1 **Highly selective and efficient removal and extraction of heavy metals by**
2 **layered double hydroxides intercalated with the diphenylamine-4-**
3 **sulfonate: A comparative study**

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Six new NiCr layered double hydroxides (LDHs) intercalated with different inter-layer anions, including diphenylamine-4-sulfonate (DPA), dodecyl sulfonate (DS), pentansulfonate (PS), terephthalate (TA), fumarate (FA) and 2-ethylhexyl hydrogenphosphate (EHP), were synthesized and used to removal of Cd^{2+} , Pb^{2+} , Cu^{2+} , and Zn^{2+} ions from water samples. The maximum adsorption capacities (q_m) for the mentioned LDHs based on their inter-layer anions were $\text{DPA} > \text{DS} > \text{PS} > \text{TA} > \text{FA} > \text{DEHP}$. This observation highlights the key role of the structure of the inter-layer anions in the adsorption behavior of LDHs. The sulfonate-based LDHs showed better adsorption efficiency than carboxylate-based LDHs, and phosphonate-based LDHs showed the lowest adsorption efficiency. Also, at both high and low concentrations of the metal ions, the length of R- groups and the type of functional groups of inter-layer anions play a key role in the adsorption process. Subsequently, DPA-LDH, due to having the highest q_m value among intercalated-LDHs, was chosen as an efficient sorbent for the removal of the metal ions from aqueous samples and its selectivity for adsorption of metal ions was investigated. DPA-LDH displayed a selectivity order of $\text{Zn}^{2+} < \text{Cu}^{2+} < < < \text{Cd}^{2+} < \text{Pb}^{2+}$ for their adsorption, providing good separation of much more toxic metal ions of Cd^{2+} and Pb^{2+} from Zn^{2+} and Cu^{2+} . For the highly toxic Pb^{2+} and Cd^{2+} , enormous q_m values as large as 479 and 282 mg g^{-1} can be obtained, respectively; and these are among the highest q_m values reported for Pb^{2+} and Cd^{2+} sorbents. The very high distribution coefficient (K_d) values for Pb^{2+} ($1.99 \times 10^8 \text{ mL g}^{-1}$) and Cd^{2+} ($1.99 \times 10^7 \text{ mL g}^{-1}$), obtained using a V/m ratio of 2000 mL g^{-1} , place the DPA-LDH at the top of materials known for such removal.

Key words: Layered double hydroxides; Removal, Heavy metal ions; Water samples; Inter-layer anions

1. Introduction

The increasing worldwide contamination of fresh water systems has become one of the key environmental problems facing humanity. Among various contamination sources, heavy metals ions, such as Cd(II), Pb(II), Zn(II) and Cu(II), can cause severe health problems for animals and human beings because, unlike organic contaminants, these heavy metal ions are not biodegradable, tend to accumulate in living organisms, and are known to be toxic or carcinogenic [1-4]. At trace levels, some of the heavy metals such as copper and zinc are essential micronutrients for plants, living organisms, and the human body, whereas, in large amounts, they cause Wilson's, Menkes, and Prion diseases [5]. On the other hand, lead, cadmium are well recognized to be highly toxic and hazardous to human health even at low concentrations [6, 7]. Lead can cause central nervous system damage. It can also damage the kidneys, liver, reproductive system, basic cellular processes and brain functions [8]. Exceeding its critical level, nickel might create serious lung and kidney problems as well as gastrointestinal distress, pulmonary fibrosis and skin dermatitis [8]. Hence, given the catastrophic effects of toxic metal ions on the ecosystem and human health, the presence of elevated levels of Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} in almost argons is a serious matter of concern. As a result, the removal and determination of heavy metal ions in different samples is necessary. Hence, recent research in the area of heavy metal removal has focused on the development of materials with increased affinity, capacity, and selectivity for the target metals. In particular, with resent developments in nanotechnology, the use of different sorbents such as activated carbon, bio materials, zeolites and clay minerals, thanks to their numerous advantages such as high separation efficiency, easy operation and low cost is considered as an efficient technique for removing toxic metal ions from the aqueous medium [9-13]. Among these sorbents, the use of clays as sorbents to remove contaminants has increasingly received attention because they are cheaper than other materials such as

activated carbon and zeolites [14-17]. However, they suffer from low selectivity and weak affinity for heavy metals [10]. In any case, the selectivity of clay minerals for specific metal ions can be improved by intercalating suitable inter-layer anions.

The layered double hydroxides (LDHs) are anionic clays with positively-charged host layers and counter-anions found in the inter-layer space. Their excellent intercalation and anion-exchange properties allow the use of LDHs for versatile applications such as catalysts [18, 19], ion exchange [20, 21], sorbents [10, 22], batteries [23] and supercapacitors [24]. The structural formula of LDHs can be expressed as $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent metal cations, respectively[25]. A^{n-} denotes the inter-layer anions that balance the positive charges on the layers, and x is defined as the molar ratio of M^{2+} to $(M^{2+} + M^{3+})$. The removal capacity of LDHs for specific metal ions can be improved by intercalating the suitable inter-layer anion. Recently, composite materials prepared by intercalation of well-known interlayer anions, such as ethylene diaminetetraacetate ($R-CO_2^-$) [26], aromatic acid anions ($R-CO_2^-$) [27], MoS_4^{2-} ($R-S^-$) [10], chromotropic acid ($R-SO_3^-$) [2], dodecyl sulfate ($R-SO_3^-$) [28], CO_3^{2-} [29], and amino tris (methylene phosphonic acid) ($R-PO_3^-$) [30], into LDHs were reported to be able to adsorb cationic species, which means that LDH-based materials are promising sorbents for metal cations. However, the detailed effect of the structure of inter-layer anions on metal ions adsorption by LDHs has not been reported. It is expected that combination of suitable inter-layer anion with the LDH layers can produce materials capable of possessing suitable binding sites, to remove heavy metal ions.

Therefore, the aim of this work was to investigate effect of anion head groups, type and length of R- groups of inter-layer anions on the adsorption efficiency of intercalated-LDH for some metal ions, including Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+} , from aqueous solutions. For this purpose, six new intercalated-LDHs using different inter-layer anions, namely sodium

diphenylamine-4-sulfonate-LDH (DPA-LDH), dodecyl sulfonate-LDH (DS-LDH), pentansulfonate-LDH (PS-LDH), terephthalate -LDH (TA-LDH), fumarate-LDH (FA-LDH), and 2-ethylhexyl hydrogenphosphate-LDH (EHP-LDH), were synthesized and structurally and morphologically characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), Barret-Joyner-Halender (BJH), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). In the first step, two factors, the sample solution pH and adsorption time affecting the performance of the target metal ions adsorption, were evaluated and the extraction efficiency of intercalated-LDHs was investigated. Then, adsorption isotherm studies were performed and based on the maximum adsorption capacity values of intercalated-LDHs, DPA-LDH was selected as an efficient adsorbent for studying the adsorption selectivity of target metal ions and, next, their distribution coefficients were calculated. Finally, the applicability of DPA-LDH as an efficient solid-phase extraction (SPE) sorbent for the extraction and pre-concentration of trace amounts of target metal ions was evaluated. Also, the use of a DPA intercalated-LDH for removal of heavy metal ions has not been reported.

2. Experimental

2.1. Materials and apparatus

All chemicals were of analytical reagent grade. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Pb}(\text{NO}_3)_2$ salts were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Diphenylamine-4-sulfonate sodium salt, sodium dodecyl sulfonate, sodium pentansulfonate, sodium terephthalate, sodium fumarate, and sodium 2-ethylhexyl hydrogenphosphate were purchased from Sigma-Aldrich. Other chemicals applied were of analytical reagent grade or of the highest purity available. Apparatus information is completely explained in supporting information section.

2.2. Synthesis and modification of Ni/Cr-LDH with different inter-layer ligands

(NO₃)-LDH was prepared using the co-precipitation method under a constant pH similar to what is reported in the literature [31, 32]. Also, DS-LDH (theoretical formula (Tf): Ni_{0.75}Cr_{0.25}(OH)₂(C₁₂H₂₅NaO₄S)_{0.25}), TA-LDH (Tf: Ni_{0.75}Cr_{0.25}(OH)₂(C₈H₆Na₂O₄)_{0.125}), FA-LDH (Tf: Ni_{0.75}Cr_{0.25}(OH)₂(C₄H₄Na₂O₄)_{0.125}), PS-LDH (Tf: Ni_{0.75}Cr_{0.25}(OH)₂(C₅H₉NaO₂)_{0.25}), DPA-LDH (Tf: Ni_{0.75}Cr_{0.25}(OH)₂(C₁₂H₁₀NNaO₃S)_{0.25}) and EHP-LDH (Tf: Ni_{0.75}Cr_{0.25}(OH)₂(C₈H₁₈O₄Na₂P)_{0.125}) were prepared by dropwise addition of the Ni/Cr solution to the ligands solutions at a constant pH of 10. The ideal co-precipitation reaction can be expressed as follows:

The stoichiometric coefficients for anions were calculated based on the neutralization of the excess positive charge in the Cr-bearing brucite-like octahedral layers due to the replacement of Ni with Cr at a Ni/Cr molar ratio of 3. In the synthesis procedure, a stoichiometric amount of Ni(NO₃)₂·6H₂O (0.015 mol) and Cr(NO₃)₃ (0.005 mol) in 100 mL of deionized water was slowly added to 100 mL of a solution containing 0.005 mol of DS, DPA, or PS and 0.0025 mol of TA, FA, or EHP. The pH of the reaction mixture was adjusted to 10.0 by adding 2 mol L⁻¹ NaOH solution. The resulting gelatinous precipitate was aged at

65 °C for 24 h. The final product was collected by centrifugation (4000 rpm for 5 min), washed with water and ethanol five times, and dried at 70 °C for 24 h.

2.3. Extraction procedure

To investigate the extraction efficiency of heavy metal ions by intercalated-LDHs at low concentrations (ng mL⁻¹), the solid-phase extraction (SPE) technique was applied. In order to increase the accuracy and precision of the results and to decrease analysis time, a simple online system, namely on-line packed SPE, was designed. The procedure for the on-line packed SPE of the target metal ions is completely explained in supporting information.

2.4. Heavy metal ions removal experiments

The removal of heavy metal ions by LDHs was studied by batch experiments. To investigate the metal ions adsorption at high concentrations, 10 mg of intercalated-LDHs were added to 20 mL of metal ion solution (the concentration of metal ion varying from 30 to 200 mg L⁻¹) and stirred for 20 min at a constant temperature of 25 °C. After mixing the solid sorbents with the solutions, centrifugation was performed and the metal concentrations in the supernatant solutions were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

The adsorption isotherm data were fitted to the Langmuir equation to obtain maximum adsorption capacity of the intercalated-LDHs as shown in equation 1:

$$q_e = q_m \frac{bC_e}{1+bC_e} \quad \text{or} \quad \frac{q_e}{C_e} = \frac{q_m}{b} - q_e \quad (1)$$

where C_e (mg L⁻¹) and q_e (mg g⁻¹) are the equilibrium adsorbate concentrations in the aqueous and solid phases, respectively; q_m (mg g⁻¹) is the maximum adsorption capacity and b is the Langmuir adsorption equilibrium constant [2, 30]. In the next step, the adsorption capacity of the intercalated-LDHs were compared and the effect of the type of anionic groups (CO₂⁻,

SO₃⁻ and PO₃²⁻) and R- groups of inter-layer anions on the adsorption capacity of the LDHs was investigated and consequently, the intercalated-LDH with the best adsorption capacity was selected. The distribution coefficient (K_d) and removal % of this solid sorbent was calculated. The distribution coefficient K_d is defined by equation 2:

$$K_d = (V[(C_0 - C_f)/C_f])/m \quad (2)$$

Where C_0 and C_f are the initial and final concentration of M^{n+} ($\mu\text{g mL}^{-1}$) after the contact, respectively. V is the volume (mL) of the testing solution and m is the amount of the solid sorbent (g) used in the experiment. In our experiments, a V/m ratio of 2000 mL g^{-1} was used. The capture efficiency, referred to as removal (%), was calculated via equation 3:

$$\% \text{Removal} = 100 \times (C_0 - C_f)/C_0 \quad (3)$$

Finally, to determine the selectivity of the selected sorbent for ions of Cu²⁺, Cd²⁺, Zn²⁺ and Pb²⁺, some experiments were conducted using solutions containing mixtures of all four ions at a concentration of $10 \mu\text{g mL}^{-1}$. The separation factor for A and B (SF_A^B) was used to indicate the selectivity of intercalated-LDH for the heavy metal ions. The SF_A^B defined by K_d^A/K_d^B is a scale used to determine whether a material can be utilized to separate out certain ions from one another[30].

3. Results and discussion

3.1. Characterization of the intercalated-LDHS

The XRD, BET, BJH, SEM and FT-IR spectroscopy techniques were applied to characterize the synthesis products and to confirm the intercalation of the inter-layer anions into the inter-layer of the NiCr-LDH.

The XRD patterns of the LDHs samples are shown in Fig. 1 and XRD indexes (basal spacing and inter-layer spacing) are listed in Table 1. As shown in Fig. 1, NO₃-LDH and

intercalated-LDHs display the characteristic (003), (006), (009) and (110) reflections corresponding to hydrotalcite-like materials which also establish the purity of the LDHs obtained from the co-precipitation method. The intense reflection strongly indicated that NO₃-LDH and all of intercalated-LDHs possessed a high degree of crystallinity and layered structure. The basal spacing (d) of the layered materials could be calculated from the basal reflection using Bragg's equation $\lambda = 2d\sin\theta$ (where λ was the wavelength of Cu-K α radiation and equal to 0.15406 nm; and θ was the half of the basal reflection). For NO₃-LDH, the observed basal spacing, d (003), was 7.27 Å, due to the LDH host layer thickness of approximately 4.8 Å and the inter-layer spacing of 2.47 Å. For the DPA-LDH, DS-LDH, PS-LDH, TA-LDH, FA-LDH, and EHP-LDH, the basal spacing's were 16.30, 35.0, 12.63, 11.50, 10.84, and 23.55 Å, respectively, indicating that the inter-layer spacing's were larger than that of the NO₃-LDH. The intercalation of the inter-layer anions is clearly seen in each case from the significant increase in the basal spacing (Table 1) compared with that in the nitrate precursor. On the other hand, the different inter-layer anions cause a slight change in the positions of the (110) diffraction reflections (Insets in Fig. 1). Since d (110) depends on the Ni/Cr ratio, can be concluded that the molar ratio of Ni/Cr in intercalated-LDHs and so the chemical composition and consequently the morphology of the LDHs were changed [34-36].

FTIR spectra for the NO₃-LDH and intercalated-LDHs are shown in Fig. 2. The FTIR spectrum of NO₃-LDH was roughly attributed to what follows: 3479 cm⁻¹ to the O-H stretching vibration (ν_{O-H}) of the metal hydroxide layer and inter-layer water molecules; 1633 cm⁻¹ to the OH stretching band of H₂O; 1372 cm⁻¹ to the stretching vibration of NO₃⁻; 500-850 cm⁻¹ to the M-O, M-O-M, and O-M-O (M = Ni or Cr) lattice vibrations. These observations confirmed the formation of NO₃-LDH. Compared with the spectrum of NO₃-LDH, the spectra of intercalated-LDHs were more complicated, especially in the range from

2000 cm^{-1} to 1000 cm^{-1} . The most interesting features in the DPA-LDH spectrum are the bands at: 3419 cm^{-1} due to the O–H and N–H stretching vibrations; 1500 cm^{-1} due to the aromatic C=C bending ($\gamma_{\text{C}=\text{C}}$); 1126 cm^{-1} due to the $\nu_{\text{S}=\text{O}}$ (symmetric); and 1088 cm^{-1} due to the $\nu_{\text{S}=\text{O}}$ (asymmetric). In the DS-LDH spectrum, bands were observed at: 3419 cm^{-1} due to the $\nu_{\text{O}=\text{H}}$; 2855 and 2923 cm^{-1} due to the alkyl C–H stretching (ν_{CH_2}); 1201 cm^{-1} due to the $\nu_{\text{S}=\text{O}}$ (symmetric); and 1077 cm^{-1} due to the $\nu_{\text{S}=\text{O}}$ (asymmetric). Because of their close structures, PS-LDH and DS-LDH showed similar spectrums. In the FA-LDH spectrum, bands were observed at: 3419 cm^{-1} due to $\nu_{\text{O}=\text{H}}$ and carboxylic acid O–H stretching; 2198 cm^{-1} due to the alkenyl C=C stretching ($\nu_{\text{C}=\text{C}}$); 1763 cm^{-1} due to the carboxylic acid C=O stretching; 1568 cm^{-1} due to the ν_{COO^-} (asymmetric); and 1519 cm^{-1} due to the ν_{COO^-} (symmetric). For the TA-LDH spectrum, strength bands can be seen at: 3439 cm^{-1} due to the $\nu_{\text{O}=\text{H}}$ and carboxylic acid O–H stretching; 1782 cm^{-1} due to the carboxylic acid C=O stretching; 1580 cm^{-1} due to the ν_{COO^-} (asymmetric) and $\gamma_{\text{C}=\text{C}}$; 1520 cm^{-1} due to the ν_{COO^-} (symmetric). In the EHP-LDH spectrum, important bands are: 3439 cm^{-1} due to the $\nu_{\text{O}=\text{H}}$; 2870 and 2932 cm^{-1} due to the alkyl C–H stretching (ν_{CH_2}); 1126 cm^{-1} due to the $\nu_{\text{P}=\text{O}}$; 1034 and 1085 cm^{-1} due to the $\nu_{\text{P}=\text{O}-\text{C}}$. These observations confirmed the formation of intercalated LDHs. In the spectra of all of the intercalated-LDHs, the absence of the strength peak at 1372 cm^{-1} corresponding to NO_3^- confirmed the result of XRD analysis that indicated the inter-layer NO_3^- was displaced by organic anions.

The NO_3^- -LDH and intercalated LDHs were characterized by means of SEM measurements. Figs. 3A and B show SEM images of NO_3^- -LDH at different magnifications. From the SEM images, it can be clearly seen that NO_3^- -LDH consists of nanosheets with an average length of about 1.5–2.5 μm and a thickness of approximately 20 nm. Figs. 3C, D and E show that PS-LDH, TA-LDH, and FA-LDH particles contain interconnected nanosheets thicker than that of NO_3^- -LDH due to the enlarged inter-layer distance, as described by XRD

analysis. However, some small particles were absorbed on the surface of the sheets of PS-LDH. On the contrary, Figs. 3 F, G, and H show that the DPA-LDH, DS-LDH, and EHP-LDH consist of completely different structures. DPA-LDH, DS-LDH, and EHP-LDH present a slightly irregular plate-like morphology, and the plate size is about 0.2-0.7 μm , and has a thickness of approximately 20-60 nm. The different morphology can affect the specific surface area, pore size and consequently, adsorption capacities and extraction efficiencies of the sorbents. Interestingly, although the same method was adopted to synthesize NO_3 -LDH and intercalated-LDHs, the morphologies of all of the LDHs were different, which was confirmed by the XRD reflections results. The different morphologies of the synthesized LDHs indicated that the effect of organic anions on the growth habits of the LDHs (growth direction, direction of stacking) was very complicated.

The typical nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves of the NO_3 -LDH and intercalated-LDHs are shown in Fig. 4A and listed in Table 2. All of the curves show typical IV isotherms with an H_3 -type hysteresis loop ($P/P_0 > 0.4$), demonstrating the existence of mesopores in all the samples. The surface areas of the intercalated-LDHs (Table 2) are in the range of 66.98-293.69 $\text{m}^2 \text{g}^{-1}$ which is much larger than those of NO_3 -LDH with a 49.92 $\text{m}^2 \text{g}^{-1}$ surface area. It is worthy to note that the specific surface areas have significant increase as a result of the addition of inter-layer anions. The observed surface area order for LDHs based on their anions was $\text{DS} > \text{DPA} > \text{EHP} > \text{PS} > \text{FA} > \text{TA} > \text{NO}_3$. Generally, the larger surface area of the sorbent can offer much more active adsorption sites. Based on the obtained results, the modified LDHs with large ligands such as DPA might be helpful for enhancing the adsorption capacity of sorbents in water treatment. Fig. 4B shows the BJH desorption pore size distributions of the NO_3 -LDH and the intercalated-LDHs. It can be seen that all of the LDHs show a uniform mesopores size distribution of 10.90-18.68 nm. The observed pore size order for the LDHs based on

their anions was $\text{NO}_3^- > \text{FA} = \text{PS} > \text{EHP} > \text{DPA} > \text{TA} > \text{DS}$. Based on the above data, it was expected that the intercalation of the inter-layer anions into the NiCr-LDH should cause changes in the texture, surface morphology and adsorption capacity of the NiCr-LDH.

3.2. Optimization of the extraction parameters

To better understand the effect of inter-layer anions on the extraction efficiency of intercalated-LDHs, two important experimental parameters including sample pH and adsorption time were investigated by the on-line packed SPE method. All the experiments were performed in triplicates, and their averages were used as analytical signals. Finally, the extraction efficiencies of the target metal ions by the intercalated-LDHs were calculated and compared.

The pH of the sample solution plays an important role in the whole adsorption process and particularly in the adsorption capacity. In order to evaluate the effect of pH on the adsorption of metal ions in the studied LDH sorbents, a series of sample solutions containing metal ions at concentrations of 50 ng mL^{-1} were prepared with pHs in the range of 4.0–10.0 and the recommended procedure was conducted. The results for Cd are shown in Fig. 5 (all the metal ions showed a similar behavior). The obtained results for EHP-LDH, which contains the phosphonate group, showed that the adsorption efficiency increases rapidly when the pH is raised above 6.0. This effect can be related to the complete deprotonation of phosphonate groups at high pH values ($pK_2 = 6.4$), which enhances the electrostatic interactions between metal cations and the phosphonate groups, resulting in higher retention of metal species in inter-layer of LDH. For TA- and FA-LDH that have carboxylate groups, the extraction efficiency (EE%) increased dramatically as the pH increased from 4.0 to 8.0 and then decreased. By increasing the pH of the solution from 4.0 to 8.0, the inter-layer anion was negatively charged and an electrostatic attraction occurred between the positively charged

heavy metal ions and the sorbent particles. Similar to EHP, this effect can be related to the complete deprotonation of carboxylic groups by increasing the pH. However, DPA, DS, and PS based LDHs that have a sulfonate group showed a better EE% at a lower pH (6.0) than EHP, TA, and FA. This effect can be related to the high acidic strength of the sulfonate group which can be completely deprotonated at lower pHs. As shown in Fig. 5, the adsorption capacity of NiCr-LDHs increased by increasing the pH. The decrease in the adsorption capacity at low pHs ($\text{pH} < 4.0$) may be related to the slight dissolution of NiCr-LDHs. Based on the ICP-AES results, the released amount of Ni(II) and Cr(III) during the removal process of heavy metal ions at pH of 4.0 reached to 0.74 and 0.35 mmol g^{-1} , respectively. But ICP-AES analysis results showed that at pHs above 6.0, concentrations of Ni and Cr in solution are zero, that suggests NiCr-LDHs are more stable. The remarkable structural features enable NiCr-LDHs to exhibit a powerful ability to capture heavy metal ions pollutants from aqueous solution. In all cases, decreasing EE% at high pH values can be related to the formation of hydroxyl forms of the metal ions and their precipitation. The optimum pH values for all of the sorbents are given in Table 3.

Adsorption time is one of the key parameters affecting the distribution of metal ions between the sorbents and the sample solution. To reveal the effect of adsorption time on the EE% of the metal ions, the adsorption times were varied in the range of 3-35 min (Fig. 6). According to Fig. 6, by increasing the time, EE% also increased in all cases until reaching equilibrium. Based on Table 3, the observed adsorption time order for the different LDHs based on their inter-layer anion was $\text{DPA} > \text{PS} > \text{TA} > \text{EHP} = \text{FA} > \text{DS}$, $\text{DPA} > \text{TA} = \text{FA} > \text{PS} > \text{EHP} > \text{DS}$, $\text{DPA} > \text{TA} = \text{FA} > \text{PS} > \text{EHP} > \text{DS}$ and $\text{DPA} = \text{TA} = \text{FA} = \text{PS} > \text{EHP} > \text{DS}$ for Pb, Cu, Zn, and Cd, respectively. Interestingly, the results showed that the adsorption time of DS-LDH was lower than that of the other intercalated-LDHs and this can be explained by XRD and BET results. BET and XRD results showed that DS-LDH have the highest surface

area and inter-layer space as well as the lowest pore size, resulting in very rapid adsorption processes.

3.3. Comparison of extraction efficiency of intercalated-LDHS

Comparing EE% values (Table 3) showed that the order of EE% for intercalated-LDHs based on their inter-layer anions was DPA>DS>PS>TA>FA>EHP. Accordingly, it can be said that the structure of the inter-layer anions have a key role in the adsorption of metal ions. The obtained results indicated that sulfonate-based LDHs showed a better EE% than carboxylate-based LDHs, and phosphonate-based LDHs showed the lowest EE%. Nevertheless, the order of acidity strength of these groups is vice versa and it is expected to achieve reverse results. Comparing the results with those obtained by other published studies completely confirmed them [30], [37]. For example, the maximum adsorption capacity of different intercalated-LDHs based on amino tris(methylene phosphonic acid) with phosphonate group [30], diethylenetriaminepentaacetic with carboxylate groups [37], and chromotropic acid [2] with sulfonate groups for removal of heavy metal ions have been obtained to be 69, 179, and 980 mg g⁻¹, respectively. It seems that by decreasing the acidity property of inter-layer anions, their interactions strength with LDH hydroxide basal layer increases and reduces their freedom in LDH structure. Thus, the interaction between inter-layer anions and metal ions will be decreased. On the other hand, the results also show that inter-layer anions with similar head groups have different EE% values. For example, the order of EE% values for LDHs with inter-layer anions of DPA, DS, and PS with sulfonate head group was DPA>DS>PS, and for LDHs with inter-layer anions of TA and FA with carboxylate group, this order was TA>FA. It can be due to the different R- groups of inter-layer anions. It seems that the type of functional groups such as amine, phenyl, and ethylene groups, and the length of R- groups have a key role in EE% of intercalated-LDHs. Therefore, the presence of amine and phenyl groups in DPA ligand can have appropriate interactions,

that is acid-base and π -cation interactions, with the target metal ions and provides higher adsorption efficiencies than DS and PS. On the other hand, the greater EE% of DS-LDH, compared to that of PS-LDH, can be explained by XRD and BET results. Comparing the inter-layer spacing of DS-LDH and PS-LDH, one can understand that the increment of the inter-layer spacing in DS-LDH is clearly more than that of PS-LDH, and this might be related to the greater length of DS compared to PS. Hence, the higher surface area and more porosity of DS-LDH, in comparison with PS-LDH, leads to its better EE%. In the case of TA-LDH and FA-LDH, the better adsorption efficiency of TA-LDH can be attributed to presence of phenyl group creating better π -cation interactions with the metal ions.

3.4. Removal of the metal ions from aqueous solutions

The studies of the influence of time on the adsorption of Cd^{2+} (all metal ions have shown the similar behavior) have been included in Fig. S4. As shown in Fig. S4, EHP-LDH, TA-LDH, FA-LDH, PS-LDH, and DS-LDH reach the metal ion absorption equilibrium of 110, 80, 80, 70, and 60 min, respectively, while DPA-LDH exhibits relatively more rapid absorption kinetics of 40 min, which is higher than that of other adsorbents. The quicker adsorption kinetics of metal ions is mainly ascribed to the existence of suitable R- and head groups in the inter-layer anions structure, which can improve interactions with metal ions and accelerate the adsorption kinetics of metal ions on LDHs.

3.5. Adsorption isotherm studies

To investigate the metal ions adsorption, 10 mg of intercalated-LDHs were added to 20 mL of metal ion solution (the concentration of metal ion varying from 30 to 200 mg L^{-1}) and stirred for 20 min at a constant temperature of 25 °C. The equilibrium data were analyzed with the help of Langmuir isotherm; the values of maximum adsorption capacity (q_m , mg g^{-1}) and distribution adsorption coefficient (b , L mg^{-1}) are calculated from the intercept and the

slope of plotting q_e/C_e vs. q_e in Langmuir adsorption isotherm (Eq. 1), respectively, (see Table 4). The adsorption isotherms of Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} on intercalated-LDHs are shown in Fig. 7, and they are typical H type isotherms according to Giles classification [38]. This indicates that the adsorption of metal ions on intercalated-LDHs occurs as monolayer, which is indicative of a chemical adsorption process, and suggests the formation of complexes of the metal ions and the inter-layer anions. To investigate the effect of inter-layer anion on maximum adsorption capacity, the q_m values obtained for different intercalated-LDHs were compared and it was observed that the order of q_m for inter-layer anions was, similar to the order of the extraction efficiency, DPA>DS>PS>TA>FA>EHP for all of the metals ions. Based on these results, it can be concluded that the type of head groups, length of R-groups, and functional groups of inter-layer anions play an important role for the maximum adsorption capacities of intercalated-LDHs. Hence, it is possible to improve the adsorption efficiency of the LDH sorbents by choosing an appropriate inter-layer anion including sulfonate groups, large R- groups with more suitable functional groups. In all cases, DPA-LDH showed higher adsorption efficiency than the other intercalated-LDHs, so the maximum adsorption capacities of Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} on DPA-LDH were 479, 282, 242, and 258 mg g⁻¹, respectively (Table 4). Accordingly, DPA-LDH was selected as a suitable adsorbent for the removal of heavy metal ions from water samples and, subsequently, the affinity of DPA-LDH toward these metal ions and its relative selectivity for the metal ions was investigated. Finally, the method performance of this adsorbent for the extraction of trace amounts of heavy metals was evaluated.

To confirm the complex formation between metal cations and DPA in the interlayer, the XRD patterns of the isotherm products Pb-DPA-LDH were obtained. XRD patterns of Pb^{2+} adsorbed DPA-LDH compared with original DPA-LDH are shown in Fig. S5. It can be clearly observed that a series of (001) peaks of Pb-DPA-LDH samples appear to have almost

no change. Results revealed that the inter-layer distances were nearly not expanded by adsorbed Pb^{2+} , as also previously found in heavy metals sorption on intercalated layered double hydroxides samples [37]. The results suggest that the M-DPA complexes are accommodate into the inter-layer without apparent deformations, dissolution or structure change of DPA-LDH. Also, the remarkable structural stability of DPA-LDHs, enable them to exhibit a powerful ability to capture heavy metal cations in aqueous solution.

3.6. Evaluating the affinity of DPA-LDH toward the metal ions

The affinity of DPA-LDH toward the metal ions can be expressed in terms of the distribution coefficient K_d (for its definition, see Experimental Section). The higher the K_d value, the more effective capturing and holding the target species by the sorbent material will be occurred. In general, K_d values of 10^3 mL g^{-1} are considered good, and those above 10^4 mL g^{-1} are considered to be exceptional sorbents [39]. In this study, adsorption experiments with individual solutions of Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} were carried out. According to the results given in Table 5, the adsorption ability of DPA-LDH toward Pb^{2+} and Cu^{2+} is higher than that of the other ions. As shown in Table 5, the K_d^{Pb} , K_d^{Cu} , K_d^{Zn} , and K_d^{Cd} values were achieved to be 1.99×10^8 , 6.66×10^6 , 3.98×10^5 , and $7.49 \times 10^4 \text{ mL g}^{-1}$, respectively. Comparing the K_d values in Table 6 shows that the obtained K_d values for DPA-LDH are higher than those that were reported for previous sorbents such as metal-organic frameworks [6], dodecyl sulfate based intercalated-LDHs [28], carbonate based LDHs [29], sulfide based intercalated-LDHs and materials [10, 40, 41], polymers [42, 43], magnetic nanoparticles [44, 45], ion imprinted polymers [46], layered hydrogen metal sulfides [47], and zeolites [48]. The comparison of the q_m values of DPA-LDH with the same values of other sorbents presented in the literature (Table 6) for metal ions removal is indicative of the higher efficiency of DPA-LDH for the removal of heavy-metal ions.

3.7. Relative selectivity of DPA-LDH for Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+}

As mentioned in previous sections, the DPA-LDH can capture the Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} ions effectively, reducing their concentrations from $10 \mu g mL^{-1}$ to $\leq 1 ng mL^{-1}$ at lower than 40 min. Since Zn^{2+} and Cu^{2+} are essential micronutrients for the human body at trace levels, while Cd and Pb are extremely toxic even in low concentrations, the maximum acceptable limit for Zn^{2+} , Cu^{2+} , Cd^{2+} and Pb^{2+} are 5.0, 0.12, 0.005 and 0.01 $mg L^{-1}$, respectively [8, 49]. It seems that providing a sorbent for the highly selective removal of Cd^{2+} and Pb^{2+} from water samples in the presence of Zn^{2+} and Cu^{2+} is remarkable. Therefore, the adsorption selectivity of DPA-LDH for the metal ions was investigated and the separation factor (SF_A^B) was used to indicate selectivity. For this purpose, adsorption of the metal ions from 20 mL of a solution containing a mixture of all of the four ions at a concentration of $10 \mu g mL^{-1}$ was performed using 5 mg of DPA-LDH, which was sufficient to pick up only one of the ions. The obtained results are shown in Table 7. Generally, good separation factors are considered to be more than 100 depending on the conditions and applications for which the SF is measured [10]. According to the data in Table 7, the values of SF_{Pb}^{Cu} , SF_{Pb}^{Zn} , SF_{Cd}^{Cu} and SF_{Cd}^{Zn} can be calculated as 2.5×10^4 , 6.9×10^4 , 1.1×10^3 and 3.1×10^3 , respectively, showing an obvious higher affinity and selectivity of DPA-LDH for Pb^{2+} and Cd^{2+} than Cu^{2+} and Zn^{2+} . Also, the SF_{Pb}^{Cd} of 22.2 suggests a somewhat higher selectivity of DPA-LDH towards Pb^{2+} than Cd^{2+} . Thus, the selectivity order of $Zn^{2+} < Cu^{2+} \lll Cd^{2+} < Pb^{2+}$ was observed using DPA-LDH.

3.8. Evaluation of the On-line packed-SPE method performance

ICP-AES is considered as an appropriate technique due to its high sensitivity. However, the effects of complicated matrixes, including spectral interferences and non-spectral interferences, constitute a major limitation of this technique in carrying out an accurate

determination. In addition, it is sometimes quite difficult or even impossible to determine the trace/ultra-trace elements directly by ICP-AES. Hence, it is often necessary to apply an appropriate sample preparation step, including extraction and preconcentration, prior to the final analysis by ICP-AES. Therefore, applicability of DPA-LDH as a SPE sorbent to extract and preconcentrate trace amounts of target metal ions from aqueous sample solutions was evaluated *via* on-line packed-SPE method followed by ICP-AES determination. For this purpose, a number of method performance parameters were investigated as figures of merit, which are summarized in Table 8. Calibration curves were obtained by the extraction and determination of the metal ions using ten spiking levels of the target analytes in the concentration range of 0.04–200 ng mL⁻¹; they were found to be linear in the range of 0.01–200 ng mL⁻¹. The limits of detections (LODs) were 0.01, 0.05, 0.005 and 0.01 ng mL⁻¹ for Cd, Pb, Cu and Zn, respectively. The precision of the proposed method reported as the relative standard deviation (RSD %) was determined by intra- and inter-assays using five determinations at three different levels in the range of the expected concentrations. RSDs% values less than 4.8% for intra-day and less than 6.8% for inter-day confirm the acceptable precision of the method. These results confirm the high efficiency of DPA-LDH as a SPE sorbent for the extraction and preconcentration of trace amounts of heavy metal ions.

4. Concluding remarks

Six new NiCr-LDHs intercalated with some different inter-layer anions including DPA, DS, PS, TA, FA, and EHP were synthesized and used to study the effect of head groups and also the type and length of R-groups on the adsorption efficiency of Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ from aqueous solutions. The characterization of the intercalated-LDHs suggested that changing the inter-layer anion affects morphology, inter-layer space, and specific surface area of LDH. The adsorption of these metal ions occurred mainly through interaction with inter-layer anions. The results showed that the maximum adsorption capacity order of the LDHs

based on their inter-layer anions was DPA>DS>PS>TA>FA>EHP for all of the metal ions. So, it can be concluded that inter-layer anions with a sulfonate group show a better adsorption capacity than a carboxylate group, and that a phosphonate group shows the lowest adsorption capacity. On the other hand, the results indicated that the presence of functional groups such as amine, phenyl, and ethylene groups with inter-layer anions can improve the adsorption capacity. Also, the length of R-groups can affect the adsorption efficiency of the intercalated-LDHs through changing the length of inter-layer space, surface morphology and specific surface area of the sorbent. Because of the higher adsorption efficiency of DPA-LDH compared to the other intercalated-LDHs, it was selected as a suitable sorbent for the removal heavy metal ions from aqueous samples. The evaluation of DPA-LDH affinity toward these metal ions and its relative selectivity for metal ions adsorption showed that DPA-LDH can adsorb certain ions with extremely high adsorption capacities (476 mg g⁻¹ for Pb²⁺, 278 mg g⁻¹ for Cu²⁺, 238 mg g⁻¹ for Zn²⁺ and 250 mg g⁻¹ for Cd²⁺). Investigating the adsorption behavior toward different metal ions showed that, in a solution containing a mixture of the four ions of Cu²⁺, Zn²⁺, Pb²⁺ and Cd²⁺, the selectivity order of Zn²⁺<Cu²⁺<<<Cd²⁺<Pb²⁺ can be observed using DPA-LDH. For the highly toxic Pb²⁺ and Cd²⁺, an exceptionally rapid capture with removal ~100% within 1 hour was observed and final concentrations well below the acceptable levels in drinking water (< 1 ppb) were achieved.

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References

- [1] R.P. Schwarzenbach, B.I. Escher, K. Fenner, T.B. Hofstetter, C.A. Johnson, U. von Gunten, B. Wehrli, The challenge of micropollutants in aquatic systems, *Science* 313 (2006) 1072-1077.

- [2] Y. Chen, Y.-F. Song, 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 (2013) 4436-4442.
- [3] M.X. Tan, Y.N. Sum, J.Y. Ying, Y. Zhang, A mesoporous poly-melamine-formaldehyde polymer as a solid sorbent for toxic metal removal, *Energy Environ. Sci.* 6 (2013) 3254-3259.
- [4] D. Vilela, J. Parmar, Y. Zeng, Y. Zhao, S. Sanchez, Graphene-based microbots for toxic heavy metal removal and recovery from water, *Nano Lett.* 16 (2016) 2860-2866.
- [5] L. Mi, H. Hou, Z. Song, H. Han, Y. Fan, Polymeric zinc ferrocenyl sulfonate as a molecular aspirator for the removal of toxic metal ions, *Chem. Eur. J.* 14 (2008) 1814-1821.
- [6] E. Tahmasebi, M.Y. Masoomi, Y. Yamini, A. Morsali, Application of mechanosynthesized azine-decorated zinc(II) metal-organic frameworks for highly efficient removal and extraction of some heavy-metal ions from aqueous samples: a comparative study, *Inorg. Chem.* 54 (2015) 425-433.
- [7] Y. Pan, Z. Liu, W. Wang, C. Peng, K. Shi, X. Ji, Highly efficient macroporous adsorbents for toxic metal ions in water systems based on polyvinyl alcohol–formaldehyde sponges, *J. Mater. Chem. A* 4 (2016) 2537-2549.
- [8] R. Shawabkeh, A. Al-Harabsheh, A. Al-Otoom, Copper and zinc sorption by treated oil shale ash, *Sep. Purif. Technol.* 40 (2004) 251-257.
- [9] Y.L.-b. Du Wen, Z. Yu-qun, Catalytic oxidation and adsorption of elemental mercury over CuCl₂-impregnated sorbents [J], *Ind. Eng. Chem. Res.* 53 (2014) 582-591.
- [10] L. Ma, Q. Wang, S.M. Islam, Y. Liu, S. Ma, M.G. Kanatzidis, Highly selective and efficient removal of heavy metals by layered double hydroxide intercalated with the MoS₄(2-) ion, *J. Am. Chem. Soc.* 138 (2016) 2858-2866.
- [11] A.A. Chavan, H. Li, A. Scarpellini, S. Marras, L. Manna, A. Athanassiou, D. Fragouli, Elastomeric nanocomposite foams for the removal of heavy metal ions from water, *ACS Appl. Mater. Interfaces* 7 (2015) 14778-14784.
- [12] Y. Zhang, S. Zhang, T.-S. Chung, Nanometric graphene oxide framework membranes with enhanced heavy metal removal via nanofiltration, *Environ. Sci. Technol.* 49 (2015) 10235-10242.

- [13] A.B. Albadarin, H. Ala'a, N.A. Al-Laqtah, G.M. Walker, S.J. Allen, M.N. Ahmad, Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts, *Chem. Eng. J.* 169 (2011) 20-30.
- [14] K.R. Kumrić, A.B. Đukić, T.M. Trtić-Petrović, N.S. Vukelić, Z. Stojanović, J.D. Grbović Novaković, L.L. Matović, Simultaneous removal of divalent heavy metals from aqueous solutions using raw and mechanochemically treated interstratified montmorillonite/kaolinite clay, *Ind. Eng. Chem. Res.* 52 (2013) 7930-7939.
- [15] X. Liu, Q. Hu, Z. Fang, X. Zhang, B. Zhang, Magnetic chitosan nanocomposites: a useful recyclable tool for heavy metal ion removal, *Langmuir* 25 (2008) 3-8.
- [16] X. Zhang, J. Wang, R. Li, Q. Dai, R. Gao, Q. Liu, M. Zhang, Preparation of Fe₃O₄@ C@ layered double hydroxide composite for magnetic separation of uranium, *Ind. Eng. Chem. Res.* 52 (2013) 10152-10159.
- [17] W. Li, Q. Gu, F. Su, Y. Sun, G. Sun, S. Ma, X. Yang, Intercalation of azamacrocyclic crown ether into layered rare-earth hydroxide (LRH): Secondary host-guest reaction and efficient heavy metal removal, *Inorg. Chem.* 52 (2013) 14010-14017.
- [18] B. Sels, D.D. Vos, M. Buntinx, F. Pierard, A. Kirsch-De Mesmaeker, P. Jacobs, Layered double hydroxides exchanged with tungstate as biomimetic catalysts for mild oxidative bromination, *Nature* 400 (1999) 855-857.
- [19] B.M. Choudary, S. Madhi, N.S. Chowdari, M.L. Kantam, B. Sreedhar, Layered double hydroxide supported nanopalladium catalyst for Heck-, Suzuki-, Sonogashira-, and Stille-type coupling reactions of chloroarenes, *J. Am. Chem. Soc.* 124 (2002) 14127-14136.
- [20] G. Choi, J.-H. Yang, G.-Y. Park, A. Vinu, A. Elzatahry, C.H. Yo, J.-H. Choy, Intercalative ion-exchange route to amino acid layered double hydroxide nanohybrids and their sorption properties, *Eur. J. Inorg. Chem.* 2015 (2015) 925-930.
- [21] H. Liang, F. Meng, M. Cabán-Acevedo, L. Li, A. Forticaux, L. Xiu, Z. Wang, S. Jin, Hydrothermal continuous flow synthesis and exfoliation of NiCo layered double hydroxide nanosheets for enhanced oxygen evolution catalysis, *Nano letters* 15 (2015) 1421-1427.

- [22] X. Gu, Y. Yang, Y. Hu, M. Hu, C. Wang, Fabrication of graphene-based xerogels for removal of heavy metal ions and capacitive deionization, *ACS Sustain. Chem. Eng.* 3 (2015) 1056-1065.
- [23] M. Gong, Y. Li, H. Zhang, B. Zhang, W. Zhou, J. Feng, H. Wang, Y. Liang, Z. Fan, J. Liu, H. Dai, Ultrafast high-capacity NiZn battery with NiAlCo-layered double hydroxide, *Energy Environ. Sci.* 7 (2014) 2025.
- [24] Z. Gao, J. Wang, Z. Li, W. Yang, B. Wang, M. Hou, Y. He, Q. Liu, T. Mann, P. Yang, M. Zhang, L. Liu, Graphene nanosheet/ $\text{Ni}^{2+}/\text{Al}^{3+}$ layered double-hydroxide composite as a novel electrode for a supercapacitor, *Chem. Mater.* 23 (2011) 3509-3516.
- [25] T. Kwon, G.A. Tsigdinos, T.J. Pinnavaia, Pillaring of layered double hydroxides (LDH's) by polyoxometalate anions, *J. Am. Chem. Soc.* 110 (1988) 3653-3654.
- [26] M.R. Pérez, I. Pavlovic, C. Barriga, J. Cornejo, M.C. Hermosín, M.A. Ulibarri, Uptake of Cu^{2+} , Cd^{2+} and Pb^{2+} on Zn–Al layered double hydroxide intercalated with edta, *Appl. Clay Sci.* 32 (2006) 245-251.
- [27] S. Yu, X. Wang, Z. Chen, J. Wang, S. Wang, T. Hayat, X. Wang, Layered double hydroxide intercalated with aromatic acid anions for the efficient capture of aniline from aqueous solution, *J. Hazard. Mater.* 321 (2017) 111–120.
- [28] H. Chen, G. Qian, X. Ruan, R. L. Frost, Removal process of nickel(II) by using dodecyl sulfate intercalated calcium aluminum layered double hydroxide, *Appl. Clay Sci.* 132–133 (2016) 419–424.
- [29] J. Li, H. Cui, X. Song, G. Zhang, X. Wang, Q. Song, N. Wei, J. Tian, Adsorption and intercalation of organic pollutants and heavy metal ions into MgAl-LDHs nanosheets with high capacity, *RSC Adv.* 6 (2016) 92402-92410.
- [30] T. Kameda, T. Shinmyou, T. Yoshioka, Synthesis of Li–Al layered double hydroxide intercalated with amino tris(methylene phosphonic acid) and kinetic and equilibrium studies of the uptake of Nd^{3+} and Sr^{2+} ions, *Appl. Surf. Sci.* 366 (2016) 523-528.
- [31] S. Carlino, The intercalation of carboxylic acids into layered double hydroxides: a critical evaluation and review of the different methods, *Solid State Ionics* 98 (1997) 73-84.
- [32] S. Miyata, Synthesis of hydrotalcite-like compounds and their physico-chemical properties---The systems $\text{Mg}^{2+}\text{-Al}^{3+}\text{-SO}_4^{2-}$ and $\text{Mg}^{2+}\text{-Al}^{3+}\text{-CrO}_4^{2-}$, *Clay. Clay Miner.* 25 (1977) 14-18.

- [33] Z. Hassanzadeh Fard, C.D. Malliakas, J.L. Mertz, M.G. Kanatzidis, Direct extraction of Ag^+ and Hg^{2+} from cyanide complexes and mode of binding by the layered $\text{K}_2\text{MgSn}_2\text{S}_6$ (KMS-2), *Chem. Mater.* 27 (2015) 1925-1928.
- [34] M. Serdechnova, A.N. Salak, F.S. Barbosa, D.E. Vieira, J. Tedim, M.L. Zheludkevich, M.G. Ferreira, Interlayer intercalation and arrangement of 2-mercaptobenzothiazolate and 1, 2, 3-benzotriazolate anions in layered double hydroxides: In situ X-ray diffraction study, *J. Solid State Chem.* 233 (2016) 158-165.
- [35] D.G. Evans, R.C. Slade, *Structural aspects of layered double hydroxides*, Springer, 2006.
- [36] M. Pérez, I. Pavlovic, C. Barriga, J. Cornejo, M. Hermosin, M. Ulibarri, Uptake of Cu^{2+} , Cd^{2+} and Pb^{2+} on Zn–Al layered double hydroxide intercalated with edta, *Appl. Clay Sci.* 32 (2006) 245-251.
- [37] X. Liang, W. Hou, Y. Xu, G. Sun, L. Wang, Y. Sun, X. Qin, Sorption of lead ion by layered double hydroxide intercalated with diethylenetriaminepentaacetic acid, *Colloids Surf. A Physicochem. Eng. Asp.* 366 (2010) 50-57.
- [38] C. Giles, T. MacEwan, S. Nakhwa, D. Smith, 786. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, *J. Chem. Soci.* (1960) 3973-3993.
- [39] M.J. Manos, N. Ding, M.G. Kanatzidis, Layered metal sulfides: Exceptionally selective agents for radioactive strontium removal, *Proc. Natl. Acad. Sci. U.S.A.* 105 (2008) 3696-3699.
- [40] S. Ma, Q. Chen, H. Li, P. Wang, S.M. Islam, Q. Gu, X. Yang, M.G. Kanatzidis, Highly selective and efficient heavy metal capture with polysulfide intercalated layered double hydroxides, *J. Mater. Chem. A* 2 (2014) 10280.
- [41] Z. Hassanzadeh Fard, S.M. Islam, M.G. Kanatzidis, Porous amorphous chalcogenides as selective adsorbents for heavy metals, *Chem. Mater.* 27 (2015) 6189-6192.
- [42] J.J. Alcaraz-Espinoza, A.E. Chavez-Guajardo, J.C. Medina-Llamas, C.A. Andrade, C.P. de Melo, Hierarchical composite polyaniline-(electrospun polystyrene) fibers applied to heavy metal remediation, *ACS Appl. Mater. Interfaces* 7 (2015) 7231-7240.

- [43] B. Akhavan, K. Jarvis, P. Majewski, Plasma polymer-functionalized silica particles for heavy metals removal, *ACS Appl. Mater. Interfaces* 7 (2015) 4265-4274.
- [44] J. Li, S. Zhang, C. Chen, G. Zhao, X. Yang, J. Li, X. Wang, Removal of Cu(II) and fulvic acid by graphene oxide nanosheets decorated with Fe₃O₄ nanoparticles, *ACS Appl. Mater. Interfaces*, 4 (2012) 4991-5000.
- [45] W. Yantasee, C.L. Warner, T. Sangvanich, R.S. Addleman, T.G. Carter, R.J. Wiacek, G.E. Fryxell, C. Timchalk, M.G. Warner, Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles, *Environ. Sci. Technol.* 41 (2007) 5114-5119.
- [46] J. He, Y. Lu, G. Luo, Ca(II) imprinted chitosan microspheres: An effective and green adsorbent for the removal of Cu(II), Cd(II) and Pb(II) from aqueous solutions, *Chem. Eng. J.* 244 (2014) 202-208.
- [47] M.J. Manos, V.G. Petkov, M.G. Kanatzidis, H₂xMnxSn_{3- x}S₆ (x= 0.11–0.25): A novel reusable sorbent for highly specific mercury capture under extreme pH conditions, *Adv. Funct. Mater.* 19 (2009) 1087-1092.
- [48] K. He, Y. Chen, Z. Tang, Y. Hu, Removal of heavy metal ions from aqueous solution by zeolite synthesized from fly ash, *Environ. Sci. Pollut. Res.* 23 (2016) 2778-2788.
- [49] C.V. Mohod, J. Dhote, Review of heavy metals in drinking water and their effect on human health, *Int. J. Innov. Res. Sci. Eng. Technol.* 2 (2013) 2992-2996.

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Table 1. Assignment of XRD reflections obtained for NO₃-LDH and its modified forms

LDH	Formula	2 θ (003)	Basal spacing ^a	Hydrotalcite- layer thickness ^a	Inter-layer spacing ^a
NO ₃ -LDH	Ni _{0.75} Cr _{0.25} (OH) ₂ (NO ₃) _{0.25}	12.20	7.27	4.8	2.47
DS-LDH	Ni _{0.75} Cr _{0.25} (OH) ₂ (C ₁₂ H ₂₅ NaO ₄ S) _{0.25}	2.50	35.0	4.8	30.20
TA-LDH	Ni _{0.75} Cr _{0.25} (OH) ₂ (C ₈ H ₆ O ₄) _{0.125}	7.66	11.50	4.8	6.70
FA-LDH	Ni _{0.75} Cr _{0.25} (OH) ₂ (C ₄ H ₄ O ₄) _{0.125}	8.21	10.84	4.8	6.05
PS-LDH	Ni _{0.75} Cr _{0.25} (OH) ₂ (C ₅ H ₉ NaO ₂) _{0.25}	6.97	12.63	4.8	7.82
DPA-LDH	Ni _{0.75} Cr _{0.25} (OH) ₂ (C ₁₂ H ₁₀ NNaO ₃ S) _{0.25}	5.42	16.30	4.8	11.49
EHP-LDH	Ni _{0.75} Cr _{0.25} (OH) ₂ (C ₈ H ₁₈ O ₄ P) _{0.125}	3.75	23.55	4.8	18.75

^a All units in the table are Å°

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Table 2. Values of specific surface areas and pores for the NO₃⁻-LDH and its modified forms

LDH	Pore volume (cm ³ g ⁻¹)	Average pore size (nm)	BET surface area (m ² g ⁻¹)	
NO ₃ -LDH	0.234	18.68	49.92	
DS-LDH	0.388	10.90	293.69	7
TA-LDH	0.232	11.79	66.98	8
FA-LDH	0.198	17.15	68.28	
PS-LDH	0.281	17.15	95.96	9
DPA-LDH	0.298	12.01	168.33	
EHP-LDH	0.269	12.68	113.50	10

Table 3. Optimum condition for on-line packed SPE of target metal ions by intercalated-LDHs.

LDH	pKa	pH				Adsorption time (min)				Extraction efficiency%			
		Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd
DS-LDH	Strong acid	6.0	6.0	6.0	6.0	13	13	13	13	78	82	71	70
TA-LDH	$pK_1 = 3.5, pK_2=4.4$	8.0	8.0	8.0	8.0	23	25	23	25	64	60	59	52
FA-LDH	$pK_1 = 3.0, pK_2=4.4$	8.0	8.0	8.0	8.0	20	25	23	25	56	54	51	49
PS-LDH	Strong acid	6.0	6.0	6.0	6.0	25	23	20	25	75	66	65	63
DPA-LDH	Strong acid	6.0	6.0	6.0	6.0	27	27	30	25	94	98	87	85
EHP-LDH	$pK_1 = 1.5, pK_2=6.4$	9.0	9.0	9.0	9.0	20	20	17	20	44	39	33	34

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Table 4. Parameters of the Langmuir isotherm for the Sorption of Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} by intercalated-LDHs

LDH	q_m (mg g^{-1})				b (L mg^{-1})				R^2			
	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd
DS-LDH	309	189	164	142	0.09	0.072	0.028	0.029	0.9970	0.9908	0.9821	0.9965
TA-LDH	195	112	118	113	0.089	0.067	0.03	0.016	0.9971	0.9977	0.9866	0.9966
FA-LDH	176	110	112	92	0.05	0.072	0.023	0.019	0.9957	0.9959	0.9892	0.9923
PS-LDH	232	143	139	117	0.073	0.06	0.021	0.021	0.9995	0.9981	0.9964	0.9774
DPA-LDH	479	282	242	258	0.041	0.042	0.023	0.013	0.9968	0.9962	0.9902	0.9786
EHP-LDH	89	44	42	45	0.006	0.088	0.024	0.013	0.9886	0.9954	0.9902	0.9993

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Table 5. Adsorption results of DPA-LDH toward individual four metal ions.

Single ion	C_0^a	C_t^a -1h	Removal %	K_d^a
Cd	10.0	0.001	99.9 ₉	1.99×10^7
Cu	10.0	0.006	99.9 ₄	3.33×10^6
Zn	10.0	0.05	99.5 ₀	3.98×10^5
Pb	10.0	0.0001	100.0	1.99×10^8

^aAll concentrations mg L⁻¹.

Sample volume (V) = 20 mL; m (mass of solid sample) = 10 mg

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Table 6. Comparison of maximum adsorption capacities (q_m) and distribution coefficient (K_d) of some sorbents reported in the literature for the removal of target metal ions

sorbent	q_m (mg g ⁻¹)					K_d (mL g ⁻¹)					Ref.
	Cd	Cu	Zn	Pb	Ni	Cd	Cu	Zn	Pb	Ni	
Zinc(II)-MOF (TMU-5)	43	57	-	251	-	-	-	-	-	-	6
MoS ₄ ²⁻ -LDH	-	181	-	290	-	1.3×10^4	4.5×10^6	5.7×10^4	2.6×10^5	-	10
Polysulfide-LDH	57	127	145	483	106	396	2.4×10^3	305	3.0×10^3	47	40
Hierarchical PAN-PS	124	171	-	312	-	-	-	-	-	-	41
WP-PPT	-	25	27.4	-	-	-	-	-	-	-	43
GO/ Fe ₃ O ₄	-	18	-	-	-	-	-	-	-	-	44
Ca(II)-CS microspheres	51	55	-	79	-	-	-	-	-	-	46
H _{2x} Mn _x Sn _{3-x} S ₆	-	-	-	-	-	2.28×10^3	-	-	1.98×10^3	-	47
Na _{2-x} K _x SnSb ₂ S ₆	-	-	-	-	-	4.9×10^3	-	-	4.7×10^3	-	41
Zeolite	52.1	56	-	65.75	34.4	4.5×10^3	1.5×10^4	-	2.5×10^4	1.5×10^3	48
DMSA/ Fe ₃ O ₄	-	-	-	-	-	1×10^4	2.7×10^5	-	2.3×10^6	-	45
DS-LDH	-	-	-	-	149.8	-	-	-	-	-	28
CO ₃ -LDH	-	-	-	-	92.3	-	-	-	-	-	29
DPA-LDH	258	282	242	479		1.99×10^7	3.33×10^6	3.98×10^5	1.99×10^8		This work

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Table 7. Adsorption of DPA-LDH toward the four mixed ions.

Mixed ions	C_0^a	C_f^a -1h	Removal %	K_d^a
Cd	10.0	0.02	99.8	1.99×10^6
Cu	10.0	6.92	30.8	1780
Zn	10.0	8.61	13.9	645
Pb	10.0	0.0009	100.0	4.44×10^7

^aAll concentrations are in mg L⁻¹.
Sample volume (V) = 20 mL; m (mass of solid sample) = 5 mg

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Table 8. Figures of merit for the on-line packed SPE of target metal ions.

Analyte	Linearity			Precision ^a (RSD%, n = 3)					
	LDR ^a	R ²	LOD ^a	Inter-day			Intra-day		
				1	25	75	1	25	75
Cd	0.04-200.0	0.9990	0.01	6.0	5.3	4.8	4.5	4.2	3.3
Cu	0.01-200.0	0.9989	0.005	5.4	5.5	4.6	4.0	3.8	3.4
Zn	0.04-200.0	0.9986	0.01	6.4	5.7	4.4	4.3	3.9	3.5
Pb	0.10-200.0	0.9981	0.05	6.8	5.9	4.9	4.8	4.3	3.7

^a All concentrations are in ng mL⁻¹.

Fig. 1 Powder X-ray diffraction (XRD) patterns of NO_3 -LDH and intercalated-LDHs.

Fig. 2 FT-IR spectra of NO₃-LDH and intercalated-LDHs.

Fig. 3 SEM images of (A) and (B) NO_3 -LDH in different magnifications, (C) PS-LDH, (D) TA-LDH, (E) FA-LDH, (F) DPA-LDH, (G) DS-LDH, (H) EHP-LDH,.

Fig. 4 The N₂ adsorption/desorption isotherms (A) and pore size distributions of LDHs (B).

Fig. 5 Effect of sample pH on extraction efficiency of intercalated-LDHs.

Fig. 6 Effect of adsorption time on extraction efficiency of intercalated-LDHs.

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10 **Fig. 7** Heavy metal ions adsorption isotherms for intercalated-LDHs.