GO-SH. The kinetic experimental data for LDH@GO-NH₂ and LDH@GO-SH were found to be in good agreement with pseudo-second-order model. The thermodynamic parameters calculated from the temperature dependent adsorption isotherms indicated that the adsorption was a spontaneous and endothermic process. The possible adsorption mechanisms comprising formation of precipitation, isomorphic substitution of Mg(II), and formation of complexation with amino-groups and thiol-groups were proposed. Desorption experiments put into evidence that the LDH@GO-NH₂ and LDH@GO-SH may be promising suitable candidates for the remediation of metal ions from aqueous solutions in real work in the near future.

Key words: Adsorption capacities; Amino-group; Thiol-group; Characterization; Heavy metals; Adsorption mechanism;

1. Introduction.

Heavy metal contamination is one of the most pressing environmental concerns, affecting human health, water resources, and ecosystems. Heavy metals abundantly discharged into biosphere and natural water can cause severe deterioration of environment and great health hazard (Xie et al. 2015). Characterized by high toxicity, carcinogenicity and non-biodegradability, heavy metals represent acute toxicity to human beings even at low concentrations (Arias et al. 2002, Medellin-Castillo et al. 2017). Among heavy metals, copper and cadmium are two important cation pollutants. Cu(II) is essential to human life and health, but is potentially toxic, which can cause neurotoxicity through the deposition of Cu(II) in the lenticular nucleus of the brain and liver (Chen & Song 2013). Cd(II) is regarded as an extremely toxic metal, over-exposure to Cd(II) can cause kidney damage, hypertension, and skeletal malformation (Wang et al. 2018, Zhao et al. 2018).

In order to eliminate these metal cations, a great many technologies have been explored, including reverse osmosis (Talati et al. 2019), coagulation (Henneberry et al. 2011), and adsorption (Zheng et al. 2018). Among them, adsorption has drawn a great attention due to its simplicity, flexibility and elevated efficiency in industrial applications (Medellin-Castillo et al. 2017). Recently, the hybrid of layered double hydroxides and graphene oxide (LDH@GO) has been investigated as promising adsorbents for heavy metals owing to the advantage of larger specific surface area and versatile properties (Fang & Chen 2014, Zhang et al. 2015). LDH@GO exhibited favorable adsorption capacities for heavy metals in some reports (Liao et al. 2019a, Liao et al. 2019b). Wen et al (Wen et al. 2013). found that layered double hydroxides and graphene oxide (LDHs/GO) nanocomposites had excellent adsorption capacity for heavy

metal ions such as As(V). It is a perpetual goal to improve the removal ability of the adsorbents for practical applications. Chemical modification by introducing distinct functional groups to bring new and improved physical and chemical traits is of interest. Several functional groups such as amino (Ge & Ma 2015), thiol (Yantasee et al. 2007, Yari et al. 2015), carboxyl and hydroxyl (Zhao et al. 2017) can anchor metal ions to form stable metal complexes through a coordinate bond (Khadivi et al. 2019, Tang et al. 2018). Introducing these functional groups would modify the chemical composition of the adsorbents and produce enhanced adsorption capacities (Soltanzadeh et al. 2013). Previously, Cheng et al. (Meng et al. 2018) reported tunable removal efficiency for Fe^{3+} by the amino-functionalized magnetic composite ($\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-NH}_2$). Comprising a Fe_3O_4 core and a mesoporous silica shell, the $\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-NH}_2$ shell exhibited strong metal chelating capability. Chen et al. (Chen et al. 2016) synthesized functionalized graphene oxide with sulfhydryl group (-SH) and amino group (-NH₂) and the functionalized GO exhibited greater Cu(II) sorption ability than the original GO. Indeed, several researches have validated that introducing functional groups can modify the chemical composition of the adsorbents and produce enhanced adsorption capacities (Yao et al. 2016, Zhao et al. 2011b).

In this study, the amino- and thiol-functionalized LDH@GO (LDH@GO-NH₂ and LDH@GO-SH) were prepared. Cu(II) and Cd(II) removal abilities of the two composites in aqueous solution were contrasted. The effect of adsorption properties, such as temperature, pH effect and ionic strength, on the adsorption process were discussed and the data of adsorption isotherms, kinetics and thermodynamics were analyzed in detail. The surface characteristics of adsorbents and adsorption mechanisms were elucidated through Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis. Moreover, the regeneration performance of the prepared adsorbents was tested by 0.1 M MgCl_2 .

2. Experimental

2.1. Materials

The graphite powder was obtained from Sinopharm Chemical Reagent Co. Ltd. Other chemicals were analytical grade and were purchased from Sigma Aldrich (Shanghai) Co. Ltd. without further purification. All test solutions contained 0.01 M NaCl as the background electrolyte.

2.2. Fabrication of the adsorbents

The grapheme oxide (GO) was prepared by Hummers methods (Jr &Offeman 1958).

For preparation of GO-NH₂, 5 mL triethylenetetramine was added to the suspension of GO (containing 0.2 g GO), and then the mixture was transferred to a reaction kettle and put into a pre-heated oven for 2 h at 378 K. After that, the kettle was taken out and cooled down at room temperature. The mixture was washed by acetone (3×), ethanol (3×), and deionized water (3×).

For preparation of GO-SH, 1.0 g 4-aminothiophenol and 40 mL 1 M HCl was added to a three-necked flask under stirring condition, and the temperature of the reaction was increased to 323 K until 4-aminothiophenol was completely dissolved. Then, NaNO₂ solution (2 g NaNO₂ dissolved into 50 mL deionized water) was dropwise added to the reacting mixture under ice-bath condition. After that, 80 mL suspension of GO (containing 0.2 g GO) was added to the reacting solution. After 12 h stirring under ice-bath, the mixture was washed by acetone (3×), ethanol (3×), and deionized water (3×).

For preparation of the amino- and thiol-functionalized LDH@GO, the as-prepared GO-SH or GO-NH₂ was dispersed in 100 mL deionized water and stirred vigorously with a magnetic stirrer. Solution A was prepared by dissolving 3.05 g MgCl₂·6H₂O and 1.21 g AlCl₃·9H₂O in 100 mL deionized water. Solution B was prepared by dissolving 1.2 g NaOH and 1.05 g Na₂CO₃ in 100 mL deionized water. Solution A and B were simultaneously added to the above suspension drop by drop under vigorous

stirring at room temperature. The pH was maintained at 10 during the process. The resulted suspension was stirred for another 4 h at room temperature, and then was aged in a water bath at 338 K for 4 h. The precipitate was centrifuged, washed by ethanol (3×), and deionized water (3×). The precipitate was then dried at 338 K overnight.

2.3. Characterization of as-prepared composites

The Brunauer-Emmett-Teller (BET) nitrogen specific surface areas of the materials were estimated by N₂ adsorption-desorption at 77 K on a surface area and porosity analyzer (ASAP2020, USA). The X-ray powder diffraction (XRD) patterns were measured using a powder diffractometer (PANalytical B.V., Holland). The X-ray photoelectron spectroscopy (XPS) tests were obtained with an AXIS Ultra DLD (Shimadu, Japan) using monochromatic Al K α X-ray source. Fourier transform infrared spectroscopy (FTIR) spectrums were obtained by FTIR spectrometer using KBr pellets over a range of 4,000–400 cm⁻¹ (Nicolet 6700, USA). The metal ion concentrations were determined by flame emission spectrometry (Shimadzu, Japan).

2.4. Adsorption Experiments

Adsorption kinetics of Cu(II) and Cd(II) were carried out by adding 0.5 g/L of each adsorbent to 250 mL Erlenmeyer flasks containing 200 mL Cu(II) and Cd(II) solution at 298 K in a Submersible Stirrers. The initial concentrations of Cu(II) and Cd(II) were 100 mg/L and 20 mg/L, respectively. Adsorption isotherms were studied at various initial concentrations (2-100 mg/L for Cd(II) and 2-200 mg/L for Cu(II)) under three different temperatures of 288 K, 298 K and 308 K, respectively. The initial pH of the solution was adjusted to 5 by 0.1 M HCl and NaOH solution. 0.01 M NaCl was added as the background electrolyte. The effect of pH on adsorption was investigated by varying the pH between 2 and 6 using 0.1 M HCl and NaOH solutions. The influence of solution ionic strength on adsorption was investigated

by varying the concentrations of NaCl (0.001-0.1 M). The initial concentrations of Cu(II) and Cd(II) were maintained at 100 mg/L and 20 mg/L, respectively. The solid and liquid phases were separated by filtration through a 0.45-μm membrane filter.

2.5. Experimental analysis

For kinetic adsorption study, the pseudo-first-order model and pseudo-second-order model were applied to simulate the experimental data and the correlation coefficient (R^2) was considered as a measurement of the agreement between the experimental data and the proposed models. The two kinetic models can be described as (Yao et al. 2017):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

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

where q_e and q_t (mg/g) are the amounts of metal ions adsorbed at equilibrium and at time t (min), respectively. k_1 (1/min) is the rate constant of the pseudo-first-order model and k_2 is the rate constant of the pseudo-second-order model (g/(mg min)).

Langmuir and Freundlich isotherms were employed to calculate adsorption capacity. The Langmuir model is based on monolayer adsorption onto a surface of finite identical adsorption sites, which represents chemisorption on a set of distinct localized adsorption sites. The linear form of the isotherm can be depicted by the following equation (Zhou et al. 2018):

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m} \quad (3)$$

The Freundlich model explains multilayer adsorption on the heterogeneous solid surfaces with adsorption on each class of sites, which can be described as (Zhou et al. 2018):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (4)$$

In the thermodynamic study, three important parameters namely the Gibbs free energy change ΔG° (kJ/mol), standard enthalpy change ΔH° (kJ/mol) and standard entropy change ΔS° (J/(mol·K)) were calculated from the temperature dependent adsorption isotherms.

The standard free energy change (ΔG°), the standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) can be calculated from the relationships (Zhang et al. 2013):

$$\Delta G^\circ = -RT \ln K_0 \quad (6)$$

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

where K_0 is the adsorption equilibrium constant, the values of $\ln K_0$ obtained by plotting $\ln(q_e/c_e)$ versus q_e at different temperature. R is universal gas constant (8.314 J/mol·K). T is the temperature in Kelvin (K).

2.6. Desorption and regeneration of the adsorbents

Desorption experiments were conducted using eluents including 0.1 M MgCl_2 . Firstly, adsorption was performed using 0.05 g of the adsorbents (LDH@GO- NH_2 or LDH@GO-SH) with 100 mL metal ions (20 mg/L for Cd(II) or 100 mg/L for Cu(II)) at 298 K for 24 h. Then the metal-loaded adsorbents were filtrated from solutions through ash-free filter paper on a Buchner funnel. Desorption treatment was then carried out by adding the metal-loaded adsorbents to 50 mL of 0.1 M MgCl_2 and vigorously stirred for 4 h. The desorbed adsorbents were washed thoroughly with distilled water and subjected to the next cycle. The regeneration performances were examined by adsorption-desorption process for four cycles.

3. Results and discussion

3.1. Characterization of the adsorbents

The N₂ adsorption-desorption isotherms of the LDH@GO-NH₂ and LDH@GO-SH were presented in Fig.S1 and the pore structural parameters were summarized in Table 1. According to the IUPAC classification, both isotherms exhibited typical type-III curves with H3 hysteresis loops. Compared with LDH@GO, both the BET specific surface area (S_{BET}) and the pore volume reduced after modification. This might be due to the pore structure in LDH@GO was partially or completely blocked, or even destroyed by the corrosive effect during the modification process. The damage to LDH@GO-NH₂ was more remarkable, and the specific surface area of LDH@GO-SH (59.44 m²/g) was much larger than that of LDH@GO-NH₂ (18.11 m²/g).

XRD patterns of the LDH@GO, LDH@GO-NH₂ and LDH@GO-SH in Fig.1 exhibited structures similar to the unmodified LDH@GO (Liao et al. 2019b), showing the characteristic diffraction peaks of the LDH-phase (JCPDS No. 51-1528). The d_{003} values of LDH@GO-NH₂ and LDH@GO-SH were 0.78 and 0.76 nm, respectively. The XRD results indicated that the as prepared LDH@GO-NH₂ and LDH@GO-SH were principally composed of a hexagonal LDHs phase and no diffraction peaks of impurities were discerned, suggesting the high purity of the sample.

FTIR spectra of GO-NH₂, GO-SH, LDH@GO-NH₂, and LDH@GO-SH are shown in Fig. 2. The broad bands at ~3450 cm⁻¹ and ~1630 cm⁻¹ can be assigned to hydrogen bonded O-H stretching vibration arising from surface hydroxyl groups and bending vibration of water molecules in the interlayer (Huang et al. 2016, Zhang et al. 2012). The bands at ~660 cm⁻¹ and ~420 cm⁻¹ correspond to metal oxide stretching vibrations in the spectra of the composites (Huang et al. 2016). After the modification with triethylenetetramine, the absorbance at wavenumber of 1629 cm⁻¹ in GO-NH₂ corresponds to N-H (Wu

et al. 2013, Yu et al. 2016), suggesting -NH_2 group was successfully grafted onto GO. The absorption peaks at 2924 cm^{-1} and 2835 cm^{-1} in LDH@GO-NH_2 were caused by C-H stretching vibration of methylene groups of alkyl chains (Wu et al. 2013). The absorption of N-H stretching ($\sim 1629\text{ cm}^{-1}$) (Wu et al. 2013) in LDH@GO-NH_2 was overlapped with the absorption peak of water molecules. The bands at 1372 cm^{-1} was due to the vibration mode of CO_3^{2-} , which may be introduced into the interlayer of LDH by absorption of CO_2 during the preparation procedure (Yue et al. 2017). After adsorption of Cu(II) and Cd(II) , the peaks of amine group shifted to lower waves, suggesting amino groups on LDH@GO-NH_2 promoted the adsorption process. For GO-SH , the adsorption band of thiol group was too weak to be detected. Nevertheless, the successful introduction of thiol group were confirmed by the characteristic peaks at 1159 , 1116 , and 617 cm^{-1} , which corresponds to the stretching vibration of S-O (Yao et al. 2016) and C-S bond (Tang et al. 2018). Unfortunately, these peaks were not detected in LDH@GO-SH , which may due to GO-SH was wrapped in the internal region of LDH. Additionally, the peak appeared around 1622 cm^{-1} of GO-SH , LDH@GO-SH , and adsorbed LDH@GO-SH were attributing to the bending vibrations of C=O, demonstrating the existence of oxygen-containing functional groups (Chen et al. 2016).

Fig. S2 shows the XPS spectra of GO-NH_2 , GO-SH , LDH@GO-NH_2 , and LDH@GO-SH in a narrow scan N 1s and S 2p. For GO-NH_2 and LDH@GO-NH_2 , the observed N element at binding energy of 399.5 eV , demonstrating the presence of -NH_2 group. For GO-SH , S element was detected, which suggested that -SH was existed in GO-SH . While for LDH@GO-SH , S element was not detected, which confirmed GO-SH was wrapped inside of LDH.

3.2. Adsorption kinetics.

Adsorption kinetics of Cu(II) and Cd(II) by the LDH@GO-NH_2 and LDH@GO-SH are shown in

Fig. 3. For Cu(II) adsorption on LDH@GO-NH₂ and LDH@GO-SH, there was a fast initial stage in the first few hours and about 60% Cu(II) was removed during the first stage. And then the adsorption slowed down until equilibrium. For Cd(II) adsorption on LDH@GO-SH, the removal rate was fast and the adsorption equilibrium achieved in the first 1 h. While, the removal rate and adsorption capacity were relatively lower by LDH@GO-NH₂ than LDH@GO-SH.

Table 2 illustrated the adsorption kinetics data of pseudo-first-order and pseudo-second-order models. It was obvious that the adsorption of Cu(II) and Cd(II) on LDH@GO-NH₂ and LDH@GO-SH were better fitted with the pseudo-second-order kinetic model than pseudo-first-order model, suggesting that strong chemical forces caused by exchanging electrons at the solid/solution interface (Wang et al. 2017) and the adsorption rate relying on the available sites on the surface of adsorbents (Fang et al. 2014).

3.3. Adsorption isotherm.

Fig. 4 presents the adsorption isotherm LDH@GO-NH₂ and LDH@GO-SH for Cu(II) and Cd(II) at three different temperatures (288 K, 298 K and 308 K). It was clearly shown that the adsorption amount increased with the increase of initial metal ion concentration and temperature. The equilibrium adsorption q_e increased with the increase in Cu(II) and Cd(II) concentrations. The higher concentrations of Cu(II) and Cd(II) provided a driving force to overcome the mass transfer resistance for ion transfer between the solution and the surface of the adsorbents (Długosz & Banach 2018). The equilibrium adsorption capacities of LDH@GO-SH for both Cu(II) and Cd(II) were higher than that of LDH@GO-NH₂ at different concentrations.

The equilibrium adsorption (q_e) of LDH@GO-NH₂ and LDH@GO-SH to Cu(II) was higher than that of Cd(II). Arias et al. (Arias et al. 2002) investigated the adsorption of Cu(II) and Cd(II) on kaolin

and found that the adsorption on kaolin of Cu(II) was stronger than that of Cd(II), which was in agreement with our study. The adsorption affinity is related to adsorbate characteristics in terms of electronegativity and ionic radius (bin Jusoh et al. 2005). The electronegativity of Cu(II) is higher than Cd(II) (Arias et al. 2002), which means Cu(II) has stronger strength to attach electron at adsorbents. Moreover, Cu(II) has a relatively smaller ionic radius than that of the Cd(II), which is 0.0075 and 0.0095 nm, respectively. The smaller ionic radius of Cu(II) made it easier to penetrate into the micropores of the adsorbents. The facts implied that Cu(II) exhibited a stronger affinity than Cd(II) to LDH@GO-NH₂ and LDH@GO-SH.

The relative parameters calculated from Langmuir and Freundlich models are listed in Table 3. The adsorption isotherms were fitted well with both Langmuir model and Freundlich model, suggesting the multiple adsorption of Cu(II) and Cd(II) on LDH@GO-NH₂ and LDH@GO-SH. This phenomenon also indicated that chemisorption was the principal adsorption mechanism in the adsorption process. According to the fitted results of Langmuir model, the adsorption capacity (q_m) increased with the temperature increasing from 288 K to 308 K, indicating the adsorption process was endothermic process. Moreover, LDH@GO-SH appeared to be a more excellent adsorbent than LDH@GO-NH₂ for removing Cu(II) and Cd(II) from aqueous solution. The adsorption capacity for Cd(II) on LDH@GO-SH was nearly three times than that on LDH@GO-NH₂. The maximum adsorption of Cd(II) on LDH@GO-NH₂ and LDH@GO-SH at 308 K were 37.99 and 102.77 mg/g, respectively, based on the Langmuir isotherm. The values of $1/n$ calculated from Freundlich isotherm were less than unity, suggesting that Cu(II) and Cd(II) were adsorbed favorably by LDH@GO-NH₂ and LDH@GO-SH at all temperatures studied. The increase in Freundlich constants with increase of temperature confirmed that adsorption was favorable at high temperatures and the process was endothermic in nature.

3.4. Sorption thermodynamics

With the purpose of investigating the spontaneity and the thermodynamic properties of the adsorption process, the thermodynamic studies were carried out. The values of ΔH° and ΔS° can be acquired from the slopes and intercepts of the plots of $\ln K_C$ versus $1/T$, and the thermodynamic parameters are summarized in Table 4. As listed in Table 4, the negative values of ΔG° indicated that the investigated adsorption processes were spontaneous in the range of testing temperature and the decrease of ΔG° with the increasing temperature illuminated a more favorable adsorption process at higher temperature. The positive values of ΔH° enunciated all the investigated adsorption processes were endothermic and the higher temperature was beneficial to the adsorption processes, which was consistent with the conclusion of the isothermal discussion. Positive values of ΔS° implied some structural changes in sorbate and sorbent during the adsorption process, which lead to an increase in randomness of the solid-solution system (Zhao et al. 2011a). Besides, the values of ΔS° and ΔH° obtained from LDH@GO-SH systems were evidently larger than those obtained from LDH@GO-NH₂ systems, also implying LDH@GO-SH had higher affinity for metal ions.

3.5. Effect of pH and ionic strength

The solution pH has great influence on adsorption of heavy metal ions from aqueous solution since the concentration of protons affects both the surface charge of adsorbent and the speciation of metal ions (Dinari &Tabatabaeian 2018). The effect of solution pH on the adsorption capacities of LDH@GO-NH₂ and LDH@GO-SH for adsorbing Cu(II) or Cd(II) was investigated by varying solution pH values from 2 to 6, and the results are graphed in Fig. 5. The adsorption amount increased as the pH rise from 2 to 4, but further increasing the initial pH to 6 only slightly changed the adsorption amount. In addition, LDH@GO-SH performed greater adsorption ability for Cu(II) and Cd(II) than LDH@GO-NH₂, while

LDH@GO-NH₂ showed a better buffering capacity to acid than LDH@GO-SH.

Generally, a low pH value would abate metal ions retention because of H⁺ competition or protonation of functional groups (Hua et al. 2013). In acidic conditions, the concentration of hydrogen ions increased and the surface of LDH@GO-NH₂ and LDH@GO-SH became positively charged due to the protonation reaction (i.e., S-NH₂+H⁺=S-NH₃⁺ or S-SH+H⁺=S-SH⁺) (Liu et al. 2016). The surface of the adsorbent was gradually blocked by hydrogen ions, and the competition with H⁺ inhibited the adsorption of Cu(II) and Cd(II). The electrostatic repulsion occurred between heavy metal ions and the edge groups with positive charge (S-NH₃⁺ or S-SH₂⁺) on adsorbent surface, which also lead to low adsorption efficiencies of Cu(II) and Cd(II). Thus, minimal metal ions were adsorbed onto the LDH@GO-NH₂ and LDH@GO-SH at pH of 2. At high pH values, the surface of LDH@GO-NH₂ and LDH@GO-SH became negatively charged due to the deprotonation process (i.e., S-NH₂⇌S- NH⁻ +H⁺), which intensified the adsorption of the positively charged metal ions through electrostatic attraction. Moreover, the amount of complex hydrated forms of the metals increased with pH value increased may also played an important role in the adsorption of metal ions (Sprynskyy et al. 2006).

Fig. 5 also shows that the effect of ionic strength on the adsorption of Cu(II) and Cd(II) onto LDH@GO-NH₂ and LDH@GO-SH. The adsorption capacities of Cd(II) decreased with the increase of ionic strength. The reason for this phenomenon might be the facts: (i) the activity coefficients of Cd(II) would be influenced by the ionic strength of solution so that the sorption process would be inhibited; (ii) sodium ions would compete with Cd(II) for the limited adsorption sites onto the adsorbents; (iii) the increased ionic strength impeded the loading of Cd(II) onto the adsorption sites due to the electrostatic repulsion (Chen et al. 2016, Zhao et al. 2011a). As for Cu(II), the adsorption capacities of Cu(II) on LDH@GO-NH₂ and LDH@GO-SH were not dramatically influenced as the concentration of NaCl

increased from 0.001 mol/L to 0.01 mol/L. This revealed that Na^+ did not compete with Cu(II) for the negatively charged adsorption sites (Zhou et al. 2018). While, as the concentration of NaCl further increased to 0.1 mol/L, the adsorption capacities of Cu(II) on LDH@GO-NH_2 and LDH@GO-SH increased. This phenomenon could be ascribed to the reason that with the increasing ionic strength, Cu(II) ions and Na^+ collided with each other and formed particle aggregations, and then the aggregations were favorable to precipitate and adsorb onto the adsorbents surface.

3.6. Adsorption mechanisms

To investigate the mechanisms of the LDH@GO-NH_2 and LDH@GO-SH composites for Cu(II) and Cd(II) removal, the samples after adsorbing Cu(II) and Cd(II) were characterized by XRD, FTIR, and XPS techniques. The Cu(II) -loaded LDH@GO-NH_2 and LDH@GO-SH ($\text{LDH@GO-NH}_2/\text{Cu}$ and LDH@GO-SH/Cu) samples were prepared at $C_0=100$ mg/L, $\text{pH}=5$, and $C_s=0.5$ g/L, and the Cd(II) -loaded LDH@GO-NH_2 and LDH@GO-SH ($\text{LDH@GO-NH}_2/\text{Cd}$ and LDH@GO-SH/Cd) samples were prepared at $C_0=20$ mg/L, $\text{pH}=5$, and $C_s=0.5$ g/L.

After adsorption, all the samples maintained the characteristic diffraction peaks of the LDH-phase, but appeared a number of new peaks (Fig.1). After Cu(II) adsorption, the d_{003} values were changed to 7.9 nm and 7.7 nm for $\text{LDH@GO-NH}_2/\text{Cu}$ and LDH@GO-SH/Cu , respectively. While the d_{003} values of $\text{LDH@GO-NH}_2/\text{Cd}$ and LDH@GO-SH/Cd were barely changed. This may be due to Cu(II) (0.073 nm) has similar ionic radius with Mg(II) (0.072 nm), Cu(II) was more-favorable in the isomorphic substituted with Mg(II) compared to Cd(II) (0.095 nm). Thus, Cu(II) was inserted into the LDH layer during the adsorption process. The “Jahn-Teller” effect caused the distortion of the octahedron in the laminate, and then increased the thickness of the LDH layer (Feng et al. 2003). Moreover, the XRD patterns of $\text{LDH@GO-NH}_2/\text{Cu}$ and LDH@GO-SH/Cu appeared a number of strong peaks, indicating the formation

of $\text{Cu}_2(\text{OH})_3\text{Cl}$ phase (Fig.1). Al_2O_3 phase was also observed, which may because of the insertion of Cu led the LDH layer distorted and unstable. The peaks appeared at $2\theta \approx 23.5, 30.4, 36.4, 43.8, 48.1, 50.0, 58.2,$ and 65.4 was attributing to cadmium-containing compounds after adsorption of Cd(II) onto LDH@GO-SH. No new minerals were detected in the XRD analysis after adsorption of Cd(II) onto LDH@GO-NH₂, which may be due to only a small amount of Cd(II) adsorbed onto LDH@GO-NH₂ and cannot be detected by XRD.

XPS technique was used to analyze the chemical and bonding environment of the LDH@GO-NH₂ and LDH@GO-SH before and after adsorption. The survey spectra of LDH@GO-NH₂ and LDH@GO-SH are shown in Fig. 6.

The Mg 1s, Al 2p, O 1s, and C 1s signals were the most significant features in these spectrums. For LDH@GO-NH₂, the observed N element demonstrated that -NH₂ was existed in LDH@GO-NH₂. While for LDH@GO-SH, N and S elements were not significantly detected. The presence of Cu and Cd in fully scanned survey were obviously observed after adsorption (Fig.6a and Fig.6b), indicating that these metal ions were successfully adsorbed on the adsorbents. The high resolution XPS spectrum of Cu 2p showed the Cu 2p_{3/2} and its shakeup satellites at 934.3 eV and 943.6 eV, and the Cu 2p_{1/2} and its shakeup satellites at the higher BE peaks around 954.8 eV and 962.0 eV, implying the formation of Cu hydroxides during the removal of Cu(II) (Fig.6c) (Wang et al. 2014, Yue et al. 2017). As for Cd, the binding energies of 405.3 eV for 3d_{5/2} and 411.9 eV for 3d_{3/2} were detected, which were attributed to Cd(OH)₂ or CdCO₃ (Fig.6d) (He et al. 2018). In XRD patterns (Fig.1), the appearance of new peaks after adsorption also confirmed the precipitation occurred during the adsorption of Cu(II) and Cd(II). The results indicated the precipitation was an important mechanism for Cu(II) and Cd(II) removal. Besides, a significant decrease of the Mg 1s spectra intensity and a remarkably spectra shift of Mg 1s were observed after Cu(II) and

Cd(II) adsorption, especially for the case of LDH@GO-NH₂ (Fig. 6e), implying an intense variation of Mg bonding environment. Thus, Mg atoms likely played an important role in the adsorption process, which may be due to the isomorphic substitution of Mg by Cu and Cd. Interestingly, one more peak in Al 2p high resolution spectra appeared after adsorption of Cu (Fig. 6f), suggesting the formation of new Al-O bands (Sherwood 1998), probably Al₂O₃. In addition, the O 1s spectra of LDH@GO-NH₂ and LDH@GO-SH after metal ions adsorption were slightly different, indicating the alteration of oxygen constituents (Fig. 6g). On the other hand, the peak at 399.41 eV (N 1s) decreased after Cu and Cd adsorption, implying the strong interactions between -NH₂ and metal ions (Fig. 6h).

The N and S atoms were expected to exhibit a strong affinity for cadmium and copper ions (Li et al. 2015, Tang et al. 2018). The N-containing and S-containing functional groups could provide active adsorption sites to form strong chelation with cadmium and copper ions in the aqueous solution. The S and N atoms have long pair electrons, and it is this which attached amino- and thiol- groups to the LDH@GO. The S atoms own two pairs of long pair electrons, and the N atoms only have a pair of long pair electrons, indicating that the electron giving ability of S is stronger than that of N. The thiol- group has stronger affinity than amino- group to attach the original composites. The thiol- group and amino- group decorated the original composites in different ways. The amino- group was decorated on the surface of LDH@GO-NH₂, and the N-containing groups were identified by FTIR (Fig.2). While, the thiol group grafted GO (GO-SH) was wrapped inside LDH, which could explain the -SH group on LDH@GO-SH was not identified by FTIR and XPS tests. The decoration of thiol- and amino- group weakened the internal force of the layer, and made the bond energy of Al-O and Mg-O decreased and the bond length increased, as a result of a great decrease in the stability of the layer structure. During the adsorption of Cu(II), Cu substituted part of Mg (the releasing of Mg was detected) to form a twisted

octahedral coordination structure, resulting in the intensification of the layer distortion and tend to be structurally unstable. Thus, few Al_2O_3 was formed during the formation of Mg-Al-Cu ternary composites, which were verified by XRD and XPS tests.

In order to further verify the isomorphic substitution, the releasing of Mg in the aqueous solutions were tested by adding 0.5 g/L of LDH@GO-NH₂ and LDH@GO-SH to 100 mg/L Cu(II) and Cd(II) solutions. The concentration of Mg in the solution were detected by AAS after reacting for 24 h. Blank experiment was conducted by adding 0.5 g/L of LDH@GO-NH₂ and LDH@GO-SH to deionized water. The results are showed in Fig.S3. The concentrations of Mg in the solution after Cu(II) adsorption were higher than that in the solution after Cd(II) adsorption. This confirmed that more Mg was substituted by Cu(II) during the adsorption process, which was consistent with the above discussion. For Cd(II) adsorption, LDH@GO-SH released more Mg than LDH@GO-NH₂, indicating thiol- group weakened the internal force of the layer, which promoted substituted of Mg by Cd.

The LDH@GO-SH exhibited higher adsorption capacities for Cu(II) and Cd(II) compared with LDH@GO-NH₂, and the maximum adsorption capacity of LDH@GO-SH to Cd(II) was almost triple that of LDH@GO-NH₂. This could be explained by the hard-soft acid-base theory. According to the hard-soft acid-base theory, hard acid tends to bind with hard base and vice-versa. Cu(II) was considered as a medium acid, and it was easily to bound to all available sites(Vu et al. 2017). While, Cd(II) was considered as a soft acid, it preferred the specific binding sites. -SH groups (soft base) can provide the soft binding unit for soft acid, so it was more-favorable in the binding with Cd(II) compared to -NH₂ (a hard base).

Above all, the adsorption mechanisms of LDH@GO-NH₂ and LDH@GO-SH for adsorption of Cu(II) and Cd(II) were proposed, which generally involved: (i) formation of precipitation; (ii)

isomorphic substitution between Mg and the metal ions (mainly for Cu(II)); (iii) formation of complexation with the functional groups on the surface of LDH@GO-NH₂ and LDH@GO-SH (i.e., -NH₂ and -SH), (mainly for Cd(II)). The enhanced uptake of Cu(II) and Cd(II) on LDH@GO-SH occurred due to the co-operative effect of LDH and GO-SH, the thiol groups in GO-SH weakened the internal force of the layer and then promoted isomorphic substitution. Moreover, thiol group had a stronger affinity for metal ions than amino group. The mechanism of adsorption of Cu(II) and Cd(II) on LDH@GO-SH is illustrated in Fig.7.

3.7. Desorption and reusability

The reusability is an important indication to evaluate the potential of prepared adsorbents in practice application. Therefore, a series of regenerative experiments were conducted by using 0.1 M MgCl₂ as eluant. The adsorption capacities of LDH@GO-NH₂ for Cu(II) and Cd(II) still maintained over 90% after five consecutive adsorption-desorption cycles, while those of LDH@GO-SH left above 85% in the same condition. The result of regeneration experiments demonstrated that both LDH@GO-NH₂ and LDH@GO-SH possessed high potential to remove heavy metal ions from polluted water.

4. Conclusion

Two novel adsorbents, thiol- and amino-functionalized GO grafted onto LDH (LDH@GO-NH₂ and LDH@GO-SH) were synthesized through graft modification with 4-aminothiophenol and triethylenetetramine for Cu(II) and Cd(II) removal from aqueous solutions. The pseudo-second-order model fitted the experimental data effectively than the pseudo-first-order model. The adsorption kinetics, isotherms and thermodynamics were investigated in detail. The adsorption processes were well represented by Langmuir and Freundlich isotherms and were driven by spontaneous endothermic entropy reduction. LDH@GO-SH showed better adsorption capacities for both Cd(II) and Cu(II), due to

the high affinity of thiol group. The maximum adsorption capacities of LDH@GO-SH predicted by the Langmuir isotherm at 298 K were 92.08 mg/g for Cd(II) and 213.67 mg/g for Cu(II). The adsorption mechanisms involve formation of precipitation, isomorphic substitution of Mg(II), and formation of complexation with the functional groups on the surface of LDH@GO-NH₂ and LDH@GO-SH. Additionally, the synthesized adsorbents showed excellent regeneration performance after five adsorption/desorption cycles, hinting that LDH@GO-NH₂ and LDH@GO-SH can be used repeatedly as efficient adsorbents for practical wastewater treatment.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analysed during this study are included in this published article [and its supplementary information files].

Competing interests

The authors declare that they have no competing interests.

Funding

This research was supported by the International Scientific and Technological Innovation and Cooperation Project of Sichuan (No. 2019YFH0170).

Authors' contributions

WL: Methodology, Validation, Formal analysis, Writing- Original draft preparation.

DB: Visualization, Validation.

HQL: Conceptualization, Writing- Reviewing and Editing.

PY: Resources, Supervision.

Reference:

Arias M, Barral MT, Mejuto JC (2002): Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids. *Chemosphere*

bin Jusoh A, Cheng WH, Low WM, Nora'aini A, Megat Mohd Noor MJ (2005): Study on the removal of iron and manganese in groundwater by granular activated carbon. *Desalination* 182, 347-353

Chen D, Zhang H, Yang K, Wang H (2016): Functionalization of 4-aminothiophenol and 3-aminopropyltriethoxysilane with graphene oxide for potential dye and copper removal. *J Hazard Mater* 310, 179-87

Chen Y, Song Y-F (2013): Highly Selective and Efficient Removal of Cr(VI) and Cu(II) by the Chromotropic Acid-Intercalated Zn–Al Layered Double Hydroxides. *Ind Eng Chem Res* 52, 4436-4442

Dinari M, Tabatabaeian R (2018): Ultra-fast and highly efficient removal of cadmium ions by magnetic layered double hydroxide/guargum bionanocomposites. *Carbohydr Polym* 192, 317-326

Długosz O, Banach M (2018): Kinetic, isotherm and thermodynamic investigations of the adsorption of Ag⁺ and Cu²⁺ on vermiculite. *J Mol Liq* 258, 295-309

Fang F, Kong L, Huang J, Wu S, Zhang K, Wang X, Sun B, Jin Z, Wang J, Huang XJ, Liu J (2014): Removal of cobalt ions from aqueous solution by an amination graphene oxide nanocomposite. *J Hazard Mater* 270, 1-10

Fang Q, Chen B (2014): Self-assembly of graphene oxide aerogels by layered double hydroxides cross-linking and their application in water purification. *J. Mater. Chem. A* 2, 8941-8951

439 Feng YJ, Li DQ, Li CX, Wang ZH, Duan X (2003): Synthesis and structural analysis of
 440 Cu-Ni-Mg-Al-CO₃ hydrotalcite-like materials. *Acta Chimica Sinica -Chinese Edition-* 61, 78-83

441 Ge H, Ma Z (2015): Microwave preparation of triethylenetetramine modified graphene oxide/chitosan
 442 composite for adsorption of Cr(VI). *Carbohydr Polym* 131, 280-7

443 He S, Li Y, Weng L, Wang J, He J, Liu Y, Zhang K, Wu Q, Zhang Y, Zhang Z (2018): Competitive
 444 adsorption of Cd(2+), Pb(2+) and Ni(2+) onto Fe(3+)-modified argillaceous limestone: Influence of pH,
 445 ionic strength and natural organic matters. *Sci Total Environ* 637-638, 69-78

446 Henneberry YK, Kraus TEC, Fleck JA, Krabbenhoft DP, Bachand PM, Horwath WR (2011): Removal of
 447 inorganic mercury and methylmercury from surface waters following coagulation of dissolved organic
 448 matter with metal-based salts. *Sci Total Environ*

449 Hua M, Jiang Y, Wu B, Pan B, Zhao X, Zhang Q (2013): Fabrication of a new hydrous Zr(IV)
 450 oxide-based nanocomposite for enhanced Pb(II) and Cd(II) removal from waters. *ACS Appl Mater*
 451 *Interfaces* 5, 12135-42

452 Huang G, Jiang L, Wang D, Chen J, Li Z, Ma S (2016): Intercalation of thiacalix[4]arene anion via
 453 calcined/restored reaction into LDH and efficient heavy metal capture. *J Mol Liq* 220, 346-353

454 Jr WSH, Offeman RE (1958): Preparation of Graphitic Oxide. *J.am.chem.soc* 80, 1339

455 Khadivi SM, Edjlali L, Akbarzadeh A, Seyyedi K (2019): Enhanced adsorption behavior of amended
 456 EDTA-graphene oxide for methylene blue and heavy metal ions. *International Journal of Environmental*
 457 *Science and Technology* 16, 8151-8160

458 Li X, Zhou H, Wu W, Wei S, Xu Y, Kuang Y (2015): Studies of heavy metal ion adsorption on
 459 chitosan/sulfhydryl-functionalized graphene oxide composites. *J Colloid Interface Sci* 448, 389-97

460 Liao W, Wang H, Li H-q, Yang P (2019a): Cd(ii) removal by Fe(ii) surface chemically modified layered

double hydroxide–graphene oxide: performance and mechanism. RSC Adv. 9, 38982-38989

Liao W, Wang HL, Hui-Qiang, Yang P (2019b): Fe(II) Removal from Aqueous Solution by Layered Double Hydroxide/Graphene Composites: Adsorption Coupled with Surface Oxidation. Environ Eng Sci 37

Liu J, Liu W, Wang Y, Xu M, Wang B (2016): A novel reusable nanocomposite adsorbent, xanthated Fe₃O₄-chitosan grafted onto graphene oxide, for removing Cu(II) from aqueous solutions. Applied Surface Science 367, 327-334

Medellin-Castillo NA, Padilla-Ortega E, Regules-Martínez MC, Leyva-Ramos R, Ocampo-Pérez R, Carranza-Alvarez C (2017): Single and competitive adsorption of Cd(II) and Pb(II) ions from aqueous solutions onto industrial chili seeds (*Capsicum annuum*) waste. Sustainable Environment Research 27, 61-69

Meng C, Zhikun W, Qiang L, Chunling L, Shuangqing S, Songqing H (2018): Preparation of amino-functionalized Fe₃O₄@mSiO₂ core-shell magnetic nanoparticles and their application for aqueous Fe(3+) removal. J Hazard Mater 341, 198-206

Sherwood PMA (1998): Introduction to Studies of Aluminum and its Compounds by XPS. Surface Science Spectra 5, 1-3

Soltanzadeh M, Kiani G, Khataee A (2013): Adsorptive capacity of polyacrylonitrile modified with triethylenetetramine for removal of copper and cadmium ions from aqueous solutions. Environ Prog Sustain 33, n/a-n/a

Sprynskyy M, Buszewski B, Terzyk AP, Namiesnik J (2006): Study of the selection mechanism of heavy metal (Pb²⁺, Cu²⁺, Ni²⁺, and Cd²⁺) adsorption on clinoptilolite. J Colloid Interface Sci 304, 21-8

Talati S, Mohebbi A, Dorrani H (2019): Investigation of the Capability of Carbon Nanotube Membranes

483 in Separating the Heavy Metal Ions from Aqueous Solutions by Molecular Dynamics Simulation. *J Eng*
 484 *Thermophys* 28, 123-137
 485 Tang N, Niu CG, Li XT, Liang C, Guo H, Lin LS, Zheng CW, Zeng GM (2018): Efficient removal of
 486 Cd(2+) and Pb(2+) from aqueous solution with amino- and thiol-functionalized activated carbon:
 487 Isotherm and kinetics modeling. *Sci Total Environ* 635, 1331-1344
 488 Vu HC, Dwivedi AD, Le TT, Seo S-H, Kim E-J, Chang Y-S (2017): Magnetite graphene oxide
 489 encapsulated in alginate beads for enhanced adsorption of Cr(VI) and As(V) from aqueous solutions:
 490 Role of crosslinking metal cations in pH control. *Chem Eng J* 307, 220-229
 491 Wang H, Wang X, Ma J, Xia P, Zhao J (2017): Removal of cadmium (II) from aqueous solution: A
 492 comparative study of raw attapulgite clay and a reusable waste-struvite/attapulgite obtained from
 493 nutrient-rich wastewater. *J Hazard Mater* 329, 66-76
 494 Wang Y-Y, Ji H-Y, Lu H-H, Liu Y-X, Yang R-Q, He L-L, Yang S-M (2018): Simultaneous removal of
 495 Sb(iii) and Cd(ii) in water by adsorption onto a MnFe₂O₄-biochar nanocomposite. *RSC Adv.* 8,
 496 3264-3273
 497 Wang Y, Zhao H, Li M, Fan J, Zhao G (2014): Magnetic ordered mesoporous copper ferrite as a
 498 heterogeneous Fenton catalyst for the degradation of imidacloprid. *Applied Catalysis B: Environmental*
 499 147, 534-545
 500 Wen T, Wu X, Tan X, Wang X, Xu A (2013): One-pot synthesis of water-swellable Mg-Al layered double
 501 hydroxides and graphene oxide nanocomposites for efficient removal of As(V) from aqueous solutions.
 502 *ACS Appl Mater Interfaces* 5, 3304-11
 503 Wu L, Wang H, Lan H, Liu H, Qu J (2013): Adsorption of Cu(II)-EDTA chelates on
 504 tri-ammonium-functionalized mesoporous silica from aqueous solution. *Sep Purif Technol* 117, 118-123

505 Xie Y, Wang J, Wang M, Ge X (2015): Fabrication of fibrous amidoxime-functionalized mesoporous
 506 silica microsphere and its selectively adsorption property for Pb(2+) in aqueous solution. J Hazard Mater
 507 297, 66-73

508 Yantasee W, Warner CL, Sangvanich T, Addleman RS, Carter TG, Wiacek RJ, Fryxell GE, Timchalk C,
 509 Warner MG (2007): Removal of heavy metals from aqueous systems with thiol functionalized
 510 superparamagnetic nanoparticles. Environ Sci Technol 41, 5114-5119

511 Yao T, Xiao Y, Wu X, Guo C, Zhao Y, Chen X (2016): Adsorption of Eu(III) on sulfonated graphene
 512 oxide: Combined macroscopic and modeling techniques. J Mol Liq 215, 443-448

513 Yao W, Yu S, Wang J, Zou Y, Lu S, Ai Y, Alharbi NS, Alsaedi A, Hayat T, Wang X (2017): Enhanced
 514 removal of methyl orange on calcined glycerol-modified nanocrystalline Mg/Al layered double
 515 hydroxides. Chem Eng J 307, 476-486

516 Yari M, Rajabi M, Moradi O, Yari A, Asif M, Agarwal S, Gupta VK (2015): Kinetics of the adsorption of
 517 Pb(II) ions from aqueous solutions by graphene oxide and thiol functionalized graphene oxide. J Mol Liq
 518 209, 50-57

519 Yu J-x, Xiong W-l, Zhu J, Chen J-d, Chi R-a (2016): Removal of Congo red from aqueous solution by
 520 adsorption onto different amine compounds modified sugarcane bagasse. Clean Technologies and
 521 Environmental Policy 19, 517-525

522 Yue X, Liu W, Chen Z, Lin Z (2017): Simultaneous removal of Cu(II) and Cr(VI) by Mg-Al-Cl layered
 523 double hydroxide and mechanism insight. J Environ Sci (China) 53, 16-26

524 Zhang C, Sui J, Li J, Tang Y, Cai W (2012): Efficient removal of heavy metal ions by thiol-functionalized
 525 superparamagnetic carbon nanotubes. Chem Eng J 210, 45-52

526 Zhang F, Song Y, Song S, Zhang R, Hou W (2015): Synthesis of magnetite-graphene oxide-layered

double hydroxide composites and applications for the removal of Pb(II) and 2,4-dichlorophenoxyacetic acid from aqueous solutions. *ACS Appl Mater Interfaces* 7, 7251-63

Zhang J, Zhai S, Li S, Xiao Z, Song Y, An Q, Tian G (2013): Pb(II) removal of Fe₃O₄@SiO₂-NH₂ core-shell nanomaterials prepared via a controllable sol-gel process. *Chem Eng J* 215-216, 461-471

Zhao D, Sheng G, Hu J, Chen C, Wang X (2011a): The adsorption of Pb(II) on Mg₂Al layered double hydroxide. *Chem Eng J* 171, 167-174

Zhao G, Li J, Wang X (2011b): Kinetic and thermodynamic study of 1-naphthol adsorption from aqueous solution to sulfonated graphene nanosheets. *Chem Eng J* 173, 185-190

Zhao J, Niu Y, Ren B, Chen H, Zhang S, Jin J, Zhang Y (2018): Synthesis of Schiff base functionalized superparamagnetic Fe₃O₄ composites for effective removal of Pb(II) and Cd(II) from aqueous solution. *Chem Eng J* 347, 574-584

Zhao N, Zhao C, Lv Y, Zhang W, Du Y, Hao Z, Zhang J (2017): Adsorption and coadsorption mechanisms of Cr(VI) and organic contaminants on H₃PO₄ treated biochar. *Chemosphere* 186, 422-429

Zheng C, Zheng H, Wang Y, Wang Y, Qu W, An Q, Liu Y (2018): Synthesis of novel modified magnetic chitosan particles and their adsorption performance toward Cr(VI). *Bioresour Technol* 267, 1-8

Zhou Q, Liao B, Lin L, Qiu W, Song Z (2018): Adsorption of Cu(II) and Cd(II) from aqueous solutions by ferromanganese binary oxide-biochar composites. *Sci Total Environ* 615, 115-122

List of Figures.

Fig.1 The XRD patterns of (a) LDH@GO-NH₂ and (b) LDH@GO-SH before and after adsorption.

Fig.2 The FTIR spectra of (a) LDH@GO-NH₂ and (b) LDH@GO-SH before and after adsorption.

Fig.3 The adsorption kinetics of (a) Cu(II) and (b) Cd(II) onto LDH@GO-NH₂ and LDH@GO-SH.

Fig.4 The adsorption isotherms of Cu(II) onto (a) LDH@GO-NH₂, (b) LDH@GO-SH and Cd(II) onto (c) LDH@GO-NH₂, (d) LDH@GO-SH at 288 K, 298 K and 308 K.

Fig.5 The effect of pH and ionic strength on the adsorption capacities of Cu(II) onto (a) LDH@GO-NH₂, (b) LDH@GO-SH and Cd(II) onto (c) LDH@GO-NH₂, (d) LDH@GO-SH.

Fig.6 XPS spectra of (a), (b) survey, (c) Cu 2p, (d) Cd 3d, (e) Mg 1s, (f) Al 2p, (g) O 1s, and (h) N 1s of LDH@GO-NH₂ and LDH@GO-SH.

Fig.7 Mechanism of adsorption of Cu(II) and Cd(II) on LDH@GO-SH.

Fig.1 The XRD patterns of (a) LDH@GO-NH₂ and (b) LDH@GO-SH before and after adsorption.

Fig.2 The FTIR spectra of (a) LDH@GO-NH₂ and (b) LDH@GO-SH before and after adsorption.

Fig.3 The adsorption kinetics of (a) Cu(II) and (b) Cd(II) onto LDH@GO-NH₂ and LDH@GO-SH.

Fig.4 The adsorption isotherms of Cu(II) onto (a) LDH@GO-NH₂, (b) LDH@GO-SH and Cd(II) onto (c) LDH@GO-NH₂, (d) LDH@GO-SH at 288 K, 298 K and 308 K.

Fig.5 The effect of pH and ionic strength on the adsorption capacities of Cu(II) onto (a) LDH@GO-NH₂, (b) LDH@GO-SH and Cd(II) onto (c) LDH@GO-NH₂, (d) LDH@GO-SH.

Fig.6 XPS spectra of (a), (b) survey, (c) Cu 2p, (d) Cd 3d, (e) Mg 1s, (f) Al 2p, (g) O 1s, and (h) N 1s of LDH@GO-NH₂ and LDH@GO-SH.

Fig.7 Mechanism of adsorption of Cu(II) and Cd(II) on LDH@GO-SH.

671 List of Tables.

672 Table 1 Textural properties of the samples.

673 Table 2 Kinetics parameters of Cu(II) and Cd(II) adsorption on LDH@GO-NH₂ and LDH@GO-SH.

674 Table 3 The correlated parameters for the adsorption of Cu(II) and Cd(II) on LDH@GO-NH₂ and

675 LDH@GO-SH from aqueous solution according to Langmuir and Freundlich isotherm models.

676 Table 4 Thermodynamic data for the adsorption of Cu(II) and Cd(II) on LDH@GO-NH₂ and

677 LDH@GO-SH.

678

679

680

681

682

683

684

685

686

687

688

689

690

691

692

693

694

695

696

697 Table 1 Textural properties of the samples.

adsorbents	BET surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹	Pore size/nm
LDH@GO-NH ₂	18.11	0.044	9.88
LDH@GO-SH	59.44	0.139	10.70

698

699

700

701

702

703

704

705

706

707

708

709

710

711

712

713

714

715

716

717

718

719

720

721

722

723

724

725

726

727

728

729

730

731

732

733

734

735

736

Table 2 Kinetics parameters of Cu(II) and Cd(II) adsorption on LDH@GO-NH₂ and LDH@GO-SH.

adsorbates	adsorbents	q _{e,exp} (mg/g)	Pseudo-first-order			Pseudo-second-order		
			q _{e, cal} (mg/g)	k ₁ (h ⁻¹)	R ²	q _{e, cal} (mg/g)	k ₂ (g/mg h)	R ²
Cu(II)	LDH@GO-NH ₂	149.60	137.65	0.9103	0.8966	150.67	0.00792	0.9834
	LDH@GO-SH	143.89	156.78	0.8842	0.9290	173.93	0.00637	0.9906
Cd(II)	LDH@GO-NH ₂	16.37	14.39	1.4298	0.6392	15.49	0.1249	0.8603
	LDH@GO-SH	27.19	28.12	4.6845	0.9243	28.46	0.6293	0.9538

Table 3 The correlated parameters for the adsorption of Cu(II) and Cd(II) on LDH@GO-NH₂ and LDH@GO-SH from aqueous solution according to Langmuir and Freundlich isotherm models.

Adsorbate	Adsorbent	T (K)	Langmuir isotherm			Freundlich isotherm		
			q _m	K _L	R ²	K _F	1/n	R ²
Cd(II)	LDH@GO-NH ₂	288	28.23	0.1513	0.9548	7.29	0.2904	0.9657
		298	32.78	0.1870	0.9743	8.46	0.3045	0.9817
		308	37.99	0.2302	0.9864	9.75	0.3192	0.9933
	LDH@GO-SH	288	85.18	0.1355	0.9675	11.11	0.5007	0.9866
		298	92.08	0.2041	0.9595	17.71	0.3966	0.9772
		308	102.77	0.3228	0.9799	23.20	0.3824	0.9799
Cu(II)	LDH@GO-NH ₂	288	161.29	0.1913	0.9711	21.22	0.4706	0.9057
		298	182.82	0.3754	0.9952	27.95	0.4709	0.8982
		308	204.08	0.4495	0.9924	34.59	0.4575	0.8930
	LDH@GO-SH	288	196.08	0.7183	0.9980	40.29	0.4068	0.9418
		298	213.67	1.4312	0.9993	55.41	0.3654	0.7983
		308	235.29	1.2248	0.9989	64.44	0.3653	0.8363

791 Table 4 Thermodynamic data for the adsorption of Cu(II) and Cd(II) on LDH@GO-NH₂ and
 792 LDH@GO-SH.

Adsorbate	Adsorbent	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(mol·K))
Cd(II)	LDH@GO-NH ₂	288	-20.79	20.35	142.85
		298	-22.22		
		308	-23.64		
	LDH@GO-SH	288	-22.42	53.11	262.57
		298	-25.33		
		308	-27.65		
Cu(II)	LDH@GO-NH ₂	288	-25.92	30.21	194.81
		298	-27.79		
		308	-29.82		
	LDH@GO-SH	288	-28.34	43.57	250.26
		298	-31.35		
		308	-33.32		

793

Figures

Figure 1

The XRD patterns of (a) LDH@GO-NH₂ and (b) LDH@GO-SH before and after adsorption.

Figure 2

The FTIR spectra of (a) LDH@GO-NH₂ and (b) LDH@GO-SH before and after adsorption.

Figure 3

The adsorption kinetics of (a) Cu(II) and (b) Cd(II) onto LDH@GO-NH₂ and LDH@GO-SH.

Figure 4

The adsorption isotherms of Cu(II) onto (a) LDH@GO-NH₂, (b) LDH@GO-SH and Cd(II) onto (c) LDH@GO-NH₂, (d) LDH@GO-SH at 288 K, 298 K and 308 K.

Figure 5

The effect of pH and ionic strength on the adsorption capacities of Cu(II) onto (a) LDH@GO-NH₂, (b) LDH@GO-SH and Cd(II) onto (c) LDH@GO-NH₂, (d) LDH@GO-SH.

Figure 6

XPS spectra of (a), (b) survey, (c) Cu 2p, (d) Cd 3d, (e) Mg 1s, (f) Al 2p, (g) O 1s, and (h) N 1s of LDH@GO-NH₂ and LDH@GO-SH.

Figure 7

Mechanism of adsorption of Cu(II) and Cd(II) on LDH@GO-SH.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryMaterial.docx](#)