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A study on the intercalation of heavy metal ions in a wastewater by synthetic layered inorganic adsorbents

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ABSTRACT

This study examined the intercalation mechanism of Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Fe^{3+} ions into synthetic layered inorganic adsorbents—hydrotalcite and gyrolite under different conditions. It was observed that the process parameters above depend on the chemical nature of both solutions and adsorbents. An extremely high and selective uptake of Fe^{3+} ions was observed in both cases (~98–99%). The selectivity sequence of studied metal ions by gyrolite can be written as follows: $Co^{2+} > Zn^{2+}/Mn^{2+}/Ni^{2+} > Fe^{3+}$, while with calcined hydrotalcite: $Co^{2+}/Ni^{2+}/Mn^{2+} > Zn^{2+} > Fe^{3+}$. It was determined that, during simultaneous adsorption, the intercalation of heavy metal ions into the structure of gyrolite or calcined hydrotalcite proceeds differently, because the amount of adsorbed Me^{x+} ions is higher than the amount of leached Ca^{2+} and Mg^{2+} ions, resulting in the occurrence of two types of chemical reactions – substitution and addition. It should be noted that almost all heavy metal ions (~99.84%) are chemisorbed by both adsorbents. Moreover, after chemisorption, no other compounds were observed in X-ray powder diffraction patterns of both adsorbents. It was observed that hydrothermally treated and calcined hydrotalcite reconstructs its structure during the chemisorption process, while the structure of gyrolite remains stable.

Keywords: Waste management technologies; Hydrotalcite; Gyrolite; Synthetic layered inorganic adsorbents

1. Introduction

To remain compliant with increasingly stringent environmental legislation, it is recommended that manufacturing processes be updated to include the use of advanced recuperative waste removal technologies, to reduce the amounts of contaminants [1].

Heavy metals released into the environment poses a significant threat to the aquatic environment and human health [2–4]. Pb, Cd, Fe, Mn, Cu, Zn, Cr and Ni are common metals that are known to accumulate in living organisms, causing numerous diseases and disorders, and often found in surface water, groundwater and soil. Removal of heavy metals from wastewater is of crucial importance due to their high toxicity, solubility in the presence of water, non-biodegradable and persistent nature [5,6]. It should be noted that it is necessary to treat metal-contaminated effluents prior to their discharge to the environment.

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For this reason, various techniques have been employed for removing dissolved heavy metals, including chemical precipitation, ion exchange and electrochemical removal [5–7]. However, these methods have several known disadvantages: incomplete removal, high-energy requirements and production of toxic sludge [5–7].

Currently, numerous approaches have been investigated for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent [5,8–10]. Among them, the adsorption technique is considered to be the most appealing process because of its simplicity, convenience and high removal efficiency [10–15]. The search for low-cost adsorbents, with metal-binding capacities, has been a focus. The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products, agricultural wastes or polymeric materials [10,12,16,17]. However, the design and exploration of novel adsorbents are still necessary to improve their adsorption capacity and enhance the separation rate.

Over three decades ago, by seeking to resolve various environmental problems, including removal of toxic heavy metal ions, calcium silicate hydrates had been proposed as adsorbents [18–21]. Due to their variety in chemical composition and crystalline lattice structure, which influence the calcium silicate hydrates adsorption capacity, a new family of inorganic cation exchangers was created [18]. However, it was published that most of natural and synthetic calcium silicate hydrates have a low ion exchange capacity, presumably, defined by the fact that Ca^{2+} ions in these compounds are intercalated between separate layers, and chemical bonds are formed by connection with oxygen atoms [22]. The guest ions may be incorporated into their crystal lattice structure only if these bonds are broken.

In previous works [23,24], the adsorption capacity of gyrolite, calcium silicate hydrates family compound, was investigated. It was determined that this compound shows very good cation exchange properties, because almost all of the Cu^{2+} ions (99.5% removal efficiency) were intercalated depending on the initial concentration of copper ions in the $Cu(NO_3)_2$ solution in alkaline medium [23]. However, the experimental data of Kasperaviciute's work showed that, in acidic medium, gyrolite acts as chemosorbent, which can adsorb only 41.48% of Cu^{2+} ions [24]. It should be noted that ion exchange capacity of gyrolite substituted with Na^+ ions is greater (92.30 mg Cu^{2+}/g) than $\sum X$ of tobermorite substituted with Al and Na ions (53.22 mg Cu^{2+}/g) [25].

By comparing with other calcium silicate hydrates, gyrolite, due to its larger interlayer thickness of about 2.2 nm, can adsorb more new guests. It should be noted that pure as well as substituted with metal ions gyrolite can be synthesised in the laboratory to form mixtures with the molar ratio calcium oxide/silicon dioxide $(CaO/SiO_2) = 0.66$ in aqueous suspension at temperatures of about 150–200°C [26–28]. Thus, it is necessary to explore the sorption and textural properties of gyrolite because of its crucial importance in a search of low-cost adsorbents.

In response to environmental remediation, another group of compounds, layered double hydroxides (LDHs), have received significant attention. These materials have a well-defined layered structure with nanometer (0.3–3 nm) interlayer distances and contain important functional groups, where relatively weak bonding occurs between the interlayer ions or molecules and the host sheets; they are widely used as adsorbents for liquid ions [29–31]. Hydrotalcite, a hydroxycarbonate of magnesium and aluminium, can be considered a prototype of this materials class. It consists of stacks of brucite-like layers in which Mg^{2+} cations are replaced in part by Al^{3+} cations, thus generating sheets having a net positive charge that is compensated in interlamellar anions, which commonly are carbonates [29–31]. The key features of this material are the ability to exchange charge-compensating interlayer ions with a variety of organic and inorganic guests and so-called "memory effect" property [32,33].

Manju and Anirudhan performed the adsorption of As(III) from aqueous solutions using hydrotalcite, and evaluated the effect of contact time, agitation rate, As (III) concentration, pH and equilibrium temperature on its removal efficiency. They determined that maximum removal was equal to 78.2% at a pH of 8.5, and maximum desorption – 85.2% [34]. Lazaridis et al. [35] studied adsorption of chromates from water by calcined and uncalcined hydrotalcites, and almost complete removals were obtained from batchwork dispersed-air flotation in the presence of a flocculant. The removal of Cr(VI) by Mg–Al, Ni–Al and Zn–Cr synthetic LDHs was also investigated by Goswamee [36]. Their results showed that ion exchange with uncalcined LDH is slower in rate, smaller in amount and more pH dependent than in calcined ones. Other researchers [37,38] also investigated calcined hydrotalcites, which showed better adsorption capacity for F^- and Br^- anions than uncalcined samples. Parks et al. explored the ion exchange capacity of hydrotalcite for Cu^{2+} and Pb^{2+} cations from aqueous solutions and found that surface adsorption proceeds, leading the precipitation of Cu^{2+} and Pb^{2+} complex compounds [39].

While much preliminary work has been done to demonstrate hydrotalcite ability to remove some ions from contaminated waters, a thorough investigation on its textural and adsorption properties is still needed.

The aim of this study was to evaluate the intercalation mechanism of heavy metal ions into the structure of synthetic adsorbents, and determine the selectivity sequences for mentioned ions in acidic and alkaline solutions.

2. Materials and methods

2.1. Synthesis of layered inorganic adsorbents

The synthesis of layered inorganic adsorbents was based on the hydrothermal method. Fine-grained $SiO_2{\cdot}nH_2O$ (Reaktiv, Russia; ignition losses, 7.84%; specific surface area $S_a = 1{,}804$ m/kg by Blaine) and calcium oxide (CaO was burned at 950°C for 0.5 h; $S_a = 1{,}234\ m^2/kg$; purity, 98.83%) were used as starting materials for pure gyrolite crystallization, when isothermal curing duration at 200°C was equal to 48 h ($CaO/SiO_2 = 0.66$). For hydrotalcite synthesis (200°C, 4 h, Mg/Al = 2:1), the following reagents were used: γ-Al_2O_3 (γ-Al_2O_3 was produced by burning aluminium hydroxide (Reachim, Russia) at 475°C for 5 h) and basic magnesium carbonate (Reachim, Russia; the purity is 99%).

The resulting products were filtered off, dried at 50 ± 5°C, and put through a sieve with an 80 μm mesh. According to [37–39] references, synthetic hydrotalcite was pre-heated at 475°C for 4 h to obtain nano-sized compounds, which allows to gain better sorption properties.

In order to determine the stability of adsorbents, the leaching tests were performed in the thermostatic absorber Grant SUB14 at 25°C temperature for 60 min. One gram of gyrolite or calcined hydrotalcite was added to 100 ml of distilled water in a 250 ml conical flask. All tests were carried out in triplicates. After separation, the aqueous medium/water was analysed for Ca^{2+} and Mg^{2+} ions using a Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer. It was determined that, after 60 min, the amount of Ca^{2+} ions leached from gyrolite to aqueous medium was below the detection limit (0.0155 mmol/g). Meanwhile, the quantity of released Mg^{2+} ions from calcined hydrotalcite was equal to 0.29 mmol/g.

2.2. Adsorption experiments

Adsorption experiments were carried out at 25°C in the thermostatic absorber Grant SUB14 with different time periods (0.5, 1, 2, 3, 5, 10, 15 and 60 min). A series of suspensions in conical flasks was prepared, each containing 1 g of gyrolite or calcined hydrotalcite and 100 ml of 0.25 g Me/dm^3 aqueous solutions (where Me is Ni^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Zn^{2+} ions, respectively). The percentage of adsorbed ions was determined using the variations of cations concentration, both in the solution and in gyrolite or hydrotalcite. The saturated adsorbents were rinsed with distilled water, dried at 50 ± 5°C, and dissolved in HCl (1:1). The concentration of Ni^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Zn^{2+} ions in aqueous solution were determined using a Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer. All tests were repeated three times. The same methodology was applied for the simultaneous adsorption with a mixture of Ni^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Zn^{2+} ions solutions, which concentration was equal to 0.25 g Me/dm^3.

In order to determine kinetic parameters of adsorption reactions, kinetic models have been developed and fitted for the adsorption process of the heavy metal ions into calcined hydrotalcite and gyrolite. The Largergren model [30] assumes *first-order adsorption kinetics*, and can be represented by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

where q_e and q_t are the amounts of adsorbed ions at equilibrium and at time t_e, respectively ($mg\,g^{-1}$), and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}).

After integration and applying boundary conditions $t = 0$ to $t = t_e$ and $q_t = 0$ to $q_t = q_e$, the integrated form becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{2}$$

The pseudo-second-order adsorption kinetic rate equation [31–33] is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where k_2 is the rate constant of the pseudo-second-order adsorption ($g\,mg^{-1}\,min^{-1}$).

For the boundary conditions $t = 0$ to $t = t_e$ and $q_t = 0$ to $q_t = q_e$, the integrated form of the equation becomes (the integrated rate law for the pseudo-second-order reaction):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \tag{4}$$

2.3. Analytical techniques

The analysis of the surface area of synthetic gyrolite was performed by a BET surface area analyser "KELVIN 1042 Sorptometer" (Costech Instruments). The specific surface areas of calcined hydrotalcite and gyrolite were calculated by the BET equation using the data of the lower part of N_2 adsorption isotherm ($0.05 < p/p_0 < 0.35$):

$$\frac{1}{X\left(\frac{p_0}{p}-1\right)} = \frac{C-1}{X_m \cdot C} \cdot \frac{p}{p_0} + \frac{1}{X_m \cdot C} \tag{5}$$

where X is the mass of adsorbate, adsorbed on the sample at relative pressure p/p_0 (p: the partial pressure of adsorbate, p_0: the saturated vapour pressure of adsorbate); X_m is the mass of adsorbate adsorbed at a coverage of one monolayer; and C is a constant which is a function of the heat of the adsorbate condensation and heat of adsorption (C_{BET}).

The X-ray powder diffraction (XRD) data were collected with a DRON-6 X-ray diffractometer with Bragg–Brentano geometry using Cu Kα radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2°–60° (2θ) in steps of $2\theta = 0.02°$.

The specific surface area of the raw materials was determined by the Blaine's method with air permeability apparatus (Model 7201, Toni Technik Baustoffprufsysteme GmbH).

3. Results and discussion

It was observed that the amount of adsorbed heavy metal ions by calcined hydrotalcite and gyrolite depends on the chemical nature of adsorbents and solutions used.

As expected, the adsorption of Co^{2+} ions proceeded slower at the beginning of the process. After 30 s, the amount of adsorbed ions by gyrolite was equal to 3 mg Co^{2+}/g when the initial concentration was 0.25 g/dm^3 (Fig. 1, curve 1).

It was determined that the adsorption rate slightly increased, when the experiment was prolonged to 15 min; this is due to exchange in the quantity of incorporated Co^{2+} ions (14.66 mg Co^{2+}/g). After 15 min, the equilibrium is attained and the removal of mentioned ions is complete (Fig. 1, curve 2).

It should be noted that the uptake of Co^{2+} ions is different when using calcined hydrotalcite. In this case, after 30 s of reaction, 10.47 mg Co^{2+}/g is intercalated into its crystal structure. In comparison with gyrolite, the amount of adsorbed Co^{2+} ions by calcined hydrotalcite was higher, and, after 60 min, was equal to 20.09 mg Co^{2+}/g.

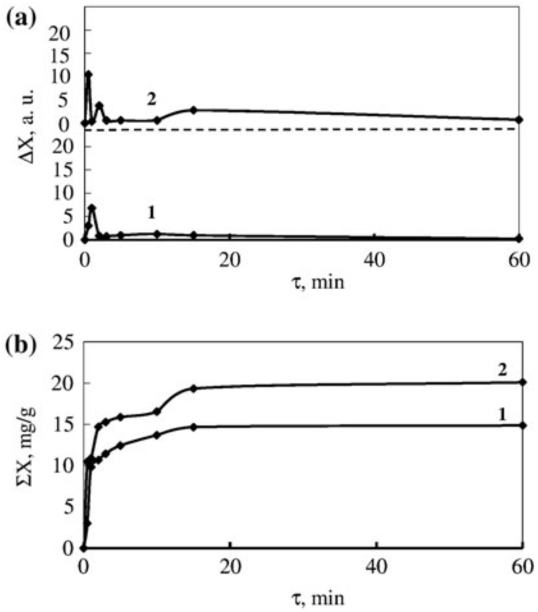

Fig. 1. Co^{2+} adsorption from $Co(NO_3)_2 \cdot 6H_2O$ solution, when Co^{2+} initial concentration is equal to 0.25 g·Co^{2+}/dm^3, differential (a) and integral (b) kinetic curve; adsorbents: 1—gyrolite; 2—calcined hydrotalcite.

The obtained experimental data confirmed that the type of heavy metal ion, as well as the nature of synthetic layered inorganic adsorbents, influences the uptake of Zn^{2+} ions.

It was found that, within 30 s of adsorption experiment, the removal efficiency of both adsorbents reaches 50%, i. e. approximately from 12 to 13 mg Zn^{2+}/g (Fig. 2, curve 1). Moreover, the reaction equilibrium is achieved at different period of time: after five minutes, when gyrolite was used, and after 2–3 min—with calcined hydrotalcite (Fig. 2, curve 2). However, at the end of the process, a considerable amount of Zn^{2+} ions (21.75 mg Zn^{2+}/g) was incorporated into the structure of gyrolite, while calcined hydrotalcite adsorbed a smaller quantity (16.63 mg Zn^{2+}/g).

It was observed that the kinetics of Mn^{2+} ions uptake is more rapid than with zinc ions.

In this case, after 30 s of reaction, the removal efficiency of both adsorbents reaches 70%, i. e. approximately from 17 to 18 mg Mn^{2+}/g (Fig. 3, curve 1). Furthermore, the elimination of ions from manganese nitrate solution by gyrolite (20.73 mg Mn^{2+}/g) is completed after 5 min because of the reached equilibrium, while calcined hydrotalcite shows slightly higher

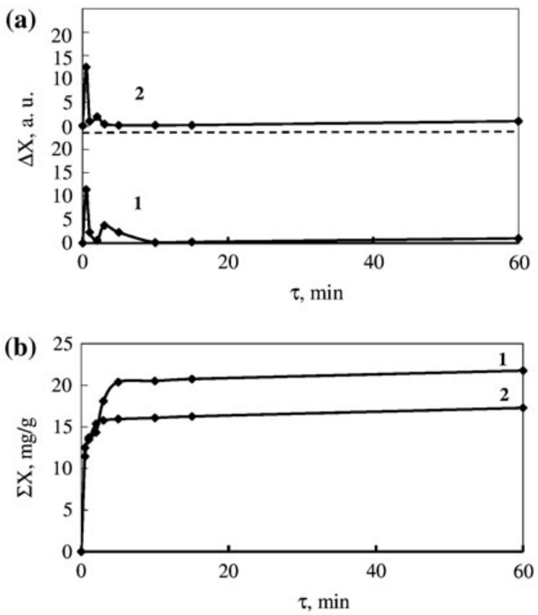

Fig. 2. Zn^{2+} adsorption from $Zn(NO_3)_2{\cdot}6H_2O$ solution, when Zn^{2+} initial concentration is equal to $0.25\,g\,Zn^{2+}/dm^3$, differential (a) and integral (b) kinetic curves; adsorbents: 1—gyrolite; 2—calcined hydrotalcite.

adsorption rate. However, the maximum amount of intercalated manganese ions (23.66 mg Mn^{2+}/g) is obtained only after 15 min (Fig. 3, curve 2).

The adsorption dependency on the chemical nature of adsorbents and heavy metal solutions is confirmed by experimental data of Ni^{2+} removal from aqueous solution (Fig. 4). As shown in curve 1, during the first minute, the uptake of mentioned ions is very slow due to a small quantity of adsorbed ions, i.e. only ~10 mg Ni^{2+}/g is taken by both synthetic layered inorganic adsorbents. The process equilibrium using calcined hydrotalcite is attained only after 15 min, while in comparison with gyrolite, it reached two times faster (after 5 min; Fig. 4, curve 2). However, the calcined hydrotalcite adsorbed a larger amount of Ni^{2+} ions (24.39 mg Ni^{2+}/g) in comparison with gyrolite (18.96 mg Ni^{2+}/g).

It should be noted that the intrusion of metal ions into adsorbent structures depends also on the pH of solution, due to the extremely high and selective uptake of Fe^{3+} ions. It was determined that the elimination of mentioned ions is completed within 30 s because all iron ions (~98–99%) are adsorbed (Fig. 5).

It was observed that the adsorption of Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Fe^{3+} from aqueous solutions by synthetic layered inorganic adsorbents is a complex process. It was determined that, during ion exchange process, $Ca^{2+} \leftrightarrow Me^{x+}$ and $Mg^{2+} \leftrightarrow Me^{x+}$ reactions, typical to gyrolite and calcined hydrotalcite, were found to be non-stoichiometric (Table 1). The uptake of Me^{x+} ions by the solids was lower than the amount

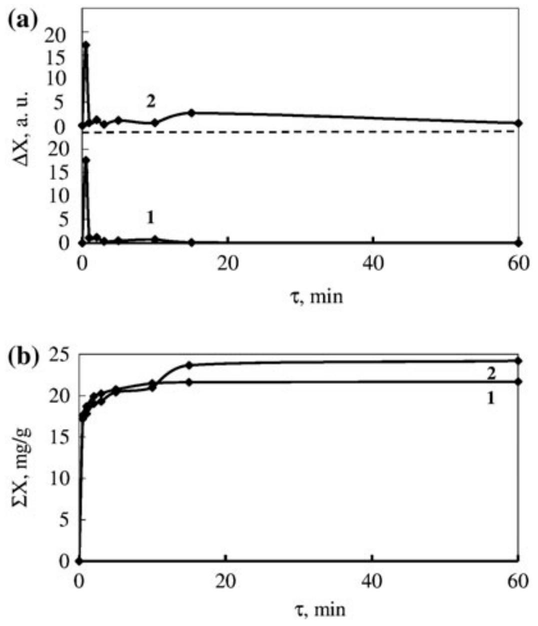

Fig. 3. Mn^{2+} adsorption from $Mn(NO_3)_2{\cdot}4H_2O$ solution, when Mn^{2+} initial concentration is equal to $0.25\,g\,Mn^{2+}/dm^3$, differential (a) and integral (b) kinetic curves; adsorbents: 1—gyrolite; 2—calcined hydrotalcite.

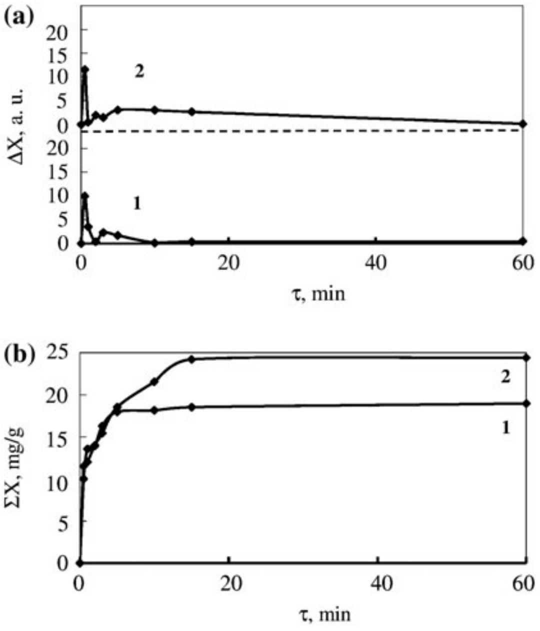

Fig. 4. Ni^{2+} adsorption from $Ni(NO_3)_2{\cdot}6H_2O$ solution, when Ni^{2+} initial concentration is equal to $0.25\,g{\cdot}Ni^{2+}/dm^3$, differential (a) and integral (b) kinetic curves; adsorbents: 1—gyrolite; 2—calcined hydrotalcite.

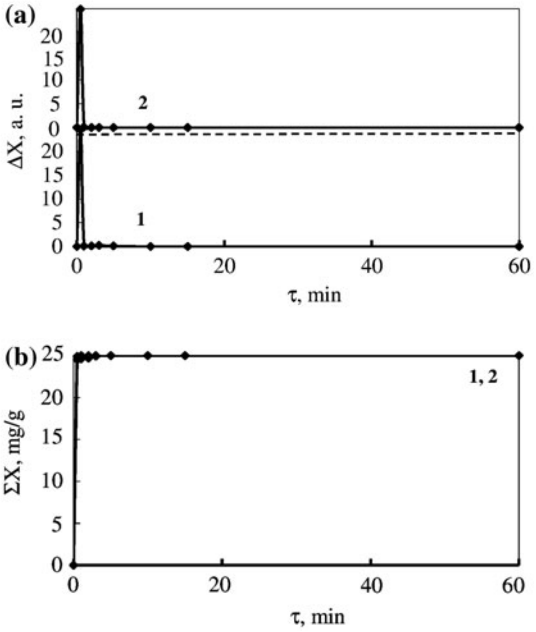

Fig. 5. Fe^{3+} adsorption from $Fe(NO_3)_3 \cdot 6H_2O$ solution, when Fe^{3+} initial concentration is equal to 0.25 g.Fe^{3+}/dm^3, differential (a) and integral (b) kinetic curves; adsorbents: 1—gyrolite; 2—calcined hydrotalcite.

of Ca^{2+} or Mg^{2+} ions leached. In the case of Co^{2+} ions, after 60 min, the amount of adsorbed Co^{2+} was equal to 0.31 mmol/g, while the amount of leached Ca^{2+} ions—0.51 mmol/g. The non-stoichiometry arouse due to the leaching of Ca^{2+} ions from interlayers of gyrolite crystal lattice. The same trend was observed with calcined hydrotalcite. The observations of three times higher quantity of leached Mg^{2+} ions (e. g. with cobalt nitrate; $\sum X = 0.34$ mmol Co^{2+}/g $\sum X = 0.90$ mmol Mg^{2+}/g) can be explained by this compound's ability to reconstruct its structure. During this process, due to the initial pH value of heavy metal ion solutions, the crystallinity of hydrotalcite is changed: in acidic and neutral medium, the intensity of main diffraction maximum varies from 1,130 to 1,734 a.u., respectively. Meanwhile, the intensity of diffraction peak typical to as-synthesized HT is equal to 9,590 a.u. For this reason, an extra amount of Mg^{2+} ions are leached to the reaction medium, suggesting that not all of them are participating in reconstruction process.

Thus, the selectivity sequence of adsorption (according to the duration of mentioned process: from slower to faster intercalation of investigated ions into adsorbent structure) can be represented as:

$$Co^{2+} > Zn^{2+}/Mn^2 + /Ni^{2+} > Fe^{3+}$$

and in the case of calcined hydrotalcite:

$$Co^{2+}/Ni^{2+}/Mn^{2+} > Zn^{2+} > Fe^{3+}$$

In order to evaluate multiple adsorbates, which are commonly found in wastewaters, the experiments of simultaneous adsorption were performed in a mixture of Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Fe^{3+} ion solutions (0.25 g Me/dm^3). The obtained results showed that, for all examined metal ions, the removal efficiency of calcined hydrotalcite is equal to 99.76%, while gyrolite reaches only 96.03% of elimination yield (Fig. 6).

Table 1
The amount of adsorbed and leached metal ions

		Layered inorganic adsorbents			
		Calcined hydrotalcite		Gyrolite	
Composition of adsorption medium	Me^{x+} ions	The amount of adsorbed Me^{x+}, mmol/g	The amount of leached Mg^{2+}, mmol/g	The amount of adsorbed Me^{x+}, mmol/g	The amount of leached Ca^{2+}, mmol/g
Single adsorbates	Fe^{3+}	0.45	1.4	0.45	0.68
	Co^{2+}	0.34	0.9	0.31	0.51
	Ni^{2+}	0.41	1.2	0.35	0.44
	Zn^{2+}	0.26	0.5	0.33	0.55
	Mn^{2+}	0.44	1.0	0.39	0.55
Multiple adsorbates	Fe^{3+}	0.44	1.04	0.45	0.45
	Co^{2+}	0.42		0.37	
	Ni^{2+}	0.42		0.36	
	Zn^{2+}	0.38		0.38	
	Mn^{2+}	0.45		0.42	

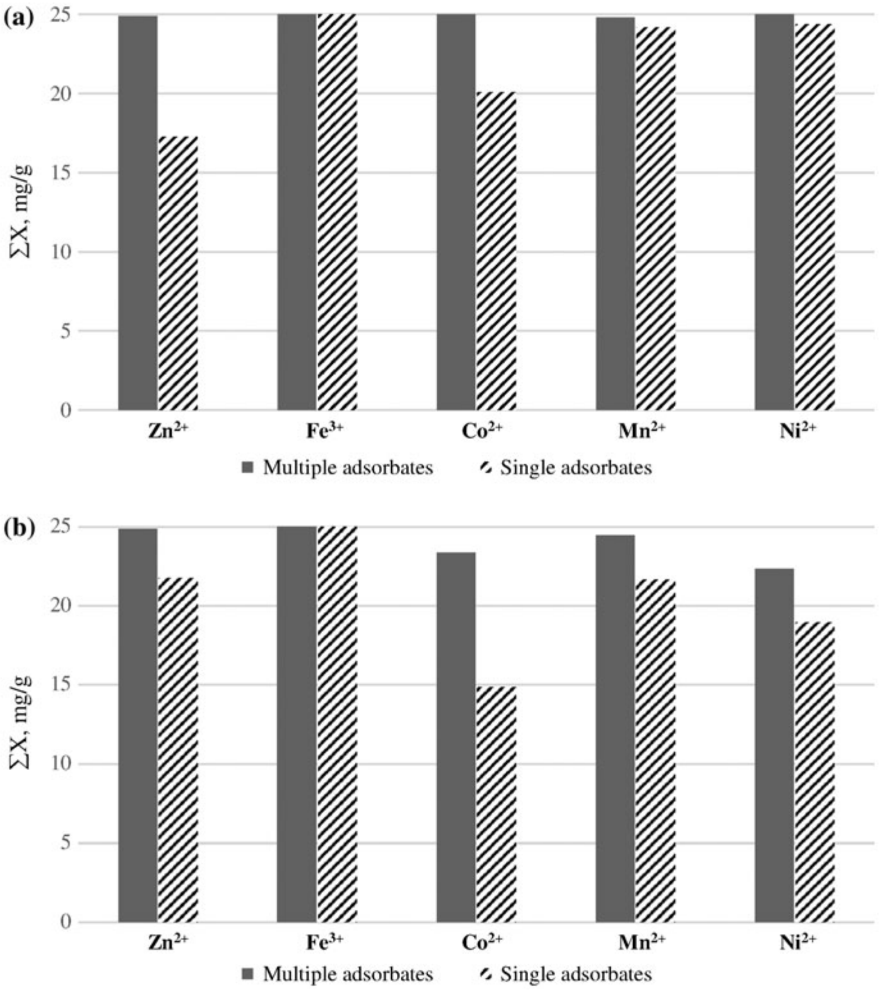

Fig. 6. The diagrams of total amount of adsorbed ions by calcined hydrotalcite (a) and gyrolite (b) after 60 min of experiment at 25℃.

It was estimated that, during simultaneous adsorption, the ion exchange reactions proceed differently than during single ions adsorption; the amount of adsorbed Me^{x+} ions is higher than the amount of leached Ca^{2+} and Mg^{2+} ions (Table 1). The intercalation of heavy metal ions into the structure of gyrolite or calcined hydrotalcite proceeds by two types of chemical reactions: substitution and addition. The ion exchange occurs between divalent or trivalent ions, because Ca^{2+} or Mg^{2+} ions are replaced by 0.45 mmol Me^{x+}/g or 1.04 mmol Me^{x+}/g, and the remaining part of these ions are combined by gyrolite (1.53 mmol

Table 2
The amount of heavy metal ions leached to aqueous solution

		The amount of heavy metal ions leached to aqueous solution, mmol/g				
Composition of adsorption medium	Layered inorganic adsorbents	Ni^{2+}	Co^{2+}	Mn^{2+}	Zn^{2+}	Fe^{3+}
Single adsorbates	Calcined hydrotalcite	0.00008	0.00007	0.00011	0.00020	0.00008
	Gyrolite	0.00237	0.00077	0.00016	0.00058	0.00221
Multiple adsorbates	Calcined hydrotalcite	0	0	0.00005	0.00008	0
	Gyrolite	0.00003	0.00007	0.00003	0.00028	0.00078

Table 3
The kinetic parameters of the pseudo-second-order kinetic models for adsorbents in multiple adsorbates

Adsorbent	Me^{x+} ions	R^2	$q_{e(\text{exp.})}$, mg g^{-1}	$q_{e(\text{cal.})}$, mg g^{-1}	k_2, g mg^{-1} min^{-1}
Calcinated hydrotalcite	Fe^{3+}	1	25.00	25.00	3.20
	Co^{2+}	1	25.00	24.63	1.10
	Ni^{2+}	0.9996	25.00	24.86	0.24
	Zn^{2+}	0.9999	24.89	24.88	0.77
	Mn^{2+}	1	24.80	24.81	1.35
Gyrolite	Fe^{3+}	1	23.54	23.47	1.65
	Co^{2+}	0.9999	24.51	24.39	0.45
	Ni^{2+}	1	23.71	23.70	1.37
	Zn^{2+}	1	24.73	24.69	1.26
	Mn^{2+}	1	24.95	25	1.00

Me^{x+}/g) or calcined hydrotalcite (1.07 mmol Me^{x+}/g) according to addition reaction.

Thus, it should be noted that the adsorption of heavy metal ions in the mixture of their solution differs slightly from single adsorbates. In the case of gyrolite, the selectivity sequence, according to the duration of adsorption, can be proposed as follows:

$$Co^{2+}/Mn^{2+}/Ni^{2+} > Zn^{2+}/ > Fe^{3+}$$

meanwhile, with calcined hydrotalcite:

$$Zn^{2+}/Ni^{2+}/Mn^{2+} > Co^{2+} > Fe^{3+}$$

It should be noted that the adsorption reactions are not reversible processes. To confirm this fact, after the latter process, synthetic layered inorganic adsorbents with substituted heavy metal ions were dried up and immersed in distilled water, it was proved that mentioned metal ions did not appear in the solution after 60 min at 25˚C (Table 2). Thus, the data given in Table 2 shows that almost all heavy metal ions (~99.84%) are chemisorbed by calcined hydrotalcite and gyrolite.

In order to determine adsorption kinetic parameters, the reactions mentioned previously were described by pseudo-first-order and pseudo-second-order equation.

It was determined that pseudo-first-order A. Largergren Eq. (2) did not describe the simultaneous adsorption mechanism for both synthetic layered adsorbents, because the calculated $q_{e(\text{cal})}$ values disagreed with the experimental $q_{e(\text{exp})}$ values, as well as the values of correlation coefficients (R^2) are quite low (varied in 0.3–0.8 range).

R^2: correlation coefficient; $q_{e(\text{exp})}$: the amount of adsorbed ions, mg g^{-1}, calculated from experimental data (Table 1, Fig. 6); $q_{e(\text{cal})}$: the amount of adsorbed

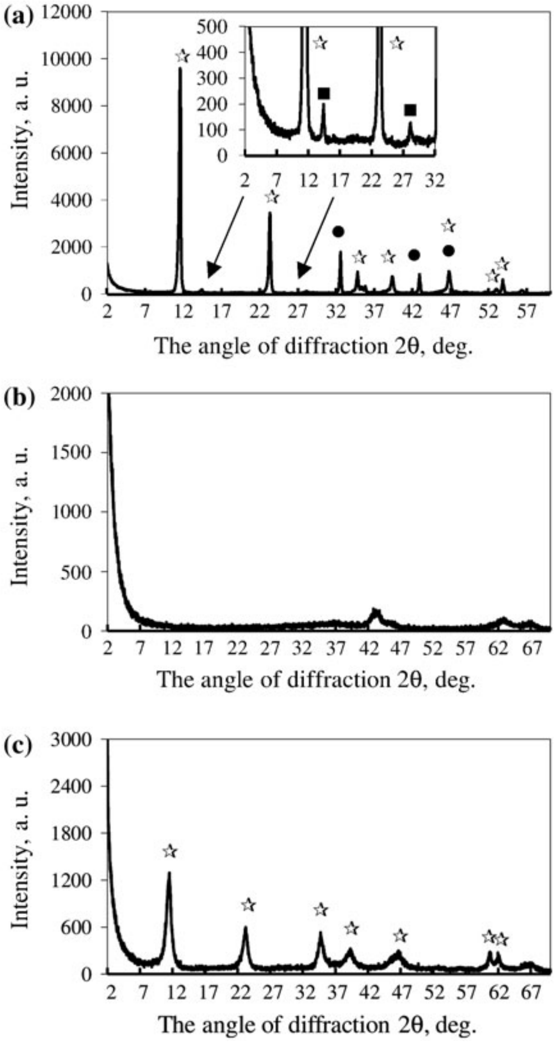

Fig. 7. X-ray diffraction patterns of hydrotalcite samples: (a) after hydrothermal synthesis (200˚C, 4 h); (b) after calcination (475˚C, 4 h); and (c) after chemisorption of a mixture of heavy metal ions (25˚C, 60 min). Indexes: ☆—hydrotalcite, ●—magnesium carbonate; ■—boehmite.

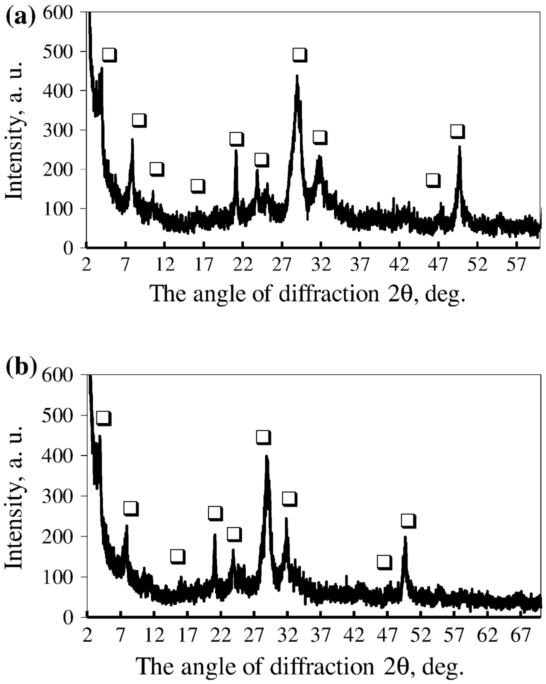

Fig. 8. X-ray diffraction patterns of gyrolite samples: (a) after hydrothermal synthesis (200°C, 48 h); (b) after chemisorption of a mixture of heavy metal ions (25°C, 60 min). Indexes: ❑—gyrolite.

ions, mg g^{-1}, calculated by using Eqs. (3) and (4) of kinetic models.

It was observed that simultaneous adsorption process follows the pseudo-second-order Ho equation. The correlation coefficients (R^2) of this model were greater than 0.99, which indicate that pseudo-second-order equation adequately describe the experimental data (Table 3). Moreover, an agreement between $q_{e(\mathrm{exp})}$ experimental and $q_{e(\mathrm{cal})}$ calculated values was observed. It was found that adsorption rate of Fe^{3+} ions is the highest for calcined hydrotalcite ($k_2 = 3.2\ \mathrm{g\ mg^{-1}\ min^{-1}}$) and gyrolite ($k_2 = 1.65\ \mathrm{g\ mg^{-1}\ min^{-1}}$) (Table 3). These observations based off the data agree with the experimental results (Table 1 and Fig. 6).

In order to identify the stability of both adsorbents, the products of chemisorption were explored. It should be noted that no other compounds were observed in XRD patterns of both adsorbents.

It was determined that, during calcination of hydrotalcite, sharp diffraction maximums characteristics to the mentioned compound (*d*-spacing—0.766, 0.381, 0.250, 0.229 and 0.194 nm) as well as diffraction peaks of magnesium carbonate (*d*-spacing—0.274, 0.257, 0.210, 0.194 and 0.170 nm), and boehmite (*d*-spacing—0.615, 0.309, 0.235 and 0.186 nm) were unidentified in XRD curve (Fig. 7(a) and (b)). Thus, only broader diffraction maximums (humps) typical to nano-sized compound are observed in calcinated hydrotalcite sample (Fig. 7(b)).

Unexpected results were obtained; hydrotalcite reconstructs its structure and so-called "memory effect" happens during chemisorption process (Fig. 7(c)).

X-ray diffraction analysis showed that, after chemisorption experiment, the structure of gyrolite remains stable in the solution, although the intensity of typical diffraction peaks (*d*-spacing—2.21; 1.1264; 0.8369; 0.4196; 0.3731; 0.3510; 0.2804; and 0.2143 nm) slightly decreases due to calcium ions desorption (18.03 mg Ca^{2+}/g) into the solution (Fig. 8).

Moreover, obtained results allow us to state that the crystal lattice of calcinated hydrotalcite contains extra quantity of Mg^{2+} ions (1.04 mmol/g), which, after chemisorption, have no effect on its structural properties (Table 1 and Fig. 7(c)). The observations

Table 4
Calculated parameters of adsorbents' specific surface area (S_{BET}) after synthesis and chemisorption process

		BET equation constants		Capaticy of monolayer $X_m = \frac{1}{S+I}, g$	S_{BET}, m^2/g	$C_{\mathrm{BET}} = \frac{1}{I \cdot X_m}$	Reliability coefficient
	Adsorbent mass m, g	Slope $S = tg\alpha$	Intercept I				R^2
After synthesis							
Calcinated hydrotalcite	0.1648	379.16	2.5894	0.0026	55.82	147.43	0.9999
Gyrolite	0.0323	1188.70	0.7088	0.000841	91.52	1678.06	0.9986
After chemisorption process							
Calcinated hydrotalcite	0.1563	221.97	2.1305	0.0045	100.27	105.19	0.9998
Gyrolite	0.0657	514.95	2.3755	0.0019	103.33	217.78	0.9981

were made in a case of gyrolite as well—the additional amount of Ca^{2+} ions is only equal to 0.45 mmol/g and has no influence on the stability of gyrolite (Table 1 and Fig. 8(b)).

Moreover, S_{BET} of hydrotalcite significantly increases after heavy metal ions are inserted into its crystal lattice ($S_{BET} = 100.27\,m^2/g$) (Table 4). This can be explained by the "memory effect", during which, in the presence of water, the transformation of compound proceeds, resulting in reconstruction of layered structure. Moreover, due to chemisorption of mentioned ions, gyrolite exhibits slightly larger specific surface area, which is equal to $103.33\,m^2/g$ (Table 4).

4. Conclusions

(1) It was observed that, during adsorption with single adsorbates, the ion exchange reactions of $Ca^{2+} \leftrightarrow Me^{x+}$ and $Mg^{2+} \leftrightarrow Me^{x+}$, typical to gyrolite and calcined hydrotalcite, were found to be non-stoichiometric, because the amount of adsorbed Me^{x+} ions by the solids was lower than the quantity of leached Ca^{2+} or Mg^{2+} ions. Meanwhile, in a case of simultaneous adsorption, the intercalation of heavy metal ions into the structure of adsorbents proceeds differently, because the amount of adsorbed Me^{x+} ions is higher than the amount of leached Ca^{2+} and Mg^{2+} ions and two types of chemical reactions—substitution and addition—occur.

(2) It was estimated that the adsorption reactions are not reversible process, because almost all heavy metal ions (~99.84%) are chemisorbed by calcined hydrotalcite and gyrolite. The data were confirmed by pseudo-second-order Ho kinetic model.

(3) It was determined that heavy metal ions intercalate in the crystal structure of synthetic layered inorganic adsorbents and do not form other compounds. Hydrothermally treated and calcined hydrotalcite reconstructs its structure, and the "memory effect" happens during the above-mentioned process. Meanwhile, the intensity of typical gyrolite diffraction peaks slightly decreases due to calcium ions desorption. It should be noted that the specific surface area of calcined hydrotalcite significantly increases when heavy metal ions are inserted into its crystal lattice ($S_{BET} = 100.27\,m^2/g$), while gyrolite exhibits slightly larger S_{BET}, which is equal to $103.33\,m^2/g$.

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