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Research concerning the influence of several factors on Pb^{2+}, Cu^{2+} and Zn^{2+} ions adsorption by natural zeolite tuff from Maramureş county, Northern Romania

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Abstract. The purpose of this research is to highlight the influence that certain parameters have on the removal efficiency of Pb^{2+}, Cu^{2+} and Zn^{2+}ions from industrial wastewater using natural zeolite tuff. Environmental and human health damage arising due to heavy metal content in surface water and groundwater have been challenging for researchers to find the most effective treatment methods with a high yield and relatively low cost (Carland & Aplan 1995; Curkovic et al 1997; Inglezakis et al 2003; Inglezakis et al 2005). They may well be achieved by using natural zeolites whose properties such as: molecular sieves, adsorption, hydration-dehydration without modifying their structural network, which give them an important role in the removal of heavy metal ions from wastewater (Alvarez-Ayuso et al 2003; Peric et al 2004). For this experiment the zeolite tuff sample was taken from a perimeter with volcanic tuffs located in the Bârsana area, Maramures County, Romania. During the batch experiment the influence of certain factors on the ion exchange process was observed, like: particle diameter of zeolite tuff and the pH of the contact solution. After processing the data it was found that the highest levels of specific adsorption for all studied heavy metal ions has been obtained for the lowest average diameters (d = 0.037 mm) of the ground natural zeolite used in the experiment and the best adsorption has been done at the highest pH used in the experiment (pH = 4).

Key Words: Bârsana zeolitic tuff, wastewater, heavy metals, ion exchange, adsorption

Rezumat. Cercetările privind eficienţa utilizării tufurilor zeolitice în diferite procese de epurare a apelor uzate au luat amploare în ultimul timp datorită faptului că ele asigură o alternativă fiabilă la procedurile clasice care sunt mult mai costisitoare şi de multe ori mai ineficiente. În această lucrare s-a urmărit influenţa pe care o au diametrele medii ale granulelor de tuf zeolitic de Bârsana măcinat şi a pH-ului soluţiei de contact asupra eficientei reţinerii ionilor de Pb^{2+}, Cu^{2+} and Zn^{2+} din soluţii sintetice. Adsorbţia ionilor de metale grele studiaţi este cu atât mai ridicată cu cât diametrele granulelor de tuf zeolitic folosit în experiment sunt mai mici, asigurându-se în acest fel o suprafaţă specifică mai mare. În ceea ce priveşte influenţa pH ului soluţiei de contact s-a constatat că eficienţa reţinerii ionilor de metale grele de către tuful zeolitic de Bârsana este mai mare la pH uri ale soluţiei mai ridicate (pH4, pH5).

Cuvinte cheie: tuf zeolitic de Bârsana, ape uzate, metale grele, adsorbţie.

Introduction. Due to their high content of heavy metals, wastewaters resulted from different operations of metallurgical industry have attracted a growing concern in finding the most efficient methods of cleaning them (Carland & Aplan 1995). The high concentrations of some elements including Pb, Cu and Zn represent a danger to the environment and human health due to their bioaccumulation and bioconcentration in living organisms. Also, the high concentrations of these elements in industrial effluents create severe pollution of the surface waters and groundwater (Curkovic et al 1997; Inglezakis et al 2003).

Conventional methods of removing heavy metals are not efficient in treating these wastewaters in order to achieve the quality standards for surface waters, expressed by maximum admissible concentrations. Natural zeolites are very appreciated especially because of the cost-effectiveness of their usage given by their very high capacity of adsorption, molecular sieve, hydration-dehydration without changing their network, and by the low costs related to their exploitation (Bailey et al 1999; Alvarez-Ayuso et al 2003; Vaca-Mier et al 2001; Cerjan-Stefanovici et al 1996; Ouki et al 1994; Inglezakis et al 2005; Peric et al 2004; Nicula et al 2010).

Different parameters determine the removal efficiency of the heavy metals from solutions. The aim of the experiment performed on the Bârsana zeolitic tuff was to determine the influence of the mean mineral particle diameters and the pH of the contact solutions on the adsorption rates of the Pb^{2+}, Cu^{2+} and Zn^{2+} ions.

Material and Method. The volcanic zeolitic tuff used in this experiment was sampled in Bârsana area, Maramureş County (Romania) (Figure 1).

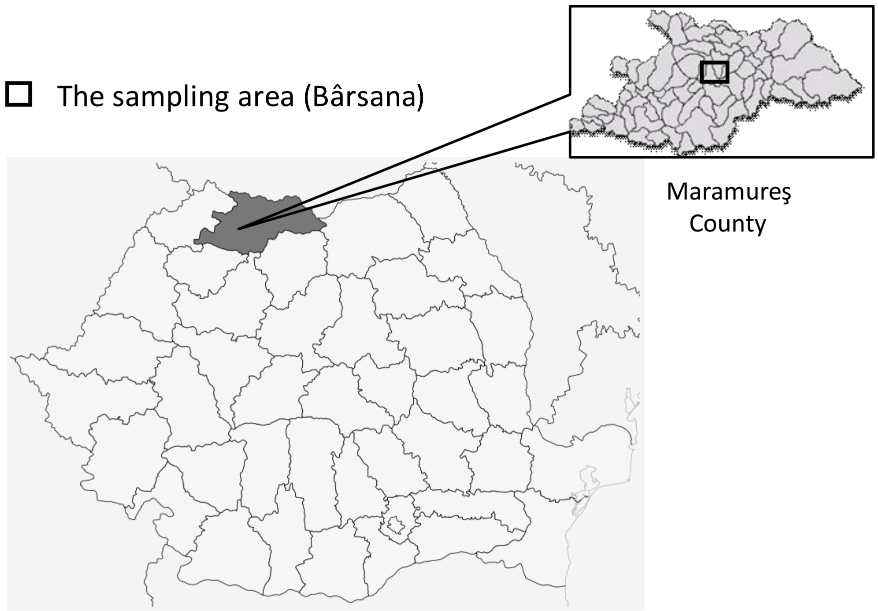

Figure 1. The Bârsana sampling area in Maramureş county, Romania.

The ground tuff with micronic sizes was analyzed by X-ray diffraction (XRD) (Figure 2) and chemical analysis (Table 1, Table 2). DRX measurements were performed using the MiniFlex-Rigaku equipment (radiation: CuKα; XG power: 30 KV, 15 mA; receiving slit 0.3 mm; Step size: 0.05º 2 θ; Scan setting: 5º - 70º 2 θ; counting time: 5 s).

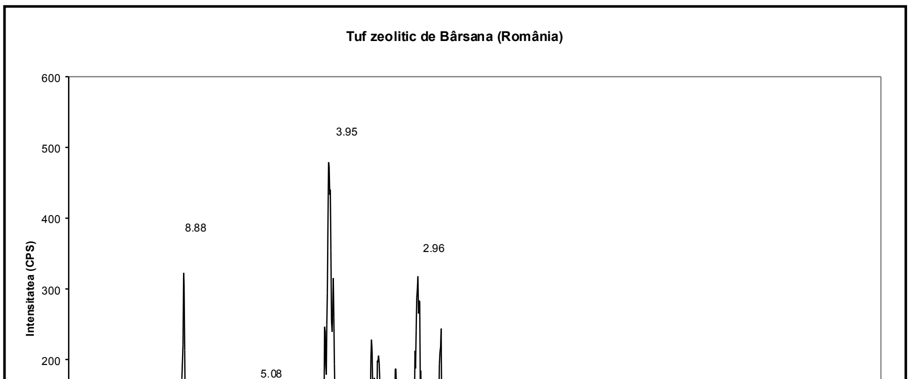

Figure 2. Characterization of Bârsana Tuff zeolites by X-ray diffraction (DRX).

Clinoptilolite is the main zeolitic mineral, small quantity of quartz, albite and cristobalite were also determined. Their specific diffraction lines are very clear on X-ray diagram. The 8.88 Å, 7.89 Å, 5.08 Å, 4.62 Å peaks are well marked (Figure 2.).

The zeolite tuff chemical analyses were performed using the methods of X-ray fluorescence (XRF) for major elements, and flame spectroscopy for minor elements. X-ray fluorescence analyses were performed using Cr Kα radiation and Philips difractometer (spectrometer PW 1410/20 generator PW 1732/10, PW 1390 channel control, restrict and crystal LFI 8203 AM). A Corning 400 spectrophotometer was used for performing the analyses by flame spectroscopy.

Table 1

The chemical composition of Bârsana Tuff - major elements (weight percent)

SiO_2 (%)	**Al_2O_3 (%)**	**Fe_2O_3 T (%)**	**MnO (%)**	**MgO (%)**	**CaO (%)**	**Na_2O (%)**	**K_2O (%)**	**TiO_2 (%)**	**P_2O_5 (%)**	**L.O.I.* (%)**	**TOTAL (%)**
72.42	12.22	1.48	0.05	0.20	1.36	2.76	2.80	0.17	0.04	6.51	100

* loss on ignition

Table 2

The chemical composition of Bârsana Tuff - minor elements (ppm)

Sc	**V**	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**Ga**	**Cd**	**Sn**	**Sb**	**Pb**	**Th**
2.5	10.5	23.0	357.2	42.4	115.2	237.1	11.7	4.0	10.6	4.4	306.6	13.1
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Cs**	**Ba**	**La**	**Ce**	**Nd**	**U**	
114.7	185.2	15.5	85.0	7.8	1.0	3.6	717.5	31.2	51.8	15.6	3.2	

It is noted the presence of quartz and aluminum oxide in a high proportion (Table 1). Following the analysis performed for the sample tuff subjected to the experiment, it was determined the pH of 9.97 and conductivity of 390 mS / cm.

After grading classification of the of Bâasana zeolite tuff fractions it was passed to prepare the zeolite material required for experiments by washing it with distilled water to remove foreign elements, followed by filtration and drying for 48 hours in the oven (Binder, Germany) at a temperature of 105 ^{0}C.

To determine the influence of particles diameter of the zeolite tuff on the efficiency of retention of Pb^{2+}, Cu^{2+} and Zn^{2+} ions by the zeolite tuff five grading fractions of zeolite material were used, presented in Table 3 and Figure 3.

Table 3

Zeolitic tuff particle diameters of Bârsana after grinding and classifying

No.	*sieve*	*d min*	*d max*	*d mean*	*difference*	*±%*
1	2	2				
2	1	1	2	1.5	0.5	33.33
3	0.25	0.25	1	0.625	0.375	60.00
4	0.125	0.125	0.25	0.1875	0.0625	33.33

The synthetic solutions containing Pb^{2+}, Cu^{2+} and Zn^{2+} ions were prepared using salt of $CuSO_45H_2O$, $Pb(CH_3COO)_2 \cdot 3H_2O$, respectively salt of $ZnSO_4 \cdot 7H_2O$, produced by the E. Merck, Darmstadt (Germany). The initial pH of solutions was adjusted to 4.0 using a solution of H2SO4 and CH3COOH, respectively.

The pH was measured with a digital pH-meter Consort P901 (Belgium. In order to dissolve the salts, distillated water was used produced by water distiller Fistreem Cyclone (United Kingdom).

After preparing the materials, an amount of one gram of zeolite tuff in each size grading fraction was contacted, stirring continuously for 24 hours (long enough to attain equilibrium) in terms of thermostatic temperature of 25 0C, using an orbital shaker

Heidolph Unimax 1010 - Germany with a volume of 50 ml of synthetic solutions of Pb^{2+}, Cu^{2+} and Zn^{2+} ions, respectively.

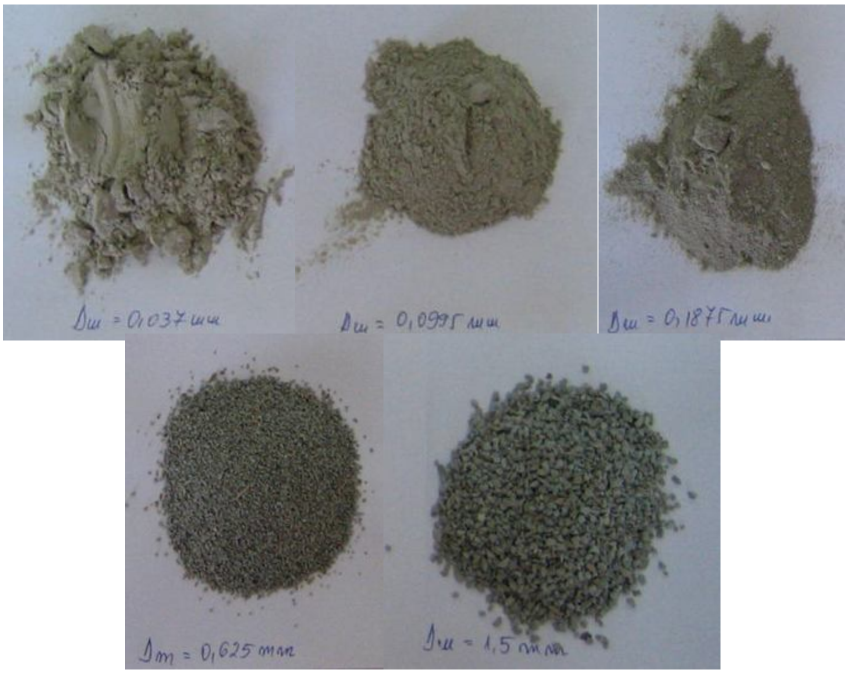

Figure 3. The classified fractions of the ground zeolite tuff used in the experiment.

The shaking of the zeolite tuff with the contact solution was done in polyethylene bottles with volume of 75 ml. After this contact, the mixtures were filtered using blue belt filter paper (with small pores < 65 µm). The equilibrium concentrations were determined by atomic absorption spectrometry using a Perkin Elmer atomic absorption spectrometer AAS800 (Shelton USA).

Using the solution concentration in equilibrium conditions the specific adsorption q (mg M^{2+}/g) were calculated (Zuhair 2003):

$$q = \frac{(c_0 - c) \cdot V}{1000 \cdot m} \quad (1)$$

where:

q = amount of heavy metal removed from solution (mg/g)
c_0 = the initial concentration of the solution (mg M^{2+}/L)
c = equilibrium concentration (mg M^{2+}/L)
V = volume of the contact solution (mL)
m = sorbent weight (g).

In the study of the influence of the mean particles diameter (d = 0.037 mm, d = 0.0995 mm, d = 0.1875 mm, d = 0.625 mm, d = 1.5 mm) on the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} ions in terms of contacting 1 g of ground Bârsana zeolite tuff with 50 ml of each type of solution of Pb^{2+}, Cu^{2+} and Zn^{2+} ions at pH = 4, for 6 concentrations of solution (100 mg/l to 200 mg/l to 400 mg/l, 600 mg/l, 800 mg/l and 1000 mg/l) different values of equilibrium concentration and specific adsorption were obtained.

To follow the influence of pH on the adsorption efficiency of studied heavy metal ions by the Bârsana zeolite tuff the procedure applied was the same as that used for studying the influence of diameter of particles adsorption process but in this case the contact solutions were brought to four values of pH, namely: pH 4, pH 3, pH 2 and pH = 1 using a solution of H2SO4, respectively CH3COOH. The distribution ratio (Kd) was calculated using the following equations (Menhage-Bena et al 2004):

$$K_d = \frac{C_i - C_f}{C_f} \cdot \frac{V}{m} \quad (L/g) \tag{2}$$

$$Kd = \frac{Qe}{Ce}(L/g) \tag{3}$$

K_d – is a parameter showing the strength of the relationship between metal adsorption and the adsorption surface of the zeolite material. The higher value of Kd, the stronger the relationship.

Results and Discussion. In Figures 4, 5, and 6 there are shown the isotherms of adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} ions, function of mean particle diameters of the Bârsana zeolite tuff for the concentrations of the studied heavy metals solutions of 100 mg/l, 200 mg/l, 400 mg/l, 600 mg/l, 800 mg/l and 1000 mg/l.

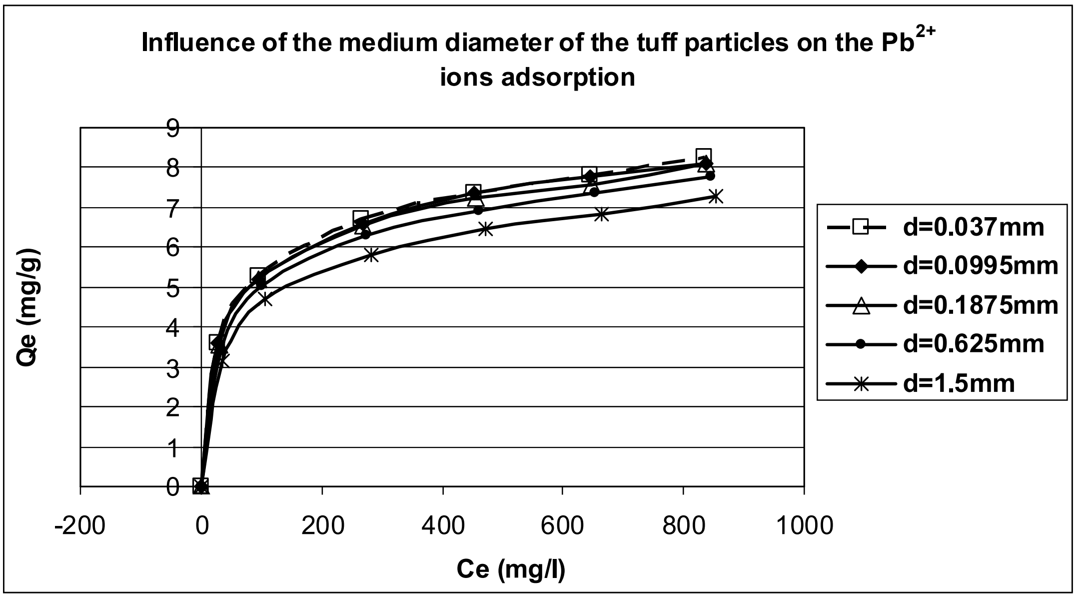

Figure 4. Adsorption isotherm of Pb^{2+} ions by the Bârsana zeolite tuff according to the mean particle diameters.

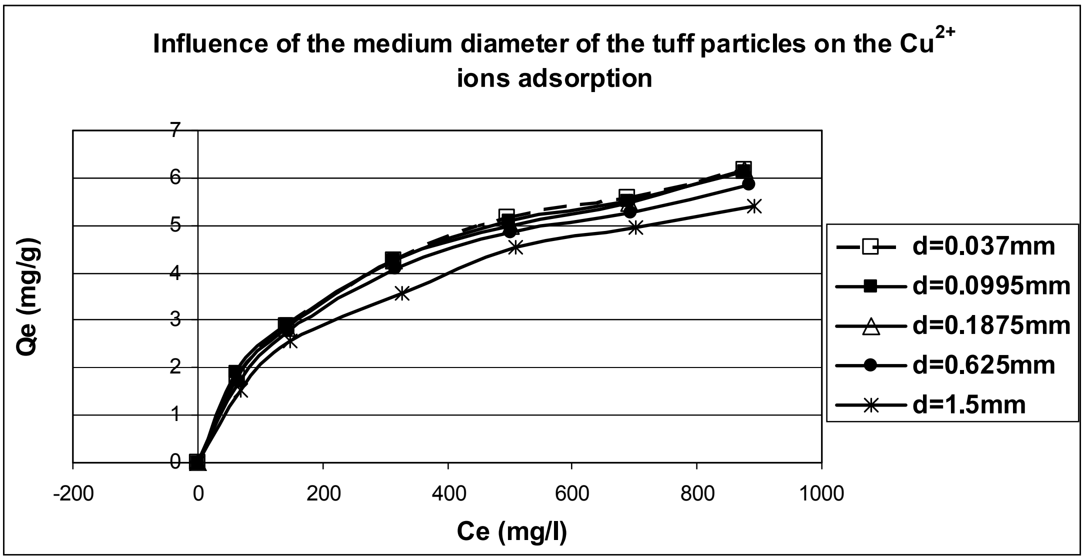

Figure 5. Adsorption isotherm of Cu^{2+} ions by the Bârsana zeolite tuff according to the mean particle diameters.

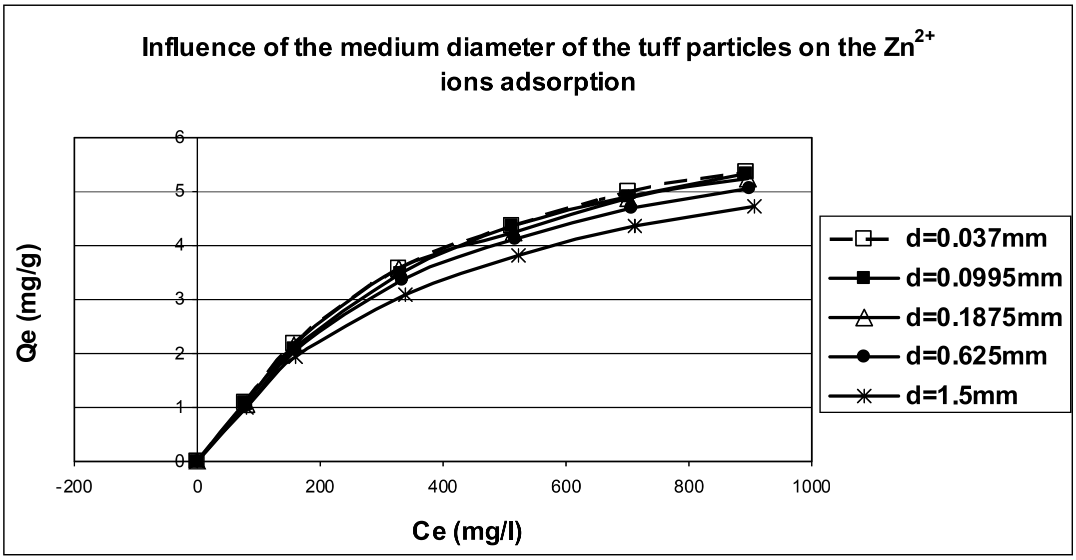

Figure 6. Adsorption isotherm of Zn^{2+} ions by the Bârsana zeolite tuff according to the mean particle diameters.

In Tables 4 and 5 there are presented the comparative experimental data resulted from the contact of the Bârsana zeolite tuff having mean particle diameters of 0.037 mm, 0.0995 mm, 0.1875 mm, 0.625 mm and 1.5 mm with 50 ml solution of Pb^{2+}, $Cu^{2+}$and Zn^{2+} ions of 1000 mg/l concentration at pH 4 and temperature conditions of 25 0C.

Table 4

Specific adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} ions by Bârsana tuff at pH=4 and 25 ^{0}C

No.		*d (mm)*	*Q_e (mg/g)*		
			Pb^{2+}	Cu^{2+}	Zn^{2+}
1	1000 mg/l pH=4 t=25 ^{0}C	0.037	8.261	6.1855	5.3715
2		0.0995	8.102	6.1355	5.3275
3		0.1875	8.096	6.16	5.246
4		0.625	7.766	5.8665	5.068
5		1.5	7.2995	5.416	4.7155

It is noted that the highest levels of specific adsorption is recorded for the smallest mean particles diameters of the Bârsana zeolite tuff for all heavy metal ions studied. This is explained by the fact that these particles have the largest area surface and thus greater adsorption sites of heavy metals.

Table 5

Percentage retention of Pb^{2+}, Cu^{2+} and Zn^{2+} ions by the Bârsana zeolite tuff having different mean diameters

No.		*d (mm)*	*Q_e (mg/g)*		
			Pb^{2+}	Cu^{2+}	Zn^{2+}
1	1000 mg/l pH=4 t=25 ^{0}C	0.037	100	100	100
2		0.0995	98.075294	99.1916579	99.18086196
3		0.1875	98.002663	99.5877455	97.6635949
4		0.625	94.007989	94.8427775	94.34980918
5		1.5	88.360973	87.5596152	87.78739644

From the experimental data analysis related to the usage of the 5 mean diameters of the zeolitic tuff, at a 1000 mg/l concentration of Pb^{2+}, Cu^{2+} and Zn^{2+} ions, at a pH=4 and a temperature of 25 ^{0}C, as it results from the graphical illustrations of the presented results in diagrams 4, 5 and 6 there is not a too big difference between the influence degree of the studied heavy metals ions at small diameters (d=0.037 mm and d=0.0995 mm).

The biggest difference is recorded for larger diameters (d = 1.5 mm). As it can be seen in the Figure 4 regarding the influence of mean particle diameter of the Bârsana tuff on the Pb^{2+} ion adsorption, at its equilibrium concentrations, due the initial concentration of 100mg/l and 200 mg/l, the specific adsorption records high levels after that the shape of curves gradually becomes flattened.

In Figure 5 and Figure 6 regarding the influence of the mean particle diameters of the Bârsana zeolite tuff on the adsorption of Cu^{2+} and Zn^{2+} ions it can be observed a proportionality between equilibrium concentration increase and specific adsorption of Cu^{2+} and Zn^{2+} ions by the Bârsana zeolite tuff.

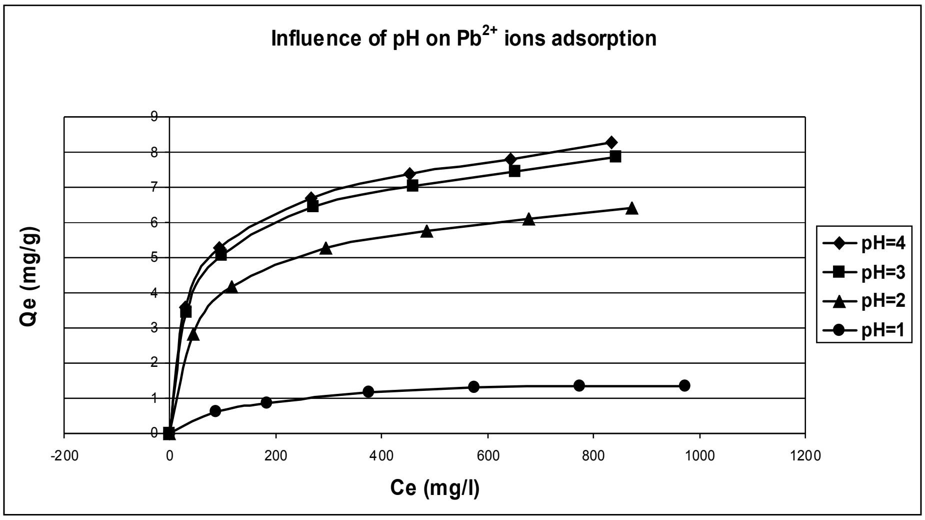

Figure 7. The influence of the mean particle diameters of the Bârsana zeolitic tuff on the Pb^{2+}, Cu^{2+} and Zn^{2+} ions adsorption.

Under the same experimental conditions for the three heavy metals studied, as illustrated in Figure 8, the highest adsorption is recorded for Pb^{2+} ions followed by Cu^{2+} and the Zn^{2+} ions.

The diagrams shape shows a decrease in retaining efficiency of Pb^{2+}, Cu^{2+} and Zn^{2+} ions due to the growth of the mean particle diameters of Bârsana zeolite tuff used in the experiment.

In the Figure 8 the influences of the four values of pH (pH=4, pH=3, pH=2 and pH=1) on the Pb^{2+} ions adsorption efficiency by the Bârsana zeolite tuff with a particle diameter of 0,037 mm are presented.

The graph reflects the variation of specific adsorption of Bârsana zeolite tuff depending on the concentration of the four values obtained at equilibrium pH of the solution.

There is a higher growth of specific adsorption of Pb^{2+} ions by the zeolite tuff in the case of solutions with a higher pH (pH 4, pH 3) and much lower for solution with a lower pH (pH = 1).

In the graph in Figure 9 the influences of the four values of pH (pH=4, pH=3, pH=2 and pH=1) on the efficiency adsorption of Cu^{2+} ions by the Bârsana zeolite tuff with particle diameters of 0.037 mm are presented.

As in the case of adsorption of Pb^{2+} ion in the case of Cu^{2+} ion adsorption by zeolite tuff can notice a higher specific adsorption capacity when using solutions with lower pH (pH = 1).

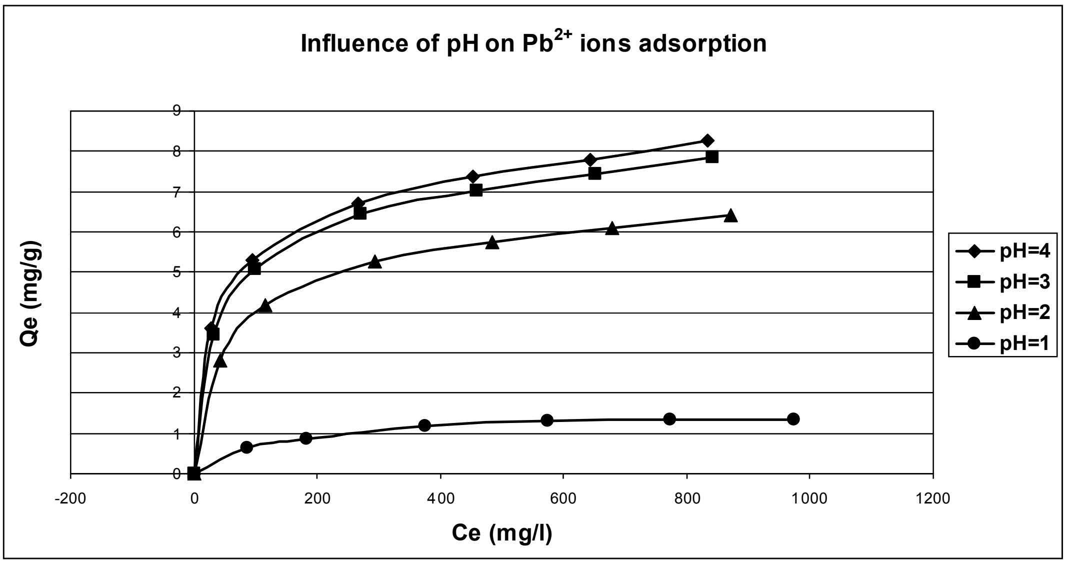

Figure 8. The influence of solution pH on the Pb^{2+} ions adsorption by the Bârsana zeolite tuff (D = 0.037 mm).

The graph in Figure 10 illustrates the variation degree of restraint of Zn^{2+} ion by the Bârsana zeolite tuff with a mean particle diameter of 0.037 mm at four pH values (4, 3, 2, 1).

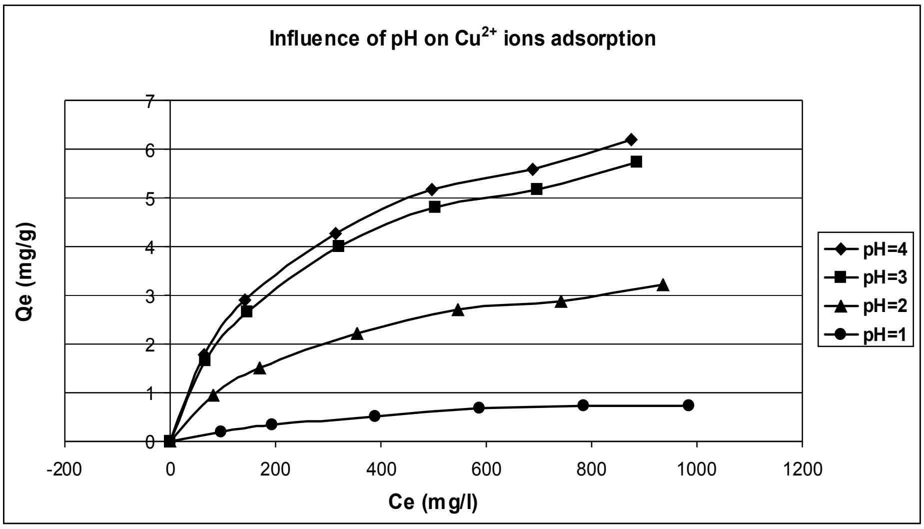

Figure 9. The influence of solution pH on the Cu^{2+} ions adsorption by the Bârsana zeolite tuff (D = 0,037 mm).

Figure 10 also expresses the variation of the specific adsorption of Zn^{2+} ions by the Bârsana zeolite tuff with a mean particle diameter of 0.037 mm under the conditions of contacting a solution of Zn^{2+} having different concentrations (100 mg/l to 200 mg/l, 400 mg/l, 600 mg/l 800 mg/l and 1000 mg/l) at different sites pH (pH 4, pH 3, pH 2 and pH = 1).

As in the cases of experiments with solutions of Pb^{2+} and Cu^{2+} ions it can be observed a very good adsorption capacity of the zeolite tuff for the solutions with higher pH (pH=4, pH=3) and a lower adsorption in the conditions of using a solution with a lower pH (pH=1).

This fact can be explained by that at low pH (under 3) an excessive protonation of the active centers on the zeolitic material surface happened that leads to a weight in establishing links between heavy metals ions and active centers.

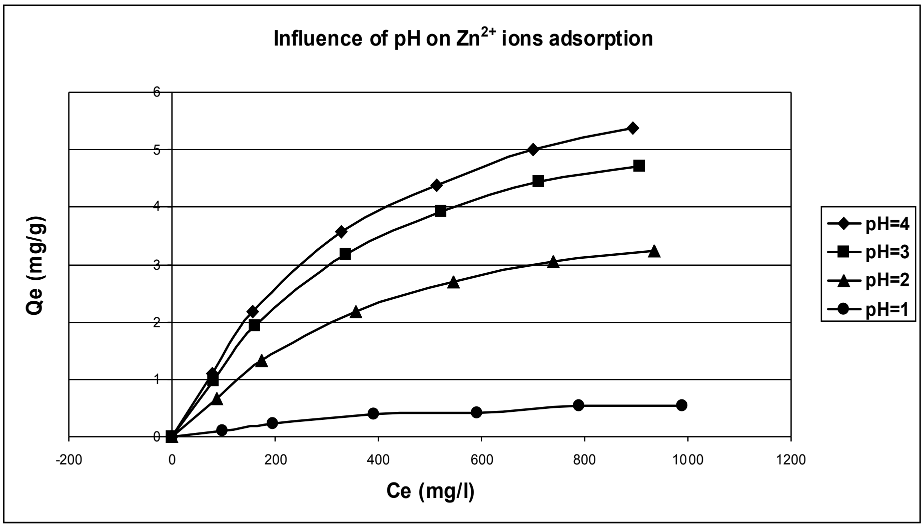

Figure 10. The influence of solution pH on the Zn^{2+} ions adsorption by the Bârsana zeolite tuff (D = 0.037 mm).

At moderate pH (3 and 4), H^+ ion is released from the active centers and the adsorbed amount of heavy metal ions is increasing. At higher pH (above 4) there is even a better adsorption; a possibility of precipitation of heavy metals exists.

Comparing the shapes of the graphs in the case of specific adsorption for the three studied heavy metals it can be remarked a better adsorption for Pb^{2+} ions in the similar pH conditions of the other studied metals.

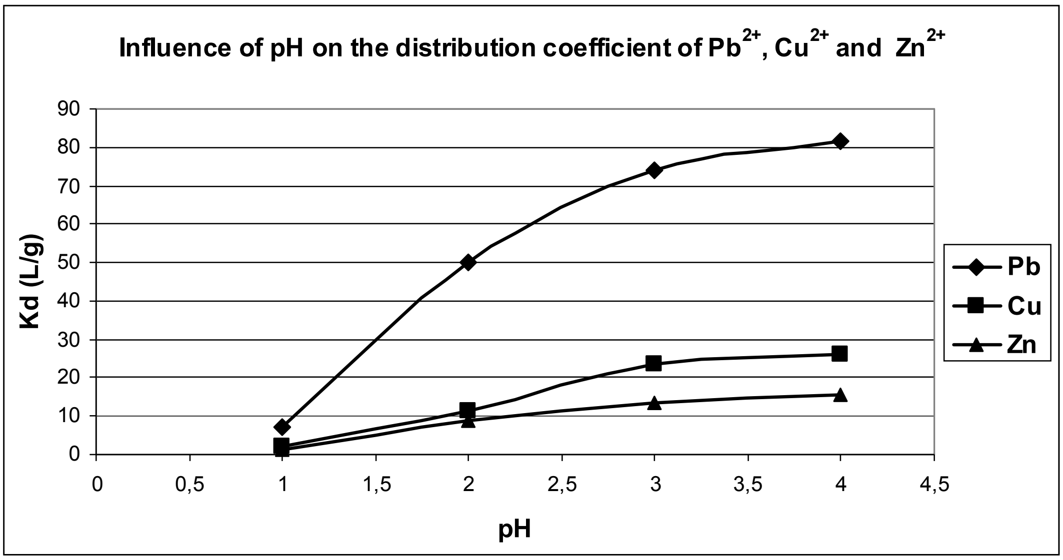

Figure 11. Kd variation of Pb^{2+}, Cu^{2+} and Zn^{2+} ions on the adsorption surface of the Bârsana zeolite tuff according to the pH of the contact solution.

From the graphical representation of Kd variation with pH of contact solution (Figure 11) it can be observed that the lower the pH of contact solution decreases the lower the distribution coefficient Kd decreases. This may be correlated with the increase of the adsorption capacity of the zeolite tuff with the increase of the solution contact pH.

Conclusions. Natural zeolites are a highly valued source for environmental decontamination in general and wastewater cleaning in particular. This performance is due to their special qualities (ion exchange, molecular sieve, adsorption and desorption capacity etc.). Retention efficiency of heavy metal ions from wastewater by natural zeolite tuffs may be influenced by several factors such as: grain size of tuff grains, pH of the contact solution, temperature etc.

Data presented in this paper show that the efficiency of the heavy metal ions in their retention by the Bârsana zeolite tuff, increases with the decrease of the tuff particles dimension and with increase of the contact solution pH, which is also confirmed by the distribution coefficient which increases with the decreasing pH of the contact solution.

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