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# Removal of Cu(II), Co(II) and Cd(II) from water solutions by layered-double hydroxides with different [Mg(II)]/[Fe(III)] molar ratios

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**Abstract.**    This work presents a study of sorption of heavy metals (HMs)—Cu(II), Co(II) and Cd(II)—from water media by carbonated and calcined forms of layered-double hydroxides (LDH) with various Mg(II)/Fe(III) molar ratios, which are obtained by precipitation. It is ascertained that the maximum sorption (99.9%) of the HM ions stated is observed with the use of calcined forms of LDH at pH > 2.8 (pH after sorption $\geq$ 8.3). Such an increase in the pH of the aqueous suspension causes sorption of the HM ions by the mechanism of their precipitation in the form of hydroxides or hydroxocarbonates (for Cu(II)). Sufficiently high degrees of sorption of HMs, even at low pH of the aqueous medium, are apparently caused not only by the precipitation of their hydroxide forms, but also due to the complex formation with ferrinol groups of brucite sorbent layers. An increase in the Mg/Fe ratio from 2 to 4 and a corresponding decrease in the positive charge of the layers, which determines the size of the interlayer space in the LDH, have virtually no effect on the degree of extraction of HMs. The presented results suggest that the use of the studied-LDH in practice might be promising.

**Keywords.**    Heavy metals; water treatment; layered-double hydroxide of Mg and Fe; sorption.

## 1. Introduction

Removal of highly toxic heavy metals (HMs) from polluted waters is an important current problem. HMs are highly soluble in water, hence cannot be biologically degraded and can be bioaccumulated and biomagnified, which can lead to carcinogenic and pathogenic effects on living organisms [1,2]. Cu(II), Co(II) and Cd(II) belong to HMs with the highest toxicity. Therefore, their removal from water media is of interest to guarantee ecological safety of the natural environment and to prevent contamination of drinking water sources.

Layered-double hydroxides (LDH) and their calcination products—mixed oxides—are currently being investigated for the removal of anionic and cationic forms of inorganic toxicants because of simplicity of their synthesis [3–15]. LDH are anion-exchange clays that can be represented by the following formula: $[(M^{II})_{1-x}(M^{III})_x(OH)_2]^{x+} \cdot [(A^{n-})_{x/n} \cdot mH_2O]$, where $M^{II}$ and $M^{III}$ denote metal cations in oxidation states +2 and +3, respectively, $A^{n-}$ is an anion (organic or inorganic), $n$ is a valence state of the anion and $x$ is the coefficient that denotes molar fraction $[M^{III}]/[M^{II}]+[M^{III}]$ [14,16]. The excessive positive charge of brucite-like layers of LDH, which is determined by a partial isomorphic substitution of $M^{II}$ by $M^{III}$, is compensated by inclusion of anions in the interlayer regions of LDH. The aimed change in the cation content and cation ratio allows to change the size of the interlayer channel, and, therefore, the sorption capacity of LDH, by an increase in the concentration of the reaction centres in the sorbent matrix.

The use of Zr-modified Mg/Fe–LDH(CO$_3$) is known [15]; re-usable Mg/Fe–LDH(Cl) for water treatment against phosphate ions [17], as well as Mg/Fe–CO$_3$ and their oxide form for isolation of uranium(VI) [18] are also known. It is important that the production of these sorbents uses widely available and cheap reagents, and the synthesis can be easily reproduced by means of co-precipitation of metals that are analogues of natural hydrotalcite.

The aim of this work is to investigate the sorption capacity of carbonated and calcined forms of LDH with different [Mg(II)]/[Fe(III)] molar ratios for the removal of Cu(II), Co(II) and Cd(II) from water media. This research task is due to the fact that the composition of the cations, their ratio in the LDH, as well as the shape of the sorbent can affect the dimensions of the interlayer channel, the sorption capacity of the LDH due to an increase in the concentration of reaction centres in the sorbent matrix, the mechanism of ecotoxicant extraction and, accordingly, the degree of purification of water media.
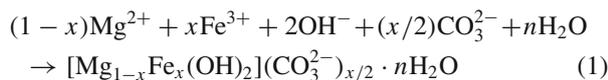
## 2. Experimental

### 2.1 *Materials and methods*

$CuSO_4 \cdot 5H_2O$, $CoSO_4 \cdot 7H_2O$, $CdSO_4$ ('pro-analysis' grade) and deionized water were used for the preparation of the metal containing solutions. NaCl ($1 \, mol \cdot l^{-1}$ solution) was used as a background electrolyte. pH values of water solutions were regulated by addition of $HNO_3$ and NaOH ($0.1 \, mol \cdot l^{-1}$).

### 2.2 *Synthesis of LDH samples*

The experiments were based on the use of Mg/Fe–LDH in their carbonated and calcined (at 400°C) forms and with [Mg(II)]/[Fe(III)] molar ratios in brucite-like layers that were equal to 2:1, 3:1 and 4:1.

LDH in their carbonated form with a 2:1 $[Mg^{II}]/[Fe^{III}]$ molar ratio ($Mg_2Fe$–LDH) and also a 3:1 molar ratio ($Mg_3Fe$–LDH), were obtained by co-precipitation from Mg(II) and Fe(III) nitrates by NaOH in the presence of $Na_2CO_3$ at constant pH, in accordance with the scheme [18]:

$$(1 - x)Mg^{2+} + xFe^{3+} + 2OH^- + (x/2)CO_3^{2-} + nH_2O$$
$$\rightarrow [Mg_{1-x}Fe_x(OH)_2](CO_3^{2-})_{x/2} \cdot nH_2O \qquad (1)$$

At the start of the synthesis procedure, $0.3 \, dm^3$ of distilled water were added in a $1 \, dm^3$ 3-neck round-bottom flask with pockets for electrodes to control pH. After this, NaOH was added until $pH \sim 10$ was reached (stirring was performed by a mechanical mixer), and then, during intensive stirring, two solutions were added in parallel by a peristaltic pump at a speed of $1 \, cm^3 \cdot min^{-1}$. The first solution contained the necessary amount of a mixture of $2 \, mol \cdot l^{-1}$ of $Mg(NO_3)_2$ and $1 \, mol \cdot l^{-1}$ of $Fe(NO_3)_3$, and the second solution contained the necessary amount of $2 \, mol \, dm^{-3}$ solution of NaOH for the production of LDH and the threefold amount, compared to the necessary, of $Na_2CO_3$. During the reaction, pH of the mixture was maintained at $\sim 10 \pm 0.5$ by addition of NaOH and $HNO_3$. After the formation of the precipitate, the flask was closed and placed in an oven for 24 h for aging of the sediment at 80°C. After this, the sediment was transferred on a glass filter #4 and washed with hot-distilled water until a negative reaction for the test of nitrates with the use of diphenylamine. The thermal treatment of the obtained carbonated forms of Mg/Fe–LDH was performed in air in an oven at 400°C for 1 h.

X-ray diffraction (XRD) and infrared spectroscopy (IR) were used for characterization of the structure of the synthesized-LDH samples. The phase composition of the synthesized sorbents was investigated by an X-ray diffractometer DRON-2.0 with filtered Co-Kα emission (30 kV and 10 mA) in an interval of 2–80° ($2\theta$) at the speed of the counter of $1 \, deg \cdot min^{-1}$. IR spectra were obtained with the use of Spectrum BX FT-IR (Perkin-Elmer) ($4000-400 \, cm^{-1}$). The LDH samples were ground with KBr, after which the tablets were made from the obtained powder by pressing ($1700 \, kg \, cm^{-2}$).

### 2.3 *Sorption experiments*

Sorption experiments were carried out under static conditions. Air-dried weighted LDH samples ($0.050 \, g$, $\leq 0.25 \, mm$ fraction) were put in conical flasks ($100 \, cm^3$) with the investigated solutions with $V/m$ ratio equal to $1000 \, cm^3 \cdot g^{-1}$. The suspensions were shaken on a shaker AVU-6S for 2 h at room temperature (20°C). The initial HM concentration in the modelled solutions was $1 \times 10^{-4} \, mol \cdot l^{-1}$. For the investigation of the sorption isotherms, the aqueous solutions ($pH_0$ 4.0) of the stated-inorganic toxicants with concentrations $0.5 \times 10^{-4}$ to $6.0 \times 10^{-4} \, mol \cdot l^{-1}$ were used. After sorption, the liquid phase was separated by centrifugation (5000 RPM) and HM concentrations in supernatants were analysed by the AAS method using a spectrophotometer C-115-M1 at wavelengths λ nm: for Cu(II) — 324.7, for Co(II) — 240.7 and for Cd(II) — 228.8.

The sorption properties were assessed by the amount of sorption $a_s$ ($mmol \cdot g^{-1}$), which was calculated by the following formula [5–7]:

$$a_s = (C_0 - C_p)V/m, \qquad (2)$$

where $C_0$, $C_p$ are ion concentrations of the studied metals in the water solution before and after sorption ($\mu mol \cdot l^{-1}$); $V$ the volume of the water phase (l) and $m$ the mass of the weighted sample of LDH (g).

The pH values of the initial-HM solution ($pH_0$), pH of the solution after sorption ($pH_{eq}$) and $pH_{ZCP}$ (pH of the point of zero charge) were measured by an ionometer I-160 M with a glass electrode 'EVL-1M3.1' (the experiments were carried out at $pH_0$ of the model solutions $\leq 6$ to prevent the formation of metal hydroxides and their precipitation).

## 3. Results and discussion

### 3.1 *XRD analyses of the sorbents*

The diffraction lines, observed on the XRD patterns of the synthesized samples, are shown in table 1. It is seen that all

**Table 1.** The values of the interlayer distances and Miller indexes of the diffraction lines of the synthesized Mg/Fe–LDH.

| hkl | Mg/Fe 2:1 | Mg/Fe 3:1 | Mg/Fe 4:1 |
|-----|-----------|-----------|-----------|
| 003 | 7.76 | 7.82 | 7.94 |
| 006 | 3.862 | 3.891 | 3.957 |
| 012 | 2.639 | 2.636 | 2.246 |
| 015 | 2.364 | 2.341 | 2.379 |
| 018 | 1.997 | 1.989 | 2.024 |
| 116 | 1.556 | 1.556 | 1.559 |
| 113 | 1.552 | 1.523 | 1.528 |
| 116 | 1.440 | 1.442 | 1.445 |
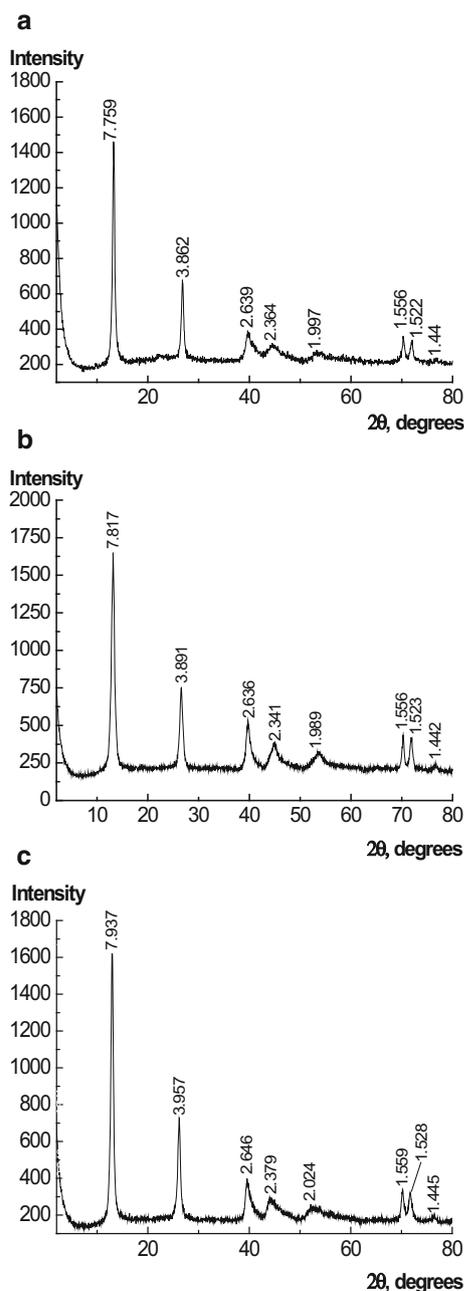
**Figure 1.** XRD patterns of the samples: (**a**) $Mg_2Fe$–LDH; (**b**) $Mg_3Fe$–LDH and (**c**) $Mg_4Fe$–LDH.



**Figure 2.** Effect of the initial pH values of the water solutions on the amounts of sorption of (**a**) Cu(II), (**b**) Co(II) and (**c**) Cd(II) onto the samples: 1 — $Mg_3Fe$–LDH, 2 — $Mg_2Fe$–CLDH, 3 — $Mg_3Fe$–CLDH and 4 — $Mg_4Fe$–CLDH. $V$ — $50\,cm^3$, $m$ — $0.050$ g, $C_0^{Me(II)}$ — $1 \times 10^{-4}$ mol $\cdot$ l$^{-1}$, $I$ — $0.01$, $t_{sorp}$ — $2$ h.

the diffraction lines are related to LDH and can be indexed in the hexagonal cells, which does not contradict the literature data about the crystallization of synthetic Mg/Fe–LDH in the rhombohedral structure [19]. It is seen from the data presented in table 1 and figure 1 that the values of the basal reflections 003 and 006 decrease with an increase of Fe content in Mg/Fe–LDH, which is connected with an increase of electrostatic interactions between the positively charged brucite-like layers and carbonate anions in the interlayer regions. From t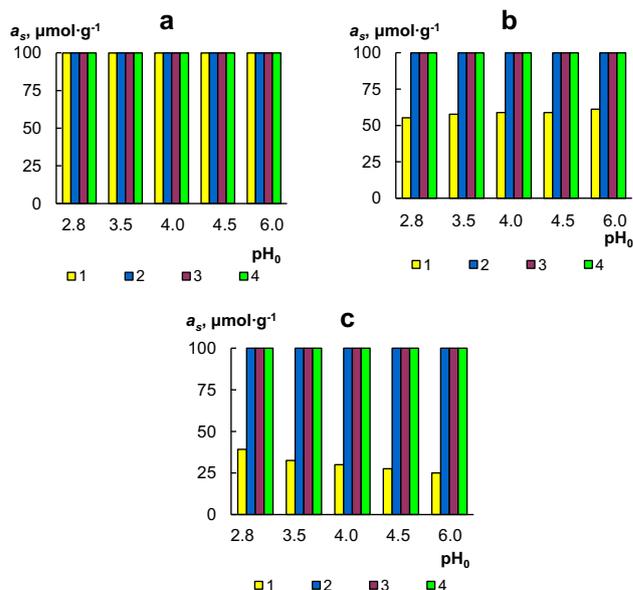he analysis of XRD graphs, a tendency can be seen for the decrease of the parameter $a$ of the hexagonal cells of LDH with an increase of the substitution of magnesium by ferric iron. It should be noted that there is a lack of strict overlap between the measured and calculated interlayer distances for the obtained synthetic products, which may be connected with defects in the structures of the obtained LDH samples.

### 3.2 *Effect of the pH of water solution*

One of the most important parameters that influence the sorption process is the pH value of water solution. Figure 2a–c shows the dependence of the amount of sorption of Cu(II), Co(II) and Cd(II) onto Mg/Fe–LDH on the $[Mg^{II}]/[Fe^{III}]$ molar ratios in the structure of brucite-like layers (2:1, 3:1 and 4:1) of calcined forms of LDH ($Mg_2Fe$–CLDH, $Mg_3Fe$–CLDH and $Mg_4Fe$–CLDH), and also, for comparison, of their carbonated ($Mg_3Fe$–LDH) form on pH of the model water medium.

It is seen that at $pH_0 > 2.8$ there occurs almost complete removal of HM ions by the calcined sorbents, and also by $Mg_3Fe$–LDH for Cu(II). During this process, there can be seen strong shifts of $pH_{eq}$ in the slightly acidic and alkaline pH regions (table 2), which was noted previously in the literature [6]. This is due to the presence of the studied LDH of an alkaline element Mg(II), and also, apparently, to anion-exchange of OH$^-$ ions, which partly compensate positive charge of the brucite-like layers. In accordance with the data [20], and also with data calculated on the basis of the hydrolysis constants [21], the

**Table 2.**  The $pH_{eq}$ values after HM ion sorption on the synthesized Mg/Fe–LDH.

| pH$_0$ | pH$_{eq}$ | | | |
|---|---|---|---|---|
| | Mg$_3$Fe–LDH | Mg$_2$Fe–CLDH | Mg$_3$Fe–CLDH | Mg$_4$Fe–CLDH |
| 2.8 | 8.3 | 9.3 | 9.5 | 9.9 |
| 3.5 | 8.5 | 9.5 | 9.7 | 10.0 |
| 4.0 | 8.6 | 10.0 | 9.9 | 10.1 |
| 4.5 | 8.7 | 10.1 | 10.0 | 10.1 |
| 6.0 | 8.7 | 10.1 | 10.1 | 10.1 |

studied ions Cd(II), Co(II) and Cu(II) in water solutions at $1 \times 10^{-4}$ mol · l$^{-1}$ concentrations in acidic and neutral pH of the solutions are predominantly present in cationic and monomeric hydroxoforms. The initiation of precipitation of the insoluble hydroxides starts at pH $\approx 7.5 - 8$ (the constants of the precipitate formation for Cu(OH)$_2$ – log $K_S = 18.2$, Co(OH)$_2$ – log $K_S = 14.8$ and Cd(OH)$_2$ – log $K_S = 14.61$ [21]).

Apparently, the maximum values of sorption of HM ions onto the calcined forms of LDH are determined by sedimentation of Me(OH)$_2$ in the form of a separate phase on the surface of the LDH material, as well as in the form of a part of the structure of the investigated sorbents due to the substitution mechanism [22].

An increase in the amount of sorbed-Cu(II) ions on the carbonated form of Mg$_3$Fe–LDH at pH$_0 > 2.8$ (pH$_{eq} > 8.3$) occurs as a result of its co-precipitation in the form of hydroxycarbonate (the solubility product of Cu$_2$CO$_3$(OH)$_2$ is $7.8 \times 10^{-34}$). This is confirmed by the light-green colouring of the solid phase of the carbonated form of the sorbent after the sorption of Cu(II), which is characteristic of Cu(II) hydroxycarbonate, as shown for Zn/Al−CO$_3$ forms of LDHs at pH$_0 \geq 7$ [23].

Additionally, the removal of the studied toxicants by Mg$_3$Fe–LDH in the stated pH range occurs, apparently, as a result of their bonding with hydroxyl groups on the surface of the brucite-like layers, and also as a result of possible isomorphic substitutions of Mg(II) by HM ions in the structure of Mg/Fe–LDH, especially those, which have values of ionic radii close to that of magnesium ($r_{Mg(II)} = 78$ pm, $r_{Cu(II)} = 70$ pm, $r_{Co(II)} = 82$ pm and $r_{Cd(II)} = 97$ pm) [24].

### 3.3  Sorption mechanism

For Cu(II), Co(II) and Cd(II) the sorption isotherms were obtained experimentally for carbonated (Mg$_3$Fe–LDH) and calcined (Mg$_3$Fe–CLDH) forms of LDH at pH$_0$ 4 (figure 3). As is seen, the character of the sorption isotherms for the studied sorbents is significantly different. For Mg$_3$Fe–CLDH in a wide range of the initial concentrations ($0.5 \times 10^{-4}$ to $6 \times 10^{-4}$ mol · l$^{-1}$) of Cu(II), Co(II) and Cd(II) there can be seen almost complete removal of HMs by the surface of the sorbent.
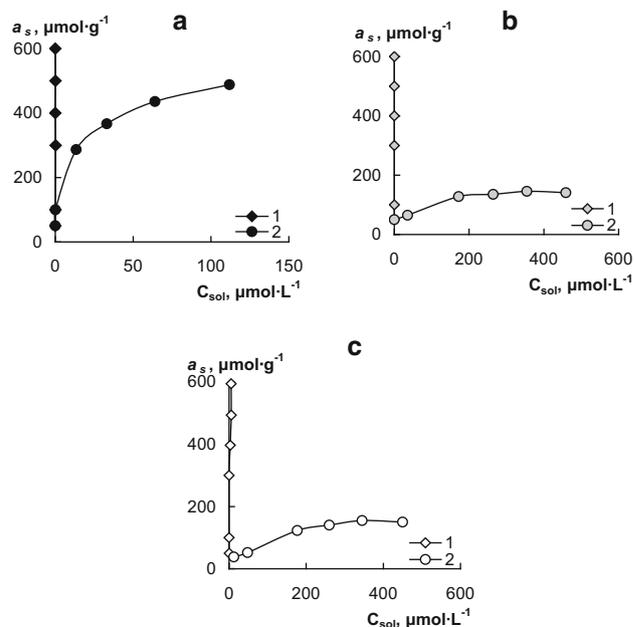


**Figure 3.**  Sorption isotherms of (**a**) Cu(II), (**b**) Co(II) and (**c**) Cd(II) from water solutions by sorbents: 1 — Mg$_3$Fe–CLDH, 2 — Mg$_3$Fe–LDH. pH$_0$ 4, $V$ — 50 cm$^3$, $m$ — 0.050 g, $I$ — 0.01, $t_{sorp}$ — 2 h.

For isotherms of sorption of Cu(II), Co(II) and Cd(II) on Mg$_3$Fe–LDH in the range of low-HM concentrations there is a gradual increase, and with a further increase of HM ion concentrations there occurs saturation of the surface of the studied-sorption material.

Langmuir and Freundlich equations were used for the analysis of the experimental results of HM ion sorption onto the studied sorbents:

$$a_s = \frac{K_L a_\infty C_p}{1 + K_L C_p}, \tag{3}$$

$$a_s = K_F C_p^{1/n}, \tag{4}$$

where $K_L$ is Langmuir constant, $a_\infty$ the theoretically calculated maximum sorption value (μmol · g$^{-1}$), $1/n$ and $K_F$ are Freundlich constants.

**Table 3.** The coefficients of Langmuir and Freundlich equations for the adsorption of Cu(II), Co(II) and Cd(II) on $Mg_3Fe$–LDH.

| Me(II) | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|
| | $K_L$ | $a_\infty$, $\mu$mol $\cdot$ g$^{-1}$ | $R^{2*}$ | $K_F$ | $1/n$ | $R^2$ |
| Cu(II) | 0.196 | 500.0 | 0.986 | 316.22 | 0.871 | 0.950 |
| Co(II) | 0.022 | 158.73 | 0.997 | 50.12 | 0.200 | 0.987 |
| Cd(II) | 0.021 | 163.93 | 0.998 | 81.28 | 0.128 | 0.999 |

*$R$ — correlation coefficient.

**Table 4.** Composition (by macrocomponents) of the sample of surface natural water studied.

| Indicator | Surface water sample |
|---|---|
| pH | 7.15 |
| Mineralization, mg$\cdot$l$^{-1}$ | 2227 |
| Hardness, mEq$\cdot$l$^{-1}$ | 23.6 |
| Alkalinity, mEq$\cdot$l$^{-1}$ | 10.0 |
| $NO_3^-$, mg$\cdot$l$^{-1}$ | 430 |
| $Cl^-$, mg$\cdot$l$^{-1}$ | 153 |
| $SO_4^{2-}$, mg$\cdot$l$^{-1}$ | 182.4 |
| $Na^+$, mg$\cdot$l$^{-1}$ | 49 |

The presented equations describe well the obtained experimental data for the carbonated form $Mg_3Fe$–LDH (table 3). The limit adsorption values for Cu(II), Co(II) and Cd(II) that were calculated by the Langmuir equation for $Mg_3Fe$–LDH are 500, 158.73 and 163.93 $\mu$mol $\cdot$ g$^{-1}$, respectively.

The composition of natural waters from which Cu(II), Co(II) and Cd(II) were extracted with the $Mg_3Fe$–CLDH sample is shown in table 4. To assess the effect of typical macrocomponents of natural waters on the efficiency of extracting HM ions in the sample of water, HM ions were additionally introduced to establish their concentration at $1 \times 10^{-4}$ mol $\cdot$ l$^{-1}$, after that they were kept for 24 h until concentration equilibrium was established.

Figure 4 represents the results of the removal efficiency of Cu(II), Co(II) and Cd(II) from the natural water sample of the above composition with the $Mg_3Fe$–CLDH sorbent at a sorbent dose of 1 g $\cdot$ l$^{-1}$: the recovery rate for Cu(II) is 95%, for Co(II) is 85% and for Cd(II) is 78%. With an increase in the sorbent dose to 6 g $\cdot$ l$^{-1}$, almost complete extraction of the studied HM from natural water ($\sim$95–99%) is achieved.

To ascertain some aspects of the sorption mechanism of Cu(II) ions from water media, IR spectra of the calcined form of Mg/Fe–CLDH were obtained before and after the sorption of Cu(II) ions (figure 5).

For the Mg/Fe–CLDH sample (figure 5, curve 1) the IR spectrum in the 3460–3466 cm$^{-1}$ range reveals intensive and wide-absorption bands of valence oscillations $\nu$(OH) of the brucite-like layers of the sorbent and of water molecules which are present in the interlayer regions or are bonded *via*
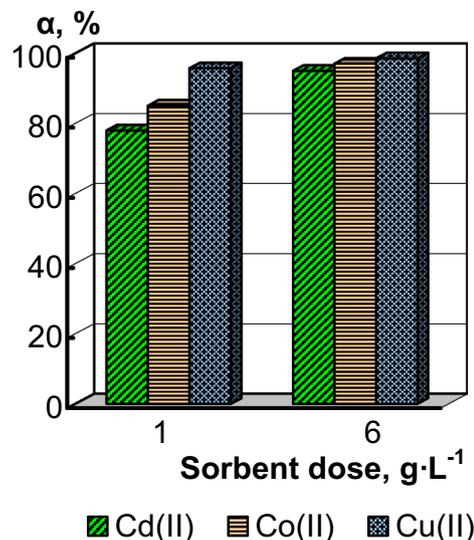


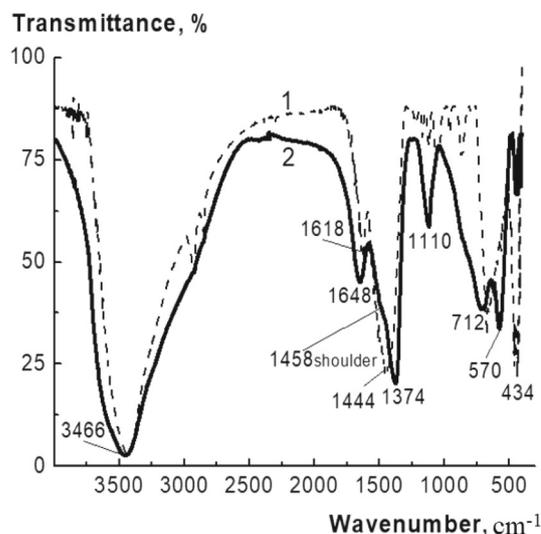**Figure 4.** Effect of the dose of sorbent on the removal of Cu(II), Co(II) and Cd(II) from surface water with $Mg_3Fe$–CLDH.



**Figure 5.** IR spectra of the samples: 1 — $Mg_3Fe$–CLDH and 2 — $Mg_3Fe$–CLDH–Cu(II).

hydrogen bonds with water molecules of the neighbouring layers. Absorption bands in the 1640–1650 cm$^{-1}$ range of

both samples belong to deformational oscillations of water molecules $\delta$(HOH).

There is an absorption band in the $1400\,cm^{-1}$ range of the initial sorbent that belongs to the valence oscillations of $CO_3^{2-}$ ions, not bonded to metal ions, which appear as a result of the contact of the solution with air.

In the IR spectrum of Mg/Fe–CLDH–Cu (figure 5, curve 2) there is partial splitting of the band of valence oscillations $\nu$(CO) at 1374 and $1458\,cm^{-1}$ (shoulder). This splitting shows a decrease in symmetry of $CO_3^{2-}$ ions, which can be a consequence of the formation of small quantities of Cu(II) hydroxycarbonate. An appearance of a band of deformational oscillations $\delta$(CuOH) at $1110\,cm^{-1}$ is a confirmation of the formation of $Cu_2(OH)_2CO_3$. This confirms the stated supposition that sorption of Cu(II) occurs predominantly by bonding with the interlayer $OH^-$ and $CO_3^{2-}$ ions with the formation of basic-copper carbonate.

Absorption bands in the $\sim$400–600 $cm^{-1}$ range can be understood to be valence metal–oxygen oscillations, and in the $\sim$700 $cm^{-1}$ range—deformational oscillations of $CO_3^{2-}$ ions [25,26].

## 4.  Conclusions

Thus, this work shows a possibility of the use of carbonated and calcined forms of Mg/Fe–LDH with various $[Mg^{II}]/[Fe^{III}]$ molar ratios for highly effective removal of Cu(II) from water media. For Cd(II) and Co(II) the calcined forms of LDH are more promising sorbents for the treatment of water media as compared to the carbonated forms. The ratio of Mg/Fe in the synthesized LDHs had practically no effect on the magnitude of the sorption of all the studied HMs, which further confirms their extraction from aqueous media by the mechanism of precipitation of their hydroxides (for copper—also hydroxocarbonates). A considerable advantage of the sorbents presented is their ecological safety, cheap price and the ease of synthesis.

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