Investigating the role of the morphology of the Zn-Al LDH on the adsorption of humic acid from aqueous solutions

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ABSTRACT

Flake Zn-Al layered double hydroxides (FLDHs) and microspheres of LDH (MLDHs) were fabricated with a simple hydrothermal method to investigate the role of the morphology of Zn-Al LDH for humic acid (HA) adsorption from synthetic solutions and natural water. The effect of process variables, i.e. contact time, initial concentration of HA, pH, and competitive ions on the adsorption was investigated. HA removal mechanism was also studied. The two adsorbents exhibited different adsorption behaviors for HA in the presence and absence of background ions, which may be highly correlated with the various adsorption mechanisms involved. Comparison of the HA removal capacity of these two adsorbents implies the superior adsorption capability of FLDH for removal of HA from synthetic solutions (9.5 mg/g), while the adsorption capacity of MLDH was higher for natural organic matters present in natural water samples containing co-existing ions (8.9 mg/g). The pseudo-second-order kinetics model and Longmuir isotherm model could adequately interpret the HA adsorption process for the studied adsorbents. Both LDHs exhibited good regeneration and recycling abilities.

Key words: adsorption, flake Zn/Al LDH, humic acid, water treatment, Zn/Al LDH microspheres

HIGHLIGHTS

- Morphology of LDH and presence of salts affect the removal mechanism of HA.
- Presence of electrolytes in solution resulted in reducing the size of the HA.
- In the absence of salts, removal of HA by MLDH was more through ligand exchange.
- For FLDH, removal mechanism was an equal combination of both ligand and ion exchange.
- MLDH could be a promising adsorbent for HA removal in multi-salt solutions.

GRAPHICAL ABSTRACT

INTRODUCTION

Humic acid (HA), one of the major components of humic substances (Zhang et al. 2012) which mainly arises from microbial degradation of plants and animals, is commonly present in soils and natural waters. The presence of HA in the water environment adversely affect its quality in different ways: introducing a yellowish to brown color, bringing undesirable taste and odor to water, providing nutrition for bacterial growth in water distribution systems, binding with various pollutants including heavy metals and enhancing their transportation in water, generating carcinogenic disinfection by-products (e.g., trihalomethanes (THMs), haloacetic acid, haloacetonitriles (HANs), haloketones (HKs), trichloronitromethanes and trichloroacetic...
aldehyde) (Li et al. 2019; Li et al. 2020), and fouling membranes and ion-exchange resins. Hence, this material must be removed from aqueous systems. However, HA concentration cannot be effectively reduced by traditional drinking water treatment processes (including coagulation, flocculation, sedimentation, filtration, and disinfection) (Tao et al. 2010; Zhang et al. 2012). So, it is of significant importance and interest to develop efficient treatment methods to minimize HA in drinking water.

Different methods have been used for remediation of HA up to now including ozonation (Seredynska-Sobecka et al. 2006; Jampa et al. 2020), biofiltration (Seredynska-Sobecka et al. 2006; Yang et al. 2020), membrane technology (Tang et al. 2007), coagulation (Ji et al. 2008; Yang et al. 2020), flotation (Zouboulis et al. 2003), ion-exchange (Baker & Khalili 2005), and adsorption (Uyguner et al. 2007). Among these methods, adsorption is considered the most effective and economical method for the removal of HA from aqueous solutions (Douila et al. 2009). So far, several adsorbents such as fly ash (Wang & Zhu 2007), modified rice husk ash (Imyim & Prapalirmungsri 2010), bentonite and montmorillonite nanoparticles (Derakhshani & Naghizadeh 2018), chitosan-H2SO4 beads (Ngah et al. 2011), magnetic chitosan nanoparticles (Dong et al. 2014), carbon nanotubes into zeolitic imidazolate framework (Li et al. 2019), oxidized galena (Wang et al. 2019), granular activated carbon (Barhoumi et al. 2019), and hematite and silicates (Tohry et al. 2021) have been successfully applied to remove humic substances but the adsorption performance is expected to be further improved by developing new adsorption materials.

Layered double hydroxides (LDHs), which are a kind of anionic clay with a layered structure and exchangeable interlayer anions, have received great research attention as adsorbents to eliminate environmental pollutants from aqueous solutions due to their high surface area, unique memory effect, low cost, eco-friendly features, and versatility in chemical composition and morphology (Hatami et al. 2018; Zhang et al. 2019; Hou et al. 2020; Hu et al. 2020). LDHs are represented by the general formula [M2++M3++(OH)2]x·(An-)y/mH2O, where M2+ is a divalent metal ion like Ni, Zn, Cu, and Mg while M3+ represents trivalent metal cations such as Al, Fe, and Cr that occupy octahedral sites in the hydroxide layers, A− is an intercalated exchangeable anion, and x is the ratio of M3+/M2++M3+ (Gasser et al. 2008). Some LDHs and their calcination products (LDOs) have been successfully fabricated and employed to effectively remove natural organic materials from water (Gasser et al. 2008; Fang et al. 2018; Li et al. 2020). However, recently LDH microspheres with porous structures, high specific surface areas, and structural stabilities have been confirmed to possess enhanced adsorption properties compared to typical monodispersed nano/mesosheets (Lin et al. 2015). For instance, Cao et al. (2019) adopted a hydrothermal method to prepare 3D MgAl-LDOs and investigated their adsorption properties for methyl orange dye. Lin et al. (2015) synthesized core-shell structured ZnAl-LDH microspheres and used them successfully for the removal of methyl orange dye. Flower-like MgAl-LDH and MgAl-LDO microspheres were prepared via a precursor method by Jia & Liu (2019) and exhibited good adsorption performance for Congo red anionic dye. Although previous studies have suggested that the morphology of the LDH (typical layered versus microsphere) plays a significant role in its adsorption properties, the information about the effect of LDH’s morphology on its adsorption capability is limited.

Another important factor affecting the process of HA removal from water is the presence of background ions in the solution. While the importance of the presence of background ions in solution on the size of HA molecules has been reported by several researchers (Douila et al. 2009; Zhang et al. 2012), most studies tried to investigate the elimination of HA molecules from synthetic solutions containing only HA and water. Actually, it should be noted that the adsorbent that has the best performance in a synthetic solution may not necessarily be the best one in natural waters containing many different salts.

In this study, in order to investigate the role of the morphology of the LDHs on the adsorption properties, flake Zn-Al LDH (FLDH) and microspheres of Zn-Al LDH (MLDH) were synthesized and compared for adsorptive removal of HA from both the synthetic aqueous solutions and a real water sample. The morphology and structure of as-prepared adsorbents were characterized and their adsorption kinetics, isotherms, and regeneration were also highlighted. Moreover, the contribution of different adsorption mechanisms to the HA removal by FLDH and MLDH was investigated with an emphasis on the effect of the presence of background ions in solution on the size of HA molecules and subsequently the removal mechanism.

MATERIALS AND METHODS

Chemicals

Sodium nitrate (NaNO3), zinc nitrate hexahydrate (Zn(NO3)2.6H2O), aluminum nitrate nonahydrate (Al(NO3)3.9H2O), sodium hydroxide (NaOH), hydrochloric acid (HCl), and urea (CO(NH2)2) were purchased as the analytical grade from chemicals. Sodium nitrate (NaNO3), zinc nitrate hexahydrate (Zn(NO3)2.6H2O), aluminum nitrate nonahydrate (Al(NO3)3.9H2O), sodium hydroxide (NaOH), hydrochloric acid (HCl), and urea (CO(NH2)2) were purchased as the analytical grade from chemicals. Sodium nitrate (NaNO3), zinc nitrate hexahydrate (Zn(NO3)2.6H2O), aluminum nitrate nonahydrate (Al(NO3)3.9H2O), sodium hydroxide (NaOH), hydrochloric acid (HCl), and urea (CO(NH2)2) were purchased as the analytical grade from chemicals. Sodium nitrate (NaNO3), zinc nitrate hexahydrate (Zn(NO3)2.6H2O), aluminum nitrate nonahydrate (Al(NO3)3.9H2O), sodium hydroxide (NaOH), hydrochloric acid (HCl), and urea (CO(NH2)2) were purchased as the analytical grade from chemicals. Sodium nitrate (NaNO3), zinc nitrate hexahydrate (Zn(NO3)2.6H2O), aluminum nitrate nonahydrate (Al(NO3)3.9H2O), sodium hydroxide (NaOH), hydrochloric acid (HCl), and urea (CO(NH2)2) were purchased as the analytical grade from chemicals. Sodium nitrate (NaNO3), zinc nitrate hexahydrate (Zn(NO3)2.6H2O), aluminum nitrate nonahydrate (Al(NO3)3.9H2O), sodium hydroxide (NaOH), hydrochloric acid (HCl), and urea (CO(NH2)2) were purchased as the analytical grade from chemicals. Sodium nitrate (NaNO3), zinc nitrate hexahydrate (Zn(NO3)2.6H2O), aluminum nitrate nonahydrate (Al(NO3)3.9H2O), sodium hydroxide (NaOH), hydrochloric acid (HCl), and urea (CO(NH2)2) were purchased as the analytical grade from chemicals.
Merck company. Humic acid (technical grade) was obtained from Aldrich Company and purified following the procedure of a previous researcher (Imyim & Prapalimrungsi 2010) to remove all inorganic impurities. In all experiments, MilliQ water was used.

Preparation of LDHs

Preparation of FLDH

FLDH was synthesized via a hydrothermal heating process (Hayatdavoudi & Rahsepar 2017). In a typical synthesis for producing FLDH with a molar ratio of Zn to Al of 2:1, 50 mL of a solution containing 1 M Zn(NO₃)₂·6H₂O and 0.5 M Al(NO₃)₃·9H₂O was added gradually to a 100 mL solution of 1.5 M NaNO₃ under stirring. During the process, nitrogen gas was blown into the solution and the pH value of the solution was kept at 10 by slowly adding appropriate amounts of a 2 M NaOH solution. The final solution was poured into the autoclave and held for 24 h at 65 °C. Synthesized LDH was separated by centrifugation and washed four times with boiled MilliQ water.

Preparation of MLDH

MLDH was prepared using a hydrothermal method and urea was also employed as a precipitating agent. Briefly, similar to FLDH preparation, a 50 mL solution of 1 M Zn(NO₃)₂·6H₂O and 0.5 M Al(NO₃)₃·9H₂O was prepared. Afterward, 6.37 g NaNO₃ was added to the solution under vigorous stirring until a uniform solution was obtained, and then a 0.4 M urea solution was added at once. After obtaining a clear solution, it was poured into the autoclave and was placed in the oven for 18 h at a temperature of 60 °C. Centrifugation and washing of MLDH were performed similarly to the method described for FLDH.

Characterization

X-ray diffraction (XRD) data were recorded with a Philips X’pert diffractometer using Cu Kα radiation source (λ = 1.54178 nm) over the range from 10° to 80° in 0.05° steps. SEM (Scanning Electron Microscopy) analysis was carried out using TESCAN-Vega3 to observe the morphology of the LDH particles. A Bruker TENSOR II spectrometer was used to record the Fourier transform infrared (FT-IR) spectra of the LDHs in the range 400–4,000 cm⁻¹.

HA adsorption experiments

All the batch experiments were carried out in 50 mL Erlenmeyer flasks with glass caps under magnet stirring at room temperature, pH = 7, 0.5 (g L⁻¹) adsorbent, and 25 (mg L⁻¹) HA solution unless otherwise noted. The pH of the solutions was adjusted with NaOH or HCl. HA concentrations were determined by using a DR-5,000 UV-Vis spectrophotometer (Hach, US) at a wavelength of 254 nm. The removal rate and adsorption capacity of HA were calculated according to Equations (1) and (2), respectively (Azadi et al. 2018a, 2018b).

\[
\%\text{Removal} = \frac{C_0 - C_t}{C_0} \times 100
\]  
\[
q_t = \left(\frac{C_0 - C_t}{M}\right) \frac{V}{M}
\]

where, \(C_0\) and \(C_t\) are the concentrations of HA (mg L⁻¹) at the beginning and at time \(t\), respectively; \(q_t\) is the adsorption capacity (mg g⁻¹) at time \(t\); \(V\) is the volume of solution (L), and \(M\) is the mass of adsorbent (g).

To investigate the adsorption kinetics, the suspensions of adsorbents/HA solutions were stirred and samples were withdrawn at a given time and then filtered through a 0.45 μm membrane filter to determine HA concentration. Adsorption isotherm experiments were conducted in various concentrations of HA solution (5–500 mg L⁻¹). The effect of four inorganic salts (NaCl, Na₂SO₄, NaNO₃, and Na₂CO₃) on HA molecular size and adsorption was evaluated by adding different amounts of them (5–100 (mmol L⁻¹)) to the HA solution. The initial pH effect on HA removal was studied in the pH range of 4–10. For the analysis of HA molecular size, prepared solutions were stirred for 100 min and finally, the ratio of the absorbance at 250 nm to the absorbance at 365 nm (E₂/E₃) was reported. It should be noted that all the ranges have been chosen based on the previous studies (Dehghani et al. 2018; Hu et al. 2018; Grover et al. 2019) and experimental limits.

In order to investigate the adsorption mechanism of HA on FLDH and MLDH, CO₃-intercalated LDHs were prepared by reconstruction method according to the procedure reported by Vreysen & Maes (2008). For each adsorbent, Equation (3) was
used to determine the share of the ligand exchange in the HA removal mechanism (Hashim et al. 2021):

\[ C = \frac{B}{A} \times 100 \]  

(3)

where, \( A \) and \( B \) are the removal percentage of HA (%) by the conventionally coprecipitated LDHs and CO\(_3\)-intercalated LDHs, respectively.

For the investigation of the ability of prepared LDHs in removing natural organic matters (NOMs) from natural waters, water samples from a nearby river (Dalaki River) were taken. Then, batch experiments were performed by adding 0.25 g adsorbent to a 1 L water sample and the amount of NOM removed was determined spectrophotometrically. In all tests, the average value of three replicates was reported.

RESULTS AND DISCUSSION

Characterizations of MLDH and FLDH

The XRD patterns of the adsorbents before adsorption and after the thermal desorption process are presented in Figure 1(I). This figure shows that for MLDH, a series of reflections appeared at 2\( \theta \) = 11.60, 23.50, 34.54, 39.15, 47.70, 60.20 and 62.95, corresponding to the crystal plane of (003), (006), (012), (015), (018), (110) and (113), respectively (Li et al. 2020). Furthermore, FLDH exhibited several similar reflections, indicating that the typical layered structure of Zn/Al LDH was obtained. According to Bragg’s law, the (003) plane was applied to measure the basal space of the MLDH and FLDH particles, which were determined to be 0.76 and 0.88 nm, respectively. The FLDH diffraction pattern showed a slightly negative shift of the (003) plane original peak to 10.05° in comparison with the MLDH pattern due to the change in the LDH morphology or the difference in the synthesis method. However, after calcination of MLDH and FLDH at 440 °C and desorption process, several characteristic reflections belonging to LDHs disappeared and three new reflections appeared at (100), (002) and (101) planes, which agreed well with the typical characteristic reflections of ZnO. The result was consistent with Li et al. (2020) and Hu et al. (2018).

FT-IR spectra of MLDH and FLDH before and after adsorption are presented in Figure 1(II). As is obvious, highly similar patterns were obtained for both adsorbents. Before adsorption, the broad band at 3,454 and 3,435 was attributed to the O-H stretching vibration of hydroxyl groups or physically adsorbed water molecules in LDH (Chakraborty et al. 2011; Grover et al. 2019). The presence of water molecules can also be evidenced by the bands at around 1,607 and 1,504 cm\(^{-1}\), which was attributed to the H-O-H deformation mode (Carpenter et al. 2017; Lu et al. 2017; Hadjiivanov et al. 2020). The strong band at 1,384 was assigned to the nitrate groups (Hatami et al. 2018). Moreover, the bands appearing at 400–800 cm\(^{-1}\) corresponded with M-O, O-M-O, and M-O-M lattice vibrations (M represents Zn and Al) (Hu et al. 2020). After adsorption, the O-H stretching vibration band at 3,444 and 3,465 cm\(^{-1}\) appeared, and took a shift compared to FLDH and MLDH, indicating that layered double hydroxides structure reconstructed and hydrogen bonds participated in adsorption of HA (Li et al. 2020). Moreover, the new bands at 2,960 and 2,956 cm\(^{-1}\) show the stretching vibration of C-H while the new bands at 1,584 and 1,586 cm\(^{-1}\) demonstrate the aromatic ring skeleton, both confirmed the adsorption of HA on FLDH and MLDH (Li et al. 2020).

The morphologies of FLDH before HA adsorption, and MLDH before adsorption and after desorption characterized by SEM are shown in Figure 2. The well-crystallized, irregular sheet-like structure (Figure 2(a)), which is the typical morphology for LDH material (Hatami et al. 2018), could be observed for the FLDH sample. Figure 2(b) shows that numerous thin sheets of FLDH aggregated, interconnected, and formed 3D hierarchical microspheres with a diameter of about 8 \( \mu \)m in MLDH. After calcination, there was no evident change of MLDH and FLDH morphology (Figure 2(c) and 2(d)), indicating that the microsphere structure of prepared LDH was maintained.

Adsorption kinetics and isotherms

The kinetic curves of the prepared FLDH and MLDH are illustrated in Figure 3. This figure shows that the adsorption of HA into the FLDH increased quickly and achieved equilibrium at 80 min, which was significantly faster than the MLDH (about 240 min). The faster adsorption of HA into the FLDH compared to the MLDH was likely due to the easy accessibility of its active adsorption sites. Therefore, in the next adsorption experiments, the adsorption time was chosen as 120 and 280 min for FLDH and MLDH, respectively. The kinetic data were then fitted with pseudo-first-order (Equation (4)) and
pseudo-second-order (Equation (5)) models that can be expressed in their linearized forms as:

\[
\log\left(\frac{q_e - q}{q_e}\right) = \log\left(\frac{q_e}{q_0}\right) - \frac{K_1}{q_e} t
\]

(4)

\[
\frac{t}{q} = \frac{1}{K_2 q_e} + \frac{1}{q_e} t
\]

(5)

**Figure 1** | (I) X-ray diffraction of (a) MLDH, (b) FLDH, (c) MLDH after calcination and (d) FLDH after calcination; (II) FTIR spectra of (a) FLHD before adsorption, (b) MLDH before adsorption, (c) FLDH after adsorption, and (d) MLDH after adsorption.
Figure 2 | SEM images of (a) FLDH, (b) MLDH, (c) MLDH after calcination, and (d) FLDH after calcination.

Figure 3 | Variation in adsorption amount with time (including error bars less than 5%).
where $q_e$ and $q_t$ (mg g$^{-1}$) are the amount of HA adsorbed at equilibration and time $t$, correspondingly; and $K_1$ (min$^{-1}$) and $K_2$ (g mg$^{-1}$ min$^{-1}$) are the rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively.

The fitted lines of the pseudo-first-order and pseudo-second-order models are displayed in Figure 4(a) and 4(b) and the corresponding parameters for the two adsorbents are listed in Table 1. As illustrated in Figure 4 and Table 1, the correlation coefficients indicated that the pseudo-second-order model fitted better to the experimental data, as compared to the pseudo-first-order model. Hence, the pseudo-second-order model was more appropriate for depicting the adsorption process of the prepared LDHs for HA removal. In addition, the $q_{e,cal}$ values calculated from the pseudo-second-order model were closer to the experimental values than the values calculated from the pseudo-first-order model.

The adsorption isotherms were employed to explore the relationship between the amounts of HA adsorbed by a unit mass of prepared adsorbents and the amounts of HA remaining in the aqueous phase at equilibrium. Figure 5 displays the experimental adsorption isotherms of HA onto FLDH and MLDH at 25 °C. The isotherms showed a sharp rise at low HA concentrations and then reached a plateau at elevated concentrations, reflecting that initially there were numerous readily available adsorption sites. FLDH exhibited higher adsorption capacities toward HA compared with MLDH. Two classic isotherm models, namely Langmuir (Equation (6)) and Freundlich (Equation (7)), were employed to analyze the experimental data further.

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}
\]

(6)

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

(7)

where $q_e$ (mg g$^{-1}$) is the adsorption capacity at equilibrium, $q_m$ (mg g$^{-1}$) is the saturated adsorption capacity, $C_e$ (mg L$^{-1}$) is the HA concentration at equilibrium, $K_L$ (L mg$^{-1}$) is the Langmuir model constant and $K_f$ ((mg g$^{-1}$)(L mg)$^{1/n}$) and $n$ are Freundlich isotherm constants.

Figure 4 | Fitted results for HA adsorption onto FLDH and MLDH by (a) linearized pseudo-first-order and (b) pseudo-second-order kinetic models (including error bars less than 5%).
The relevant parameters of these models are summarized in Table 2. Based on the results achieved, the experimental data were best fitted to the Langmuir model, suggesting that the adsorption of HA onto both FLDH and MLDH was probably dominated by a chemisorption process (Wang et al. 2014). Based on the Langmuir isotherm model, the predicted maximum adsorption capacity of HA on FLDH (84 mg g$^{-1}$) was higher than that of MLDH (60 mg g$^{-1}$), and was also comparable with other adsorbents reported in the literature such as calcined Mg-Al LDH (39.9 mg g$^{-1}$) (Fang et al. 2018), activated carbon modified by multi-wall carbon nanotubes (73.3 mg g$^{-1}$) (Noorimotlagh et al. 2020), MWCNTs/ZIF-8 (55.7 mg g$^{-1}$) (Li et al. 2019), Fe$_3$O$_4$-chitosan hybrid nano-particles (44.8 mg g$^{-1}$) (Zulfikar et al. 2016), calcined Mg-Al LDH nanocrystalline particles (98.8 mg g$^{-1}$) (Fang et al. 2018), Mg-Fe LDH (76.7 mg g$^{-1}$) (Gasser et al. 2008), and so on.

### Adsorption mechanism and effect of background anions

Previous research (Vreysen & Maes 2008) has addressed two main mechanisms for the removal of humic acids from aqueous solutions by LDHs, i.e. ion exchange with both the intercalated and surface anions of the LDHs and ligand exchange with surface groups. Actually, in the latter case, carboxylic groups on HA molecules are known to be involved in chemical reactions with the LDH surface groups, especially AL-OH groups. To investigate the contribution of the ligand exchange mechanism to the total HA removal by prepared nitrate-intercalated LDHs, adsorption data onto carbonate-intercalated

### Table 1 | Kinetic parameter values for HA adsorption by as-prepared LDHs

| Adsorbents | $q_{e,exp}$ (mg g$^{-1}$) | $q_{e,cal}$ (mg g$^{-1}$) | $K_1$ (min$^{-1}$) | $R^2$ | $q_{e,cal}$ (mg g$^{-1}$) | $K_2$ (g mg$^{-1}$ min$^{-1}$) | $R^2$ |
|------------|--------------------------|--------------------------|------------------|------|--------------------------|--------------------------|------|
| MLDH       | 31.2                     | 28.9                     | 0.004            | 0.9698 | 28.9                     | 1.4 × 10$^{-4}$         | 0.9998 |
| FLDH       | 48.8                     | 42.8                     | 0.013            | 0.7615 | 43.1                     | 2.9 × 10$^{-4}$         | 0.9997 |

### Table 2 | Isotherm parameters for HA adsorption onto LDHs

| Adsorbent type | Linear-Langmuir isotherm model | | Linear-Freundlich isotherm model | |
|----------------|---------------------------------|---|---------------------------------|---|
|                | $K_l$ (L mg$^{-1}$) | $q_{max}$ (mg g$^{-1}$) | $R^2$ | $n$ | $K_r$ ((mg g$^{-1}$)/(L mg$^{-1}$)$^n$) | $R^2$ |
| M-LDH          | 0.084                          | 59.9 | 0.9997                          | 4.28 | 16.11 | 0.8972 |
| F-LDH          | 0.094                          | 84.0 | 0.9940                          | 3.78 | 23.31 | 0.8495 |
FLDH and MLDH were recorded and presented in Figure 6. Compared to nitrate ions, carbonate ions cannot be easily separated from the LDH structure and exchanged with other ions in the solution. Thus, HA removal by carbonate-intercalated LDH is generally known to occur almost only by the ligand exchange mechanism. The relation described by Equation (3) was used to determine the percentage of HA removed by LDHs by ligand exchange. The contribution of ion exchange was then calculated by subtracting the percentage of ligand exchange from the total HA removal percentage. The total HA adsorption onto the FLDH was significantly larger, compared to the HA adsorption onto the MLDH. This can be interpreted with almost equal involvement of both mentioned mechanisms in the removal of HA by FLDH (56.6% and 43.4% for ligand exchange and ion exchange mechanisms, respectively). However, these results suggest that there was most likely more participation of ligand exchange (63.6%) compared to the ion exchange mechanism (36.4%) in the adsorption of HA onto the MLDH. Increasing of the ligand exchange contribution can be attributed to the enhanced specific surface area of LDH microspheres which resulted in the improvement of the electrostatic interactions between the anion groups on the HA and the positive adsorption sites on the surface of the MLDH. On the other hand, the reduction of the role of ion exchange may be ascribed by the intercalation of only small parts of HA molecules in-between the brucite-like sheets of the MLDH, which was also confirmed by the smaller interlayer space (003) of this adsorbent (0.76 nm) compared to FLDH (0.88 nm). In other words, in order for effective ion exchange to take place, the HA molecules should enter the interlayer space of LDH. Since the penetration of the HA molecules into the interlayer space of MLDH is difficult due to its special structure and its shorter interlayer space, the role of the ion exchange mechanism in HA removal by MLDH was reduced, while in the case of FLDH, the contribution of both the ion exchange and the ligand exchange mechanisms in the adsorption resulted in higher adsorption capacity of FLDH than MLDH.

The presence of background ions in the solution affects the adsorption mechanism of HA onto LDHs mainly through its effect on the size of HA molecules. Figure 7 shows the effect of different salts on the adsorption of HA onto MLDH and FLDH. As shown in these figures, the distinct differences in structures of the FLDH and MLDH resulted in the different adsorption behaviors of HA on them in the presence of background salts. The adsorption of HA onto the FLDH decreased slightly with the increase of ionic strength, while the adsorption onto the MLDH increased rapidly with the increase of salts concentration, but with further increasing of Na₂SO₄, NaNO₃, and Na₂CO₃ content beyond 20 mg L⁻¹ and NaCl beyond 40 mg L⁻¹, the HA removal decreased. These different adsorption trends can be explained by the different mechanisms of HA adsorption onto the two adsorbents as previously mentioned. In the absence of background ions, HA adsorption onto the MLDH was mainly through ligand exchange-surface complexation and ion exchange did not play a major role in HA removal, mainly due to the low interlayer space. However, it is known that an increase of ionic strength can cause the coiling of an HA macromolecule as a result of the neutralization of its negatively charged carboxylic and phenolic groups and the

![Figure 6](http://iwaponline.com/wst/article-pdf/84/7/1663/948498/wst084071663.pdf)
minimization of the electrostatic repulsion between ionized oxygen groups (Zhang et al. 2012; Dong et al. 2014). Consequently, the resultant smaller and more hydrophobic HA molecule could approach the interlayer space of MLDH where the interchangeable ions were located; therefore, there was more contribution from the ion exchange mechanism, in addition to ligand exchange, resulting in enhanced HA adsorption onto MLDH. Similar positive ionic strength effects on the adsorption of HA molecules onto LDHs have also been observed in other studies (Weng et al. 2007; Doulia et al. 2009; Wang et al. 2012). A further increase in the concentration of background salts caused a slight decrease in percentage removal of HA by MLDH. This could be attributed to the competition between the ionic groups on the HA with anionic electrolyte ions for the same adsorption sites on the MLDH.

Due to the larger interlayer space of FLDH, as confirmed by the XRD results, the original HA molecules could approach the intercalated anions; therefore, no obvious difference in ion exchange capacity of FLDH was observed during the adsorption process in the presence of background ions. Meanwhile, the total removal percentage of HA molecules was slightly reduced with increasing ionic strength. This may be related to the competitive adsorption of SO$_4^{2-}$, Cl$^-$, NO$_3^-$ and CO$_3^{2-}$ which were introduced by salts in excess amounts.

Figure 7 | Effect of background ions on HA removal by (a) FLDH and (b) MLDH (including error bars less than 2%).
Effect of inorganic salts on HA molecular size

To understand the effect of background ions on the size of the humic acid molecules, the ratio of absorbance at 250 nm to that at 365 nm ($E_{2}/E_{3}$) of the HA solutions in the presence and absence of different concentrations of salts were recorded and are presented in Figure 8. It is known that a higher $E_{2}/E_{3}$ ratio reflects a lower average molecular mass and aromaticity (Vreysen & Maes 2008). As is obvious from Figure 8, the $E_{2}/E_{3}$ ratio increased with increasing amount of background salts in solution, indicating the positive impact of the presence of electrolytes in solution on reducing the size of the HA molecules. The highest and lowest effect was related to NaNO₃ and NaCl, respectively.

Effect of solution pH

Solution pH is a critical factor for the adsorption of HA by adsorbents. The curves of FLDH and MLDH removal efficiency and final pH versus initial pH are demonstrated in Figure 9. It is obvious that for both adsorbents the overall range of the final pH was narrower than the range of the initial pH. This may be attributed to the buffering capacity of the FLDH and MLDH. At low pH values, the neutralization of hydrogen ions in solutions by the hydroxyl groups of FLDH and MLDH was the main mechanism that provided the buffering capacity to these adsorbents. While at high pH values, the buffering properties of FLDH and MLDH were mainly due to the deprotonation of these solids.

The HA removal efficiency did not change much with increasing pH value from 4 to 8, but with further pH rise, the removal efficiency decreased sharply. This can be interpreted by the electrostatic attraction between the protonated (positively charged) LDHs and the negative functional groups (especially carboxylic and phenolic) of HA below pH 8, and the repulsion between the deprotonated (negatively charged) LDHs and negatively charged HA above pH 8. However, even at pH 10, the HA removal efficiency was still high enough, especially for FLDH (about 70% for FLDH and 40% for MLDH), which may be ascribed to the responsibility of another adsorption mechanism (intercalation) in addition to electrostatic interaction. The results of the influence of pH on HA adsorption were consistent with the research by Li et al. (2020) and Zhang et al. (2012).

HA desorption study

Considering the feasibility of the practical application of an adsorbent, regeneration and reusability of it is important. Here, the recyclability of prepared LDHs was tested using two successive methods (i.e., thermal desorption following the regeneration of exhausted LDHS using KNO₃). The choice of KNO₃, as one of the available electrolytes in soil, was for evaluating the recoverability of HA-exhausted adsorbent as a fertilizer. In other words, in this study, LDHs exhausted after five cycles of adsorption and thermal desorption were soaked in 0.03 M KNO₃ solution, and samples were taken in different time intervals and analyzed for HA content.

**Figure 8** | Effect of different inorganic salts on HA molecular size (including error bars less than 2%).
In the first stage of the regeneration study, sequential thermal regeneration experiments were conducted by calcining the HA-laden LDHs at 455 ± 10 °C for 6 h. It can be seen from Figure 10(a) that for both the MLDH and FLDH, the adsorbed HA has increased in the second cycle and then has begun to fall off during the next three adsorption-desorption cycles. Increasing the adsorption capacity of HA in the second cycle may be due to the effect of calcination at high temperatures in converting LDHs into mixed oxide-hydroxide phases with higher specific surface areas, pore volumes and porosities. These layered double mixed oxides (LDOs) reconstruct the LDH structure through rehydration and simultaneously incorporate anions into the interlayers (Cao et al. 2019; Jia & Liu 2019). This finding is consistent with the result reported by Fang et al. (2018). As can be seen, after five cycles, the amount of HA adsorbed onto the regenerated MLDH and FLDH reached 64 and 60 mg/g, respectively, which was only less than 20% capacity reduction compared to that of the second adsorption cycle and was still higher than the original LDHs adsorption capacity. The slight decrease in adsorption capacity of calcinated LDHs might be ascribed to both incomplete desorption of HA molecules and gradual damaging of the crystal structure of LDHs by successive mechanical agitation during experiments.

In the second stage of the regeneration study, the LDH samples after five cycles of adsorption-calcination were regenerated by desorption with 0.03 M KNO₃. As shown in Figure 10(b), the amount of desorption increased dramatically in the first 20 h and then decreased gradually with the increasing contact time from 20 to 120 h. The gradual release of HA from prepared LDHs indeed reveals that the spent LDHs can be applied to agricultural fields to improve soil fertility, therefore requiring no need to spend money on their disposal. As expected, the HA recoverability of FLDH was found to be greater than that of MLDH during the test time. This likely can be associated with the harder release of HA molecules from the smaller interlayer space of MLDH than FLDH.

**Removal of natural organic matter from a real water sample**

An experimental investigation to further verify the practical applicability of prepared LDHs was performed on a local river water sample. As was expected, the adsorption efficiency of MLDH for removing natural organic matters (NOMs) from the river water sample (93.3%) was obviously higher than that of the synthetic water sample (84.4%), whereas the adsorbed amount of NOMs onto the FLDH from the real sample (90.5%) decreased slightly compared to the synthetic sample (100%). These results confirmed the positive impact of existing background ions in solution on improving the adsorption properties of MLDH, as was discussed in section 3.4. Accordingly, the application of MLDH for the removal of NOMs from natural water samples may be more effective than using FLDH.
CONCLUSION

In summary, FLDH and MLDH were synthesized using a facile approach and their structural and surface properties were fully characterized. The crystalline FLDH nanosheets and regular three-dimensional structures of MLDH were well formed and remained the same even after thermal regeneration, according to the SEM analysis. The pseudo-second-order kinetics model and the Langmuir isotherm model best described the HA adsorption process on both adsorbents. The maximum adsorption capacities of FLDH and MLDH for removal of HA from synthetic solutions were 84 and 60 mg/g, respectively. The findings in this study demonstrated that both the morphology of LDH and the presence of salts in solution affect the removal mechanism of HA. In the absence of background salts, the removal of HA by MLDH was more through the ligand exchange (63.6%) than the ion exchange (36.4%) due to the easier access of HA molecules to surface bonding sites induced by the special structure of LDH microspheres, whereas for FLDH, the removal mechanism was an almost equal combination of both the ligand exchange (56.6%) and the ion exchange (43.4%). This was likely due to the higher interlayer distance of FLDH compared to MLDH, which allows HA molecules to penetrate the interlayer space and exchange with the intercalated anions. In the presence of
other salts in the solution, the removal efficiency for MLDH was greatly improved and even reached 100% due to a decrease in the size of HA molecules and consequently an enhancement in the ion exchange participation. In other words, it seems that MLDH could be a promising adsorbent for HA removal in multi-salt solutions such as natural waters because of effectively using both the ligand exchange and ion exchange mechanisms in HA uptake. The gradual desorption of HA from prepared LDHs especially could be a promising adsorbent for HA removal in multi-salt solutions such as natural waters because of effectively using both the size of HA molecules and consequently an enhancement in the ion exchange participation. In other words, it seems that MLDH was observed during contact with KNO₃, which allows us to use them as slow-release HA fertilizer in the soil.

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DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

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