

# Sorption Characteristics of Zinc and Cadmium by some Natural-, Modified- and Synthetic Zeolites

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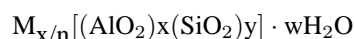
## Abstract

Sufficient knowledge of sorption capacities as well as comprehensive understanding of complex sorption properties and processes performed by natural and synthetic zeolites and their chemically modified forms belong to basic necessities of the utilisation of the above mentioned materials for increasing some nutrient concentrations and/or decreasing toxic metal's concentration in soils. The following research was undertaken to quantify the ability of a synthetic zeolite and two in Slovakia occurring zeolite tuffs (in their natural and modified forms) to adsorb zinc and cadmium. The results suggest that clinoptilolite and zeolon P4A have a particularly high potential for Zn and Cd sorption.

## 1 Introduction

As it is generally known zeolites are hydrated microcrystalline aluminosilicates containing exchangeable cations of alkaline metals and of alkaline earth metals. They are made up of three-dimensional cage-like frameworks of silica ( $\text{SiO}_4^{4-}$ ) and alumina ( $\text{AlO}_4^{5-}$ ) molecules linked together through oxygen atoms. Zeolites belong to a large group of some 45-55 different minerals, from which seven occurs in sufficient amount and purity in the nature (clinoptilolite, mordenite, erionite, ferrierite, phillipsite, chabazite and analcime). The most significant resources in Slovakia can be found in the region of the East-Slovakian lowland and the Kremnica-mountains. Beside these minerals a large group of synthetic zeolites have been designed/synthesized and a number of these products are commercially available on the market.

From several types of zeolite's empirical formula the following is used with the highest frequency:



where  $n$  is the charge of the cation  $M$ ,

$w$  represents the number of water molecules contained in the zeolite,

$x$  and  $y$  are the number of  $\text{SiO}_4^{4-}$  and  $\text{AlO}_4^{5-}$  tetrahedrons contained in a basic cell.

The tetrahedron units form cavities of various size, total volume of which is usually 20 – 50%. The effective size of channels and cavities is 0.3 – 0.7 nm. The most important properties of zeolites are as follows:

- Vigorous and partially selective cation exchange properties.
- Adsorption ability of different capacity for a number of compounds (including metal-ions, vapors and gases).
- High chemical-, temperature- and radiation stability.
- Low density and large void volume of dehydrated samples.
- Specific physical and catalytic properties.

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Natural zeolites (their modified forms) are utilized when the processes of interest require high amounts of relatively low purity and/or homogeneity of materials showing the above mentioned properties. They are applied in radioactive waste treatment, in agriculture as carriers of herbicides, pesticides and fertilizers, in environmental protection as sorbents of a number of different pollutants in different media, as soil-additives to modify their water regime, physical properties, pH, etc.

**Zinc** is an essential trace element for flora and fauna including humans. It is a component of numerous enzymes actuating in energy metabolism and genetic transcription. Zinc deficiency results in humans and animals inappetence, severe growth depressions, skin lesions and sexual immaturity. For humans depression of immunocompetence and change of taste acuity is observed as an effect of zinc-deficiency. The recommended safe and adequate dietary intake for adults is as much as  $15 \text{ mg day}^{-1}$  (MERTZ). Zn content in general plays an important role in biochemical processes of plants as well.  $\text{Zn}^{2+}$  seems to be the predominating chemical form in which zinc is absorbed by plants as a functional, structural and regulatory cofactor of a large number of enzymes. The presence of zinc is unavoidable for activity of various dehydrogenases, aldolases, isomerases and polymerases.

The ion radius of  $\text{Zn}^{2+}$  is 0.083 nm and of hydrated ion 0.43 nm. In its compounds Zn forms covalent bonds, and has significant affinity to form complex, and organometal compounds.

The zinc content of soils is largely dependent on the composition of the parent rock material. The average Zn concentrations in soils is  $50 \text{ mg kg}^{-1}$  (ALLOWAY). The total Zn content and their acceptability by plants is important to know for eventually artificial addition of elements into soils, not to exceed limit levels. Biologically accessible Zn is water-soluble and fractions solubilised by biological processes.

The total amount of zinc in soils is distributed in several forms as follows:

- free ions  $\text{Zn}^{2+}$  and organo-zinc complexes in the soil solution,
- adsorbed and exchangeable zinc in the colloidal fraction of the soil (composed of clay particles humic compounds, Fe and Al hydroxides),
- zinc in secondary minerals and insoluble complexes in the solid phase of the soil.

The factors affecting availability of Zn in soils are total soil content, pH, climatic conditions, moisture regime and interaction between Zn and other macro- and micronutrients (Zn-P, Zn-Fe, Zn-Cu, Zn-N) at the soils (ALLOWAY).

**Cadmium** has no essential biological function and has a markedly toxic effect for fauna and flora. For human health the highest risk represents the accumulation of Cd in kidney, where the cadmium concentration  $> 200 \text{ mg kg}^{-1}$  brings about its dysfunction (FASSET).

Cadmium abundance results in humans and animals extraction of calcium from the bones, their demineralisation, softening, shortening, deformation and their increased brittleness (STYK).

Cd is an analogue of zinc and it can be accepted in considerable amount by plants at the absent of zinc in soil, which causes suppression of their growth (HRONEC).

The ion radius of  $\text{Cd}^{2+}$  is 0.103 nm and of hydrated ion 0.426 nm. It has significant affinity to form cations, complex and organometal compounds. The toxic effect and bioavailability of Cd depends on its chemical forms existing in soil matrices. The average Cd content of soils is  $0.53 \text{ mg kg}^{-1}$  (ČURLÍK).

Cadmium is known in several forms: water-soluble, exchangeable, organic bounded, occluded by Fe and Mn oxides, different compounds (carbonates, phosphates, sulfides) and bounded in silicates. (MAKOVNÍKOVÁ)

$\text{Cd}^{2+}$  ions represent up to 40% of the total cadmium content in soil solutions of both neutral and acid soils.

## 2 Material and Methods

An adsorption equilibrium study of aqueous solutions of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  in contact with natural- and modified zeolitized tuffs of clinoptilolite type (Nižný Hrabovec, East Slovakia) and of mordenite type (Jastrabá-Bartošova Lehôtka, Central Slovakia), as well as with the synthetic zeolite-zeolon Z P4A (MAL, Ajka, Hungary) including their modifications has been realized using batch procedure of experiments. For zinc  $^{65}\text{Zn}$  and for cadmium  $^{109}\text{Cd}$  have been utilized as radiotracers. The determination of applied  $\gamma$ -emitters was carried out as follows: The detection of  $^{65}\text{Zn}$  was realized using the  $\gamma$ -spectrometer assembly consisted of a well type scintillation crystal NaI(Tl), Scionix, The Netherlands, emulated by the data processing software Scintivision 32, Ortec, USA; the detection of  $^{109}\text{Cd}$  was carried out by a 16-channel well type scintillation detector JNG-401, ÚRVJT Košice, Slovakia.

The natural zeolite samples have been milled and sieved to fraction of grain-size 0.25 – 0.315 mm and dried at  $105^\circ\text{C}$ .

The modification of examined samples has been carried out by shaking 50 g of particular natural/synthetic zeolites with 2 M NaCl water-solution and 2 M NH<sub>4</sub>Cl water-solution respectively for 72 hours.

The studied adsorption isotherms have been performed at 25 °C using metal concentrations in solutions ranged from 0,1 to 50 mmol dm<sup>-3</sup>. The applied solid to liquid ratio was 10 g dm<sup>-3</sup>.

The shaking time for particular sorption processes (uniform shaking parameters: 20 mm amplitude and 320 oscillations min<sup>-1</sup> for all realized experiments) has been determined as the time required for reaching the equilibrium conditions for solution/sorbent metal-concentrations. We applied a uniform shaking time for all sorption processes - 180 min.

The determination of Zn and Cd contents in tested zeolites (before and after sorption) has been carried out using radionuclide röntgen-fluorescence analysis (RRFA), namely by a detection assembly made up a Ge(Li) detector connected to a multichannel analyser (Ortec, USA) utilizing 1100 MBq <sup>238</sup>Pu as radiation source.

### 3 Results and discussion

The zinc content of tested sorbents before and after the sorption as well as the cadmium content after sorption - using 50 mmol dm<sup>-3</sup> water solutions of ZnCl<sub>2</sub> and CdCl<sub>2</sub> - determined by RRFA illustrates Table 1. Cadmium contents of tested sorbents before sorption processes have not been determined as the relevant concentrations of Cd were under the detection limit.

Table 1. Zn and Cd contents of the zeolite samples.

Sample	Zn concentration before sorption [μmol g <sup>-1</sup> ]	Zn concentration after sorption [μmol g <sup>-1</sup> ]	Cd concentration after sorption [μmol g <sup>-1</sup> ]
Nat - CLI	0,180	267,66	108,11
Na - CLI	0,216	370,14	299,81
NH <sub>4</sub> - CLI	0,236	301,31	218,65
Nat - MOR	0,148	not determined	47,73
Na - MOR	0,239	224,84	174,94
NH <sub>4</sub> - MOR	0,228	229,43	180,08
Z A4P	0,057	2370,76	709,75
Na - P4A	not determined	2052,62	1074,65
NH <sub>4</sub> - P4A	not determined	1711,53	876,32

The main objectives of our experiments have been the study of adsorption isotherms concerning the relevant systems with the aim to quantify the sorption characteristics and to determine the reaction orders of studied sorption procedures.

Fig 1-9 illustrate adsorption isotherms of tested zeolite samples

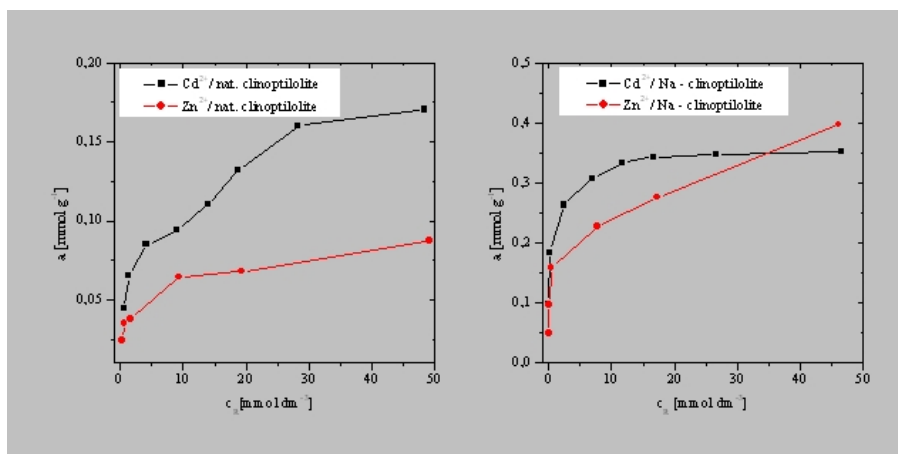


Fig 1

Fig 2

Fig. 1 Adsorption isotherms of Zn<sup>2+</sup> and Cd<sup>2+</sup> on natural clinoptilolite

Fig. 2 Adsorption isotherms of Zn<sup>2+</sup> and Cd<sup>2+</sup> on Na - clinoptilolite

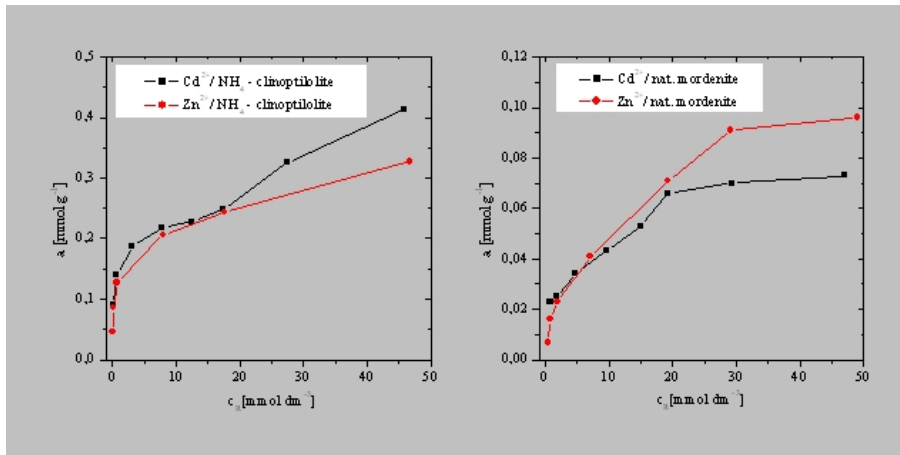


Fig 3

Fig 4

Fig 3 Adsorption isotherms of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  on  $\text{NH}_4$  - clinoptilolite  
 Fig 4 Adsorption isotherms of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  on natural mordenite

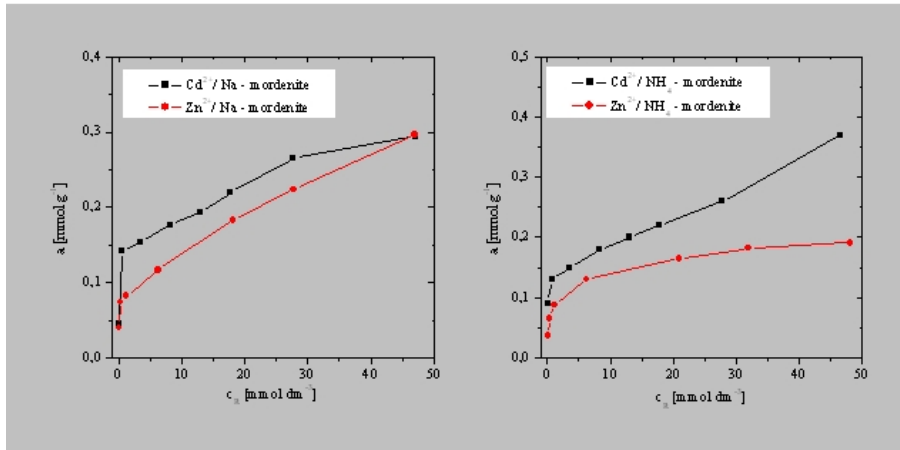


Fig 5

Fig 6

Fig 5 Adsorption isotherms of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  on Na - mordenite  
 Fig 6 Adsorption isotherms of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  on  $\text{NH}_4$  - mordenite

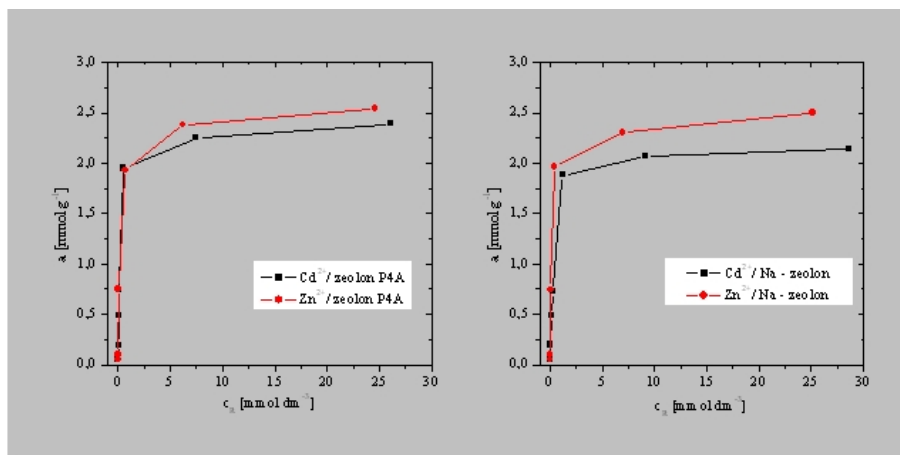


Fig.7

Fig. 8

 Fig. 7 Adsorption isotherms of  $Zn^{2+}$  and  $Cd^{2+}$  on zeolon P4A

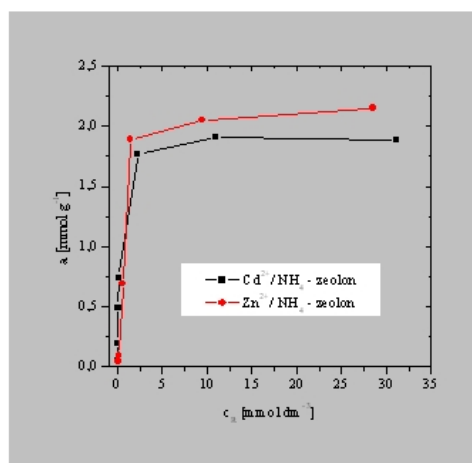
 Fig. 8 Adsorption isotherms of  $Zn^{2+}$  and  $Cd^{2+}$  on Na - zeolon


Fig. 9

 Fig. 9 Adsorption isotherms of  $Zn^{2+}$  and  $Cd^{2+}$  on  $NH_4$  - zeolon

The judgement of first vs. second reaction order for zinc sorption on Na-clinoptilolite, and on zeolon P4A are presented in Fig. 10, 11, 12, 13. The linearization of Langmuir- and Freundlich isotherms for zinc sorption for Na-clinoptilolite and for zeolon P4A are presented in Fig. 14, 15, 16, 17. The judgement of first vs. second reaction order for cadmium sorption on Na-clinoptilolite, and on zeolon P4A are presented in Fig. 18, 19, 20, 21. The linearization of Langmuir- and Freundlich isotherms for cadmium sorption for Na-clinoptilolite and for zeolon P4A are presented in Fig. 22, 23, 24, 25.

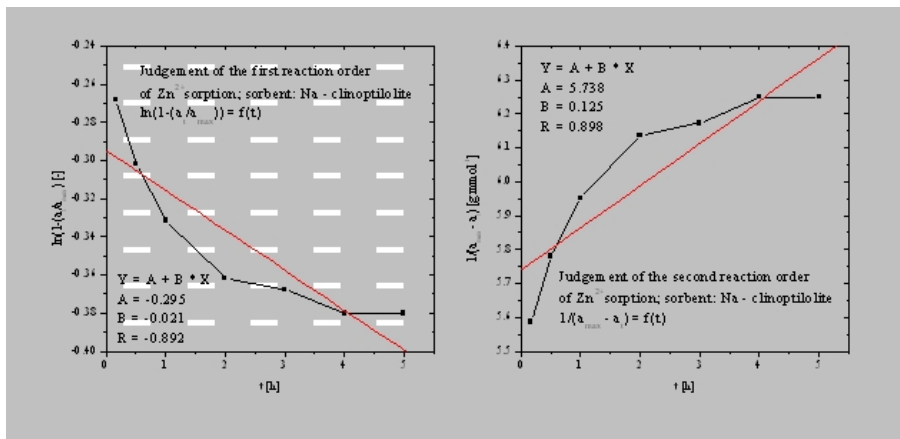


Fig 10

Fig 11

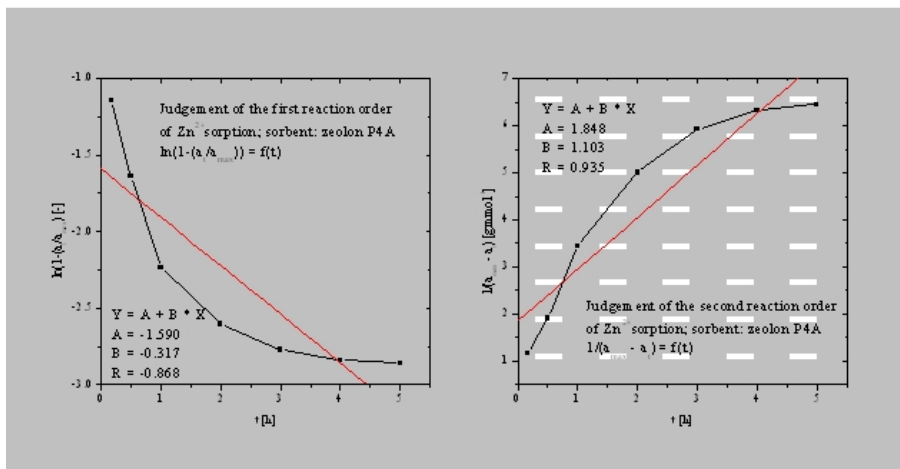
 Fig. 10 – 11 The judgement of the first and second reaction order resp. of Zn<sup>2+</sup> sorption on Na-clinoptilolite.


Fig 12

Fig 13

 Fig. 12 – 13 The judgement of the first and second reaction order resp. of Zn<sup>2+</sup> sorption on synthetic zeolon P4A.

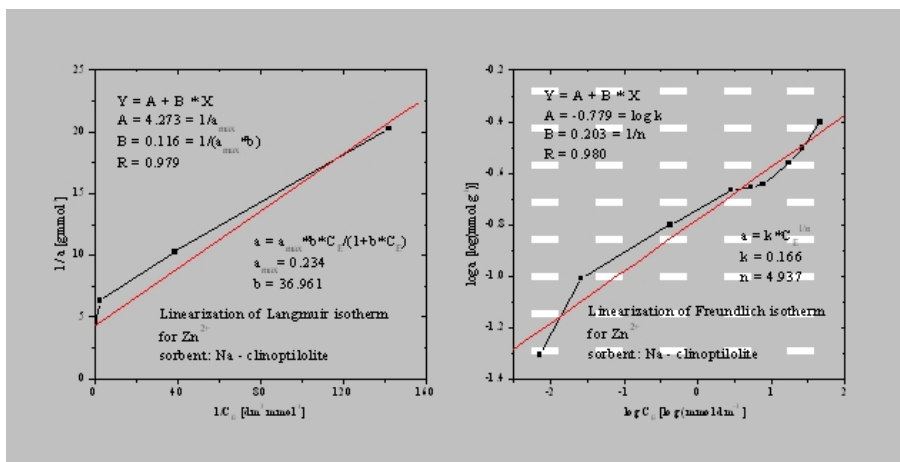


Fig. 14

Fig. 15

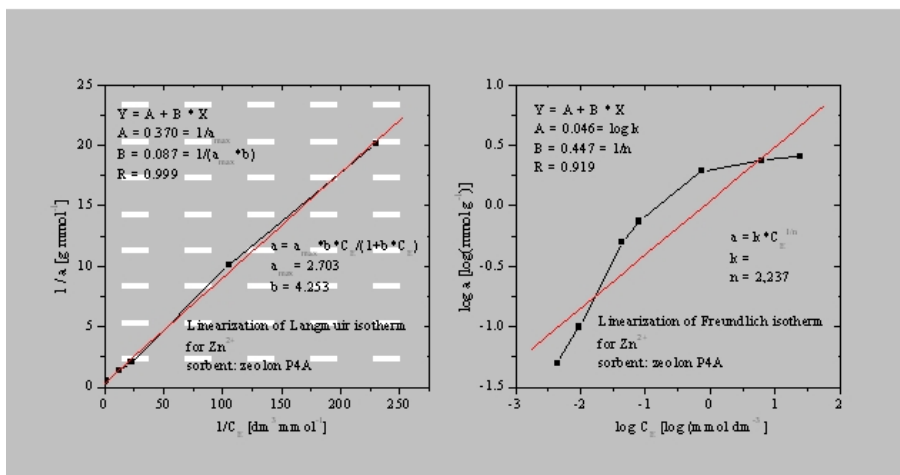
 Fig. 14 – 15 Linearization of Langmuir and Freundlich isotherms resp. for Zn<sup>2+</sup> sorption on Na-clinoptilolite.


Fig. 16

Fig. 17

 Fig. 16 – 17 Linearization of Langmuir and Freundlich isotherms resp. for Zn<sup>2+</sup> sorption on synthetic zeolon P4A.

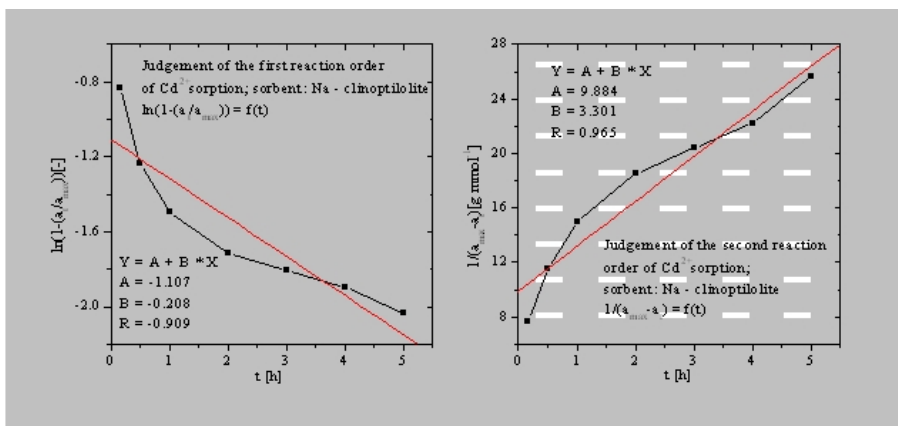


Fig 18

Fig 19

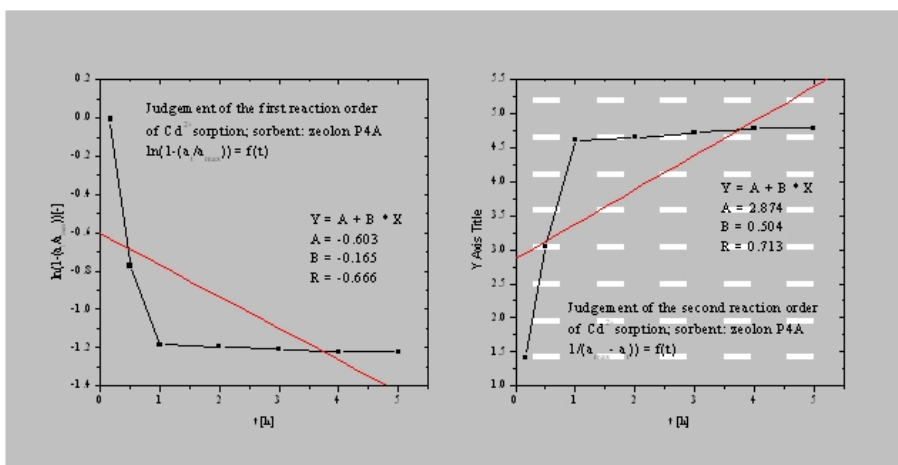
 Fig 18 – 19 The judgement of the first and second reaction order resp. of Cd<sup>2+</sup> sorption on Na-clinoptilolite.


Fig 20

Fig 21

 Fig 20 – 21 The judgement of the first and second reaction order resp. of Cd<sup>2+</sup> sorption on synthetic zeolon P4A.



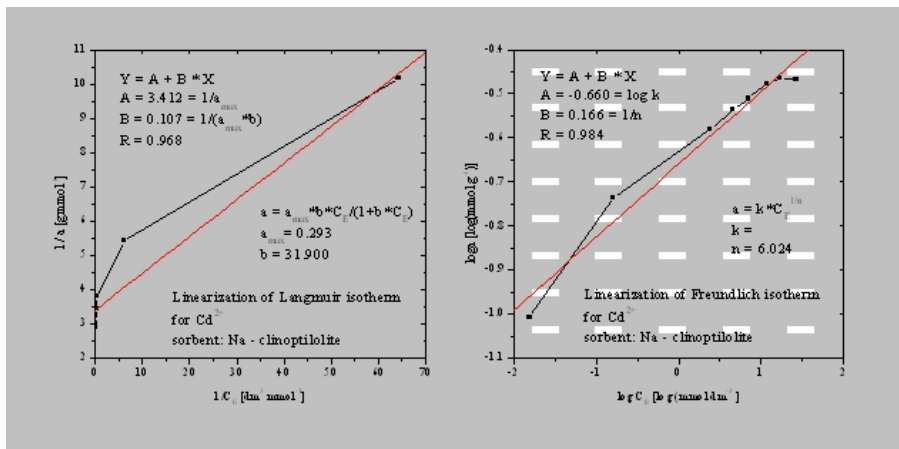


Fig 22

Fig 23

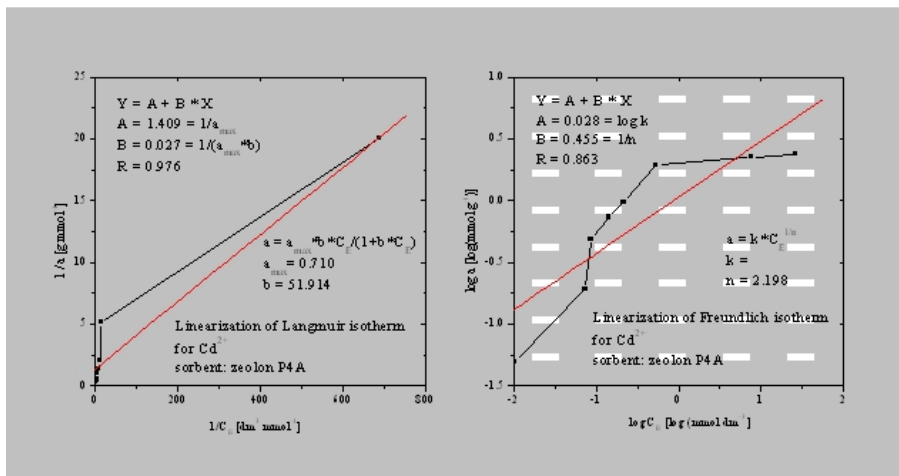
 Fig. 22 – 23 Linearization of Langmuir and Freundlich isotherms resp. for Cd<sup>2+</sup> sorption on Na-clinoptilolite.


Fig 24

Fig 25

 Fig. 24 – 25 Linearization of Langmuir and Freundlich isotherms resp. for Cd<sup>2+</sup> sorption on synthetic zeolon P4A.

## 4 Conclusions

The studied species showed considerable variations in Zn and Cd sorption properties. Sorption equilibrium by synthetic zeolite (Zeolon P4A) was achieved in shorter time than by Na-form of the tested natural clinoptilolite and the sorption capacity of synthetic zeolon P4A was much higher than the capacity of natural zeolites and their modified forms.

The highest sorption capacity for Cd<sup>2+</sup> and Zn<sup>2+</sup> among the modified as well as the natural forms of zeolites was found for Na-zeolon P4A and the lowest sorption capacity was determined for the natural mordenite and its modified forms. The highest Zn and Cd sorption capacity among the modified natural zeolites was found in the case of Na-clinoptilolite.

Sorption capacity of NH<sub>4</sub>mordenite was higher for Cd<sup>2+</sup>, while the capacity of Na-mordenite was higher for Zn<sup>2+</sup>.

Characteristics of Zn<sup>2+</sup> and Cd<sup>2+</sup> sorption on natural zeolites and synthetic zeolon were certified by radionuclide röntgenfluorescence analysis.

The intensive acidification of soils emphasizes the need of effective tools to solve the problem of increasing bioavailability of toxic elements for plants (SCHMIDT-SZAKÁL). The obtained results offer a feasible chance of Zn-zeolite utilization in agriculture. Zn-zeolites added to soils may primarily cure the Zn-deficiency, and in the same time they may be profitable from the point of view of the antagonism between Cd and Zn in suppression of

Cd levels in soils rich of Zn.

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