Cu(II) and Cd(II) removal from aqueous solution with LDH@GO-NH\(_2\) and LDH@GO-SH: kinetics and probable mechanism

Wei Liao \(^1\) · Di Bao \(^1\) · Hui-qiang Li \(^1\) · Ping Yang \(^1\)

Received: 14 January 2021 / Accepted: 17 July 2021 / Published online: 28 July 2021
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2021

Abstract
Two novel adsorbents (LDH@GO-NH\(_2\) and LDH@GO-SH) were successfully synthesized by grafting thiol- or amino-functionalized GO onto LDH and their adsorption capacities for heavy metal ions (Cu(II) and Cd(II)) were significantly enhanced. Characterization experiments illustrated that the thiol group (–SH) or amino group (–NH\(_2\)) was grafted onto LDH@GO-NH\(_2\) or LDH@GO-SH. Adsorption isotherms 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-NH\(_2\). The enhancement in adsorption capacity of LDH@GO-SH was due to the cooperative effect of LDH and GO-SH. The kinetic experimental data for LDH@GO-NH\(_2\) and LDH@GO-SH were found to be in good agreement with the pseudo-second-order model. The thermodynamic parameters calculated from the temperature-dependent adsorption isotherms indicated that the adsorption was spontaneous and an endothermic process. The possible adsorption mechanisms comprising formation of precipitation, isomorphic substitution of Mg(II), and formation of complexation with amino groups or thiol groups were proposed. Desorption experiments put into evidence that LDH@GO-NH\(_2\) 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.

Keywords Surface functionalization · Amino group · Thiol group · Heavy metals removal · Adsorption mechanism

Introduction
Heavy metal contamination is one of the most pressing environmental concerns, affecting human health, water resources, and ecosystems. Heavy metals abundantly discharged into the biosphere and natural water can cause severe deterioration of the environment and great health hazard (Xie et al. 2015). Characterized by high toxicity, carcinogenicity, and non-biodegradability, heavy metals can cause acute toxicity in 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 it is potentially toxic, which can cause neurotoxicity through the deposition of Cu(II) in the lenticular nucleus of the brain and liver (Chen and Song 2013). Cd(II) is regarded as an extremely toxic metal; overexposure 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 from aqueous solution, 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 (Medellín-Castillo et al. 2017). Owing to the advantage of a larger specific surface area and versatile properties, the hybrid of layered double hydroxides and graphene oxide (LDH@GO) has been investigated as a...
promising adsorbent of heavy metals (Fang and Chen 2014; Zhang et al. 2015). In previous reports, LDH@GO exhibited favorable adsorption capacities for heavy metals (Liao et al. 2019a, b). 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 and 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 (Tang et al. 2018; Khadivi et al. 2019). Introducing these functional groups would modify the chemical composition of the adsorbents and produce enhanced adsorption capacities (Zhao et al. 2011a, b). Previously, Cheng et al. (Meng et al. 2018) reported tunable removal efficiency for Fe3+ by the amino-functionalized magnetic composite (Fe3O4@mSiO2–NH2). The Fe3O4@mSiO2–NH2 shell comprised a Fe3O4 core and a mesoporous silica shell, which exhibited strong metal chelating capability. Chen et al. (2016) synthesized functionalized graphene oxide with a sulfydryl group (–SH) and an amino group (–NH2), and the functionalized GO exhibited greater Cu(II) sorption abilities than the original GO.

In this study, two novel adsorbents (LDH@GO-NH2 and LDH@GO-SH) were successfully synthesized by grafting thiol- or amino-functionalized GO onto LDH. Cu(II) and Cd(II) removal abilities of these two adsorbents in aqueous solution were contrasted. The effect of adsorption properties, such as temperature, pH effect, and ionic strength, on the adsorption process was 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 X-ray powder diffraction (XRD), scanning electron microscopy (SEM), 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 MgCl2.

**Experimental**

**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.

**Fabrication of the adsorbents**

The graphene oxide (GO) was prepared by Hummers methods (Hummers and 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 were 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 of stirring under the ice bath, the mixture was washed by acetone (3×), ethanol (3×), and deionized water (3×).

For preparation of LDH@GO-NH2 or LDH@GO-SH, the as-prepared GO-NH2 or GO-SH 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 resulting suspension was stirred for another 4 h at room temperature, and then the mixture was aged in a water bath at 338 K for 4 h. The precipitate was centrifuged and washed by ethanol (3×), and deionized water (3×). The precipitate was then dried at 338 K overnight.

**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 (Shimadzu, Japan) using a monochromatic Al Kα X-ray source. Fourier transform infrared spectroscopy (FTIR) spectra were obtained by an FTIR spectrometer using KBr pellets over a range of 4000–400 cm−1 (Nicolet 6700, USA). The metal ion concentrations were determined by flame emission spectrometry (Shimadzu, Japan). The scanning electron
microscope (SEM) was used to measure the surface morphology (JSM-7500F, Japan).

**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) or Cd(II) solution at 298 K in 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 from 2 to 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.

**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):

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

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

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. 2018b):

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m}$$

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. 2018b):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e$$

In the thermodynamic study, three important parameters namely the Gibbs free energy change ($\Delta G^\circ$ (kJ/mol)), standard enthalpy change ($\Delta H^\circ$ (kJ/mol)), and standard entropy change ($\Delta S^\circ$ (J/(mol·K))) were calculated from the temperature-dependent adsorption isotherms.

The standard free energy change ($\Delta G^\circ$), the standard enthalpy change ($\Delta H^\circ$), and the standard entropy change ($\Delta S^\circ$) can be calculated from the following relationships (Zhang et al. 2013):

$$\Delta G^\circ = -RT \ln K_0$$

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

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 the universal gas constant (8.314 J/mol·K). $T$ is the temperature in Kelvin (K).

**Desorption and regeneration of the adsorbents**

Desorption experiments were conducted using eluents including 0.1 M MgCl₂. Firstly, adsorption was performed using 0.05 g of the adsorbents (LDH@GO-NH₂ or LDH@GO-SH) with 100 mL metal ions solution (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 0.1 M MgCl₂ solution 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 the adsorption-desorption process for four cycles.

**Results and discussion**

**Characterization of the adsorbents**

The N₂ adsorption-desorption isotherms of the LDH@GO-NH₂ and LDH@GO-SH are presented in Fig. S1, and the pore structural parameters are 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 were reduced after modification. This might be because 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; 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).

The SEM micrograph of LDH@GO-NH₂ and LDH@GO-SH is shown in Fig. S2. LDH@GO-NH₂ and LDH@GO-SH exhibited similar morphologies, which were composed of aggregates of inhomogeneous flakes. Both LDH@GO-NH₂ and LDH@GO-SH showed a well-developed layered porous structure.

The XRD patterns of LDH@GO, LDH@GO-NH₂, and LDH@GO-SH in Fig. 1 exhibited structures similar to the unmodified LDH@GO (Liao et al. 2019a), showing the characteristic diffraction peaks of the LDH phase (JCPDS No. 51-1528). The d₀₀₃ 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, indicating that the samples were of high purity.

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 were assigned to hydrogen bonded O–H stretching vibration arising from surface hydroxyl groups and bending vibration of water molecules in the interlayer (Zhang et al. 2012; Huang et al. 2016). The bands at ~660 cm⁻¹ and ~420 cm⁻¹ corresponded 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 corresponded to N–H (Wu et al. 2013; Yu et al. 2016), suggesting the –NH₂ group was successfully grafted onto GO. The absorption peaks at 2924 cm⁻¹ and 2835 cm⁻¹ in LDH@GO-NH₂ were caused by C–H stretching vibration of methylene groups of alkyl chains (Wu et al. 2013). The absorption of N–H stretching (~1629 cm⁻¹) (Wu et al. 2013) in LDH@GO-NH₂ was overlapped with the absorption peak of water molecules. The bands at 1372 cm⁻¹ were due to the vibration mode of CO₃²⁻, which may be introduced into the interlayer of LDH by absorption of CO₂ during the preparation procedure (Yue et al. 2017). After adsorption of Cu(II) and Cd(II), the peaks of the amine group shifted to lower waves, suggesting amino groups on LDH@GO-NH₂ promoted the adsorption process. For GO-SH, the adsorption band of the thiol group was too weak to be detected. Nevertheless, the successful introduction of the thiol group was confirmed by the characteristic peaks at 1159, 1116, and 617 cm⁻¹, which corresponds to the stretching vibration of the S–O (Yao et al. 2016) and C–S bonds (Tang et al. 2018). Unfortunately, these peaks were not detected in LDH@GO-SH, which might be because 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).

Figure S3 shows the XPS spectra of GO-NH₂, GO-SH, LDH@GO-NH₂, and LDH@GO-SH in a narrow scan N 1s and S 2p. For GO-NH₂ and LDH@GO-NH₂, the observed N element was at a binding energy of 399.5 eV, demonstrating the presence of the –NH₂ group. For GO-SH, the S element was detected, which suggested that –SH existed in GO-SH.

### Table 1: Textural properties of the samples

| Adsorbents | BET surface area/m² g⁻¹ | Pore volume/cm³ g⁻¹ | Pore size/nm |
|------------|--------------------------|---------------------|--------------|
| LDH@GO-NH₂ | 18.11                    | 0.044               | 9.88         |
| LDH@GO-SH  | 59.44                    | 0.139               | 10.70        |
while for LDH@GO-SH, the S element was not detected, which confirmed GO-SH was wrapped inside of LDH.

**Adsorption kinetics**

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

**Adsorption isotherm**

Figure 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 is 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 (Dlugosz and 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. (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 more strength to attach electron at adsorbents. Moreover, Cu(II) has a relatively smaller ionic radius than 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 the 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 fitting results of the Langmuir model, the adsorption capacity ($q_m$) increased with the temperature increasing from 288 to 308 K, indicating that the adsorption processes were endothermic processes. 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 maximum adsorption of Cd(II) on LDH@GO-NH₂ and LDH@GO-SH at 308 K was 37.99 and 102.77 mg/g, respectively, based on the Langmuir isotherm. The adsorption capacity for Cd(II) on LDH@GO-SH was nearly three times that on LDH@GO-NH₂. The values of $1/n$ calculated from the Freundlich isotherm were less than unity, suggesting that Cu(II) and Cd(II) were adsorbed

| Adsorbates | Adsorbents | $q_e$ (mg/g) | $q_e$ 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-NH₂ | 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-NH₂ | 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 |

Fig. 4 The adsorption isotherms of Cu(II) onto a LDH@GO-NH₂ and b LDH@GO-SH, and Cd(II) onto c LDH@GO-NH₂ and d LDH@GO-SH at 288 K, 298 K, and 308 K.
favorably by LDH@GO-NH2 and LDH@GO-SH at all temperatures studied. The increase in Freundlich constants with the increase of temperature confirmed that adsorption was favorable at high temperatures and the process was endothermic in nature.

The comparison of prepared adsorbents with other adsorbents reported previously is presented in Table 4 for comparison. Compared with other adsorbents reported in the literature, LDH@GO-NH2 and LDH@GO-SH in our study have considerable or even much higher adsorption capacities, indicating that the prepared adsorbents in our study have great potential to be used as adsorbent for the removal of heavy metals from the aqueous solution.

Sorption thermodynamics

With the purpose of investigating the spontaneity and the thermodynamic properties of the adsorption process, thermodynamic studies were carried out. The values of $\Delta H^\circ$ and $\Delta S^\circ$ 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 5. As listed in Table 5, the negative values of $\Delta S^\circ$ indicated that the investigated adsorption processes were spontaneous in the range of testing temperature and the decrease of $\Delta G^\circ$ with the increasing temperature illuminated a more favorable adsorption process at higher temperature. The positive values of $\Delta H^\circ$ encapsulated 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 $\Delta S^\circ$ implied some structural changes in sorbate and sorbent during the adsorption process, which led to an increase in randomness of the solid-solution system (Zhao et al. 2011a). Besides, the values of $\Delta S^\circ$ and $\Delta H^\circ$ obtained from LDH@GO-SH systems were evidently larger than those obtained from LDH@GO-NH2 systems, also implying that LDH@GO-SH had higher affinity for metal ions.

Effect of pH and ionic strength

The solution pH has great influence on the adsorption of heavy metal ions from aqueous solution since the concentration of protons affects both the surface charge of the adsorbent and the speciation of metal ions (Dinari and 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 rose 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.

The zeta potential at various pH of LDH@GO-NH2 and LDH@GO-SH was determined. As illustrated in Fig. 6, it is obvious that the zeta potential of LDH@GO-NH2 and LDH@GO-SH decreased with the increase in pH. The surfaces of both LDH@GO-NH2 and LDH@GO-SH were positively charged in the pH range from 2 to 6. This positive surface charge of the adsorbents may initiate electrostatic repulsion.

Generally, a low pH value would abate metal ion 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-SH2+) (Liu et al. 2016). The surface of the adsorbent was

| Adsorbate | Adsorbent | $T$ (K) | Langmuir isotherm | Freundlich isotherm |
|-----------|-----------|---------|------------------|---------------------|
|           |           | $q_m$   | $K_L$ | $R^2$ | $K_F$ | $1/n$ | $R^2$ |
| Cd(II)    | LDH@GO-NH2 | 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-NH2 | 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 |
gradually blocked by hydrogen ions, and the competition with H\(^+\) inhibited the adsorption of Cu(II) and Cd(II). Electrostatic repulsion occurred between heavy metal ions and the edge groups with a positive charge (S-NH\(^3\)\(^+\) or S-SH\(^2\)\(^+\)) on the adsorbent surface, which also led to low adsorption efficiencies of Cu(II) and Cd(II). Thus, minimal metal ions were adsorbed onto the LDH@GO-NH\(_2\) and LDH@GO-SH at a pH of 2. At high pH values, the surface of LDH@GO-NH\(_2\) and LDH@GO-SH became less positively charged due to the deprotonation process (i.e., S-NH\(^2\)\(^-\) ⇌ S-NH\(^3\)\(^+\) + 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 an increase in the pH value; this may have also played an important role in the adsorption of metal ions (Sprynskyy et al. 2006).

Figure 5 also shows the effect of ionic strength on the adsorption of Cu(II) and Cd(II) onto LDH@GO-NH\(_2\) 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 following 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; and (iii) the increased ionic strength impeded the loading of Cd(II) onto the adsorption sites due to the electrostatic repulsion (Zhao et al. 2011a; Chen et al. 2016). As for Cu(II), the adsorption capacities of Cu(II) on LDH@GO-NH\(_2\) and LDH@GO-SH were not dramatically influenced as the

| Table 4 | Comparison of the adsorption capacities with other reported adsorbents. |
|-----------------|-----------------|-----------------|-----------------|
| **Materials**    | **Conditions**              | **Adsorption capacity (mg/g)** | **Ref.**       |
| Cu(II) LDH@GO-NH\(_2\) | pH = 5, T = 35 °C, C\(_0\) = 200 mg/L, t = 24 h | 204.80 | This study |
| LDH@GO-SH        | pH = 5, T = 35 °C, C\(_0\) = 200 mg/L, t = 24 h | 234.80 | This study |
| Succinylated SNCs | pH = 5, T = 25 °C, C\(_0\) = 200 mg/L | 84.07  | (Chen et al. 2019) |
| Alkali-PEI-HC    | pH = 5.5, T = 25 °C, C\(_0\) = 1000 mg/L, t = 24 h | 56.1   | (He et al. 2021) |
| TNTs-400W        | pH = 3, T = 25 °C, C\(_0\) = 40 mg/L, t = 24 h | 156.32 | (Chiang Hsieh et al. 2018) |
| CMBC-600         | pH = 5, T = 25 °C, C\(_0\) = 300 mg/L, t = 24 h | 70.42  | (Zhang et al. 2021) |
| PS/Fe\(_2\)O\(_3\)/CS-PEI | pH = 6, T = 30 °C, C\(_0\) = 1000 mg/L, t = 6 h | 212.3  | (Xiao et al. 2017) |
| Cd(II) LDH@GO-NH\(_2\) | pH = 5, T = 35 °C, C\(_0\) = 100 mg/L, t = 24 h | 37.99  | This study |
| LDH@GO-SH        | pH = 5, T = 35 °C, C\(_0\) = 100 mg/L, t = 24 h | 102.77 | This study |
| Lig800           | pH = 5.3, T = 25 °C, C\(_0\) = 100 mg/L, t = 24 h | 91.3   | (Fumihiro et al. 2020) |
| Fe\(_2\)O\(_3\)/SiO\(_2\)/PP | pH = 6, T = 25 °C, C\(_0\) = 40 mg/L, t = 24 h | 7.092  | (Liu et al. 2020) |
| MCFN             | pH = 6, T = 35 °C, C\(_0\) = 500 mg/L, t = 180 min | 97.09  | (Xue et al. 2019) |
| FeMnMg-LDH       | pH = 5.5, T = 25 °C, C\(_0\) = 250 mg/L, t = 4 h | 59.99  | (Zhou et al. 2018a) |
| Fe\(_2\)O\(_3\)/CS NPs | pH = 6.0, C\(_0\) = 150 mg/L, t = 12 h | 36.32  | (Fan et al. 2017) |
| MAC-300          | pH = 5.0, T = 25 °C, C\(_0\) = 300 mg/L, t = 12 h | 73.7   | (Zhang et al. 2020) |

| Table 5 | Thermodynamic data for the adsorption of Cu(II) and Cd(II) on LDH@GO-NH\(_2\) and 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           |                |                     |
concentration of NaCl increased from 0.001 to 0.01 mol/L. This revealed that Na+ did not compete with Cu(II) for the negatively charged adsorption sites (Zhou et al. 2018b). As the concentration of NaCl further increased to 0.1 mol/L, the adsorption capacities of Cu(II) on LDH@GO-NH2 and LDH@GO-SH increased. This phenomenon could be understood by the “salting-out effect.” A decrease in solubility of Cu(II) with increasing concentrations of added NaCl (as electrolyte) thus made Cu(II) more likely to be adsorbed (Grover and Ryall 2005).

Adsorption mechanisms

To investigate the mechanisms of LDH@GO-NH2 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-NH2 and LDH@GO-SH (LDH@GO-NH2/Cu and LDH@GO-SH/Cu) samples were prepared at \( C_0 = 100 \) mg/L, \( pH = 5 \), and \( C_s = 0.5 \) g/L, and the Cd(II)-loaded LDH@GO-NH2 and LDH@GO-SH (LDH@GO-NH2/Cd and LDH@GO-SH/Cd) samples were prepared at \( C_0 = 20 \) mg/L, \( pH = 5 \), and \( C_s = 0.5 \) g/L.

After adsorption, all the samples maintained the characteristic diffraction peaks of the LDH phase, but a number of new peaks appeared (Fig. 1). After Cu(II) adsorption, the \( d_{003} \) values were changed to 7.9 nm and 7.7 nm for LDH@GO-NH2/Cu and LDH@GO-SH/Cu, respectively, while the \( d_{003} \) values of LDH@GO-NH2/Cd and LDH@GO-SH/Cd were barely changed. This may be because Cu(II) (0.073 nm) has a similar ionic radius with Mg(II) (0.072 nm) and 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 LDH@GO-NH2/Cu and LDH@GO-SH/Cu showed a number of strong peaks, indicating the formation of the Cu2(OH)3Cl phase (Fig. 1). The Al2O3 phase was also
observed, which may be because the insertion of Cu caused the LDH layer to be distorted and unstable. The peaks appeared at $2\theta = 23.5, 30.4, 36.4, 43.8, 48.1, 50.0, 58.2,$ and 65.4 and were attributed 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-NH$_2$, which may be due to only a small amount of Cd(II) adsorbed onto LDH@GO-NH$_2$ and cannot be detected by XRD.

The XPS technique was used to analyze the chemical and bonding environment of LDH@GO-NH$_2$ and LDH@GO-SH before and after adsorption. The survey spectra of LDH@GO-NH$_2$ 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 spectra. For LDH@GO-NH$_2$, the observed N element demonstrated that –NH$_2$ existed in LDH@GO-NH$_2$, while for LDH@GO-SH, N and S elements were not significantly detected. The presence of Cu and Cd in the fully scanned survey was obviously observed after adsorption (Fig. 7a, b), 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. 7c) (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 CdCO$_3$ (Fig. 7d) (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 remarkable spectra shift of Mg 1s were observed after Cu(II) and Cd(II) adsorption, especially for the case of LDH@GO-NH$_2$ (Fig. 6e), implying an intense variation of the 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 Al$_2$O$_3$. In addition, the O 1s spectra of LDH@GO-NH$_2$ and LDH@GO-SH after metal ion adsorption were slightly changed, 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 –NH$_2$ 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 the 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-NH$_2$, 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 the thiol and amino groups weakened the internal force of the layer, making the bond energy of Al-O and Mg-O decrease and the bond length increase, 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 making it structurally unstable. Thus, few Al$_2$O$_3$ 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 isomorph substitution, the releasing of Mg in the aqueous solutions was tested by adding 0.5 g/L of LDH@GO-NH$_2$ and LDH@GO-SH to 100 mg/L Cu(II) and Cd(II) solutions. The concentration of Mg in the solution was detected by AAS after reacting for 24 h. A blank experiment was conducted by adding 0.5 g/L of LDH@GO-NH$_2$ and LDH@GO-SH to deionized water. The results are shown in Fig. S4. 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 Cu(II) adsorption, LDH@GO-SH released more Mg than LDH@GO-NH$_2$, indicating the thiol group weakened the internal force of the layer, which promoted substitution of Mg by Cd.

LDH@GO-SH exhibited higher adsorption capacities for Cu(II) and Cd(II) compared with LDH@GO-NH$_2$, and the maximum adsorption capacity of LDH@GO-SH to Cd(II) was almost triple that of LDH@GO-NH$_2$. 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 easily 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) could provide the soft binding unit for soft acid, so it was more favorable in the binding with Cd(II) compared to –NH$_2$ (a hard base).

Above all, the adsorption mechanisms of LDH@GO-NH$_2$ and LDH@GO-SH for adsorption of Cu(II) and Cd(II) were
Fig. 7  XPS spectra of a, b survey, c Cu 2p, d Cd 3d, e Mg 1 s, f Al 2p, g O 1 s, and h N 1s of LDH@GO-NH₂ and LDH@GO-SH
proposed, which generally involved the following: (i) formation of precipitation; (ii) isomorphic substitution between Mg and the metal ions (mainly for Cu(II)); and (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 cooperative 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, the thiol group had a stronger affinity for metal ions than the amino group. The mechanism of adsorption of Cu(II) and Cd(II) on LDH@GO-SH is illustrated in Fig. 8.

**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.

**Conclusion**

Two novel adsorbents, 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 solution. The adsorption kinetics, isotherms, and thermodynamics were investigated in detail. The pseudo-second-order model fitted the experimental data effectively than the pseudo-first-order model. The adsorption processes were driven by spontaneous endothermic entropy reduction, which were well represented by Langmuir and Freundlich isotherms. LDH@GO-SH showed higher 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 involved 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.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s11356-021-15558-y.

**Author contribution** WL: methodology, validation, formal analysis, writing—original draft preparation  
DB: visualization, validation  
HQL: conceptualization, writing—reviewing and editing  
PY: resources, supervision

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

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

**Declarations**

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

**References**

Arias M, Barral MT, Mejuto JC (2002) Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids. Chemosphere 48(10):1081–1088

Bin Jusoh A, Cheng WH, Low WM, Nora’aini A, Noor MJMM (2005) Study on the removal of iron and manganese in groundwater by granular activated carbon. Desalination 182(1-3):347–353

Chen Y, Song Y-F (2013) Highly selective and efficient removal of 4-aminothiophenol and 3-aminopropyltriethoxysilane with graphene oxide for potential dye and copper removal. J Hazard Mater 310:179–187

Chen QJ, Zheng XM, Zhou LL, Zhang YF (2019) Adsorption of Cu(II) and Methylene Blue by succinylated starch nanocrystals. Starch-Starke 71(7-8):1800266

Chiang Hsieh LH, Ou HH, Huang CW (2019) Adsorption of Cu(II) in aqueous solution using microwave-assisted titanate nanotubes. Appl Nanosci 9:505–514

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

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

Fan HL, Zhou SF, Jiao WZ, Qi GS, Liu YZ (2017) Removal of heavy metal ions by magnetic chitosan nanoparticles prepared continuously via high-gravity reactive precipitation method. Carbohydr Polym 174:1192–1200

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(23):8941–8951

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

Feng YJ, Li DQ, Li CX, Wang ZH, Duan X (2003) Synthesis and structural analysis of Cu-Ni-Mg-Al-CO3 hydroxylate-like materials. Acta Chim Sin (Chin Ed) 61(1):78–83

Fumihiko O, Eri N, Hirona M, Chalermpong S, Takehiro N, Naohito K (2020) Assessment of Cd(II) adsorption capability and mechanism from aqueous phase using virgin and calcined lignin. Heliyon 6(6):e04298

Ge H, Ma Z (2015) Microwave preparation of triethylenetetramine modified graphene oxide/chitosan composite for adsorption of Cr(VI). Carbohydr Polym 131:280–287

Grover PK, Ryall RL (2005) Critical appraisal of salting-out and its implications for chemical and biological sciences. Cheminform 36(1):1–10

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

He X, Zhang T, Xue Q, Zhou Y, Tsang D (2021) Enhanced adsorption of Cu(II) and Zn(II) from aqueous solution by polyethyleneimine modified straw hydrochar. Sci Total Environ 778(15):146116

Henneberry YK, Kraus TEC, Fleck JA, Krabbenhoft DP, Bachand PM, Horwath WR (2011) Removal of inorganic mercury and methylmercury from surface waters following coagulation of dissolved organic matter with metal-based salts. Sci Total Environ 409:631–637

Hua M, Jiang Y, Wu B, Pan B, Zhao X, Zhang Q (2013) Fabrication of a new hydrous Zr(IV) oxide-based nanocomposite for enhanced Pb(II) and Cd(II) removal from waters. ACS Appl Mater Interfaces 5(22):12135–12142

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

Hummers WS, Offeman RE (1958) Preparation of graphitic oxide. J Am Chem Soc 80(6):1339

Khadivi SM, Edjlali L, Akbarzadeh A, Seyyedi K (2019) Enhanced adsorption behavior of amended EDTA-graphene oxide for methylene blue and heavy metal ions. Int J Environ Sci Technol 16(12):8151–8160

Li X, Zhou H, Wu W, Wei S, Xu Y, Kuang Y (2015) Studies of heavy metal ion adsorption on chitosan/sulfydryl-functionalized graphene oxide composites. J Colloid Interface Sci 448:389–397

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(67):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(1):43–52

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. Appl Surf Sci 367:327–334

Liu C, Jiang X, Wang X, Wang Q, Liang W (2020) Magnetic polypophenol nanocomposite of Fe3O4/SiO2/PP for Cd(II) adsorption from aqueous solution. Environ Technol:1–41

Medellín-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. Sustain Environ Res 27(2):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. Surf Sci Spectra 5(1):1–3
Sprynskyy M, Buszewski B, Terzyk AP, Namiesnik J (2006) Study of the degradation of imidacloprid. J Colloid Interface Sci 304(1):21–28
Talati S, Mohebbi A, Dorrani H (2019) Investigation of the capability of carbon nanotube membranes in separating the heavy metal ions from aqueous solutions by molecular dynamics simulation. J Eng Thermophys 28(1):123–137
Tang N, Niu CG, Li XT, Liang C, Guo H, Lin LS, Zheng CW, Zeng GM (2018) Efficient removal of Cd(2+) and Pb(2+) from aqueous solution with amino- and thiol-functionalized activated carbon: isotherm and kinetics modeling. Sci Total Environ 635:1331–1344
Vu HC, Dwivedi AD, Le TT, Seo S-H, Kim E-J, Chang Y-S (2017) Synthesis of magnetite-graphene oxide encapsulated in alginate beads for enhanced adsorption of Cr(VI) and As(V) from aqueous solutions: role of crosslinking metal cations in pH control. Chem Eng J 307:220–229
Wang Y, Zhao H, Li M, Fan J, Zhao G (2014) Magnetic ordered mesoporous copper ferrite as a heterogeneous Fenton catalyst for the degradation of imidacloprid. Appl Catal B Environ 147:534–545
Wang H, Wang X, Ma J, Xia P, Zhao J (2017) Removal of cadmium (II) from aqueous solution: a comparative study of raw attapulgite clay and a reusable waste-struvite/attapulgite obtained from nutrient-rich wastewater. J Hazard Mater 329:66–76
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 Sb(iii) and Cd(ii) in water by adsorption of magnetic ordered mesoporous copper ferrite as a heterogeneous Fenton catalyst for the degradation of imidacloprid. Appl Catal B Environ 147:534–545
Yao T, Xiao Y, Wu X, Guo C, Zhao Y, Chen X (2016) Adsorption of Eu(II) on sulfonated graphene oxide: combined macroscopic and modeling techniques. J Mol Liq 215:443–448
Yao W, Yu S, Wang J, Zou Y, Lu S, Ai Y, Alharbi NS, Alsaeedi A, Hayat T, Wang X (2017) Enhanced removal of methyl orange on calcined glycercol-modified nanocrystallline Mg/Al layered double hydroxides. Chem Eng J 307:476–486
Yari M, Rajabi M, Moradi O, Yari A, Asif M, Agarwal S, Gupta VK (2015) Kinetics of the adsorption of Pb(II) ions from aqueous solutions by graphite oxide and thiol functionalized graphene oxide. J Mol Liq 209:50–57
Yu J-x, Xiong W-l, Zhu J, Chen J-d, Chi R-a (2016) Removal of Congo red from aqueous solution by adsorption onto different amine compounds modified sugarcane bagasse. Clean Techn Environ Policy 19(2):517–525
Yue X, Liu W, Chen Z, Lin Z (2017) Simultaneous removal of Cu(II) and Cr(VI) by Mg-Al-Cl layered double hydroxide and mechanism insight. J Environ Sci (China) 53:16–26
Zhang C, Sui J, Li J, Tang Y, Cai W (2012) Efficient removal of heavy metal ions by thiol-functionalized superparamagnetic carbon nanotubes. Chem Eng J 210:45–52
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
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(13):7251–7263
Zhang Z, Wang T, Zhang H, Liu Y, Xing B (2020) Adsorption of Pb(II) and Cd(II) by magnet activated carbon and its mechanism. Sci Total Environ 757:143910
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(1-3):125013
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(1):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(1):185–190
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
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
Zheng C, Zheng H, Wang Y, Yang W, 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 H, Jiang Z, Wei S, Liang J (2018a) Adsorption of Cd(II) from aqueous solutions by a novel layered double hydroxide Fe-Mn-Mg-LDH. Water Air Soil Pollut 229(3):78.71–78.16
Zhou Q, Liao B, Lin L, Qiu W, Song Z (2018b) Adsorption of Cu(II) and Cd(II) from aqueous solutions by ferromanganese binary oxide-biochar composites. Sci Total Environ 615:115–122

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.