

# Study of the selection mechanism of heavy metal ( $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Ni}^{2+}$ , and $\text{Cd}^{2+}$ ) adsorption on clinoptilolite

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Received 10 June 2006; accepted 26 July 2006

Available online 29 July 2006

## Abstract

The study was carried out on the sorption of heavy metals ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ ) under static conditions from single- and multi-component aqueous solutions by raw and pretreated clinoptilolite. The sorption has an ion-exchange nature and consists of three stages, i.e., the adsorption on the surface of microcrystals, the inversion stage, and the moderate adsorption in the interior of the microcrystal. The finer clinoptilolite fractions sorb higher amounts of the metals due to relative enriching by the zeolite proper and higher cleavage. The slight difference between adsorption capacity of the clinoptilolite toward lead, copper, and cadmium from single- and multicomponent solutions may testify to individual sorption centers of the zeolite for each metal. The decrease of nickel adsorption from multicomponent solutions is probably caused by the propinquity of its sorption forms to the other metals and by competition. The maximum sorption capacity toward  $\text{Cd}^{2+}$  is determined as 4.22 mg/g at an initial concentration of 80 mg/L and toward  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  as 27.7, 25.76, and 13.03 mg/g at 800 mg/L. The sorption results fit well to the Langmuir and the Freundlich models. The second one is better for adsorption modeling at high metal concentrations.

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**Keywords:** Clinoptilolite; Sorption; Ion exchange; Heavy metals

## 1. Introduction

The increasing levels of heavy metals in the environment represent a serious threat to human health, living resources, and ecological systems. Mobile and soluble heavy metal species are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations, and tanneries. The soils surrounding many military bases are also polluted and pose a risk of groundwater and surface water contamination. Some metals associated with these activities are  $\text{Cd}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$ . Wastewater discharged by enterprises processing ores and concentrates of nonferrous metals are usually polluted with heavy metal ions, such as  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ . Environmental contamination by metals is mainly

by the emission of liquid effluents with relatively low, although harmful, metal concentrations (up to some hundreds of mg/L) and therefore the removal of heavy metals from wastewaters is required prior to discharge into receiving waters [1–4].

Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis. Among various treatment methods ion exchange looks like the most attractive one when effective, low-cost ion exchangers are used. Generally ion exchange and sorption are also preferred for the removal of heavy metal ions due to easy handling [5,6].

In this context natural zeolites gain a significant interest among scientists, mainly due to their valuable sorption characteristics provided by combination of ion-exchange and molecular-sieve properties which can be relatively easily modified. Zeolite use as ion exchangers for environmental protection and other applications is stimulated by the good results obtained, the nontoxic nature of these materials, their availability in the many parts of the world, and the low cost [7–10]. Re-

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removal and recuperation processes of heavy metals from aqueous solutions by natural zeolites are commonly cyclic and take into account the recovery of the metals and the regeneration of the zeolite to be reused [11]. Additionally, the mineral stability of zeolites and their structural changes under treatment in various media play important roles in their potential utilization as ion exchangers.

Clinoptilolite being the most common natural zeolite belongs to the heulandite family or a structural variation of the zeolite mineral group and has the following total chemical formula  $(\text{Na}, \text{K}, \text{Ca})_4\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 24\text{H}_2\text{O}$  [7]. This mineral occurs in andesite, rhyolite, and basalt rocks as veins and impregnations. But the large industrial deposits are connected with volcanic-sedimentary high-silica rocks. Zeolite tuffs contain often more than 70% clinoptilolite proper. Associated minerals are usually quartz, cristobalite, calcite, aragonite, thenardite, feldspars, chlorite, montmorillonite, and other zeolites. Clinoptilolite differs from heulandite mineral by a higher Si/Al ratio as well as by a higher thermal stability (4.0–5.3 and 2.5–3.7, and 600–800 and 350–450 °C, respectively).  $\text{Na}^+$  and  $\text{K}^+$  dominate mainly among exchangeable cations of clinoptilolite, but  $\text{Ca}^{2+}$  with  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  in heulandite [7,10]. The heulandite family is usually divided into heulandite, high-silica heulandite, and low- and high-silica clinoptilolite species [12], but it is also classified by a dominant exchangeable cation as follows: Ca-heulandite, K-clinoptilolite, Ca-clinoptilolite, etc. This zeolite with void volume 34% and cation-exchange capacity 2.16 meq/g has received extensive attention due to its attractive selectivity for many organic and inorganic substances including heavy metal cations [7–13].

Many researchers [11–25] have investigated various aspects of heavy metal removal from wastewater [13–15] and synthetic aqueous solutions by clinoptilolite and other zeolites. The nature of the process as well as its deciding factors is usually the most interesting. The ion-exchange process in zeolites is influenced by several factors such as concentration and nature of cations and anions, the temperature, pH level, and crystal structure of the zeolites [19,20]. The influence of pH level on heavy metal removal by ion exchange as well as the role of hydrogen ions has been considered in different reports [11,12,19–21]. Many studies are also devoted to the improvement of the clinoptilolite sorption properties by chemical modification [4,12,16,22]. Investigation of hydrolysis processes and precipitation of metal hydroxides during ion exchange with zeolites is also very promising [23].

Despite the great interest in ion exchange with clinoptilolite, only few reports exist on the influence of other ions on heavy metal removal from mixed solutions. There are only some contradictory results published [11,16,24]. The limited data are also available for metal ion exchange with the clinoptilolite in terms of equilibrium isotherms and kinetics especially with consideration of the mechanism of the process on different stages. Adsorption of heavy metals on the Transcarpathian clinoptilolite under dynamic conditions was studied and reported [21,25]. The aim of the present work is to study heavy metal ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ ) uptake from single- and multicomponent synthetic aqueous solutions by raw and pre-

treated forms of the natural zeolite and Transcarpathian clinoptilolite under static conditions and to estimate the optimal operation parameters of the process.

## 2. Experimental

### 2.1. Materials

Clinoptilolite rock from Sokyrnytsya deposit (the Transcarpathian region, Ukraine) containing nearly 75% of clinoptilolite was used. Quartz, calcite, biotite, muscovite, chlorite, and montmorillonite are the main associated minerals. The exchange cations are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  with prevalence of the last one [26]. Their total contents are determined as 2.53 meq/g. Thermostability of the sorbent is from 923 to 973 K, and static water-storage capacity and relative moisture are 9.03 and 10.19%, respectively. The content of exchangeable cations is 53.5 meq/100 g [27]. Our preliminary investigation of the clinoptilolite by the analysis of low-temperature nitrogen adsorption data (obtained via ASAP 2010, version 2.00, Micrometrics, Norcross, GA) applying the CPSM model showed that the Transcarpathian clinoptilolite may be resolutely referred to natural micro- and mesoporous materials with a polymodal pore size distribution (Fig. 1). Mesopores with diameters of 37 and 120–230 Å dominate [28]. The specific surface area ( $S_{\text{BET}}$ ) was estimated as 13 m<sup>2</sup>/g for the raw zeolite and about 78 m<sup>2</sup>/g for the clinoptilolite pretreated with 2 M solution of hydrochloric acid. The basic parameters for the porous structure of raw and acid-treated samples of the clinoptilolite are demonstrated in Table 1.

The chemical treatment of the zeolite was performed by the addition of 0.25 L of the 2 M solutions of HCl and  $\text{NH}_4\text{Cl}$  to the samples of clinoptilolite fractions of 0.71–1.0 mm (15 g). After 24 h the solid phases were separated from the solutions and from  $\text{Cl}^-$  ions and dried at room temperature. Concentrations of heavy metals in the synthetic solutions correspond to real domestic wastewaters. The synthetic stock solutions were prepared by dissolving metal nitrates ( $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) in deionized water.

### 2.2. Chemical analysis

Concentrations of heavy metals and exchangeable cations of the adsorbent ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) were determined by flame

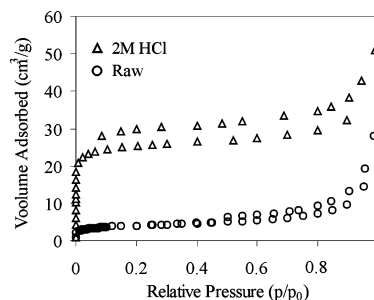


Fig. 1. Nitrogen adsorption/desorption isotherms for raw and acid-treated samples of clinoptilolite.

Table 1  
Basic parameters of clinoptilolite porous structures

Sample of clinoptilolite	$S_{\text{BET}}$ , $\text{m}^2/\text{g}$	BJH desorption, surface of mesopores, $\text{m}^2/\text{g}$	$V_{\text{mes+mic}}$ , $\text{cm}^3/\text{g}$	$V_{\text{mic}}$ , $\text{cm}^3/\text{g}$	BJH desorption, average pore diameter, Å
Raw	13.2	12.17	0.04318	0.0130	95.62
Treated by 2 M HCl	78.9	27.79	0.07873	0.0363	63.16

emission spectrometry using an AAS800 atomic absorption spectrometer, Perkin Elmer (USA). All chemicals of analytical grade used in this study were obtained from POCh, Gliwice, Poland. The average standard deviation of the measurement was from 0.01 to 0.1%. The standard reproducibility deviation was 0.1–3%.

### 2.3. Kinetics and equilibrium study

Three mechanical fractions of the clinoptilolite (2.0–1.4, 0.71–0.50, and 0.35–0.125 mm) were used in sorption kinetics study. Three replicate amounts of each size fraction of air-dried clinoptilolite (0.5 g) were placed together with 200 ml of 20 mg/L ( $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ ) and 2 mg/L Cd solutions in 330-ml glass tubes and shaken singly. Then the samples were taken periodically at 15 to 4080 min and filtrated, and heavy metal concentrations in the aqueous phase were determined. Kinetics of metals sorption onto the clinoptilolite fraction 0.71–0.5 mm was investigated at the different pH levels of solutions, in the model single solutions of each metal, and in the model mixed solution of all four metals. The raw zeolites as well as the samples pretreated by 2 M solutions of HCl and  $\text{NH}_4\text{Cl}$  were used in this study.

Sorption of heavy metals by the chosen clinoptilolite sample (0.71–0.50 mm) was studied using the batch equilibrium method. In the first phase of the runs, three replicate amounts of air-dried clinoptilolite (0.5 g) were shaken singly with 10, 20, 40, 400, and 800 mg/L of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  and 1, 2, 4, 40, and 80 mg/L of  $\text{Cd}^{2+}$  solutions, respectively. After 48 h metal concentrations in the filtrated aqueous phases were analyzed.

The equilibrium amount of metal adsorption from aqueous solution was determined applying the formula

$$q_t = m_s/m = (C_0 - C_e) V/m, \quad (1)$$

where  $q$  is the amount of metal ions sorbed at equilibrium (expressed in mg/g sorbent);  $m_s$  is the mass of metal sorbed (mg);  $m$  is the adsorbent mass (g);  $C_0$  is the initial concentration of metal ions (expressed in mg/L);  $C_e$  is the equilibrium concentration of metal ions (mg/L);  $V$  is the volume of solution from which adsorption occurs (L).

The sorption effectiveness was calculated by the following formula

$$E = 100m_s/(VC_0), \quad (2)$$

where  $E$  is the sorption effectiveness (expressed in %);  $m_s$  is the mass of metal sorbed (mg);  $C_0$  is the initial concentration of metal ions (expressed in mg/L); and  $V$  is the volume of solution from which adsorption occurs (L).

The results of the equilibrium test are used to evaluate distribution coefficients by the equation

$$K_d = q_e/C_e, \quad (3)$$

where  $K_d$  is the distribution coefficient (expressed in L/g);  $q_e$  and  $C_e$  are the solid and liquid cation concentrations (in mg/g and mg/L), respectively. Distribution coefficient data implicitly indicate the selectivity, capacity, and affinity of an ion for ion exchange.

The specific surface area ( $S$ ,  $\text{m}^2/\text{g}$ ) of the clinoptilolite occupied by the clinoptilolite-exchangeable cations and by adsorbed metals was evaluated via the following expression

$$S = qN\Omega, \quad (4)$$

where  $q$  is an amount of clinoptilolite exchangeable or metals' sorbed cations (expressed in mmol/g of the zeolite);  $\Omega$  is the area occupied by one cation ( $\text{m}^2$ ); and  $N$  is Avogadro's number.

### 2.4. Modeling of sorption kinetics and equilibrium data

The kinetics of metal adsorption was modeled applying the pseudo-first- and second-order kinetics models [29] expressed via Eqs. (5) and (6), respectively,

$$q = q_e(1 - \exp(-k_1t)), \quad (5)$$

$$q = (q_e^2 k_2 t) / (1 + q_e k_2 t), \quad (6)$$

where  $k$  is the rate constant,  $q_e$  is the equilibrium adsorption capacity, and  $t$  is the time of sorption duration.

The equilibrium metal adsorption was modeled applying the Langmuir and the Freundlich models.

The Langmuir equation may be written as

$$q_e = q_{\text{max}} b C_e / (1 + b C_e), \quad (7)$$

where  $b$  is the Langmuir model parameters,  $q_{\text{max}}$  is the adsorption maximum, with all other symbols having been explained already.

The Freundlich equation may be written as

$$q_e = K_f C_e^n, \quad n < 1, \quad (8)$$

where  $K_f$  and  $n$  are the empirical constants, with all other symbols having been explained already.

The goodness of fit of the models to experimental data was checked by comparison of the correlation coefficient  $R^2$  and standard error  $S_E$ . The CurveExpert 1.37 free ware program was used in all calculations with the confidence level set at 95%.

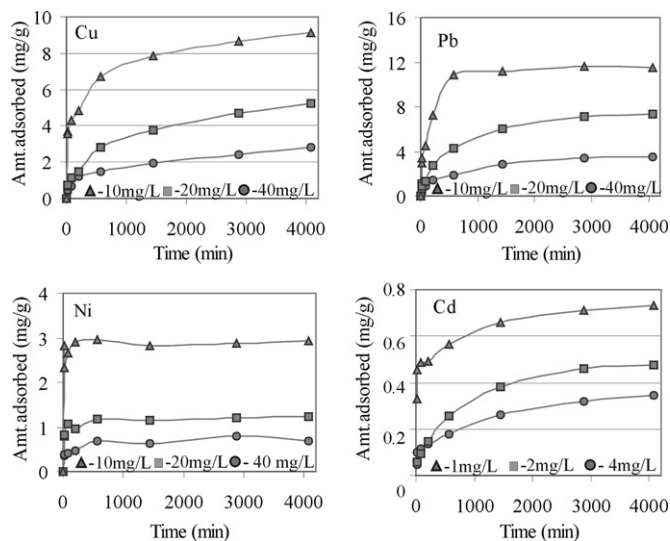


Fig. 2. Kinetics of metal sorption from single-component solutions under static conditions (0.5 g zeolite, fraction 0.71–0.50 mm, 200 ml solution, pH 6.2).

### 3. Results and discussion

#### 3.1. Kinetics study

Kinetics of ion-exchange adsorption of heavy metals from aqueous solutions onto the clinoptilolite was studied up to equilibrium. Ion-exchange adsorption of the selected heavy metals onto the clinoptilolite is a heterogeneous process with at least three different stages (Fig. 2). The first one is a very fast (instantaneous) intake corresponding to near the first 30 min for all metals. This step is established for all four metals at three different concentrations. The inversion phenomenon with desorption prevalence in ion exchange during some period is the second stage. Although all metals demonstrate this phenomenon, the sharpest one characterizes nickel. Apart from nickel the inversion is more pronounced at higher metal concentrations. The inversion was also observed in ammonium ion adsorption onto the clinoptilolite under dynamic conditions in our previous investigations [30]. During the third stage the adsorption of cadmium, lead, and copper increases but significantly slower compared with the first period and the kinetic curves are gentler. At the first stage near 25% of lead and to 40% of copper and cadmium are sorbed for 0.5 h. The rest of metal amounts are sorbed during 67 h. But the main part of nickel is taken up at the first stage with a slight sorption increase (8%) at the third one. The different stages are similar in duration for three selected concentrations.

In our opinion the noted differentiation of adsorption kinetics of the tested metals are conditioned mainly by the specific crystalline structure of the clinoptilolite. The first stage of the fast sorption corresponds to ion exchange in micropores on the microcrystal's surface of the clinoptilolite grains. According to our study the surface area of the clinoptilolite microcrystals is larger than  $30 \text{ m}^2/\text{g}$  [31]. Free access of diffusion flow of metal ions through macro- and mesopores to microcrystal surfaces provides the significant velocity of this stage. Dominance of desorption in the second stage is probably caused by counter-

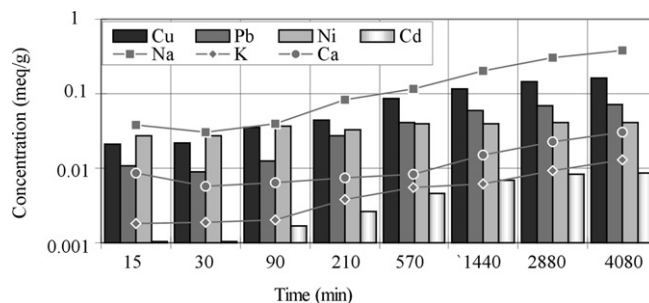


Fig. 3. Dynamics of ion exchange of heavy metals with the clinoptilolite (fraction 0.71–0.50 mm,  $C_0 = 20 \text{ mg/L}$  for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$ ;  $C_0 = 2 \text{ mg/L}$  for  $\text{Cd}^{2+}$ ).

diffusion of exchangeable cations from the deeper layers of the zeolite crystals and the subsequent occupation of exchange positions on the crystals surface by them. During the third stage of the slow metal sorption ion exchange in micropores inside separate clinoptilolite microcrystals is supposed to take place. Exchange deceleration in the close micropores inside microcrystals is connected by worse access as well as by more intensive sorption in comparison with exchange in the surface micropores. Slow and slight adsorption of nickel in the third stage confirms that the uptake of this metal occurs mainly in the micropores on the clinoptilolite microcrystal's surface. Forms and proportions of the kinetic curves are constant at different initial metal concentrations. Obviously growth of the metals ions concentrations in solutions leads to their deeper dehydration and hence to more intensive exchange between metals ions and the active surface of the zeolite. It should be noted that adsorption curves of a similar form were obtained during the study of  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Ni}^{2+}$  adsorption onto clinoptilolite [25].

Analysis of the role of different exchangeable cations of the clinoptilolite in metal uptake demonstrated (Fig. 3) that at the first period these cations form the following order  $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+$  by exchange intensity. At the same time copper and nickel are mostly sorbed from solutions. Fig. 3 shows that amounts of tested zeolite exchangeable cations are somewhat smaller than sorbed metals amounts at this stage. It is probably connected with other zeolite-exchangeable cations (Fe, Mg, Al, and Ti) taking part in the exchange, but they are not analyzed in our study. At the desorption stage the concentration of exchangeable potassium ions continues to increase in the solutions with a decrease in the quantities of sodium and calcium ions. After an inversion period exchange of nickel is practically stopped and adsorption of copper and lead prevails in the third stage. Unlike the first stage now amounts of analyzed clinoptilolite-exchangeable cations exceed sorbed metal amounts that may be caused by cation exchange with hydrogen ions of the solutions. As a whole results demonstrated in Fig. 3 testify to the ion-exchange nature of the metal uptake. At the equilibrium stage the total content of exchange cations ( $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ ) removed into solutions is 0.425 and adsorbed metal cations is 0.283 meq/g. Specific surface areas occupied by certain exchangeable cations and metal cations adsorbed by the clinoptilolite at the different stages are presented in Table 2.

Table 2

Specific surface area occupied by the clinoptilolite-exchangeable cations and metal cations adsorbed by the clinoptilolite

Parameters	K <sup>+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Cd <sup>2+</sup>
Contents of exchangeable cations (according to the clinoptilolite chemical composition)								
Surface area (m <sup>2</sup> /g)	21.74	10.44	6.1	2.3	–	–	–	–
mmol/g	0.65	0.43	0.34	0.22	1 × 10 <sup>-4</sup>	7 × 10 <sup>-5</sup>	8 × 10 <sup>-5</sup>	2 × 10 <sup>-6</sup>
Contents of exchangeable cations and adsorbed metals (after 15 min of ion exchange, C <sub>0</sub> = 20 mg/L for Cu, Ni, Pb, and C <sub>0</sub> = 2 mg/L for Cd)								
Surface area (m <sup>2</sup> /g)	0.71	0.055	0.559	–	0.133	0.123	0.115	0.008
mmol/g	0.002	0.003	0.031	n.d.	0.005	0.011	0.013	0.0005
Contents of exchangeable cations and adsorbed metals (after 4080 min of ion exchange, C <sub>0</sub> = 20 mg/L for Cu, Ni, Pb, and C <sub>0</sub> = 2 mg/L for Cd)								
Surface area (m <sup>2</sup> /g)	0.459	0.279	6.935	–	0.950	0.925	0.184	0.68
mmol/g	0.013	0.015	0.382	n.d.	0.0355	0.0828	0.0207	0.004
Contents of exchangeable cations and adsorbed metals (by the adsorption isotherm, C <sub>0</sub> = 800 mg/L for Cu, Ni, Pb, and C <sub>0</sub> = 80 mg/L for Cd)								
Surface area (m <sup>2</sup> /g)	–	–	–	–	3.57	4.51	1.97	0.64
mmol/g	n.d.	n.d.	n.d.	n.d.	0.134	0.405	0.222	0.037

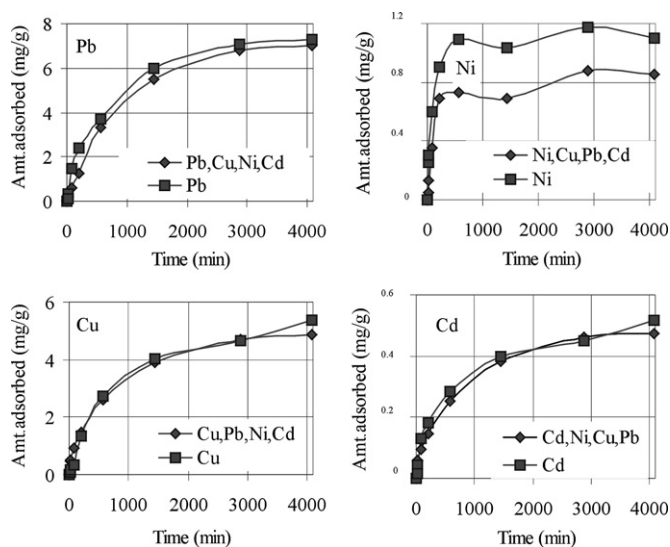


Fig. 4. Kinetics of metals sorption from single- and multicomponent (Cu<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup>) solutions under static conditions (0.5 g zeolite, fraction 0.71–0.50 mm, 200 ml solution, C<sub>0</sub> = 20 mg/L for Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> and C<sub>0</sub> = 2 mg/L for Cd<sup>2+</sup>, pH 6.2).

As a result of study of metals sorption from single- and multicomponent solutions it was found that only nickel adsorption decreases significantly due to competition (Fig. 4) while this factor is unimportant for other metals. The amounts of lead, copper, and cadmium sorbed from the single-element solutions exceed the corresponding quantities taken up from the multicomponent ones at 3–5% mainly. Only lead demonstrated slightly higher excess at the first stage. But the corresponding difference for nickel is near 40%. It may be concluded that despite the similar properties of these metals each of them interacts only with the specific sorption centers of the clinoptilolite and in different sorption forms. During the ion exchange the pH value of the solution is changed from 6.2 up to 6.7.

It should be noted that results of the previous investigations in this field are discrepant. Study of the uptake of Pb<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup> ions by natural clinoptilolite from single- and multicomponent solutions is reported in [32]. Only the sorption curves of lead were similar, but amounts of the other metals sorbed from multicomponent solutions were significantly lower than the same sorbed from the single solutions. Petrus and Warchoř [24] testing Cu<sup>2+</sup> and Cd<sup>2+</sup> ion removal by clinoptilolite found no significant difference between metal uptake from one- and two-component solutions.

Prior treatment of the zeolite by ammonium chloride increased its sorption ability more effectively in comparison with hydrochloride acid with the most evident sorption improvement at the beginning of the process as well as in nickel adsorption (Fig. 5). Adsorption of nickel by ammonium forms of the clinoptilolite is almost twice as large and by hydrogen forms is larger by 35%. But at a significant contact duration (48–64 h) the difference between nickel sorbed by treated and raw forms of the clinoptilolite rather decreases.

The chemical treatment of the clinoptilolite slightly increases sorption of the other metals (up to the first percents) with the greatest rise of copper uptake. Only at the initial period of the process (up to 90 min) the treated samples sorb two and three times as large lead and copper compared with the raw clinoptilolite with the higher ability of the ammonium form (Fig. 5). To our thinking the noted increase of metals adsorption proves that the chemical modification of the clinoptilolite is most effective on the zeolite microcrystal surfaces.

### 3.2. Equilibrium study

The sorption capacity of the clinoptilolite increased with the increase in metal concentration in the solution. The maximum sorption capacity toward cadmium was determined as 4.22 mg/g at an initial concentration of 80 mg/L and toward lead, copper, and nickel as 27.7, 25.76, and 13.03 mg/g, respec-

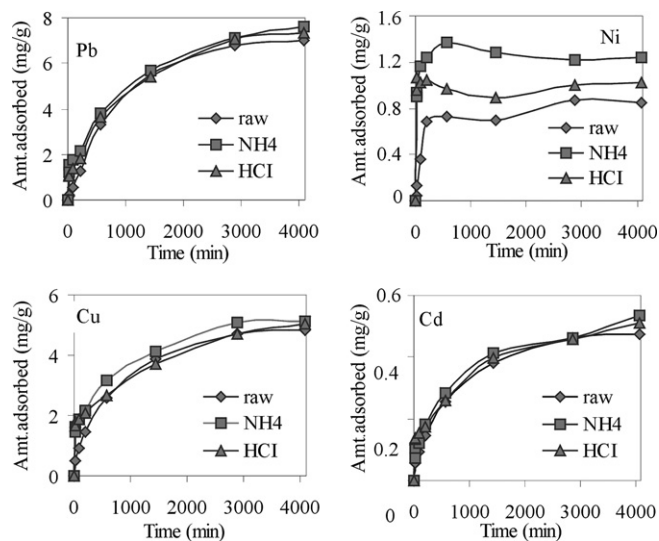


Fig. 5. Influence of chemical treatment of the clinoptilolite on heavy metal sorption (0.5 g zeolite, fraction 0.71–0.50 mm, 200 ml solution,  $C_0 = 20$  mg/L for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  and  $C_0 = 2$  mg/L for  $\text{Cd}^{2+}$ , pH 6.2).

tively, at the initial concentrations of 800 mg/L. These values of the maximum sorption capacities at the noted metal concentrations are not the ultimate clinoptilolite capacities that are confirmed by forms of the obtained sorption isotherms. Many researchers tested the sorption capacity of the clinoptilolite samples, but the obtained results are often difficult to compare. For example in [19] this value toward copper was estimated as 9.1 mg/g at the initial concentration of 400 mg/L. According to investigations using the Langmuir adsorption isotherm model the maximum sorption capacity of the clinoptilolite toward copper is equal to 6.74 mg/g [17]. Alvarez-Ayuso et al. [3] studied heavy metal uptake from solutions with metal concentrations in a range from 10 up to 200 mg/L and natural zeolite/liquid ratios from 2.5 to 10 g/L and obtained values of the sorption capacity equal to 5.91 mg/g for copper and cadmium and 1.98 mg/g for nickel. But according to Cukrovic et al. [16] the maximum adsorption of lead and cadmium from 10 mmol/L solution is equal to 91.2 and 23.6 mg/L, respectively. Maximum exchange levels for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions on natural clinoptilolite at a temperature of 27 °C and an initial concentration of 1 meq/L were estimated as 102 and 57 mg/g [33]. Under dynamic conditions the maximum sorption capacities of the Transcarpathian clinoptilolite proper toward lead from 100 mg/L solutions were evaluated as 0.5, 5.0, and 4 mg/g for raw, ammonium, and sodium forms, respectively [25]. However, the sorption capacity toward cadmium of the different treated forms of the same clinoptilolite ranged from 1.0 up to 7.4 mg/g [21]. The noted discrepancy of the published data may be caused by mineralogical and chemical features of the used sorbent as well as by experimental parameters such as sorbent–solution contact duration and equilibrium concentration values.

The selectivity series for the clinoptilolite from equilibrium isotherms follows the order  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$  for absolute and mole quantities. The established order does not correspond to the order of values of their physical–chemical parameters such as covalent and van der Waals radii, electroneg-

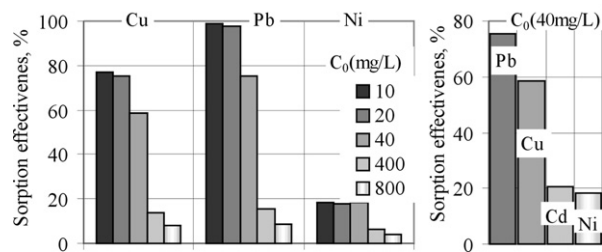


Fig. 6. Dependence of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  adsorption efficiency on their initial concentration in solutions.

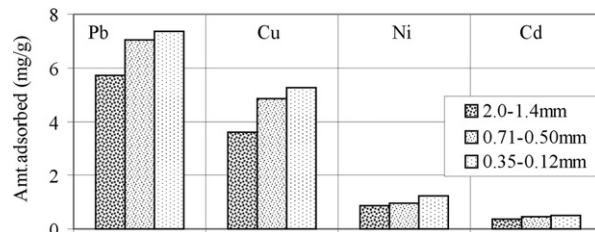


Fig. 7. Effect of clinoptilolite fraction size on sorption capacity ( $C_0 = 20$  mg/L for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  and  $C_0 = 2$  mg/L for  $\text{Cd}^{2+}$ , pH 6.2) toward metals.

activity, and ionization potential. So long as the ionic radii of these metals are several times smaller as the primary clinoptilolite pores, it is hardly probable to connect the metal selectivity with a sieve effect. Furthermore, adsorption of these metals in their hydrated forms is impossible because according to their sizes [34] they could not diffuse to the clinoptilolite micropores. It should be observed that metal selectivity order at the equilibrium concentration stage differs from the corresponding order at the first stage of ion-exchange adsorption observed in this study by kinetics curves. At this stage (Fig. 3) metals followed the sorption order  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$  for absolute and mole quantities. In our opinion this adsorption order is conditioned by metal-specific coordination in the mineral porous void. Apparently all metals except nickel are sorbed on their own sorption positions.

Efficiency of metal removal from aqueous solutions increases with a decrease of its initial concentrations that is connected with the sorption capacity and selectivity of the zeolite toward the certain metal. Lead is characterized by the highest removal efficiency (Fig. 6).

Amounts of all four metals sorbed increase with the decrease of the sorbent fraction size that may be conditioned by the better accessibility of adsorption centers in fine fractions as well as by their enrichment by clinoptilolite proper (Fig. 7).

Besides that in the fine fractions clinoptilolite crystals split easier along cleavage directions as a result of a crush. To our thinking the last factor may also influence essentially the growth of the zeolite mesoporosity and hence improve accessibility of metal diffusion flows to adsorption centers. Although according to Ouki and Kavannah [11] the sizes of zeolite grains have no influence on sorption efficiency because this process does not occur on the grain's surface but in the porous void.

The pH level of the aqueous solution is an important variable for the adsorption of metals on the adsorbents. The effect of the

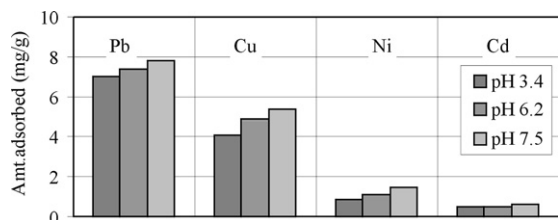


Fig. 8. Effect of pH of solution on sorption capacity ( $C_0 = 20$  mg/L for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  and  $C_0 = 2$  mg/L for  $\text{Cd}^{2+}$ ) toward metals.

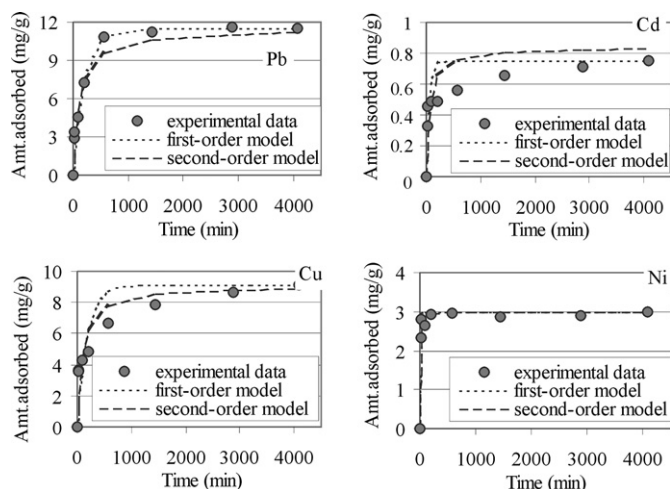


Fig. 9. Heavy metals sorption described by the pseudo-first- and the second-order kinetics models (0.5 g zeolite, fraction 0.5–0.71;  $C_0 = 40$  mg/L for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  and  $C_0 = 4$  mg/L for  $\text{Cd}^{2+}$ ).

pH on the metal adsorption by clinoptilolite was studied for pH 3.4, 6.2, and 7.5, where the material exhibits chemical stability. Efficiency of metal sorption depends on the pH level of aqueous solution. Metal adsorption decreases with the pH decrease from 7.5 up to 3.4 due to competition of hydrogen ions (Fig. 8).

As the pH level increases the concentration of the hydrogen ions as competitors decreases and this leads to an increase of the amounts of sorbed metals. The selectivity orders of the metals are constant at all pH values. The amount of complex hydrated forms of the metals increases with pH value increase that also intensifies adsorption. Thus it is possible to manage metal uptake from aqueous solutions by changing the pH value.

### 3.3. Sorption modeling

Plotting the experimental data using Eqs. (5) and (6) in Fig. 9 indicates that the pseudo-first- and second-order kinetics models do not give considerably good fit to the data. It may be connected with the complicated nature of the ion-exchange adsorption of the metals expressed in the stages of the different velocity. Fig. 9 also demonstrates that the pseudo-first-order kinetic model is somewhat closer to the experimental data for lead and nickel. But the pseudo-second-order kinetic model gives a better fit for data on copper as well as lead. The estimated kinetic coefficients (Table 3) are the average indices of the sorption process. Their values are closer to the model at the first stage. The above-noted different types of ion-exchange-active

Table 3  
Parameters of models for the sorption of heavy metals by clinoptilolite

Models	$\text{Cu}^{2+}$	$\text{Pb}^{2+}$	$\text{Ni}^{2+}$	$\text{Cd}^{2+}$
Pseudo-first-order kinetics				
$K_1$	0.0055	0.0053	0.1419	0.0216
$R$	0.6502	0.9592	0.8091	0.3759
$S$	1.7304	1.0949	0.3034	0.1508
Pseudo-second-order kinetics				
$K_2$	0.00113	0.00077	0.0041	0.0226
$R$	0.8220	0.9784	0.5057	0.4369
$S$	1.2966	0.8021	0.2642	0.1539
Langmuir model				
$b$	0.0336	0.0891	0.0058	0.0776
$q_{\text{max}}$	25.69	26.81	15.55	4.88
$R$	0.9937	0.9638	0.9971	0.9894
$S$	1.2015	2.4067	0.8025	0.2148
Freundlich model				
$K_f$	3.1404	5.7536	0.4463	0.6359
$n$	0.3254	0.2448	0.5136	0.4547
$R$	0.9935	0.9910	0.9932	0.9956
$S$	1.3721	1.6675	0.7093	0.1867

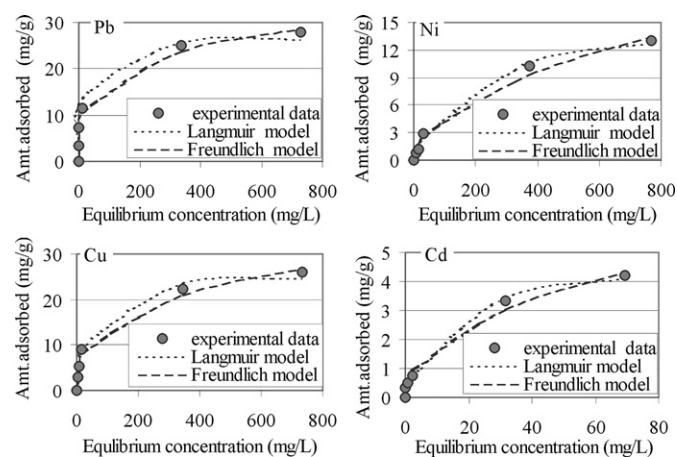


Fig. 10. Sorption isotherms of heavy metals described by the Langmuir and the Freundlich models.

surface provide significant differences between the coefficient values.

Heavy metal adsorption from aqueous solutions by the clinoptilolite is satisfactorily described by the Freundlich and the Langmuir models (Fig. 10, Table 3), although the Langmuir theory concerns sorption onto materials of homogeneous-specific surfaces. The tested metal sorption by clinoptilolite is described best by the Freundlich isotherm model with determination coefficient values over 0.99. According to the distribution coefficients estimated from the used models the metals form the following order:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ . Comparison of the distribution coefficients of the equations of the model (Table 3) with the calculated ones ( $K_d$ ) for the separate equilibrium concentrations of the metals ( $\text{Cu}^{2+}$ , 0.96, 0.77, 0.53, 0.064, and 0.035;  $\text{Pb}^{2+}$ , 2.6, 4.65, 1.02, 0.073, and 0.038;  $\text{Ni}^{2+}$ , 0.081, 0.072, 0.09, 0.027, and 0.016  $K_d$  for concentrations 10, 20, 40, 400, and 800 mg/L, respectively;  $\text{Cd}^{2+}$ , 2.6,

0.58, 0.34, 0.10, and 0.06  $K_d$  for concentrations 1, 2, 4, 40, and 80 mg/L, respectively) shows that the Langmuir model describes more correctly equilibrium of the metal adsorption at the higher concentrations contrary to Freundlich model.

#### 4. Conclusions

1. Adsorption of lead, copper, cadmium, and nickel onto clinoptilolite has an ion-exchange nature. Three different stages are observed in the ion-exchange adsorption of the metals. The process begins with fast adsorption on the zeolite microcrystal surfaces during the first 30 min. Then the inversion stage has a short-time prevalence of the desorption process connected with the diffusion flow from the clinoptilolite microcrystal's interior. The third stage is the moderate adsorption in the microcrystal's interior. Nearly 40% of copper and cadmium and nearly 90% of nickel are sorbed during the first stage on the microcrystal's surface.

2. The ion-exchange adsorption of the metals is directly proportional to pH value of aqueous solutions. Adsorption decrease in the more acidic medium is conditioned by hydrogen ion competition. The finer fractions of the clinoptilolite sorb the higher amounts of the metals due to relative enrichment by the zeolite proper as well as to higher cleavage as a result of crushing.

3. The slight difference between adsorption capacity of the clinoptilolite toward lead, copper, and cadmium from single- and multicomponent solutions may testify to individual sorption centers of the zeolite for each of these metals. Decrease of nickel adsorption from multicomponent solutions is probably caused by propinquity of its sorption forms to the other metals of the multicomponent solutions and by competition as a consequence.

4. Efficiency of metals removal from solutions by the clinoptilolite is inversely proportional to the metal concentration. The metals form the following order for adsorption efficiency:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$ . The maximum sorption capacity toward  $\text{Cd}^{2+}$  is determined as 4.22 mg/g at an initial concentration of 80 mg/L and toward  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  as 27.7, 25.76, and 13.03 mg/g, respectively, at an initial concentrations of 800 mg/L.

5. The data obtained from the batch studies are applied well to the Langmuir and the Freundlich models. The second model is better for modeling of the equilibrium adsorption by clinoptilolite at high metal concentrations and the last one is the best for low initial concentrations.

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