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Comparative Study of Zn^{2+}, Cd^{2+}, and Pb^{2+} Removal From Water Solution Using Natural Clinoptilolitic Zeolite and Commercial Granulated Activated Carbon. Equilibrium of Adsorption

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Abstract: The aim of this work is to study the effectiveness of regional, low-cost natural clinoptilolitic zeolite tuff in heavy metal ions removal from aqueous solution, through comparative study with commercial granulated activated carbon. The equilibrium of adsorption of Cd^{2+}, Pb^{2+}, and Zn^{2+} on both adsorbents have been determined at 25, 35, and 45°C in batch mode. The granulated activated carbon has shown around three times higher adsorption capacity for Cd^{2+} and Zn^{2+} than natural zeolite, and almost the same adsorption capacity for Pb^{2+} as the natural zeolite. The metal ion selectivity series $Pb^{2+} > Cd^{2+} > Zn^{2+}$, on a mass basis, has been obtained on both adsorbents. The Langmuir and Freundlich model have been used to describe the adsorption equilibrium. The thermodynamic parameters were calculated from the adsorption isotherm data obtained at different temperatures. The study of the influence of the acidity of the metal ion aqueous solution has shown an increase of metal ion uptake with increase of the pH. The sorption mechanism of Cd^{2+}, Pb^{2+}, and Zn^{2+} on natural zeolite changes from ion-exchange to ion-exchange and adsorption of metal-hydroxide with increase of the pH from 2 to 6 (and 7 for Zn^{2+}). The preliminary cost calculation, based on adsorbents maximum adsorp-

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tion capacity and their price, have revealed the potential of natural zeolite as an economic alternative to the granulated activated carbon in the treatment of heavy metal polluted wastewater.

Keywords: Adsorption; Adsorption equilibrium; Clinoptilolite; Granulated activated carbon; Heavy metals; Ion-exchange

INTRODUCTION

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Heavy metals polluted wastewaters are produced by a variety of industrial activities associated with mining and smelting operations, metal processing, and use of metals and/or substances that contain metal pollutants (1). The environmental pollution by heavy metal containing effluents is of great concern, since they are not biodegradable and tend to accumulate in organisms, causing diseases and disorders.

The conventional method for heavy metal removal from wastewater is precipitation of the metal hydroxides, followed by filtration of the sludge. This physicochemical treatment is the most widely applied due to its simple equipment, low cost, and capability to treat a large volume of wastewater. On the other hand, this method has numerous disadvantages, for example, it is inefficient in treatment of wastewater containing low concentrations of heavy metals and produces large amount of metals contaminated sludge, associated with additional costs for sludge management (2).

Other methods used for heavy metal removal from wastewater include coagulation, adsorption, ion-exchange, solvent extraction, vacuum evaporation, reverse osmosis, ultrafiltration, and electro dialysis. These methods, although usually effective, are not free of drawbacks, such as: high capital and operational cost, technical complexity, and limitation to low effluent volumes and/or low metal concentrations (3).

The sorption processes are probably the most attractive among these methods, due to their high efficiency in a wide range of metal ion concentrations, simple design and easy handling, and relatively mild operating conditions, although the cost of sorbent materials and regeneration is a limiting factor (4). Commercial activated carbon is widely used for adsorptive heavy metals removal, but its high capital and regeneration cost makes it no longer attractive for wide use in small-scale industries and developing countries. In recent years, the potential of many low-cost natural adsorbents in heavy metals removal have been investigated, among which were: chitin, chitosan, zeolite, clay, peat, agricultural wastes, dead biomass, fly-ash, lignin, red mud, seaweed, and others (5,6).

Zeolites are low-cost (0.03–0.12 US$/kg) naturally occurring hydrated aluminosilicate minerals, with wide geographic distribution and large size of deposits (5). One of the first applications of natural zeolite in removal of heavy metals from aqueous solution dates back to the late 70s (7). In the last decade there has been an increasing interest in the use of natural zeolites as cation exchangers in the treatment of heavy metal containing effluents. Besides, the ion exchange capacity natural zeolites exhibit adsorption behavior that is based on the theory of acid and basic sites in the framework structure. Sorption is the general term used to define the surface retention process without specifying the exact retention mechanism. The sorption on zeolitic particles is a complex process because of their porous structure, presence of exchangeable ions, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds, and other imperfections on the surface (8).

Some studies indicate the possibility of use of heavy metal saturated zeolites as additives to cement (9), bactericides for water disinfection (10), and antibacterial agent in paper, plastic, paint, and ceramics (11).

Clinoptilolite belongs to the Heulandite group, with the typical chemical formula $(Na, K, Ca)_{2\text{-}3}Al_3(Al, Si)_2Si_{13}O_{36}\cdot 12H_2O$, is one of the most abundant among more than 40 natural zeolite species. The porous three-dimensional structure of clinoptilolite consists of SiO_4 and AlO_4 tetrahedra connected by all their oxygen vertices forming channels. The framework negative charge due to isomorphous replacement of Al^{3+} with Si^{4+} in the structure is balanced by mono and divalent exchangeable cations such as Na^+, Ca^{2+}, K^+, and Mg^{2+}. These cations are coordinated with the defined number of water molecules, and located on specific sites in framework channels (12). The chemical composition of clinoptilolite is characterized by remarkable variations in the Si/Al ratio (between 4 and 5.5), as well as in the composition of the exchangeable cations (maximum exchange capacity up to 2.6 meq/g) (13).

In various studies several clinoptilolite containing natural zeolites have been applied in the removal of heavy metals from water solutions. The summary of clinoptilolite sorption capacity and corresponding experimental conditions is presented in Table 1. There is a big difference in clinoptilolite adsorption capacity for each metal ion listed in the table, mainly due to clinoptilolite origin, experimental conditions, and the pretreatment used. The clinoptilolite in nature is not found in a pure form. Natural zeolites from different deposits contain a different quantity of clinoptilolite in mixture with other types of natural zeolites or impurities. The metal ion removal capacity of Na homoionic form of clinoptilolite, is at least twice higher than the one of the natural, untreated clinoptilolite. One other important factor influencing the metal ion

Table 1. Summary of the clinoptilolite sorption capacity (mg/g)

Type of clinoptilolite	Cd^{2+}	Zn^{2+}	Pb^{2+}	Cu^{2+}	Ni^{2+}	$Cr3^{+}$	Co^{2+}	Mn^{2+}	pH (T)	reference
Different types of clinoptilolites	22.5–95	5.6–44.1	60.1–129.5	10.8–61.5					Solution (20°C)	(15)
Clinoptilolite		13.07	87.02	27.44					Solution (23°C)	(26)
Clinoptilolite	84.3		155.4						Solution (25°C)	(43)
Clinoptilolite	1.2		1.4						Solution (25°C)	(44)
Clinoptilolite	3.7	2.7	6.0	3.8	0.9		1.5		Solution (25°C)	(29)
Clinoptilolite		6.6							4 (20°C)	(21)
Clinoptilolite		3.6							4 (20°C)	(21)
Clinoptilolite		8.75		9.22			14.39	4.22	6–7 (30°C)	(13)
Clinoptilolite		4.40							5 (20°C)	(36)
Clinoptilolite		1.99(3.15)							Solution (20°C)	(45)
Clinoptilolite	4.88		26.81	25.69	15.55				Solution (25°C)	(20)
Clinoptilolite	4.60	3.45		5.91	1.98	4.12			4 (22°C)	(22)
Na-clinoptilolite		20.9	128						Solution (23°C)	(46)
H-clinoptilolite	7.41								5.6 (25°C)	(47)
Na-clinoptilolite			118.1						Solution (25°C)	(19)
Na-clinoptilolite			120.48						Solution (25°C)	(48)
Na-clinoptilolite		7.99							5 (20°C)	(36)
Na-clinoptilolite	39.34	50.58	145.5						Solution (25°C)	(49)
Na-clinoptilolite			142.14						4 (T = 25°C)	(24)

retention mechanism is the pH of the solution. The mechanism of metal ion retention on natural zeolites changes from ion exchange/adsorption in the acidic region to adsorption/complexation and possible precipitation in the basic region (14).

Several heavy metal cation exchange capacity (in $meq/g_{adsorbent}$) series on natural and Na-exchanged clinoptilolites have been reported in the literature, for instance: $Pb^{2+} > Cd^{2+} > Cs^{+} > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$ (15), $Pb^{2+} > Cd^{2+} > Sr^{2+} > Cs^{+} > Ni^{2+}$ (16), $Ag^{+} > Pb^{2+} > Cd^{2+} > Zn^{2+} \geq Cu^{2+} >> Ni^{2+} > Hg^{2+}$ (17), $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+} > Ni^{2+}$ (4) and $Pb^{2+} > Na^{+} > Cd^{2+} > Cu^{2+} \cong Zn^{2+}$ (18).

Determination of the sorption equilibrium is fundamental in the evaluation of the potential of the given adsorbent, and together with the kinetics and dynamics of sorption provides the necessary information for design of the adsorptive/ion-exchange units. The Langmuir and Freundlich isotherm, although based on theoretical hypotheses that are hardly satisfied even for the ideal systems, have been successfully applied in the description of heavy metal ion sorption on zeolites (13,14,19–22). Recently, the thermodynamic equilibrium models have been used to describe the heavy metal ion exchange equilibrium on the sodium form of clinoptilolite (10,18,23–25). The comparison of the thermodynamic models and Langmuir model have shown that both isotherms fit the experimental equilibrium data reasonably well, nevertheless the Langmuir isotherm is much easier to apply from the mathematical calculations point of view (24,25).

The pollution of surface water with heavy metals, caused mainly by mining and heavy metal processing industry, is a serious problem in the Republic of Macedonia. The inexistence of heavy metals polluted wastewater treatment plants and the need of low-cost treatment process is one of the country's priority environmental protection issues. The investigation of the potential of clinoptilolitic tuff, a low-cost, regionally available adsorbent, is the main goal of this work. Unlikely synthetic zeolites where the adsorption capacity for a given sorbent is quite universal, the clinoptilolite samples from different regions have shown a variety of heavy metal removal capacity, even under very similar experimental conditions (see Table 1). Therefore, the determination of the heavy metal adsorption equilibrium on each particular type of clinoptilolite containing zeolite is required for the evaluation of its potential in wastewater treatment. Regardless of the considerable research conducted to determine the chemical, surface, and ion-exchange properties, the practical application of natural zeolites to water treatment technology is still limited.

The objective of present work is to study the adsorption equilibrium of Pb^{2+}, Zn^{2+}, and Cd^{2+} on clinoptilolite from the Western Balkan

Region, regarding its application as a potential low-cost alternative to the commercial granulated activated carbon produced in the same region. The influence of the pH on the metal ion removal capacity and mechanism of sorption was studied. The thermodynamics of adsorption was evaluated from the adsorption equilibrium experiments carried out at three different temperatures.

MATERIALS AND METHODS

Chemicals

The Pb^{2+}, Zn^{2+}, and Cd^{2+} ion water solutions were prepared by dissolving the respective amount of analytical grade metal nitrate salts, $Pb(NO_3)_2$ (Merck-Germany), $Zn(NO_3)_2 \cdot 6H_2O$ (Fluka, Germany) and $Cd(NO_3)_2 \cdot 4H_2O$ (Fluka, Germany), respectively, in distilled water. The NO^{3-} anions do not influence the ion-exchange process, since they do not form any metal-anion complexes and do not hydrolyze in water solution (26). The initial metal ion concentration used in the adsorption equilibrium experiments was in the range between 10 mg/l and 500 mg/l.

Sorbent Materials

Clinoptilolite containing natural zeolite (ZEO) and commercial granulated activated carbon (GAC) were used as sorbent materials. Clioptilolitic zeolite tuff was supplied from the Vranjska Banja (Serbia) sedimentary deposit. The granulated activated carbon *K-81/B*, supplied from TRAYAL Corporation (Serbia), is a carbonized coconut shell activated by water steam, applied mainly in the filtering system for water treatment.

The adsorbents were characterized by: X-ray diffraction (XRD) using Philips X'pert X-ray diffractometer, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) using Philips XL 30 CP Scanning Electron Microscopes, and Fourier transform infrared spectroscopy (FTIR) techniques using Nicolet Impact 400 FTIR spectrometer. The ZEO specific surface area, total pore volume, and real density were measured using the multy-point-N2-BET method, using Quantachrome NovaWin2 system. The particle density was determined using Hg picnometry analysis.

According to the supplier of the zeolite tuff, the ZEO consists mainly of clinoptilolite (more than 80%), heulandite, and mordenite, also quartz, sanidine, and biotite are present in very small quantities. The XRD diffraction pattern of natural zeolite is presented in Fig. 1. XRD peaks

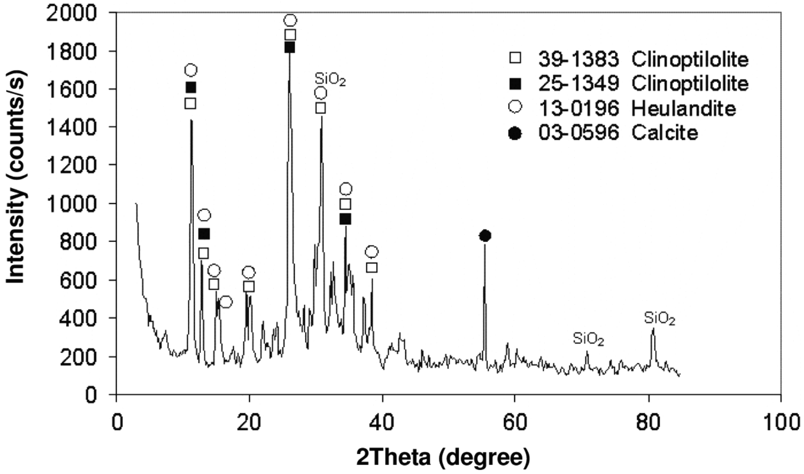
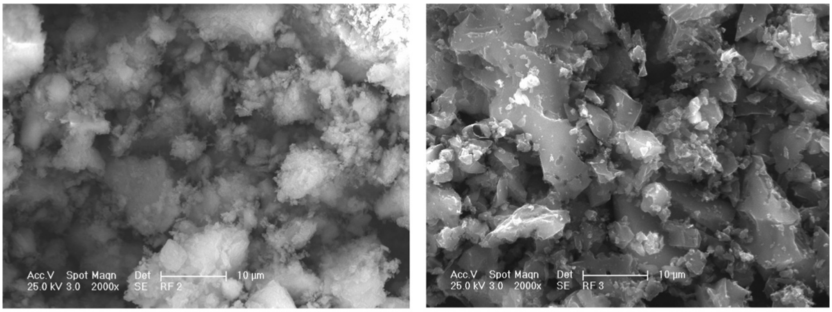


Figure 1. XRD spectrum of natural zeolite (ZEO).

of the sample were found to be in good agreement with the diffraction patterns of clinoptilolite, although some extra peaks corresponding to heulandite were also observed. In addition to the zeolitic phase, quartz and calcite were detected in the X-ray diffraction pattern. The natural zeolite (ZEO) chemical composition in weight percentage (wt%) is: 64.88 SiO_2, 12.99 Al_2O_3, 2.00 Fe_2O_3, 0.37 TiO_2, 3.26 CaO, 1.07 MgO, 0.95 Na_2O, 0.89 K_2O, and 13.59 loss of ignition. According to the chemical analysis, the total (or maximum) exchange capacity of ZEO is 2.19 meq/g, calculated as the sum of Mg, Ca, K, and Na cations. The Si(mol)/Al(mol) ratio is 4.23. In the SEM image of ZEO (Fig. 2a) typical crystals of clinoptilolite–heulandite family of zeolite were observed. The FTIR spectrum of ZEO is presented in Fig. 3a. The spectrum was measured in the range 400–4000 cm^{-1}, using a transmission technique on the germanium window, with resolution 2 cm^{-1}. IR spectrum of the natural zeolite confirms the high silica content, found by EDX analysis. Major peaks 1075–1207 cm^{-1} are attributed to the asymmetric stretching vibration of silicon – oxygen bond in the [SiO_4] tetrahedral network. Lower content of alumina in the natural zeolite is visible at weak bands 700–900 cm^{-1} (condensed AlO_4 tetrahedra) and 650–800 cm^{-1} (isolated AlO_4 tetrahedra). These regions are characteristic for stretching vibrations of the aluminum-oxygen bond in the AlO_4 tetrahedral structure (27). Intense band at 458 cm^{-1} is assigned to the rocking vibration of Si-O-Si (major contribution) and bending vibration of the Al-O-Si and Al-O-Al bonds (28). Broad band 594 cm^{-1} should be attributed to a



(a) (b)

Figure 2. SEM images of (a) natural zeolite (clinoptilolite) and (b) granulated activated carbon.

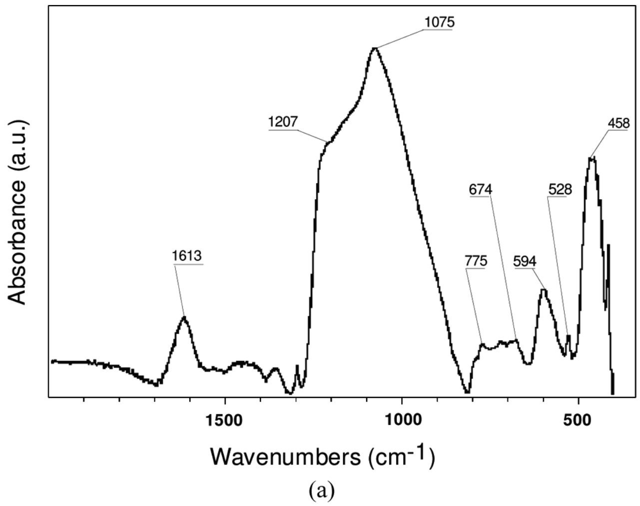
stretching vibration of the Al-O-Si bonds. The physical properties of natural zeolite are presented in Table 2.

The granulated activated carbon (GAC) X-ray diffraction pattern (not provided in the manuscript) did not show any peak, thereby indicating the amorphous nature of the material. The GAC SEM image is presented in Fig. 2b. The GAC element composition, calculated from the EDX spectra, in wt% is: 87.67 C, 11.31 O, 0.25 Si, 0.09 S, 0.41 K, and 0.28 Ca. The IR spectrum of GAC is presented in Fig. 3b. Spectrum was measured in the range 650–4000 cm^{-1} by ATR technique using ZnSe crystal, with resolution 2 cm^{-1}. The GAC have shown a very weak $C = C$ stretching bands 1573 cm^{-1} from graphite like carbon. Other broad and weak band 1071 cm^{-1} is typical for C-O and C-O-C valence bands. These bonds are result of water treatment of activated carbon. No surface water was observed. The GAC physical properties are presented in Table 2.

Prior to the experiments the ZEO was washed with distilled water in order to remove the surface dust and possible impurities and dried at 350°C for 48 h. The granulated activated carbon (GAC) was washed a few times with distilled water and dried at 120°C for 24 h. After the treatment both materials were stored in well closed glass bottles.

Determination of the Influence of pH

For the determination of the influence of the pH on the clinoptilolite (ZEO) and activated carbon (GAC) metal ion removal capacities, water solutions with given metal ion concentration were prepared at different pH values in the range between 2 and 6 (and 7 for Zn). The initial pH of the solutions was adjusted by addition of 0.01 M and 0.1 M HNO_3 and 0.01 M NaOH solutions and measured using pH Meter (PB-11,



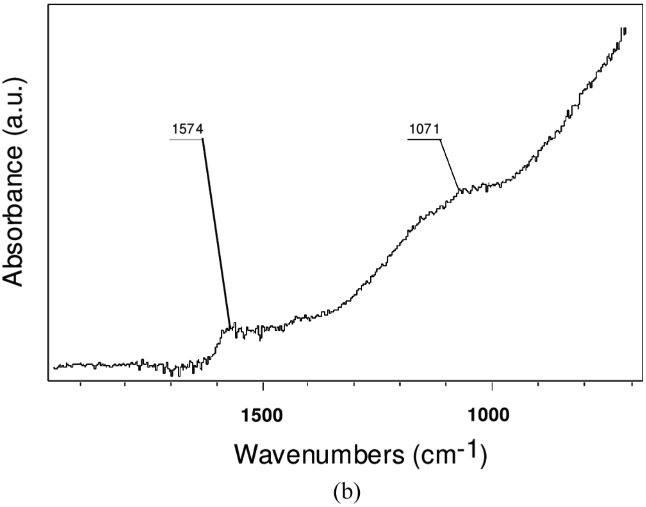


Figure 3. IR spectrum of (a) natural zeolite (clinoptilolite) and (b) granulated activated carbon.

Saratorius, Germany). 100 ml of the prepared solutions and 1 g of adsorbent were placed in 250 ml Erlenmeyer flask and shaken in rotary shaker at 25°C until the establishment of equilibrium (3 days in case of GAC and 4 days in case of ZEO). After the equilibrium has been established, the mixture was separated by filtration, and the filtrate was analyzed using an ARL 3520 atomic absorption spectrophotometer (ARL, Ecublens, Switzerland) and the pH of the filtrate was measured.

Table 2. Physical properties of natural zeolite (ZEO) and granulated activated carbon (GAC)

Property	Natural zeolite	Granulated activated carbon
Particle size (mm)	1–2	0.5–1.6
Particle density (g/cm^3)	1.425	
Real density (g/cm^3)	2.246	
Bulk density (g/cm^3)	0.70–0.75	0.44–0.48
BET area m^2/g	17.83	1200
Pore volume (cm^3/g)	0.01597*	0.8–1.0
Micropore volume (cm^3/g)		0.45–0.50
CEC (meq/g)	2.19	
Hardness (Moss scale)	3–3.5	
Ballpan hardness (%)	96–98	
Iodine number AWWA (mg/g)		1150–1250
Ash content (%)		3–5

*pores smaller than 269.8A.

Equilibrium of Adsorption

The equilibrium of adsorption of Zn^{2+}, Cd^{2+} and Pb^{2+} on ZEO and GAC was determined at 25, 35, and 45°C. Adsorption equilibrium experiments were performed in batch mode. The pH of the solution was not adjusted. 100 ml of solution with selected metal ion concentration (10–500 mg/l) and mass of adsorbent (1–4 g) were placed in 250 ml Erlenmeyer flask and shaken for a predefined time period required for the attainment of equilibrium (3 days for GAC and 4 days for ZEO) in vertical rotary shaker (150 turns/min) at constant temperature.

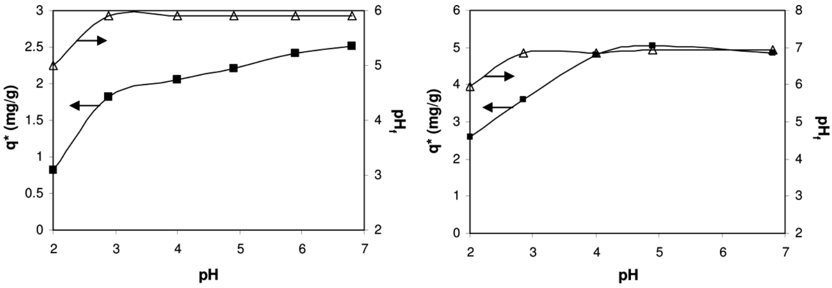
After reaching equilibrium the solid-liquid suspension was filtrated and the pH of the filtrate were than measured. The filtrates were than acidified with HNO_3 to decrease the pH below 3, before Atomic Adsorption Spectrometry (AAS) measurements.

RESULTS AND DISCUSSION

Influence of pH

The pH of the metal ion water solution is an important controlling parameter in the sorption process. The pH of the solution affects:

1. the adsorbent capacity, the metal removal typically increases with increase of pH; and



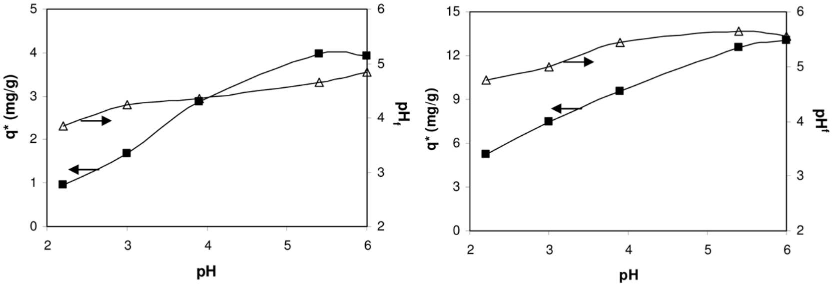
(a) (b)

Figure 4. Influence of the pH of the initial solution on the Zn^{2+} uptake and final pH in the case: a) ZEO ($C_0 = 47.0\,mg/dm^3$) and b) GAC ($C_0 = 53.3\,mg/dm^3$).

2. the mechanism of metal ions binding, by changing it from ion exchange and/or adsorption at acidic region to adsorption and/or complexation and possible precipitation at the basic region.

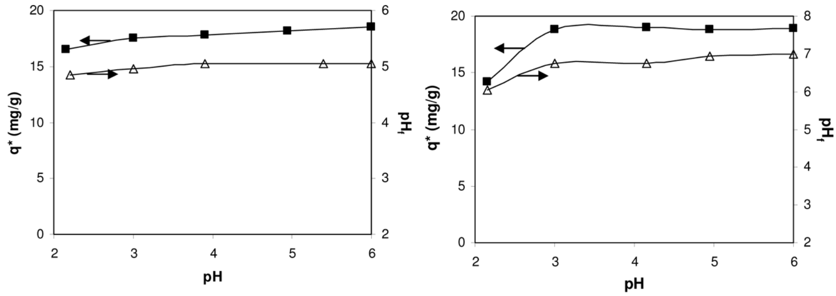
The Zn^{2+}, Cd^{2+} and Pb^{2+} uptake by ZEO and GAC as a function of pH value of the initial solution is presented in Fig. 4, Fig. 5, and Fig. 6, respectively. The change of the final pH (pH at equilibrium) as a function of initial pH is also presented in the same figures.

The metal sorption by natural zeolite (ZEO) increases with increase of the initial pH value of the aqueous solution from 2 to 6 (and 7 for Zn). This increase of the metal uptake is more pronounced in the case of Cd^{2+} and Zn^{2+} and less significant in the case of Pb^{2+}. The final pH increases in the region of the initial pH values between 2 and 4 for Cd^{2+} and Pb^{2+}, and between 2 and 5 for Zn^{2+}, during their sorption on ZEO. On the other hand, a slight decrease of the final pH has been



(a) (b)

Figure 5. Influence of the pH of the initial solution on the Cd^{2+} uptake and final pH in the case: a) ZEO ($C_0 = 118.3\,mg/dm^3$) and b) GAC ($C_0 = 135.2\,mg/dm^3$).



(a) (b)

Figure 6. Influence of the pH of the initial solution on the Pb^{2+} uptake and final pH in the case: a) ZEO ($C_0 = 189.7\,mg/dm^3$) and b) GAC ($C_0 = 190.7\,mg/dm^3$).

observed in the region of higher initial pH values, namely $pH > 5$ in the case of Cd^{2+} and Pb^{2+} and $pH > 6$ in the case of Zn^{2+}.

In the case of granulated activated carbon (GAC) the adsorbed quantity of Cd^{2+} increases significantly with increase of pH from 2 to 5, and less significantly between pH 5 and 6. Increase of the adsorption of $Pb^{2+}$and Zn^{2+} was observed until pH 3 and 4, respectively, above these values of pH the adsorbed quantity remains almost unchanged. For all metal ions the final pH is higher or equal to the initial pH in the entire studied pH range.

Similar results concerning the influence of the pH of the metal solutions on its removal by clinoptilolite and granulated activated carbon have been reported in the literature (21,29–33). The pH may affect the ionization degree of the sorbate and the surface property of the sorbent.

The formation of aquametal and hydroxo-complexes species of given metal ion depends on the pH value of the solution and the metal ion concentration. Depending on the pH level of the metal ion aqueous solution the total concentration of the metal ion in the solution is the sum of the concentration of the metal ion (X^{2+}) and present metal-hydroxy species (34):

$$\begin{aligned}[X]_{total} = {} & [X^{2+}] + [X(OH)^{+}] + [X(OH)_2^0] + [X(OH)_3^-] + [X(OH)_4^{2-}] \\ & + [X_2(OH)_3^+] + [X_3(OH)_4^{2+}] + [X_4(OH)_4^{4+}] + [X_6(OH)_8^{4+}] \\ & + [X(OH)_2(s)] \qquad (1)\end{aligned}$$

The speciation of a metal has a significant impact on the adsorbent removal efficiency and can influence the mechanism of metal ion binding. The metal ion adsorbent selectivity is also influenced by the character of the metal complex that predominates at a particular solution pH (29).

The interaction of the zeolite with hydrogen and hydroxyl ions from the water solution lead to hydrolysis of the Al-O-Si bonds and dissolution of the zeolite surface layers (35). The surface charge remaining after the detachment of framework bonds is nonhomogeneously distributed and represents active sites suitable for positive metal ionic species binding. The ionization of surface hydroxyl groups (Si-OH and Al-OH) depends on pH, (14) namely:

in acidic solution

$$>Al - OH + H^+ => AlOH_2^+ \tag{2}$$

$$>Si - OH + H^+ => SiOH_2^+ \tag{3}$$

in alkaline solution:

$$>Al - OH + OH^- => Al - OH(OH)^- => AlO^- + H_2O \tag{4}$$

$$>Si - OH + OH^- => Si - OH(OH)^- => SiO^- + H_2O \tag{5}$$

The zeolites are not only influenced by the solution pH, but they also affect the solution pH (especially in the batch system). In addition, zeolites tend to have a higher internal pH (35).

The adsorption behavior of zeolitic minerals is based on the Brønsted and Lewis theory of acidic and basic sites existing in the microporous structure (14).

In general the zeolites are weakly acidic in nature. The clinoptilolite has a negative surface charge (19,36) even at vary acidic conditions, due to:

1. the isomorphous Si^{4+}/Al^{3+} substitution,
2. the oxygen atom in the Si–O–Al species which represents the structural basic site and bears a negative charge to the lattice,
3. the broken Si-O-Si bonds at the particle surface result of the grinding process and
4. the lattice imperfections (37,38).

The governing mechanism of heavy metals removal in acidic conditions is the ion-exchange. During the ion exchange process, cations from the zeolite structure enter the solution and metal ion from the solution bind to the zeolite:

$$mX^{2+}_{(aq)} + 2M^{m+}_{(z)} \leftrightarrow mX^{2+}_{(z)} + 2M^{m+}_{(aq)} \tag{6}$$

where m is the valence of exchangeable cations M (Na, K, Ca, Mg), X is the metal ion, and the subscripts (aq) and (z) refer to solution and zeolite phases, respectively.

In very acidic conditions (pH < 3), the competitive exchange of H^+ with the exchangeable cations present in the zeolite framework is the main reason for lower retention of Zn^{2+}, Cd^{2+} and Pb^{2+} on ZEO (see Figs. 4a, 5a, and 6a, respectively). On increasing the pH of metal ion water solution from 3, the metal ion removal increases and becomes almost unchanged in the pH range 4–6 in the case of Pb^{2+}, pH range 5.3–6 in the case of Cd^{2+}, and in the pH range 6–7 in the case of Zn^{2+}. The increase of the metal ion removal as pH increased can be explained on the basis of a decrease in competition between H^+ and metal ion for the ZEO exchangeable ions. The increase of the final pH in the acidic conditions during the Zn^{2+}, Cd^{2+}, and Pb^{2+} sorption on ZEO is a result of the solution neutralization due to the exchange of the H^+, the presence of OH^- in solution resulting from hydrolysis of some species present in natural zeolite, but could be mainly attributed to the protons binding to the Lewis basic sites linked to the oxygen atom of the clinoptilolite (14,19). The increase of the solution pH promotes the formation of particular metal hydroxyl species and the contribution of the adsorption in the metal removal mechanism. This will be discussed in detail in the section Equilibrium of Adsorption. The slight decrease of the final pH in the case of higher initial pH values, namely pH > 5 in the case of Cd^{2+} and Pb^{2+} and pH > 6 in the case of Zn^{2+}, could be attributed to metal-hydroxy species formation (19,39), release of proton from the surface Bronsted acid sites, or the removal of protons from the zeolitic water that coordinate the exchangeable cations (14).

The GAC is H type carbon with pH $= 9.5$–10.5, indicating the predominance of basic functional groups on its surface. This is characteristic of the carbons activated in steam (40). The zero point charge of different carbons is in interval between 4.75 and 7.10. At pH values lower than 3, there is excessive protonation of the carbon surface resulting in decrease in the adsorption of metal ions (see Figs. 4b, 5b, and 6b, respectively). The increase in metal ion removal as increased pH can be explained on the basis of a decrease in competition between H^+ and positively charged metal ion (Zn^{2+}, Cd^{2+}, or Pb^{2+}) at the surface sites, and by decrease in the positive charge of the carbon surface which results in a lower electrostatic repulsion of the adsorbing metal ion and consecutively increased metal ion removal. Similar to other carbons of H-type, in acidic region the final pH has increased due to the neutralization, as a consequence of H^+ ion adsorption characteristic for carbons of H type.

Adsorption Equilibrium

The equilibrium of adsorption of Zn^{2+}, Cd^{2+}, and Pb^{2+} on natural zeolite and granulated activated carbon was determined at 25, 35, and 45°C. The adsorption equilibrium isotherms of Zn^{2+}, Cd^{2+}, and Pb^{2+} on ZEO and GAC at different temperatures are presented in Fig. 7. The GAC has higher adsorption capacity for Zn^{2+} and Cd^{2+} than ZEO. Both adsorbents have shown similar adsorption capacity for Pb^{2+}. The order of metal ion adsorption capacity (in $mg/g_{adsorbent}$) on both adsorbents is $Pb^{2+} > Cd^{2+} > Zn^{2+}$. Same order of ZEO selectivity was determined also by Zamzow and Murphy (15) and Kesraoui-Ouki et al. (41).

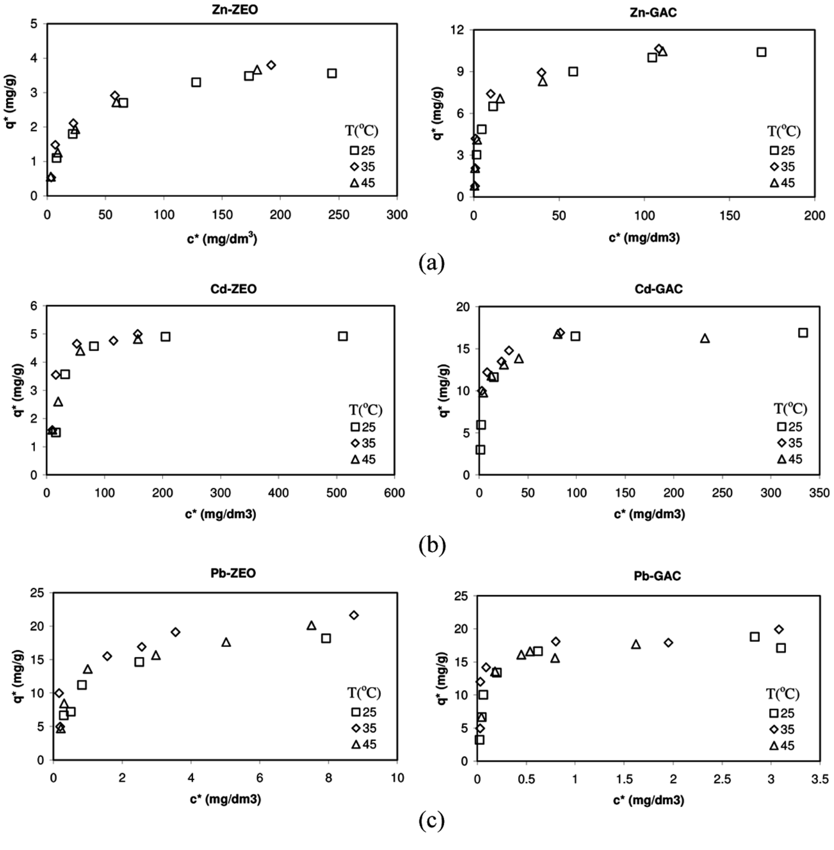


Figure 7. Metal ion adsorption equilibrium isotherms on natural zeolite (ZEO) and granulated activated carbon (GAC) at 25, 35 and 45°C: a) Zn^{2+}, b) Cd^{2+} and c) Pb^{2+}.

The experimental adsorption equilibrium data were described by Langmuir and Freundlich equations.

Langmuir Isotherm

$$q^* = \frac{Q_0 b c^*}{1 + b c^*} \tag{7}$$

where c^* (mg/dm^3) is the equilibrium concentration, q^* (mg/g) is the amount adsorbed at equilibrium, b (dm^3/mg) is the "affinity" parameter or the Langmuir constant, and Q_0 (mg/g) is the maximum adsorption capacities.

Freundlich Isotherm

$$q^* = K_F c^{*(1/n)} \tag{8}$$

where, c^* and q^* have the same definitions presented for the Langmuir isotherm. K_F and n are the constants that can be related to the adsorption capacity and the adsorption intensity, respectively.

The experimental adsorption equilibrium data of Pb^{2+}, Zn^{2+}, or Cd^{2+} adsorption on ZEO and GAC at different temperatures were correlated using the linear forms of the Langmuir and Freundlich isotherm, respectively:

$$\frac{c^*}{q^*} = \frac{1}{Q_0 b} + \frac{c^*}{Q_0} \tag{9}$$

$$\log(q^*) = \log(K_F) + \frac{1}{n}\log(c^*) \tag{10}$$

The Langmuir and Freundlich isotherm parameters for Zn^{2+}, Cd^{2+}, and Pb^{2+} adsorption on ZEO and GAC are presented in Table 3. The Langmuir isotherms fits better the experimental adsorption isotherms in all temperature ranges for all metals on ZEO and GAC. The adsorption capacity of both adsorbents increases insignificantly with the increase of the temperature. The Zn^{2+}, Cd^{2+}, and Pb^{2+} average maximum adsorption capacity on ZEO are: 4.07 mg/g, 5.35 mg/g, and 21.29 mg/g respectively. The Zn^{2+}, Cd^{2+}, and Pb^{2+} average maximum adsorption capacity on GAC are: 10.87 mg/g, 17.11 mg/g and 18.79 mg/g respectively.

The Zn^{2+}, Cd^{2+}, and Pb^{2+} adsorption capacities of different types of natural zeolites constituted mainly from clinoptilolite vary in a wide range (see Table 1). The ZEO adsorption capacity for Zn^{2+} obtained in this work is similar to that obtained by Oren and Kaya (21), Zamzow and Murphy (15), Alvarez-Ayuso et al., (22), and Athanasiadis and

Table 3. Langmuir and Freundlich isotherm parameters for Zn^{2+}, Cd^{2+}, and Pb^{2+} adsorption on natural zeolite (ZEO) and granulated activated carbon (GAC)

	Langmuir Isotherm			Freundlich isotherm		
T	b (dm^3/g)	Q^0 (mg/g)	R^2	K_F (mg/g)	n	R^2
			Zn-ZEO			
25	0.041	3.926	0.996	0.546	2.78	0.975
35	0.042	4.097	0.996	0.406	2.21	0.958
45	0.05	4.172	0.999	0.460	2.29	0.866
			Cd-ZEO			
25	0.05	5.157	0.997	0.962	3.38	0.669
35	0.054	5.435	0.997	0.795	2.62	0.892
45	0.069	5.459	0.991	1.037	3.00	0.722
			Pb-ZEO			
25	1.350	19.802	0.998	10.123	3.12	0.929
35	1.422	21.186	0.997	10.698	2.87	0.883
45	1.589	22.883	0.996	12.357	3.31	0.792
			Zn-GAC			
25	0.150	10.695	0.999	3.047	3.88	0.947
35	0.161	10.811	0.993	1.909	2.45	0.854
45	0.169	11.111	0.994	2.048	2.50	0.724
			Cd-GAC			
25	0.203	17.153	0.999	4.065	3.52	0.861
35	0.213	16.667	0.996	8.389	7.37	0.922
45	0.241	17.513	0.999	8.808	6.80	0.988
			Pb-GAC			
25	13.675	18.282	0.996	15.621	3.56	0.766
35	14.062	18.282	0.997	17.906	3.83	0.859
45	15.303	19.802	0.996	17.114	5.17	0.625

Helmreich (36). The Cd^{2+} adsorption capacity is similar to those determined by Sprynskyy et al., (20) and Alvarez-Ayuso et al., (22). The ZEO adsorption capacity for Pb^{2+} obtained in our study is similar just with the one obtained by Sprynskyy et al., (20). In the other studies the values are or much lower or much higher than 21.29 mg/g. The main reasons for different values of the metal ion clinoptilolite adsorption capacity available in the literature are: the origin of the natural zeolite (in terms of its mineralogical composition and quantity of clinoptilolite present in its composition), the initial metal ion concentration range, pH, and the mass of the adsorbent used in the adsorption equilibrium experiments.

In order to find a possible relation between Zn^{2+}, Cd^{2+}, and Pb^{2+} characteristic properties and adsorbents metal ion selectivity series

Table 4. Metal ion characteristic parameters

Metal	Ionic radius (pm)	Hydrated radius, (pm)	Electrongativity (Pauling)	Hydrolisis constant pK_{a1}	Solubility product constants pK_{sp}	Hydratation entalpy (KJ/mol)
Zn^{2+}	88[a]	430[c]	1.65[a]	9.0[a]	16.91[b]	−2044[a]
Cd^{2+}	109[a]	426[c]	1.69[a]	10.1[a]	13.6[b]	−1806[a]
Pb^{2+}	133[a]	401[c]	2.33[a]	7.7[a]	14.92[b]	−1480[a]

[a] 50.
[b] 51.
[c] 52.

$Pb^{2+} > Cd^{2+} > Zn^{2+}$ (on a mass basis) some metal ion characteristic parameters are presented in Table 4.

The conventional sorption theory on solid surfaces states that metals of higher electronegativity should adsorb more readily and the metals of higher hydrolysis constants have increased adsorptive capacity (42). The metal ions with larger ionic radius have a lower charge density and a lower electrostatic attraction that limits the interaction of the metal ions with the adsorption sites. The obtained selectivity series is in agreement with the metal ions electronegativity $Pb^{2+}(2.33) > Cd^{2+}(1.69) > Zn^{2+}(1.65)$.

The enthalpy of hydration of an ion is the amount of energy released when a mole of the ion dissolves in a large amount of water forming an infinite dilute solution; as the atomic number increases, so does the ionic size, leading to a decrease in absolute values of enthalpy of hydration. According to these parameters values, $Pb^{2+}{}_{aq}$ ions will have a greater accessibility to the adsorbent surface followed by $Cd^{2+}{}_{aq}$ and $Zn^{2+}{}_{aq}$, which would lead to the following order $Pb^{2+} > Cd^{2+} > Zn^{2+}$ (in mg/g) g) in the extent in the adsorption process. Hydration energy is an important parameter to take into account since the hydrolysis of metal ions occurs by the replacement of water ligands in the inner coordination sphere with hydroxo groups.

$$[M(H_2O)_n]^{z+} + H_2O \Leftrightarrow [M(H_2O)_{n-1}(OH)]^{(z-1)+} + H_3O^+ \qquad (11)$$

Adsorption may be related directly to the loss of the outer hydration spheres that precedes hydrolysis. It is often suggested that the tendency of metal cations to adsorb to oxide surfaces is highly correlated with their tendency to undergo hydrolysis reactions in solution. The distribution of various hydroxo-complexes depends on metal ion concentration, pH of the solution and the respective stability constants. Hydroxyl–metal complexes adsorb with a higher affinity than the completely hydrated metals because the formation of an OH^- group on the metal reduces the free energy requirement for adsorption. The pH at which the first hydrolysis product $M(OH)^+$ would appear in the solution depends on the value of the first hydrolysis constant pK_{a1}. The $M(OH)^+$ starts to appear at lower pH with decreasing of the first hydrolysis constant pK_{a1}.

From the first hydrolysis constant (pK_{a1}) and the pH of the metal ion solution measured in equilibrium (pH_f) the ratio of the metal ion (M^{2+}) and the metal hydroxid ($M(OH)^+$) concentration in equilibrium can be calculated. The hydrolysis reaction is:

$$M^{2+} + H_2O \leftrightarrow M(OH)^+ + H^+ \tag{12}$$

The equilibrium expression of this reaction is:

$$K_{a1} = \frac{\lfloor H^+ \rfloor \lfloor M(OH)^+ \rfloor}{M^{2+}} \tag{13}$$

from the values of the pH_f and fist hydrolysis constant pK_{a1} the ratio $[M(OH)^+]/M^{2+}]$ can be calculated.

The ratio $[M(OH)^+]/M^{2+}$ for each system adsorbat/adsorbent calculated using the highest measured pH_f values during the equilibrium experiments is presented in Table 5. In the case of zinc and cadmium the concentration of divalent metal ion is much higher than the concentration of $M(OH)^+$, which is not case the case of lead, where $Pb(OH)^+$ is present in significant concentration.

In published research works, metal hydroxide ($M(OH)_2$) precipitation contributed to obtainment of higher values of adsorption capacities. In these cases the degree of the insolubility of the metal hydroxides (expressed as the pK_{sp} of the corresponding metal hydroxide) approximately followed the order of the metal adsorption capacity.

The pH at which the metal ion start to precipitate (pH_{ppt}) in a form of metal hydroxides ($M(OH)_2$) at the adorbent surface or even in the

Table 5. $[M(OH)^+]/M^{2+}$ in equilibrium for different adsorbat-adsorbent systems

	pH_f	$[M(OH)^+]/M^{2+}$
Zn-ZEO	6.4	5011.9
Zn-GAC	7.1	1000.0
Cd-ZEO	5.4	3981.1
Cd-GAC	5.9	1258.9
Pb-ZEO	6.4	20.0
Pb-GAC	7	5.0

solution can be calculated from the solubility product constants (pK_{sp}):

$$pH_{ppt} = 14 - \log\sqrt{\frac{M^{2+}}{K_{sp}}} \tag{14}$$

The pH of the solution at which the precipitation starts occurring depends on the initial metal ion concentration. The pH_{ppt} values corresponding to the lowest ($c_0 = 10$ mg/l) and highest ($c_0 = 500$ mg/l) initial metal ion concentration used are: 7.5 and 6.6 for Zn^{2+}, 9.2 and 8.4 for Cd^{2+}, and 8.7 and 7.8 for Pb^{2+}, respectively. The pH values in equilibrium are almost equal or higher than the pH values of the initial metal ion solution for all studied metal ions. The comparison of the pH values in equilibrium (see Table 5) and pH of metal hydroxide formation shows that under used experimental conditions the formation of metal hydroxides $M(OH)^{2+}$ and their precipitation is not possible.

From the previous analysis we can conclude that the sorption mechanism of metal ions on ZEO is mostly ion-exchange in the case of Cd^{2+} and Zn^{2+} and ion-exchange and adsorption of $Pb(OH)^{+}$ in the case of lead. This conclusion also explains the much higher ZEO selectivity for lead, than for cadmium, and zinc. On other hand the discrepancy in the order of Cd^{2+} and Zn^{2+} adsorption capacities and first hydrolysis constant (see Table 4) is irrelevant, since $Cd(OH)^{+}$ and $Zn(OH)^{+}$ are almost not present in the water solution under the used experimental condition (initial concentration and pH) used in this research. The zinc, cadmium, and lead removal from water solution by GAC is by adsorption of M^{2+} and $M(OH)^{+}$. The quantity of first hydrolysis product present in the water solution under the used experimental conditions is much higher in the case of lead than in the case of zinc and cadmium.

THERMODYNAMICS OF ADSORPTION

The cadmium, lead, and zinc sorption capacity on ZEO and GAC increased slightly with increasing temperature, indicating the endothermic nature of the sorption process was in. Thermodynamic parameters such as standard Gibbs free energy (ΔG^0), standard enthalpy change (ΔH^0), and entropy change (ΔS^0) were calculated from following thermodynamic relations, using the results of adsorption equilibrium study:

$$\Delta G^0 = -RT\ln(b) \tag{15}$$

$$\ln(b) = \ln(b_0) - \frac{\Delta H^o}{RT} \tag{16}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{17}$$

where, b (dm^3/mol) is the Langmuir constant, b_o is a constant, R is the ideal gas constant (R = 8.31433 J/molK), and T is the temperature (K).

Calculated values of thermodynamic parameters of Zn^{2+}, Cd^{2+} and Pb^{2+} adsorption on ZEO and GAC are presented in Table 6. The positive values of the standard enthalpy change indicate that the adsorptions on both adsorbents is an endothermic phenomenon. The negative Gibbs' free energy values indicate the feasibility and spontaneous nature of adsorption of metal ions on the adsorbent. The increase in free energy change with the rise in temperature shows an increase in feasibility of adsorption at higher temperatures. The positive values of entropy show the increased randomness at the solid/solution interface during the adsorption process and metal ions adsorbents affinity.

COMPARISON OF NATURAL ZEOLITE AND ACTIVATED CARBON HEAVY METAL REMOVAL PERFORMANCES

The adsorptive removal of heavy metals is usually performed in a fixed bed system. The design of this system is based on the data for the adsorbent physical properties, adsorption equilibrium, kinetics, and dynamic parameters. The cost of the process is a sum of the capital and operational costs. In this stage of our research, just a preliminary economical evaluation of the natural zeolite heavy metal removal potential can be made based on the adsorbent price and its maximum sorption capacity. The potential of the natural zeolite was assessed by comparison of the cost for removal of given quantity of metal ion by activated carbon and natural zeolite:

$$r_i = \frac{Q0_{i(ZEO)}}{Q0_{i(GAC)}} \frac{P_{GAC}}{P_{ZEO}} \tag{18}$$

where r is the ratio of the cost of activated carbon and zeolite required for the removal of the same amount of metal ion i, P_{GAC} and P_{ZEO} are the prices of 1 kg GAC and ZEO, respectively. Taking into consideration the maximum adsorption capacity of natural zeolite and activated carbon at 25°C presented in Table 3 and the price of one kilogram adsorbent $P_{GAC} = 6.8$ EUR/kg and $P_{ZEO} = 0.08$ EUR/kg the following r_i values have been calculated: $r_{Zn} = 41.6$, $r_{Cd} = 34.1$ and $r_{Pb} = 112.8$.

These parameters are only preliminary indicators for the economical viability of natural zeolite. It is clear that for the treatment of the same capacity of heavy metal containing effluent a larger column will be

Table 6. Thermodynamic parameters ($\Delta G^0, \Delta S^0$, and ΔH^0) of Zn^{2+}, Cd^{2+}, and Pb^{2+} adsorption on natural zeolite (ZEO) and granulated activated carbon (GAC)

	ZEO			GAC		
T (°C)	−ΔG (KJ/mol)	ΔS (KJ/mol K)	ΔH (KJ/mol)	−ΔG (KJ/mol)	ΔS (KJ/mol K)	ΔH (KJ/mol)
Zn^{2+}						
25	19.57	0.0917	7.76	22.78	0.0922	4.71
35	20.28	0.0910		23.72	0.0923	
45	21.40	0.0917		24.63	0.0922	
Cd^{2+}						
25	21.40	0.1141	12.62	24.88	0.1060	6.73
35	22.32	0.134		25.83	0.1057	
45	23.69	0.1141		27.00	0.1060	
Pb^{2+}						
25	13.97	0.0683	6.40	19.70	0.0809	4.40
35	14.57	0.0680		20.44	0.0806	
45	15.33	0.0683		21.32	0.0809	

required in the case of ZEO than in the case of GAC. Anyhow, the dimensions of the fixed bed column would not be considerably larger due to the higher bulk density of ZEO than GAC (see Table 2). The bigger fixed bed unit brings a higher cost of the fixed bed column, but will not significantly influence the cost of ancillary equipment and pump lines. The cost of the adsorbent required to fill the fixed bed column is considerably lower for the case of ZEO than for the case of GAC, beside the larger unit needed when zeolite is used as adsorbent. No significant difference is expected in the operational costs, which is not the case of cost needed for adsorbent regeneration or substitution. As mentioned previously, the metal saturated zeolites could be used as additives to cement and similar materials and in water disinfection.

CONCLUSIONS

The efficiency of regional low-cost natural clinoptilolite containing zeolite tuff (ZEO) in heavy metal ions removal from aqueous solution have been evaluated through a comparative adsorption equilibrium study with commercial granulated activated carbon (GAC), from the same region. The zinc, lead, and cadmium adsorption equilibrium was determined in batch mode at three different temperatures, 25, 35, and 45°C, without the adjustment of metal ion water solution pH. The Langmuir model gives a better description of the metal ion adsorption isotherm experimental data on natural zeolite and activated carbon than the Freundlich model. The same metal ion selectivity series, $Pb^{2+} > Cd^{2+} > Zn^{2+}$ (on a mass basis) is characteristic for studied adsorbents. The granulated activated carbon has around three times higher adsorption capacity for Cd^{2+} and Zn^{2+} than natural zeolite, and almost the same adsorption capacity for Pb^{2+} was obtained on both adsorbents. The calculated thermodynamic parameters indicate feasible and spontaneous endothermic adsorption of metal ions on the natural zeolite and granulated activated carbon. The study of the effect of the pH of the metal ion aqueous solution has shown increase of metal ion uptake with increase of the pH. The sorption mechanism of Cd^{2+}, Pb^{2+}, and Zn^{2+} on natural zeolite changes from metal ion-exchange to ion-exchange/adsorption of metal-hidroxide with increase of the solution acidity from 2 to 6 (and 7 for Zn^{2+}). According to the preliminary cost calculation, in view of the price of the adsorbents and their maximum adsorption capacity, the natural zeolite could be used as a low-cost alternative to the granulated activated carbon in the treatment of heavy metals containing wastewater.

NOTATION

b	Langmuir constant (dm^3/mg)
c^*	equilibrium concentration (mg/dm^3)
K_F	Freundlich isotherm constant (mg/g)
n	Freundlich isotherm constant
pH_f	pH of the metal ion solution in equilibrium (final pH)
$\mathrm{pK}_{\mathrm{sp}}$	solubility product constants
pK_{a1}	fist hydrolysis constant
pH_{ppt}	pH at which the metal ion start to precipitate in a form of metal hydroxide
R	ideal gas constant (J/molK)
T	the temperature (K)
q^*	amount adsorbed at equilibrium (mg/g)
Q_0	maximum adsorption capacity (mg/g)
ΔG^0	Gibbs free energy (KJ/mol)
ΔH^0	standard enthalpy change (KJ/mol)
ΔS^0	standard entropy change (KJ/mol K)

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REFERENCES

1. Heavy metals. 2007 (http://www.lenntech.com/topics/heavy-metals.htm).
2. Patterson, J.W. (1989) Industrial wastes reduction. *Environ. Sci. Technol.*, *23* (9): 1032.
3. Chuah, T.G., Jumasiah, A., Azni, I., Katayon, S., Thomas Choong, S.Y. (2005) Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: An overview. *Desalination*, *175* (3): 305.
4. Kesraoui-Ouki, S., Cheeseman, C.R., Perry, R. (1994) Natural zeolite utilization in pollution control: A review of applications to metals' effluents. *J. Chem. Technol. Biotechnol.*, *59* (2): 121.
5. Kurniawan, T.A., Chan, G.Y.S., Lo, W.-h., Babel, S. (2006) Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Sci. Total Environ.*, *366* (2–3): 409.
6. Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D. (1999) A review of potentially low-cost sorbents for heavy metals. *Wat. Res.*, *33* (11): 2469.

7. Hafez, M.B., Nazmy, A.F., Salem, F., Eldesoki, M. (1978) Fixation mechanism between zeolite and some radioactive elements. *J. Radioanal. Chem.*, *47*: 115.
8. Altin, O., Ozbelge, H.O., Dogu, T. (1998) Use of general purpose adsorption isotherms for heavy metal-clay mineral interactions. *J. Coll. Interf. Sci.*, *198* (1): 130.
9. Cioffi, R., Maffucci, L., Martone, G., Santoro, L. (1998) Feasibility of manufacturing building materials by recycling a waste from ion exchange process. *Environ. Technol.*, *19* (11): 1145.
10. Top, A., Ulku, S. (2004) Silver, zinc, and copper exchange in a Na-clinoptilolite and resulting effect on antibacterial activity. *Appl. Clay Sci.*, *27* (1–2): 13.
11. Mumpton, F.A. (2000) Natural Zeolites: Where Have We Been? Where Are We Going? In: *Natural Zeolites for the Third Millenium*, Colella, C.; Mumpton, F.A., eds.; De Frede Editore: Napoli, 9.
12. Gottardi, G.; Galli, E. (1985) *Natural Zeolites*; Springer-Verlag: Berlin.
13. Erdem, E., Karapinar, N., Donat, R. (2004) The removal of heavy metal cations by natural zeolites. *J. Coll. Interf. Sci.*, *280* (2): 309.
14. Trgo, M., Peric, J. (2003) Interaction of the zeolitic tuff with Zn-containing simulated pollutant solutions. *J. Coll. Interf. Sci.*, *260* (1): 166.
15. Zamzow, M.J., Murphy, J.E. (1992) Removal of metal cations from water using zeolites. *Separation Science and Technology*, *27* (14): 1969.
16. Faghihian, H., Ghannadi Marageh, M., Kazemian, H. (1999) The use of clinoptilolite and its sodium form for removal of radioactive cesium, and strontium from nuclear wastewater and Pb^{2+}, Ni^{2+}, Cd^{2+}, Ba^{2+} from municipal wastewater. *Appl. Radiation and Isotopes*, *50* (4): 655.
17. Mondale, K.D., Carland, R.M., Aplan, F.F. (1995) The comparative ion exchange capacities of natural sedimentary and synthetic zeolites. *Minerals Eng.*, *8* (4–5): 535.
18. Langella, A., Pansini, M., Cappelletti, P., Gerraro, B., Gennaro, M., Collela, C. (2000) NH^{4+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} exchange for Na^{+} in a sedimentary clinoptilolite, North Sardinia, Italy. *Microporous Mesoporous Mater*, *37* (3): 337.
19. Kurtoglu, A.E., Atun, G. (2006) Determination of kinetics and equilibrium of Pb/Na exchange on clinoptilolite. *Sep. Purif. Tech.*, *50* (1): 62.
20. Sprynskyy, M., Buszewski, B., Terzyk, A.P., Namiesnik, J. (2006) Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite. *J. Coll. Interf. Sci.*, *304* (1): 21.
21. Oren, A.H., Kaya, A. (2006) Factors affecting adsorption characteristics of Zn^{2+} on two natural zeolites. *J. Haz. Mater.*, *131* (1–3): 59.
22. Alvarez-Ayuso, E., Garcia-Sanchez, A., Querol, X. (2003). Purification of metal electroplating waste waters using zeolites. *Wat. Res.*, *37* (20): 4855.
23. Culfaz, M., Yagız, M. (2004). Ion exchange properties of natural clinoptilolite: lead–sodium and cadmium–sodium equilibria. *Sep. Purif. Tech.*, *37* (2): 93.
24. Berber-Mendoza, M.S., Leyva-Ramos, R., Alonso-Davila, P., Fuentes-Rubio, L., Guerrero-Coronado, R.M. (2006) Comparison of isotherms for

the ion exchange of Pb(II) from aqueous solution onto homoionic clinoptilolite. *J. Coll. Interf. Sci.*, *301* (1): 40.

25. Petrus, R., Warchol, J. (2003) Ion exchange equilibria between clinoptilolite and aqueous solutions of Na^+/Cu^{2+}, Na^+/Cd^{2+} and Na^+/Pb^{2+}. *Microp. Mesop. Mater.*, *61* (1–3): 137.
26. Peric, J., Trgo, M., Vukojevic Medvidovic, N. (2004) Removal of zinc, copper and lead by natural zeolite–a comparison of adsorption isotherms. *Wat. Res.*, *38* (7): 1893.
27. Tartre, P. (1967) Infra-red spectra of inorganic aluminates and characteristic vibrational frequencies of AlO_4 tetrahedra and AlO_6 octahedra. *Spectrochimica Acta A*, *23* (7): 2127.
28. Huang, C., Behrman, E.C. (1991) Structure and properties of calcium aluminosilicate glasses. *J. Non-Cryst. Solids*, *128* (3): 310.
29. Kesraoui-Ouki, S., Kavannagh, M. (1997) Performance of Natural Zeolites for the Treatment of Mixed Metal-contaminated effluents. *Waste Manag. Res.*, *15* (4): 383.
30. Cabrera, C., Gabaldon, C., Marzal, P. (2005) Sorption characteristics of heavy metal ions by a natural zeolite. *J. Chem. Technol. Biotechnol.*, *80* (4): 477.
31. Mohan, D., Singh, K.P. (2001) Single-and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse–an agricultural waste. *Wat. Res.*, *36* (9): 2304.
32. Chen, J.P., Lin, M. (2001) Equlibrium and kinetics pf metal ion adsorption onto a commercial H-type granular activated carbon: Experimntal and modeling studies. *Water Research*, *35* (10): 2385.
33. Budinova, T.K., Gergova, K.M., Petrov, N.V., Minkova, V.N. (1994) Removal of metal ions from aqueous solution by activated carbon obtained from different raw materials. *J. Chem. Tech. Biotechnol.*, *60* (2): 177.
34. Sun, Z.X., Skold, R.O. (2001) A multi-parameter titration method for the determination of formation ph for metal hydroxides. *Minerals Engineering*, *14* (11): 1429.
35. Hui, K.S., Chao, C.Y.H., Kot, S.C. (2005). Removal of mixed heavy metal ions in wastewater by zeolite 4 A and residual products from recycled coal fly ash. *J. Haz. Mater.*, *127* (1–3): 89.
36. Athanasiadis, K., Helmreich, B. (2005) Influence of chemical conditioning on the ion exchange capacity and on kinetic of zinc uptake by clinoptilolite. *Wat. Res.*, *39* (8): 1527.
37. Breck, D.W. (1974) *Zeolite Molecular Sieves*; Wiley: New York.
38. Van Hooff, J.H.C.; Roolefson, J.W. (1991) *Introduction to Zeolite Science and Practice: Technics of Zeolite Characterization, Studies in Surface Science and Catalysis*; Elsevier: Amsterdam.
39. Inglezakis, V.J., Loizidou, M.D., Grigoropoulou, H.P. (2003) Ion exchange of Pb^{2+}, Cu^{2+}, Fe^{3+}, and Cr^{3+} on natural clinoptilolite: Selectivity determination and influence of acidity on metal uptake. *J. Coll. Interf. Sci.*, *261* (1): 49.
40. Budinova, T.K., Gergova, K.M., V., P.N., N., M.V. (1994) Removal of metal ions from aqueous solution by activated carbon obtained from different raw materials. *J. Chem. Tech. Biotechnol.*, *60* (2): 177.

41. Kesraoui-Ouki, S., Cheeseman, C., Perry, R. (1993) Effects of conditioning and treatment of chabazite and clinoptilolite prior to lead and cadmium removal. *Environ. Sci. Technol.*, *27*: 1108.
42. McBride, M.B. (1994) *Chemisorption and Precipitation of Inorganic Ions., in Environmental Chemistry of Soils*. Oxford University Press: New York.
43. Leppert, D. (1990) Heavy metal sorption with clinoptilolite zeolite: Alternatives for treating contaminated soil and water. *Mining Eng.*, *42* (6): 604.
44. Malliou, E., Loizidou, M.D., Spyrellis, N. (1994) Uptake of lead and cadmium by clinoptilolite. *Sci. Total Environ.*, *149* (3): 139.
45. Sheta, A.S., Falatah, A.M., Al-Sewailem, M.S., Khaled, E.M., Sallam, A.S.H. (2003) Sorption characteristics of zinc and iron by natural zeolite and bentonite. *Microp. Mesop. Mater.*, *61* (1–3): 127.
46. Trgo, M., Peric, J., Medvidovic, N.V. (2006) A comparative study of ion exchange kinetics in zinc/lead–modified zeolite-clinoptilolite systems. *J. Haz. Mater.*, *136* (3): 938.
47. Vasylechko, V.O., Gryshchouk, G.V., Kuz'ma, Y.B., Zakordonskiy, V.P., Vasylechko, L.O., Lebedynets, L.O., Kalytovs'ka, M.B. (2003) Adsorption of cadmium on acid-modified Transcarpathian clinoptilolite. *Microp. Mesop. Mater.*, *60* (1–3): 183.
48. Bektas, N., Kara, S. (2004) Removal of lead from aqueous solutions by natural clinoptilolite: equilibrium and kinetic studies. *Sep. Purif. Tech.*, *39* (3): 189.
49. Warchol, J., Petrus, R. (2006) Modeling of heavy metal removal dynamics in clinoptilolite packed beds. *Microp. Mesop. Mater.*, *93* (1–3): 29.
50. Wulfsberg, G. (1987) *Principles of Descriptive Chemistry*; Brooks/Cole Publishing: Monterey, CA.
51. Harris, D.C. (2002) *Quantitative Chemical Analysis*; Freeman: New York.
52. Nightingale, Jr., E.R. (1959) Phenomenological theory of ion solvation. Effective radii of hydrated ions. *J Phys Chem.*, *63*: 1381.