AACL BIOFLUX

Aquaculture, Aquarium, Conservation & Legislation
International Journal of the Bioflux Society

Sorption kinetics of Pb^{2+}, Cu^{2+} and Zn^{2+} ions by natural zeolites from Maramures County (northern Romania): potential application in wastewater reuse

Irina Smical

Faculty of Environmental Science, Babeş-Bolyai University Cluj-Napoca, 30 Fântânele Street, Cluj-Napoca City, Cluj County, Romania, European Union;
e-mail: irinadan2003@yahoo.com

Abstract. The sorption kinetics of Pb^{2+}, Cu^{2+} and Zn^{2+} ions by natural zeolite tuff from Maramureş County (northern Romania) was studied using agitated batch laboratory apparatus at two temperature levels of 25 ^{0}C and 50 ^{0}C. The sorption kinetics of studied heavy metals ions by the natural zeolitic tuff was established by fitting of experimental data using various models applied in the kinetic studies of heavy metals sorption onto ions exchangers (pseudo-order 1, pseudo-order 2 and Weber-Morris). From all of these the best results were recorded for the pseudo-order 1 model use. The interaction between metal ions and adsorbent surface is made on a single adsorption site and the adsorption mechanism is a diffusive one through the adsorbent pores.
Key Words: kinetics, natural zeolite tuff, adsorption, heavy metals, water reuse.

Rezumat. Datele prezentate în lucrare, axate pe interpretarea şi prelucrarea rezultatelor experimentale utilizând diferite modele pentru determinarea cineticii de adsorbţie, relevă faptul că tuful zeolitic natural din zona Călineşti-Bârsana, judeţul Maramureş, are proprietăţi ridicate de reţinere a metalelor grele din apele uzate. Conform rezultatelor interpretării acest proces se derulează cel mai bine la temperaturi mai ridicate. Dintre modelele cinetice utilizate (pseudo-ordin 1, pseudo-ordin 2 şi Weber-Morris) cele mai bune rezultate au fost obţinute cu ajutorul modelului cinetic de pseudo-ordinul 1. Acest lucru indică faptul că interacţiunea dintre ionii metalici şi suprafaţa adsorbantă se realizează pe câte un singur site de adsorbţie. Pe de altă parte, datele obţinute aplicând modelul cinetic Weber-Morris arată că că mecanismul de adsorbţie este de tip difuziv în porii adsorbantului.
Cuvinte cheie: cinetică, tuf natural zeolitic, adsorbţie, metale grele, reciclarea apei.

Introduction. The adsorption ability and the high ion exchange of zeolites offer the possibility of a high usage of the zeolitic tuff in various fields of economy, animal health and environment protection (Kovo & Edoga 2005; Nicula et al 2010; Smical et al 2010ab). The very long and still inexhaustible list of the conventional and unconventional application of the zeolite volcanic tuff, recommend this raw material as one of the most important in the non-metalliferous domain.

In the last half century considerable efforts have been made and technologies for zeolites usage have been developed in various applications (Wise 2005). The ion exchange by using natural zeolites may be considered one of the most attractive methods because they are abundant and the cost price is low. In addition, natural zeolites could be deposited and regenerated cheaply (Bailey et al 1999). The most applications of natural zeolites are based on their structural characteristics, excellent sorbents properties and their large specific surface (Çoruh 2008).

The cations adsorbtion, positively charged, and the complex forming are possible due to the various forms of the crystal faces, imperfection of surface, breaking the links and the margins as well as to the amphoteric nature of the hydroxil grouping [(Al/Si)-OH)] (Trgo & Peric 2003; Altin et al 1998).

Our present experimental data and their processing results give information about the adsorption rate of the Pb^{2+}, Cu^{2+} and Zn^{2+} from synthetic solution by natural zeolitic tuff from Călineşti-Bârsana area (Maramureş County) using various kinetics models.

Materials and Method. The zeolite tuff used in the experimental research was sampled from a quarry situated on the Călineşti-Văleni area (Maramureş County, northern Romania, European Union).

This natural zeolite tuff deposit is on the right slope of the Valea Mijlocie stream and close to its confluence with Valea Morii stream (see Fig. 1).

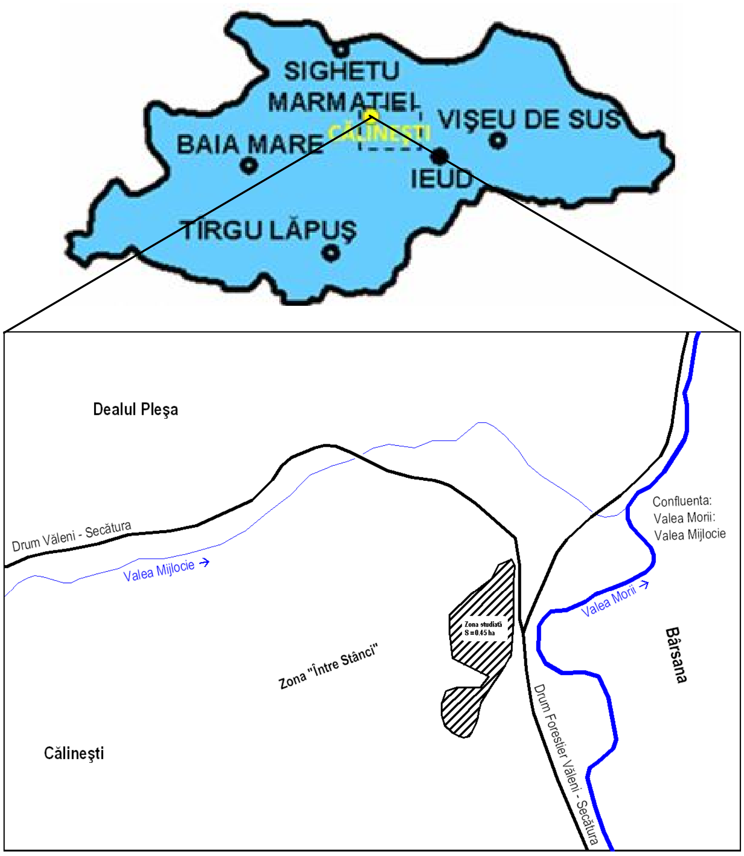

Fig. 1. The natural zeolite tuff quarry in Călineşti – Bârsana area, Maramureş County)

After grinding and granulometric classification of zeolite tuff, the material was prepared by washing of it with distilled water followed by filtration and drying in a heating (Binder-Germany) during 48 hours at temperature of 105 ^{0}C.

In order to run the experiment an amount of 1 g of zeolite tuff (d=0.037 mm) was contacted with a volume of 50 mL of Pb^{2+}, Cu^{2+} and Zn^{2+} synthetic solution, through continuously agitation during 24 hours (enough to reach the equilibrium), in thermostatic conditions at 25 ^{0}C and 50 ^{0}C, using an orbital shaker (Heidolph Unimax 1010 – Germany).

The zeolite tuff agitation together with the contact solution was made in polyethylene phials of 75 mL each one.

The synthetic solutions containing Pb^{2+}, Cu^{2+} and Zn^{2+} ions were prepared using salts of $CuSO_4 \cdot 5H_2O$, $Pb(CH_3COO)_2 \cdot 3H_2O$, respectively $ZnSO_4 \cdot 7H_2O$ p.a., made by E. Merck, Darmstadt (Germany) and the solutions initial pH was fix at 4.0 using a solution of H_2SO_4 p.a., respectively CH_3COOH.

The pH was measured with a digital pH meter Consort P901 (Belgium) and for salts dissolving distilled water was used being obtained with Fistreem Cyclon (United Kingdom) distiller.

In order to make a kinetic study on Pb^{2+}, Cu^{2+} and Zn^{2+} ions adsorption by natural zeolite tuff from Călineşti-Bârsana area, the following working conditions were met:

- Temperature of 25 ^{0}C
- Temperature of 50 ^{0}C
- Initial metal concentration in solution of 100 mg/L

- Initial solutions pH of 4.0
- mixing ratio R=S/L=1/50

At different periods, samples of solution were collected, centrifuged and subjected to procedures of establishing the heavy metals concentration by atomic spectrometry method using an atomic adsorption spectrometer Perkin Elmer AAS800 (Shelton - USA).

By studying the kinetics of adsorption process the rate was observed as well as the mechanism of reaction. The adsorption rate is generally given by equation (Senthil Kumar & Gayathri 2009):

$$\frac{da}{dt} = k(C - C_E) \qquad (1)$$

where:

a = amount adsorbed per gram of adsorbent (mol/g); t = time at the beginning adsorption (min); k = a rate constant (min^{-1}); C = the adsorbate concentration in fluid phase (mol/L);

C_E = the adsorbate concentration in fluid phase at equilibrium conditions (mol/L).

Fitting the experimental data using the pseudo-order 1, pseudo-order2 and Weber-Morris models. The experimental data were fitted using the main models for adsorption kinetics, namely: pseudo-order 1, pseudo-order 2 and Weber-Morris.

The kinetics equations used for Pb^{2+}, Cu^{2+} and Zn^{2+} ions adsorption onto the zeolite tuff might be written in the following integrated forms:

- **for kinetics of pseudo-order 1** (Namasivayam & Holl 2004; Sun et al 2004; Acemioglu & Alma 2004):

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$
$$\ln(q_e - q_t) = \ln q_e - k \cdot t \qquad (2)$$

where:

q_t = the adsorbed amount of Pb^{2+}, Cu^{2+} and Zn^{2+} (mol Pb^{2+}/g, mol Cu^{2+}/g, mol Zn^{2+}/g)

q_e = the amount of Pb^{2+}, Cu^{2+} and Zn^{2+} adsorbed in equilibrium conditions (mol Pb^{2+}/g, mol Cu^{2+}/g, mol Zn^{2+}/g)

t = time (min)

k = the adsorption constant which involves the activation energy ($g \cdot mol^{-1}$ min^{-1})

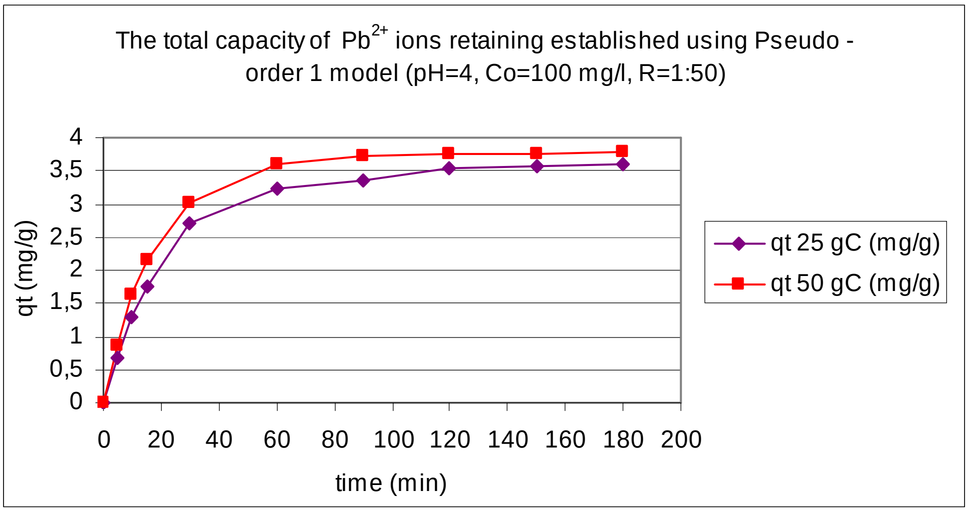

Fig. 2 The total capacity of retaining the Pb^{2+} ions by the natural zeolite tuff from Călineşti-Bârsana area, at temperatures of 25 ^{0}C and 50 ^{0}C using Pseudo-order 1 kinetic model.

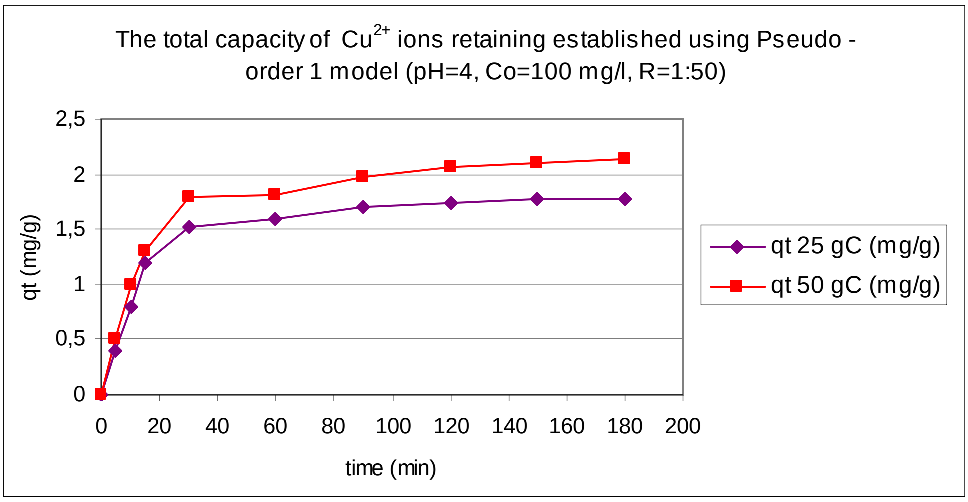

Fig. 3 The total capacity of retaining the Cu^{2+} ions by the natural zeolite tuff from Călineşti-Bârsana area, at temperatures of 25 ^{0}C and 50 ^{0}C using Pseudo-order 1 kinetic model.

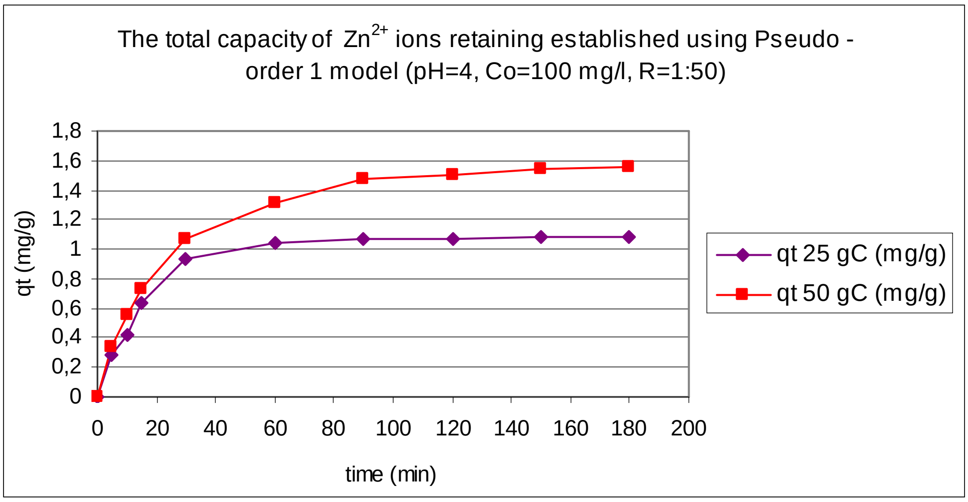

Fig. 4. The total capacity of retaining the Zn^{2+} ions by the natural zeolite tuff from Călineşti-Bârsana area, at temperatures of 25 ^{0}C and 50 ^{0}C using Pseudo-order 1 kinetic model.

- **for kinetics of pseudo-order 2** (Ho & McKay 2004; Ho 2004; Namasivayam & Holl 2004; Sun et al 2004):

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

$$\frac{t}{q_t} = \frac{1}{k \cdot q_e^2} + \frac{t}{q_e} \qquad (3)$$

where:
q_t = the adsorbed amount of Pb^{2+}, Cu^{2+} and Zn^{2+} (mol Pb^{2+}/g, mol Cu^{2+}/g, mol Zn^{2+}/g)
q_e = the amount of Pb^{2+}, Cu^{2+} and Zn^{2+} adsorbed at equilibrium conditions (mol Pb^{2+}/g, mol Cu^{2+}/g, mol Zn^{2+}/g)
t = time (min)
k = the adsorption constant which involves the activation energy ($g \cdot mol^{-1}$ min^{-1})

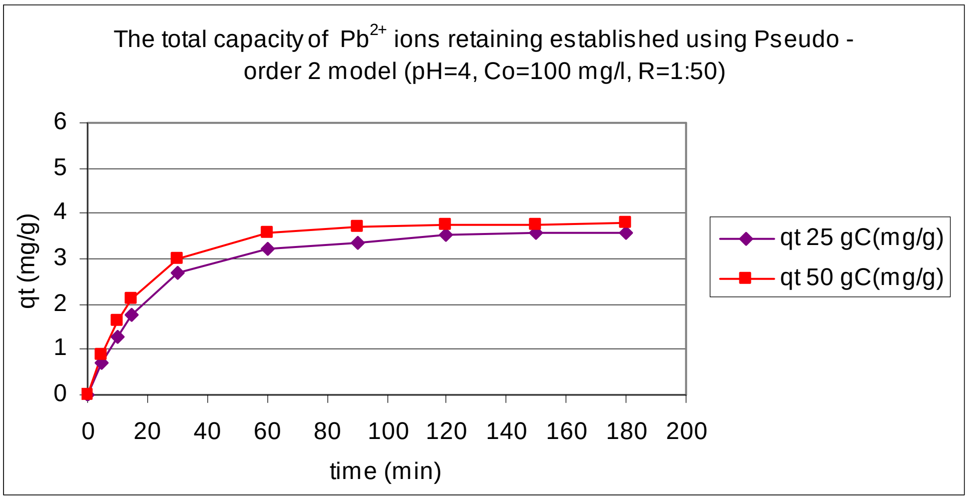

Fig. 5. The total capacity of retaining the Pb^{2+} ions by the natural zeolite tuff from Călineşti-Bârsana area, at temperatures of 25 ^{0}C and 50 ^{0}C using Pseudo-order 2 kinetic model.

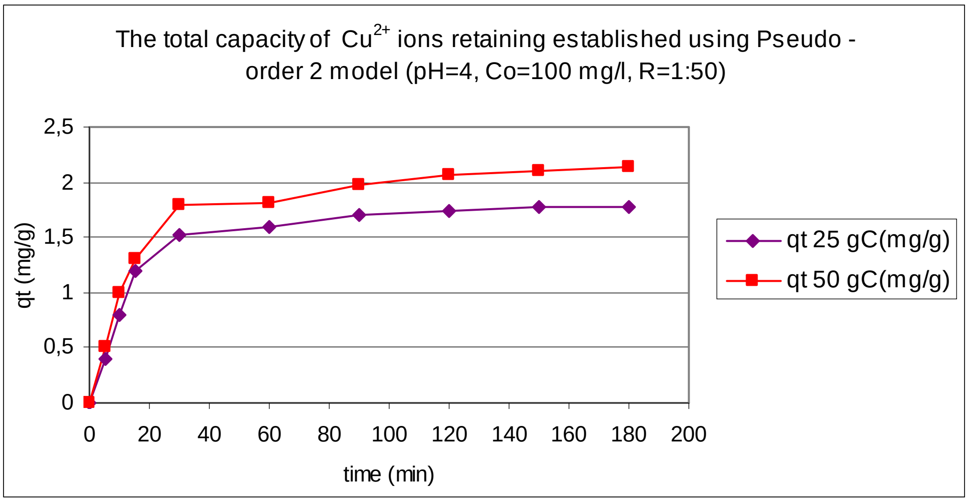

Fig. 6. The total capacity of retaining the Cu^{2+} ions by the natural zeolite tuff from Călineşti-Bârsana area, at temperatures of 25 ^{0}C and 50 ^{0}C using Pseudo-order 2 kinetic model.

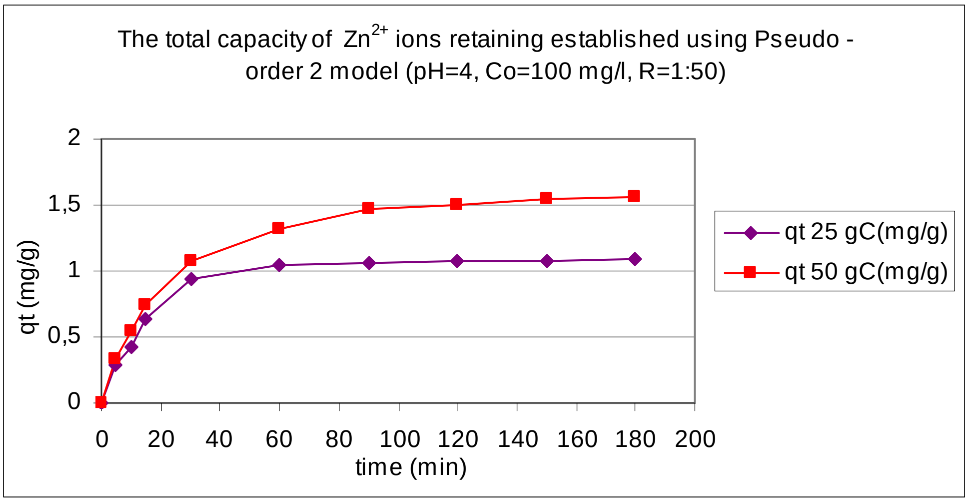

Fig. 7. The total capacity of retaining the Zn^{2+} ions by the natural zeolite tuff from Călineşti-Bârsana area, at temperatures of 25 ^{0}C and 50 ^{0}C using Pseudo-order 2 kinetic model.

- **for the kinetic model Weber-Morris (intraparticle diffusion)** (Weber Jr. & Digiano 1996; Mckay & Poots 1980):

$$q_t = I_0 + k_p \cdot t^{0.5} \quad (4)$$

$$q_t = k_i \cdot t^{0.5} \quad (5)$$

$$D_e = \pi \left[\frac{d_p \cdot k_p}{12 \cdot q_e} \right]^2 \text{ the effective diffusion coefficient} \quad (6)$$

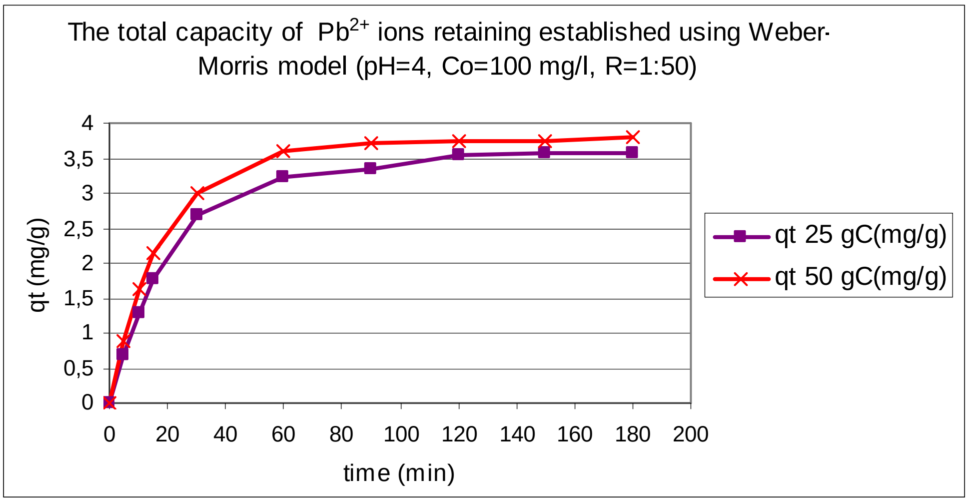

Fig. 8. The total capacity of retaining the Pb^{2+} ions by the natural zeolite tuff from Călineşti-Bârsana area, at temperatures of 25 ^{0}C and 50 ^{0}C using Weber-Morris model.

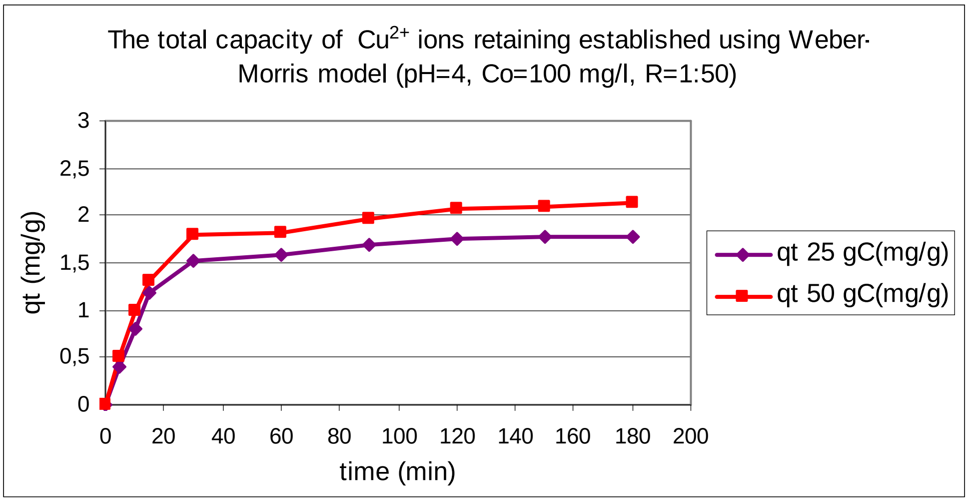

Fig. 9. The total capacity of retaining the Cu^{2+} ions by the natural zeolite tuff from Călineşti-Bârsana area, at temperatures of 25 ^{0}C and 50 ^{0}C using Weber-Morris model.

The experimental data fitting using the pseudo-order 1, pseudo-order 2 and Weber-Morris kinetic models and the calculation using the correlation coefficients are presented in Tables 1-3.

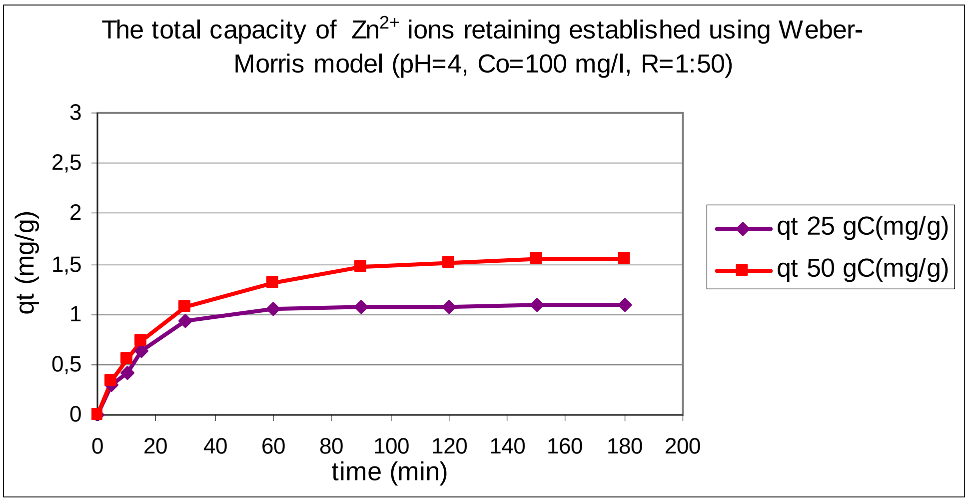

Fig. 10. The total capacity of retaining the Zn^{2+} ions by the natural zeolite tuff from Călineşti-Bârsana area, at temperatures of 25 ^{0}C and 50 ^{0}C using Weber-Morris model.

Table 1

The parameters resulted from the experimental data fitting using the pseudo-order 1 kinetic model

No.	Metal ion	A	B	r	q_e	k_1
1	Pb^{2+}	0.898066	-0.03194	0.982939	2.45485	0.031945
2	Cu^{2+}	0.118093	-0.02895	0.987578	1.125349	0.02895
3	Zn^{2+}	-0.6281	-0.02578	0.95641	0.533604	0.025783

Table 2

The parameters resulted from the experimental data fitting using the pseudo-order 2 kinetic model

No.	Metal ion	A	B	r	q_e	k_2
1	Pb^{2+}	31.22842	-167.227	0.673763	-0.00598	895.4975
2	Cu^{2+}	62.26858	-350.998	0.673183	-0.00285	1978.514
3	Zn^{2+}	85.60951	-449.809	0.512924	-0.00222	2363.384

Table 3

The parameters resulted from the experimental data fitting using the Weber-Morris kinetic model

No.	Metal ion	A	B	r	Io	Kp	De
1	Pb	0.747234	0.247777	0.923084	0.747234	0.247777	1.42E-13
2	Cu	0.589753	0.104472	0.872797	0.589753	0.104472	1.02E-13
3	Zn	0.339268	0.066838	0.876784	0.339268	0.066838	1.11E-13

Discussion and Conclusions. As it can be observed in all graphical representations the best adsorption process of the metal ions by the Călineşti-Bârsana zeolite tuff is run at higher temperatures.

The best fitting of experimental data was obtained using pseudo-order 1 kinetic model. This thing shows that the interactions between the metal ions and the adsorbent surface are made on a single adsorption site.

As it can be observed in Tables 1-3, the experimental data are fitting with the best correlation coefficients in the use of the kinetic models: pseudo-order 1, pseudo-order 2 and Weber-Morris. The medium of the correlation coefficients are: 0.9756, 0.8909 and 0.6199, respectively.

Using Weber-Morris model the values $1.42 \cdot 10^{-13}$ for Pb^{2+}, $1.02 \cdot 10^{-13}$ for Cu^{2+} and $1.11 \cdot 10^{-13}$ for Zn^{2+}, were obtained. This magnitude orders indicate that the adsorption mechanism is a diffusive one through the adsorbent pores.

From the three presented kinetic models (pseudo-order 1, pseudo-order 2 and Weber-Morris) the best fitting of the experimental data was made using the pseudo-order 1 kinetic model.

The interpretation results indicate that the interaction between metal ions and adsorbent surface was made on a single adsorption site and the adsorption mechanism is a diffusive one through the adsorbent pores.

References

Acemioglu B., Alma M. H., 2004 Sorption of copper ions by pine sawdust. Holz Roh Werkst **62**:268-272.

Altın O., Özbelge H. Ö., Dogu T., 1998 Use of general purpose adsorption isotherms for heavy metal-clay mineral interactions. Journal of Colloid and Interface Science **198**:130–140.

Bailey S., Olin T., Bricka M., Adrian D., 1999 A review of potentially low-cost sorbents for heavy metals. Water Res **33**:2469–2479.

Çoruh S., 2008 The removal of zinc ions by natural and conditioned clinoptilolites. Desalination **225**:41–57.

Ho Y. S., 2004 Pseudo isotherms using a second order kinetic expression constant. Adsorption **10**:151-158.

Ho Y. S., Mc Kay G., 2004 Sorption of copper from aqueous solutions by peat. Water, Air and Soil Pollution **158**:77-97.

Kovo A. S., Edoga M. O., 2005 Production and characterization of zeolite from Ahako Clay in Kogi State, Nigeria. Leonardo Electronic Journal of Practices and Technologies **7**:31-40.

Mckay G., Poots V. J., 1980 Kinetics and diffusion processes in colour removal from effluent using wood as an adsorbent. J Chem Technol Biotechnol **30**:279-292.

Namasivayam C., Holl W. H., 2004 Chromium (III) removal in tannery wastewaters using Chinese Reed (Miscanthus Sinensis) a fast growing plant. Holz Roh Werkst **62**:74-80.

Nicula M., Banatean-Dunea I., Gergen I., Harmanescu M., Simiz E., Patruica S., Polen T., Marcu A., Lunca M., Szucs S., 2010 Effect of natural zeolite on reducing tissue bioaccumulation and cadmium antagonism related to some mineral micro- and macronutrients in Prussian carp (*Carassius gibelio*). AACL Bioflux **3**(3):171-179.

Senthil Kumar P., Gayathri R., 2009 Adsorption of Pb^{2+} Ions from Aqueous Solutions onto Bael Tree Leaf Powder: Isotherms, Kinetics and Thermodynamics Study. Journal of Engineering Science and Technology **4**(4):381-399.

Smical I., Mihaly-Cozmuta L., Costin D., 2010a 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. AES Bioflux **2**(2):171-180.

Smical I., Mihaly-Cozmuta L., Costin D., 2010b Use of natural zeolites from Maramures county (Romania) in removal of Cu^{2+}, Pb^{2+}, Zn^{2+} ions from industrial wastewaters. AES Bioflux **2**(2):181-188.

Sun Q. Y., Lu P., Yang L. Z., 2004 The adsorption of lead and copper from aqueous solution on modified peat resin particles. Environmental Geochemistry and Health **26**:311-317.

Trgo M., Peric J., 2003 Interaction of the zeolitic tuff with Zn-containing simulated pollutant solutions. Journal of Colloid and Interface Science **260**:166-175.

Weber Jr. W. J., Digiano F. O., 1996 Process Dynamics in Environmental System; Environmental, Science and Technology Series, John Wiley and Sons: New York; p.89-94.
Wise W. S., 2005 Encyclopedia of Geology - Minerals Zeolites, University of California – Santa Barbara, Santa Barbara, CA, USA, p.591-601.

Received: 02 October 2010. Accepted: 30 December 2010. Published online: 04 July 2011.
Author:
Irina Smical, Faculty of Environmental Science, Babeş-Bolyai University of Cluj-Napoca, 30 Fântânele Street, Cluj-Napoca City, Cluj County, România, irinadan2003@yahoo.com
How to cite this article:
Smical I., 2011 Sorption kinetics of Pb^{2+}, Cu^{2+} and Zn^{2+} ions by natural zeolites from Maramures County (northern Romania): potential application in wastewater reuse. AACL Bioflux **4**(4):481-489.