

STABILIZATION OF METALS AND METALLOIDS USING Mg-Fe LAYERED DOUBLE HYDROXIDES

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Abstract

Layered double hydroxides (LDHs) and the products of their thermal treatment (mixed oxides) are highly effective adsorbents of oxyanions, but there are only few studies concerning cation sorption. Therefore, this study was focused on the synthesis and characterization of Mg-Fe LDH for adsorption of Zn^{2+} . Characterization of Mg-Fe LDH was performed using XRD, BET and FTIR-ATR analyses. Based on batch adsorption experiments, adsorption kinetics and isotherms were constructed. Concentrations of Zn after sorption were determined using ICP-OES and the solid phase was analysed using FTIR-ATR. The highest adsorption capacity for Zn^{2+} was observed for Mg-Fe LDH with the molar ratio of 4:1.

Key words:

Layered double hydroxides, adsorption, metals, adsorption isotherms, adsorption kinetics

List of abbreviations:

| | |
|--------------------------|---|
| A^{n-} | n-valence anion |
| BET | Brunauer-Emmett-Teller |
| c_0 | initial concentration (mg/L) |
| c_e | equilibrium concentration in the solution (mg/L) |
| CLDH | calcined layered double hydroxide |
| EXAFS | Extended X-Ray Absorption Fine Structure |
| FTIR-ATR | Fourier Transform Infrared Spectroscopy-Attenuated Total Reflection |
| ICP-OES | Inductively Coupled Plasma-Optical Emission Spectrometry |
| k_1 | rate coefficient of the pseudo-first kinetic order (min^{-1}) means |
| k_2 | rate coefficient of the pseudo-second kinetic order [$\text{g}/(\text{mg}\cdot\text{min})$] |
| K_F | Freundlich constant [$(\text{mg}/\text{g})(\text{L}/\text{mg})^{1/n}$] |
| K_L | Langmuir constant (L/mg) |
| LDH | layered double hydroxide |
| m | mass of the adsorbent (g) |
| M^{2+} | divalent metal cation |
| M^{3+} | trivalent cation |
| n | dimensionless constant describing the process of adsorption |
| pH_{ZPC} | pH of zero charge |
| q_e | adsorbed amount at the equilibrium (mg/g) |
| $q_{e(\text{exp})}$ | experimental value of adsorbed amount at the equilibrium |
| q_{MAX} | maximum adsorption capacity (mg/g) |
| q_t | adsorbed amount (mg/g) at time t (min) |
| R_2 | correlation coefficient |
| S_{BET} | specific surface area |
| SEM/EDX | Scanning Electron Microscopes/Energy-dispersive X-ray Spectroscopy |
| V | volume (L) |
| x | trivalent metal ratio |
| XPS | X-ray Photoelectron Spectroscopy |
| XRD | X-Ray Diffraction |

Introduction

Environmental contamination with risky elements and their remediation from the environment is a highly actual topic. Common methods of soil remediation (dumping, encapsulation, washing/flushing,

vitrification, etc.) and water (coagulation, precipitation, reverse osmosis, etc.) show a lot of significant disadvantages, e.g. higher costs, higher energy demanding and also they are more disruptive in the context of natural soil environment. Adsorption is an appropriate alternative technique that belongs to one of the mechanisms of chemical stabilization. Many various types of materials can be used for chemical stabilization of metals and metalloids, e.g. alkaline materials, clay minerals and zeolites, organic industrial waste and by-products and Fe, Mn and Al oxides (Komárek et al., 2013; Liang et al., 2013).

Layered double hydroxides (LDHs) are naturally occurring materials (hydrotalcite, pyroaurite, hydrocalumite) or they can be synthetically prepared (de Roy et al., 2010). The most important advantages of these materials are their use in different application, their unique properties, structure and a relatively simple and economical synthesis (Goh et al., 2008; Liang et al., 2013). Layered double hydroxides are layered materials with positively charged brucite-like layers consisting of octahedrally coordinated divalent and trivalent metal cations. The positive charge of layers is compensated by anions intercalated in the interlayered region, where water molecules can be also found. A general formula of LDHs is given by $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[A_{x/n}^{n-}.y\text{H}_2\text{O}]^x$, where M^{2+} and M^{3+} mean divalent and trivalent cations and A^{n-} corresponds to appropriate n-valence anions. The symbol x describes the trivalent metal ratio $M^{3+}/(M^{2+}+M^{3+})$ (Kovanda, Jakubíková 2010). Layered double hydroxides enable the sorption of metals by following mechanisms: surface precipitation of hydroxides, physical and chemical adsorption, isomorphic substitution and chelation with functional ligands (Liang et al., 2013). Heating of LDHs above 400°C leads to destruction of the layered structure and formation of mixed oxides (CLDHs) that show a larger surface area, higher thermal stability, stronger basic properties (Liang et al., 2013) and a different mechanism of sorption (mainly a reconstruction of the original layered structure of LDHs – the memory effect) (Kang et al., 2013).

Most of the studies deal with stabilization using Mg-Al LDHs and CLDHs. However, these materials contain Al that can be leached from LDHs and CLDHs at lower pH values (Boclair, Braterman, 1999). Therefore, the study is focused on Mg-Fe LDH and CLDH. Moreover, these materials show higher affinity, adsorption capacity and lower desorption rate compared with Mg-Al materials (Rojas, 2012). The main aim of the study is to describe sorption of Zn^{2+} on these materials in the solution and evaluate their efficiency during given experimental conditions. The study is a necessary step to a further use of Mg-Fe LDHs and CLDHs in soils contaminated by metals and metalloids as a potential innovative remediation technique.

Methodology

Mg-Fe LDHs with different molar ratios were synthesized by dissolution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 200 mL of demineralized water. Afterwards, the solution was titrated using 2.5 M KOH to pH 13.3. The mixture was vigorously stirred for 24 hours. Subsequently, filtration, drying at 393 K, milling and sieving under the particle size below 250 μm were performed (Seida et al., 2001).

Characterization of the structure of materials was performed by X-ray Diffraction analysis (XRD) using PANalytical X'Pert Pro diffractometer with X'Celerator detector (CuK α radiation, 40 kV, 30 mA, a measuring step 0.02° s⁻¹ in the range 10°-80°). The specific surface area was measured by N₂ adsorption at 77 K (BET analysis) using ASAP 2050 (Micrometrics Instrument Corporation, USA). Characteristic functional groups were measured using FTIR-ATR with diamond crystal (Nicolet 6700, 65 scans). The chemical analysis of solutions was performed using ICP-OES (Agilent Technologies 720 Series) after dissolution in 0.1 M HNO₃.

Solutions for batch adsorption experiments were prepared by dissolution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in demineralized water. The solid/liquid ratio was 1 g/L in all experiments. The pH value was controlled using 0.01 and 0.1 M HNO₃. The concentration of Zn^{2+} for kinetic experiments was set up to 10⁻⁴ M. Afterwards, the adsorbent was added, the mixture was vigorously stirred (550 rpm) and at given time intervals the sampling was performed (the pH 5.5 was controlled during the whole process). The concentrations of Zn^{2+} for equilibrium adsorption experiments were set up in the range 2-65 mg/L. Afterwards, the solution with added adsorbent was stirred (350 rpm) for the time needed to reach the

equilibrium (2 hours) at a constant pH value (pH=5.5). The initial concentration of Zn^{2+} for equilibrium adsorption experiments performed to analyse the solid phase after adsorption using FTIR-ATR (750 scans) was 400 mg/L. The concentration of metals in the solution was determined using ICP-OES (Agilent Technologies 720 Series). The adsorbed amount q_e (mg/g) is given by:

$$q_e = \frac{(c_o - c_e) \cdot V}{m}$$

where c_o a c_e (mg/L) is the initial and equilibrium concentration. The symbol V (L) corresponds to the given volume and m (g) to the mass of the adsorbent.

Data from kinetic experiments of Zn^{2+} were modelled using nonlinear form of pseudo-first and pseudo-second kinetic order. The pseudo-first kinetic order is represented by (Kumar, 2006):

$$q_t = q_e \cdot (1 - e^{-k_1 \cdot t})$$

where q_t a q_e (mg/g) describe the adsorbed amount at time t (min) and at the equilibrium. The constant k_1 (min^{-1}) means the rate coefficient of the pseudo-first kinetic order. The pseudo second-order is represented by (Kumar, 2006):

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

where q_t a q_e (mg/g) correspond to the adsorbed amount at time t (min) and at the equilibrium. The constant k_2 [$g/(mg \cdot min)$] means the rate coefficient of the pseudo-second kinetic order.

Data from equilibrium adsorption experiments of Zn^{2+} were modelled using Langmuir and Freundlich equation. The Langmuir equation is represented by (Langmuir, 1918):

$$q_e = \frac{q_{MAX} \cdot K_L \cdot c_e}{1 + K_L \cdot c_e}$$

where c_e and q_e correspond to the equilibrium concentration in the solution (mg/L) and the adsorbed amount at the equilibrium (mg/g). Parameters q_{MAX} and K_L are the maximum adsorption capacity (mg/g) and the Langmuir constant related to the affinity to the adsorbate (L/mg). The second type is the Freundlich equation that is given by (Freundlich, 1906):

$$q_e = K_F \cdot (c_e)^n$$

where c_e and q_e correspond to the equilibrium concentration in the solution (mg/L) and the adsorbed amount at equilibrium (mg/g). Parameters K_F and n are the Freundlich constant [$(mg/g)(L/mg)^{1/n}$] and the dimensionless constant describing the process of adsorption (the influence of the surface heterogeneity).

Results

Characterization of materials

Diffractiongrams of synthesized Mg-Fe LDH with different molar ratios are given in Fig. 1. Sharp and symmetric peaks are observed at low and high values of 2Θ (11.45; 22.75; 59.70 and 60.98). On the other hand, broad and asymmetric peaks can be found in the middle of 2Θ values (34.35; 38.23 and 45.81). The increasing intensity of reflections with the rising Mg^{2+} content is noticeable from the diffractiongrams. Moreover, the increasing Mg:Fe molar ratio means a decrease of the specific surface area ($S_{BET(2:1)} = 71.24 \text{ m}^2/\text{g}$; $S_{BET(3:1)} = 50.56 \text{ m}^2/\text{g}$ a $S_{BET(4:1)} = 40.14 \text{ m}^2/\text{g}$).

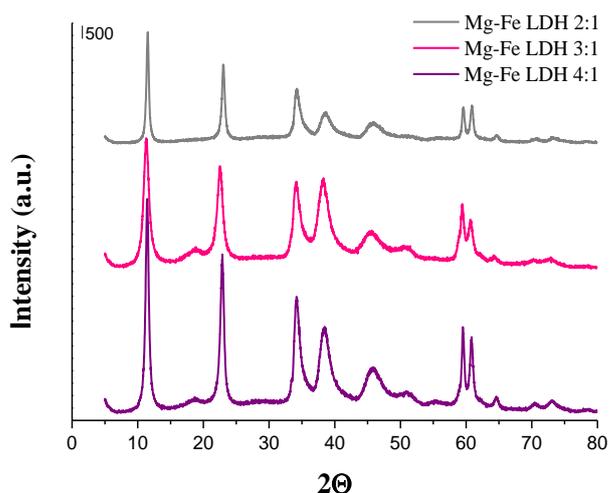


Fig. 1: Diffractograms of Mg-Fe LDHs with different molar ratios

Adsorption kinetics

Experimental values of adsorbed amounts at the equilibrium ($q_{e(exp)}$), calculated values of parameters (q_e , k_1 and k_2) and correlation coefficients (R^2) for both models are given in Table 1. The kinetic data are better fitted by the pseudo-second kinetic order (R^2 in the range 0.97-0.99) than by pseudo-first kinetic order (R^2 in the range 0.95-0.98). Values of $q_{e(exp)}$ approximately correspond to calculated values of q_e . The rate coefficient k_1 shows the highest value for LDH with molar ratio 4:1. In the case of the rate coefficient k_2 , materials with molar ratios 3:1 and 4:1 achieve similar values.

Table 1: Parameters of nonlinear modelling using pseudo-first and pseudo-second kinetic order for Zn^{2+} (pH=5.5)

| | | Mg-Fe LDH 2:1 | Mg-Fe LDH 3:1 | Mg-Fe LDH 4:1 |
|----------------------------|------------------------------|---------------|---------------|---------------|
| | $q_{e(exp)}$ (mg/g) | 3.62 | 3.97 | 5.10 |
| Pseudo-first order | q_e (mg/g) | 3.46 | 4.35 | 5.15 |
| | k_1 (min^{-1}) | 1.17 | 1.30 | 1.66 |
| | R^2 | 0.95 | 0.97 | 0.98 |
| Pseudo-second order | q_e (mg/g) | 3.60 | 4.45 | 5.28 |
| | k_2 [$g/(mg \cdot min)$] | 0.56 | 0.70 | 0.68 |
| | R^2 | 0.98 | 0.97 | 0.99 |

Adsorption isotherms

Adsorption isotherms of Zn^{2+} on Mg-Fe LDH fitted by nonlinear forms of Langmuir and Freundlich model, calculated parameters (q_{MAX} , K_L , K_F , and n) and correlation coefficients (R^2) of both models are given in Fig. 2. The equilibrium adsorption data are better fitted by the Langmuir model (R^2 in the range 0.95-0.98) than by the Freundlich model (R^2 in the range 0.87-0.94). The highest deviation from the Freundlich model is observed in the case of LDH with the molar ratio of 4:1. Better fits by both models can be found in the case of materials with lower value of q_{MAX} (LDH with molar ratios 2:1 and 3:1). The material with the molar ratio 4:1 shows the highest values of q_{MAX} and K_L (47.34 mg/g and 0.37 L/mg). Values of the parameter n are for all materials in the range 1.9-2.8. Moreover, the value of the constant K_F is the highest for LDH with the molar ratio 4:1.

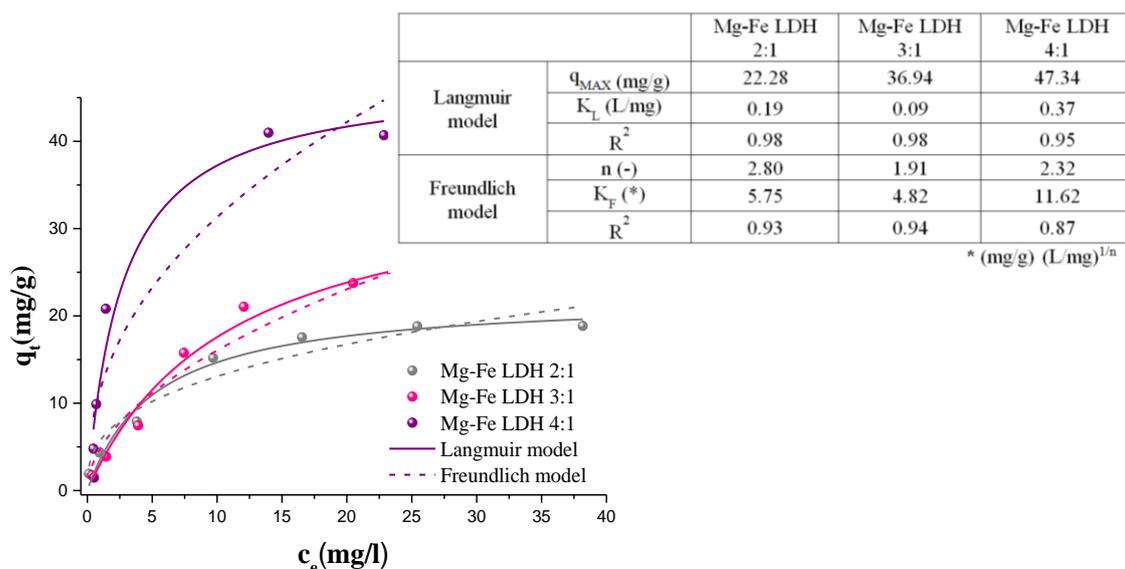


Fig. 2: Sorption of Zn^{2+} on Mg-Fe LDH with different molar ratios and parameters of nonlinear modelling using Langmuir and Freundlich model (pH=5.5)

Analysis of the solid phase after sorption

FTIR-ATR spectra of Mg-Fe LDH before and after sorption are given in Fig. 3. In the case of Mg-Fe LDH with different molar ratios before sorption, characteristic bands corresponding to important binding arrangements are observed in the ranges $3420-3443\text{ cm}^{-1}$, $1636-1637\text{ cm}^{-1}$, $1350-1360\text{ cm}^{-1}$, $660-690\text{ cm}^{-1}$ and $530-570\text{ cm}^{-1}$. The spectrum of Mg-Fe LDH with the molar ratio 4:1 after sorption of Zn^{2+} shows considerable changes of bands around 550 cm^{-1} . Due to different properties of materials before and after sorption, it was necessary to measure the spectra at different number of scans. Therefore, intensities cannot be compared.

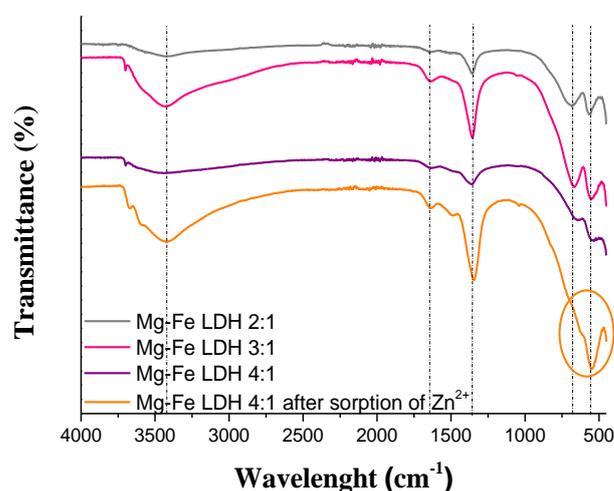


Fig. 3: FTIR-ATR spectra of Mg-Fe LDH with different molar ratios and Mg-Fe LDH 4:1 after sorption of Zn^{2+} (pH=5.5)

Discussion

Diffraction patterns that are depicted in Fig. 1 show characteristic peaks for the structure of LDHs. Reflections on basal planes (low values of 2θ) belong to Miller indexes (003), (006), (110) and (013) and reflections on nonbasal planes belong to Miller indexes (009), (015) and (018) (Kang et al., 2013). Reflections corresponding to Miller indexes (110) and (013) mean a highly crystalline structure of materials (Kurowski et al., 2005). Moreover, the increasing intensity of the reflections with the rising Mg^{2+} content means increasing crystallinity of materials (Kang et al., 2013; Seida, Nakano

2000). On the contrary, the specific surface area decreases with the increasing Mg^{2+} content (Kang et al., 2013).

Adsorption kinetics enables investigating the time necessary to reach the equilibrium and parameters describing the adsorption process (Sun et al., 2015). A validity of the kinetic model is determined by values of correlation coefficients. The values of R^2 (Tab. 1) together with the validity of the equation $q_{e(\text{exp})} \cong q_e$ confirm that measured data are better described by the pseudo-second kinetic order. These results are in accordance to many studies focused on the sorption of metals/metalloids on LDHs and CLDHs (Peng et al., 2014; Sun et al., 2015; Türk et al., 2009). Higher values of the rate constants of data describing adsorption of Zn^{2+} on materials with increasing molar ratios indicate a faster kinetic process (Peng et al., 2014).

Equilibrium adsorption experiments serve to a description of the sorption mechanism, prospectively for quantitative determination of the adsorbed amount (Kang et al., 2013). The appropriate model for the description of experimental data was chosen according to R^2 (Fig. 2). The highest values were observed in the case of the Langmuir model indicating a homogeneous distribution of centres on the surface of Mg-Fe LDH and formation of a monolayer of the adsorbate (Sun et al., 2015). In the case of studies describing the sorption of metals/metalloids on LDHs and CLDHs, higher values of R^2 for the Langmuir model are commonly observed (Peng et al., 2014; Sun et al., 2015; Türk et al., 2009). The material with the molar ratio 4:1 shows the highest value of K_L that corresponds to the highest affinity to the adsorbate (Langmuir, 1918) and the highest value of q_{MAX} is also observed. A significant increase of q_{MAX} after the thermal treatment of LDHs to CLDHs is presumed (Sun et al., 2015). All gained values of n can be found in the range 1 to 10 that means a positive adsorption process (Freundlich, 1906).

FTIR-ATR spectra of synthesized Mg-Fe LDH with different molar ratios (Fig. 3) show the stretching vibration of hydroxyl groups in the brucite-like layers at about $3420\text{-}3443\text{ cm}^{-1}$, the bending vibration of water in the interlayered region at about $1636\text{-}1637\text{ cm}^{-1}$, absorption band of interlayer CO_3^{2-} at $1350\text{-}1360$ and $660\text{-}690\text{ cm}^{-1}$ and the vibration of M-O and/or M-OH at about $530\text{-}570\text{ cm}^{-1}$ (Goh et al., 2008; Kang et al., 2013). Considerable changes of bands around 550 cm^{-1} in the spectrum of the material with adsorbed Zn^{2+} indicate possible formation of new Zn-O interactions.

The first presumption of the (ad)sorption mechanism can be drawn from results of equilibrium adsorption experiments and from the analysis of the solid phase by FTIR-ATR. Considering the low pH value during the sorption process, experiments should not be influenced by precipitation of hydroxides (Lehmann et al., 1999). Furthermore, surface complexation is significantly affected by the value of pH_{ZPC} (pH of zero charge) which reaches a value of about 10 for LDHs (positively charged surface at $\text{pH} < \text{pH}_{ZPC}$) (Liang et al., 2013). Therefore, it is assumed that the main sorption mechanism should be isomorphic substitution (Liang et al., 2013; Sun et al., 2015). However, further analyses of the solid phase (XRD, XPS, SEM/EDX and/or EXAFS) are necessary for a detailed identification of the sorption mechanisms.

Conclusion

The study was focused on the use of synthetically prepared Mg-Fe LDH for the adsorption of Zn^{2+} . Based on our results, the synthesized Mg-Fe LDH shows a promising adsorption capacity for Zn^{2+} . Kinetic data were best fitted by pseudo-second kinetic order and the equilibrium adsorption data by the Langmuir model. The highest adsorbed amount was achieved with Mg-Fe LDH with a molar ratio of 4:1. Future studies will be focused on further analyses of the solid phase in order to obtain a detailed description of the adsorption mechanisms (XRD, XPS, SEM/EDX and/or EXAFS), experiments with thermally treated materials and investigation of the sorption effectivity of chosen materials in soils contaminated by metals and metalloids. Furthermore, our recent research is also dealing with As^{5+} adsorption experiments on synthesized Mg-Fe LDHs.

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