Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1094426

57 (2016) 18748–18754
August

Taylor & Francis
Taylor & Francis Group

Binary adsorption of nickel and zinc from aqueous solutions onto the Serbian natural clinoptilolite

Djordje Stojakovic[a], Jelena Milenkovic[b], Stevan Stupar[c], Zlate Velickovic[c], Nevenka Rajic[a,*]

[a]*Faculty of Technology and Metallurgy, University of Belgrade, 11000 Belgrade, Serbia, emails: stojakovic@tmf.bg.ac.rs (D. Stojakovic), nena@tmf.bg.ac.rs (N. Rajic)*
[b]*Innovation Centre of the Faculty of Technology and Metallurgy, University of Belgrade, 11000 Belgrade, Serbia, email: jmilenkovic@tmf.bg.ac.rs*
[c]*Military Academy, University of Defence, 11000 Belgrade, Serbia, emails: stevan.stupar13@gmail.com (S. Stupar), zlatevel@yahoo.com (Z. Velickovic)*

Received 14 May 2015; Accepted 8 September 2015

ABSTRACT

Sorption of the Zn^{2+} and Ni^{2+} ions by the Na^+-enriched natural clinoptilolite (Na-CLI) from aqueous solutions containing both Zn^{2+} and Ni^{2+} ions at a range of concentrations has been studied at 298, 308, and 318 K. It was found that the sorption of a particular ion by Na-CLI increases with the increase in the initial concentration of the solution of that ion. At a given initial concentration, the sorption degree increases with temperature. Also, the sorption of a particular ion is greater when the initial solution contains a second ion than it is when the particular ion is present alone. The sorption kinetics is in accord with the pseudo-second-order reaction rate model. The values of the k_2 rate constant do not show a regular change with the initial Zn^{2+}/Ni^{2+} concentrations probably because the presence of the second ion has a significant effect on the reaction rate. Thermodynamic study has shown that the sorption is exothermic, occurring spontaneously in the 298–318 K range and with a positive entropy change.

Keywords: Adsorption; Clinoptilolite; Binary; Heavy metal; Kinetics; Zeolite

1. Introduction

Wastewaters from the mining and metal finishing industry, manufacture of batteries, pigments, chemicals, smelting of metals, etc. generally contain heavy metal cations at high concentrations. This is of great concern since these metals are toxic to human beings, animals, and plants. The process of ion exchange in which toxic heavy metal ions in solutions are replaced by more benign alkali or alkali earth cations from a solid exchanger is one of the most effective techniques in the removal of toxic heavy metal ions from industrial wastewaters. Accordingly, natural zeolites are efficiently used in ion-exchange processes due to their high abundance, beneficial ion-exchange capacities, high metal selectivity, and low cost.

Clinoptilolite is the most abundant natural zeolite. The aluminosilicate framework of clinoptilolite consists of three channels connected in two dimensions: two of them are formed by eight-membered rings and the third one by 10-membered rings [1]. The channels are occupied by exchangeable alkali and earth alkali

---

*Corresponding author.

cations and water molecules. Clinoptilolite samples from various regions show different ion-exchange abilities, the difference being mainly caused by different Si/Al molar ratios and different types of extra-framework cations. A recent structural study [2] has shown that Ni^{2+} and Zn^{2+} cations occupy mostly two extra-framework sites: the first one is in the center of the large 10-membered channel and the second one is in the center of the smaller eight-membered channel that runs parallel to the crystallographic axis *c* (the second eight-membered channel runs parallel to the crystallographic axis *a*). This study reports also that some other cations such as Cu^{2+} occupy a new extra-framework site inside the large channel.

Zlatokop in Vranjska Banja is the largest clinoptilolite deposit in Serbia. The zeolitic tuff contains more than 70 wt.% of clinoptilolite with quartz and feldspar as major mineral impurities [3]. Taking into account the high quality of this zeolitic tuff, we have investigated in detail its cation exchange behavior toward different heavy metal cations [4–7] present in water solutions as single cationic species. It should be noticed that the single metal adsorption on different naturally occurring adsorbents such as clays, activated carbons, zeolites, and biosorbents has been extensively investigated in the last decade [8,9]. The binary adsorption of metals on natural clays has been performed for a few heavy metal cations and clays [10,11]. However, such studies on clinoptilolite have been rather scarce [11].

Taking into account that Ni^{2+} and Zn^{2+} prefer similar crystallographic sites in the clinoptilolite lattice and that the presence of another metal cation can influence [refs.] the adsorption capacity of a single one, the present study deals with the exchange equilibria of Na cations from the clinoptilolite-rich zeolitic tuff and Ni^{2+}–Zn^{2+} ions present in water solutions at different concentrations. The binary adsorption was studied at three different temperatures (298–318 K).

2. Experimental

2.1. Zn and Ni sorption on the clinoptilolite tuff

The zeolite material (CLI) obtained from a large sedimentary Zlatokop deposit was used in the experiments. The particle size of the samples was in the 0.063–0.125-mm range. The sample (50 g) was pretreated with 500 cm^3 of 2.0 mol dm^{-3} solution of NaCl (p.a., Aldrich) in order to improve the tuff's exchange capacity [7]. The suspension was magnetically stirred for 48 h at 50°C. The sample (Na-CLI) was then washed with distilled water and dried in oven at 60°C. Elemental analysis showed [6] that the amount of exchangeable cations in Na-CLI theoretically allows for an uptake (by cation exchange) of appr. 46 mg of Zn or 42 mg of Ni per gram of Na-CLI. The solutions used for the experiments (Table 1) contain Zn(II) and Ni(II) either in a 2:1 (solutions I, II, and III) or 1:2 ratio (solutions IV, V, and VI). $ZnSO_4{\cdot}7H_2O$ (Zdravlje, Leskovac) and $NiSO_4{\cdot}7H_2O$ (Fluka) were used for the preparation of the solutions.

The rate of sorption of Ni^{2+}–Zn^{2+} by Na-CLI was studied at temperatures of 298, 308, and 318 K in water solutions (I–VI). 100.00 cm^3 of the appropriate solution was mixed with 1.0 g of Na-CLI and the suspension was stirred on a water bath (Memmert, WNB 22) at a rate of 105 rpm for a time period of 2, 6, and 24 h. The solid was then separated by filtration.

Preliminary investigations showed that the Zn^{2+} and Ni^{2+} removal capacity of Na-CLI increases slightly when the solution pH is raised from 4 to 7. The subsequent experiments were conducted at pH about 6 to avoid any possible hydroxide precipitation [12].

Zinc and nickel concentrations in solution were determined by AAS using Varian Spectra AA 200; at least five measurements were done for each determination.

All the experiments were carried out under controlled conditions: the temperature in the thermostated bath was maintained constant to within ±0.1°C, the clinoptilolite sample was weighed to four-digit accuracy, and the solution concentrations were determined with four-digit accuracy.

3. Results and discussion

3.1. Sorption experiments

Sorption of the Zn^{2+} and Ni^{2+} ions by the Na^{+}-enriched natural clinoptilolite (Na-CLI) from aqueous solutions containing both Zn^{2+} and Ni^{2+} ions has been examined at a range of concentrations listed in Table 1 and at temperatures of 298, 308, and 318 K. The results for the Zn^{2+} sorption are shown in Table 2, while those for Ni^{2+} are given in Table 3. Tables 2 and 3 also include the previously published data for the sorption of Zn^{2+} [6] and Ni^{2+} [5] ions, respectively, by Na-CLI from aqueous solutions containing only one of the respective ions. From Tables 2 and 3, it can be seen that the sorption of a particular ion by Na-CLI increases with an increase in the initial concentration of the solution of that ion at all three temperatures. Also, at a given initial concentration, the degree of sorption increases with temperature. Furthermore, in cases where a particular ion was in two separate experiments present at the initial concentration of 100 mg dm^{-3}, the sorption degree was greater from

Table 1
Initial Zn^{2+} and Ni^{2+} concentrations used in the experiments

Solution	Concentration ($mg\ dm^{-3}\ Zn^{2+}/mg\ dm^{-3}\ Ni^{2+}$)	Abbreviated notation
I	100/50	Zn100Ni50
II	200/100	Zn200Ni100
III	300/150	Zn300Ni150
IV	50/100	Ni100Zn50
V	100/200	Ni200Zn100
VI	150/300	Ni300Zn150

the solution in which the initial concentration of the second ion was smaller: the sorption degree of Zn^{2+} was greater from the Zn100Ni50 than from the Ni200Zn100 solution, and the sorption degree of Ni^{2+} was greater from the Ni100Zn50 than from the Zn200Ni100 solution. This is understandable since, for example, the Zn^{2+} ions in Zn100Ni50 have to compete with fewer number of Ni^{2+} ions for the sites on Na-CLI than do the Zn^{2+} ions in Ni200Zn100.

A remarkable fact to be observed from Tables 2 and 3 is that the sorption of a particular ion is greater when the initial solution contains a second ion than it is when the particular ion is present alone in the initial solution. That holds for all concentrations for which the single ion data are available, i.e. for $C_0 = 100$, 200, and 300 mg dm^{-3}, and for all three temperatures [5,6]. For example, for $C_0 = 300$ mg Zn dm^{-3} at 298 K, the sorption degree for Zn^{2+} is 15.83 mg Zn g^{-1} from the Zn300Ni150 solution and only 8.83 mg Zn g^{-1} from the solution of Zn^{2+} alone. It can be concluded that the presence of a second type of ion does not act adversely toward another cation. On the contrary, the presence of Ni^{2+} (Zn^{2+}) enhances the sorption ability of Na-CLI toward the other ion. Recently published results obtained on the binary adsorption of Cd^{2+}–Ni^{2+}, Zn^{2+}–Cd^{2+}, and Pb^{2+}–Cu^{2+} on three types of natural clays [10] indicate that the influence of a particular ion on the adsorption of the other one depends not only on the type of clay but also on the type of cations. In the Zn^{2+}–Cd^{2+} adsorption on sepiolite, Zn^{2+} inhibits the adsorption of Cd^{2+}, whereas Cd^{2+} does not influence the adsorption of Zn^{2+}. For bentonite, both Cd^{2+} and Ni^{2+} show similar antagonism toward adsorption of the other metal [10]. In the present study, it seems likely that Ni^{2+} and Zn^{2+} ions are not competitors in adsorption. This could be explained by a similarity in their hydrated radii, Ni^{2+} (83 pm), and Zn^{2+} (86 pm), and the fact that Na^{+} has a significantly larger hydrated radius in comparison to both Ni^{2+} and Zn^{2+} [13]. Since both Ni^{2+} and Zn^{2+} occupy the same two crystallographic sites, it is the increase in entropy that governs the replacement of Na^{+} from these positions in the clinoptilolite

Table 2
Equilibrium q_e values for the Zn(II) adsorption after 24 h

	q_e (mg Zn g^{-1}) two metals						q_e (mg Zn g^{-1}) one metal		
C_0 (mg Zn dm^{-3})	298 K		308 K		318 K		298 K	308 K	318 K
50	4.95 (Ni100Zn50)		4.96		4.98				
100	9.04 (Ni200Zn100)	9.85 (Zn100Ni50)	9.11	9.90	9.13	9.98	5.75	6.67	7.78
150	10.24 (Ni300Zn150)		11.46		11.95				
200	13.34 (Zn200Ni100)		13.60		14.80		7.65	9.68	11.44
300	15.83 (Zn300Ni150)		17.67		19.55		8.83	11.25	13.01

Table 3
Equilibrium q_e values for Ni^{2+} adsorption after 24 h

	q_e (mg Ni g^{-1}) two metals						q_e (mg Ni g^{-1}) one metal		
C_0 (mg Ni dm^{-3})	298 K		308 K		318 K		298 K	308 K	318 K
50	2.8 (Zn100Ni50)		3.35		3.92				
100	2.58 (Zn200Ni100)	4.65 (Ni100Zn50)	3.89	6.43	4.27	7.49	1.94	3.06	3.82
150	3.41 (Zn300Ni150)		4.39		5.28				
200	7.04 (Ni200Zn100)		8.87		10.57		2.57	4.05	5.34
300	7.61 (Ni300Zn150)		10.33		11.57		3.01	4.83	5.99

channels by the divalent ions. However, at present, we cannot offer a plausible explanation for the fact that the presence of Ni^{2+} (Zn^{2+}) increases the adsorption capacity of Na-CLI toward Zn^{2+} (Ni^{2+}) relative to the single ion adsorption.

3.2. Kinetic analysis

The time dependence of sorption of the Zn^{2+} and Ni^{2+} ions by Na-CLI has been investigated at 298 K using solutions listed in Table 1. The time dependence was followed for 24 h. Figs. 1 and 2 show the uptake values of Zn^{2+} and Ni^{2+}, respectively, from the solutions.

It is seen from the curves on Figs. 1 and 2 that at the beginning stages of sorption (i.e. approximately in the first 2 h), the Zn^{2+} and Ni^{2+} uptake increases rather sharply from $q = 0$ at $t = 0$. Afterward, the sorption proceeds more gradually. Similar behavior has been observed for the Zn^{2+} and Ni^{2+} sorption when these ions were present individually in solution [5,6]. The data from Figs. 1 and 2 were analyzed using the pseudo-second-order reaction rate model since this model has been found to give the best description of the sorption kinetics in heavy metal sorption studies [14–17]. The model is defined by Eq. (1) [17]:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{1}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order adsorption. The plot of t/q vs. t

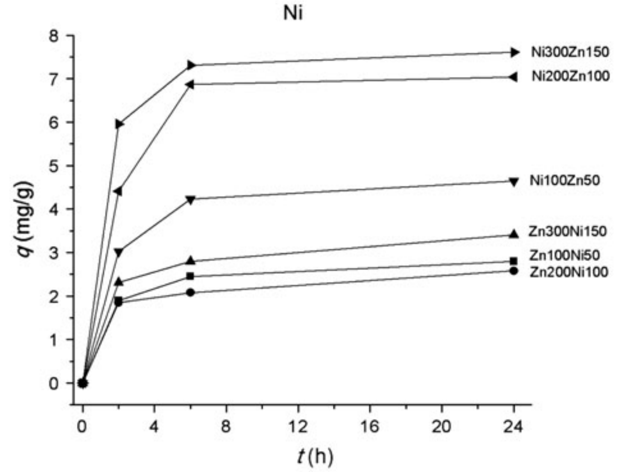

Fig. 2. Adsorption kinetics for Ni^{2+} on Na-CLI at different initial Ni^{2+} concentrations; q is the amount of the adsorbed Ni^{2+} (mg per 1 g of Na-CLI).

Table 4
Rate constants obtained by the pseudo-second-order kinetic model for the sorption of Zn^{2+}/Ni^{2+} on Na-CLI (R^2 is the coefficient of determination of linear regression)

	Zn		Ni	
Solution	k (g mg^{-1} h^{-1})	R^2	k (g mg^{-1} h^{-1})	R^2
Zn100Ni50	0.5771	1	0.303	0.999
Zn200Ni100	0.0559	0.997	0.276	0.997
Zn300Ni150	0.0391	0.998	0.201	0.998
Ni100Zn50	0.345	0.999	0.191	0.999
Ni200Zn100	0.0741	0.999	0.149	0.997
Ni300Zn150	0.0781	0.997	0.253	0.999

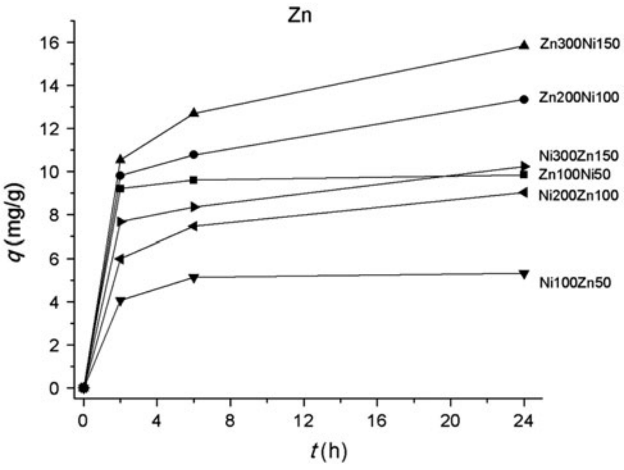

Fig. 1. Adsorption kinetics for Zn^{2+} on Na-CLI at different initial Zn^{2+} concentrations; q is the amount of the adsorbed Zn^{2+} (mg per 1 g of Na-CLI).

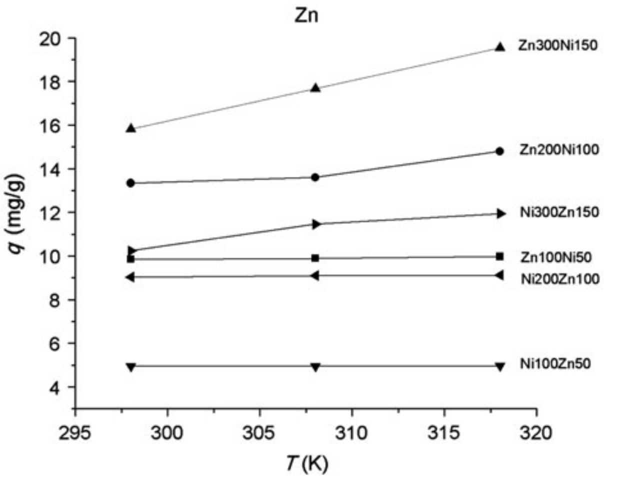

Fig. 3. Plot of q vs. T at different initial Zn^{2+} concentrations; q is the amount of the adsorbed Zn^{2+} (mg per 1 g of Na-CLI).

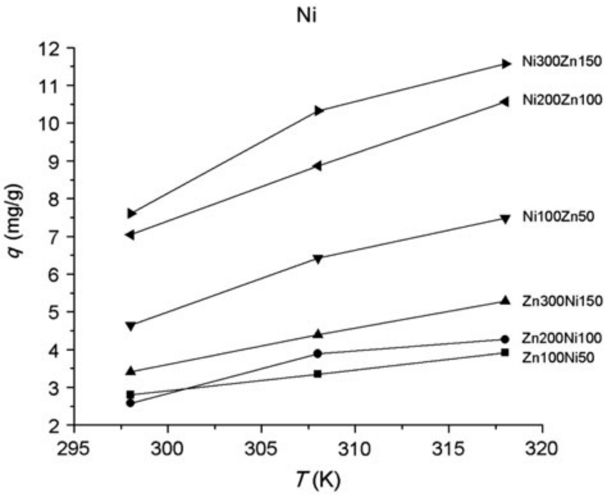

Fig. 4. Plot of q vs. T at different initial Ni^{2+} concentrations; q is the amount of the adsorbed Ni^{2+} (mg per 1 g of Na-CLI).

is a straight line if the experimental data correspond to this model; q_e and k_2 are obtained from the slope and intercept, respectively. This was the case with the data from Figs. 1 and 2, and the results of the kinetic analysis are presented in Table 4.

The results in Table 4 show that the k_2 rate constant values change rather irregularly with the initial Zn^{2+}/Ni^{2+} concentrations. This indicates that the presence of the second ion has a significant effect on the reaction rate. In addition, the sorption kinetics is probably governed not only by the ion-exchange reaction, but also by diffusional processes that have to be taken into account. Also, the Zn^{2+} species entering the clinoptilolite lattice need not be only the hydrated Zn^{2+} ions but also some more complex zinc(II) ionic moieties [6].

3.3. Thermodynamic study

The data obtained by sorption experiments at 298, 308, and 318 K for the solutions listed in Table 1 are presented in Figs. 3 (for Zn) and 4 (for Ni).

The data from Figs. 3 and 4 were used for the estimation of some thermodynamic parameters. The standard free energy of sorption (ΔG°) was calculated by Eq. (2):

$$\Delta G^\circ = -RT \ln K \tag{2}$$

where R is the universal gas constant and K is the equilibrium constant at temperature T. The constant K was calculated as the ratio of the equilibrium Zn^{2+} or Ni^{2+} concentrations on the sorbent and in solution after 24 h of exchange. The enthalpy and entropy of sorption were calculated from Eq. (3):

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{3}$$

Table 5
Thermodynamic parameters for the Zn^{2+} sorption on Na-CLI in the presence of Ni^{2+} (R^2 is the coefficient of determination of linear regression)

C_0 (mg Zn dm^{-3})	T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	R^2
50 (Ni100Zn50)	298	−19.0	−29.29	161.9	0.980
	308	−20.4			
	318	−22.3			
100 (Zn100Ni50)	298	−18.4	−16.72	117.5	0.876
	308	−19.2			
	318	−20.8			
100 (Ni200Zn100)	298	−16.8	−1.88	62.34	−0.809
	308	−17.1			
	318	−18.1			
150 (Ni300Zn150)	298	−15.3	−11.16	88.79	0.998
	308	−16.2			
	318	−17.1			
200 (Zn200Ni100)	298	−14.5	−11.23	86.07	0.864
	308	−15.1			
	318	−16.2			
300 (Zn300Ni150)	298	−13.4	−18.84	108.4	0.999
	308	−14.5			
	318	−15.7			

Table 6
Thermodynamic parameters for the Ni^{2+} sorption on Na-CLI in the presence of Zn^{2+} (R^2 is the coefficient of determination of linear regression)

C_0 (mg Ni dm^{-3})	T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	R^2
50 (Zn100Ni50)	298	−13.8	−45.85	200.0	0.998
	308	−15.7			
	318	−17.8			
100 (Ni100Zn50)	298	−12.9	−48.06	204.9	0.992
	308	−15.2			
	318	−17.0			
100 (Zn200Ni100)	298	−10.6	−13.81	85.44	0.999
	308	−12.5			
	318	−13.3			
150 (Zn300Ni150)	298	−9.3	−37.74	158.5	0.932
	308	−11.4			
	318	−12.5			
200 (Ni200Zn100)	298	−11.3	−24.98	121.9	0.999
	308	−12.6			
	318	−13.8			
300 (Ni300Zn150)	298	−10.2	−21.40	106.4	0.944
	308	−11.5			
	318	−12.4			

The plot of $\ln K$ vs. $1/T$ gives a straight line and the values of ΔS° and ΔH° are evaluated from its intercept and slope, respectively. The calculated thermodynamic parameters for the Zn^{2+} and Ni^{2+} sorption are listed in Tables 5 and 6, respectively.

The ΔG° values given in Tables 5 and 6 show that the sorption of Zn^{2+} and Ni^{2+} on Na-CLI from aqueous solutions containing both Zn^{2+} and Ni^{2+} ions occurs spontaneously in the 298–318 K range. Such spontaneity has also been observed for the Zn^{2+} and Ni^{2+} sorption when these ions were present individually in solution [5,6]. The ΔG° values slightly decrease with temperature at all initial Zn^{2+} and Ni^{2+} concentrations. The sorption of Zn^{2+} and Ni^{2+} is exothermic ($\Delta H^\circ < 0$), which is in contrast to the endothermic sorption when these ions were present individually in solution [5,6]. The Zn^{2+} and Ni^{2+} sorption proceeds with an increase in entropy, which is analogous to the situation when these ions were present individually in solution. The positive ΔS° values reflect the fact that the sorption involves the liberation of two Na^+ ions when one Zn^{2+} or Ni^{2+} ion is bound to the sorbent.

4. Conclusions

Sorption of the Zn^{2+} and Ni^{2+} ions by the Na^+-enriched natural clinoptilolite (Na-CLI) from aqueous solutions containing both Zn^{2+} and Ni^{2+} ions, studied at 298, 308, and 318 K, has shown that the sorption of a particular ion by Na-CLI increases with the increase in the initial concentration of the solution of that ion. At a given initial concentration, the sorption degree increases with temperature. It was also found that the sorption of a particular ion is greater when the initial solution contains a second ion than it is when the particular ion is present alone.

The sorption kinetics can be satisfactorily described by the pseudo-second-order reaction rate model. However, the values of the k_2 rate constant do not show a regular change with the initial Zn^{2+}/Ni^{2+} concentrations, indicating that the presence of the second ion has a significant effect on the reaction rate.

Thermodynamic study has shown that the examined sorption occurs spontaneously in the 298–318 K range. The sorption is exothermic, which is in contrast to the situation when these ions are present individually in solution. The entropy change is positive, reflecting the fact that the sorption involves an exchange of two Na^+ ions for one Zn^{2+} (or Ni^{2+}) ion.

Acknowledgements

This work was supported by the Serbian Ministry of Science (project no 172018). The authors also thank the Nemetali Company from Vranjska Banja (Serbia) for kindly providing the zeolite samples.

List of symbols

K — equilibrium constant (–)
k_2 — the rate constant of the pseudo-second-order model ($\mathrm{g\ mg^{-1}\ min^{-1}}$)
q — amount of the adsorbed M(II) ($\mathrm{mg\ g^{-1}}$)
q_e — amount of the adsorbed M(II) at equilibrium ($\mathrm{mg\ g^{-1}}$)
R — universal gas constant ($8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$)
t — time (min)

References

[1] Ath. Godelitsas, Th. Armbruster, HEU-type zeolites modified by transition elements and lead, Microporous Mesoporous Mater. 61 (2003) 3–24.

[2] Y. Garcia-Basabe, A. Ruiz-Salvador, G. Maurin, L.C. de Menorval, I. Rodriguez-Iznaga, A. Gomez: Location of extra-framework Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} cations in natural and dealuminated clinoptilolite, Microporous Mesoporous Mater. 155 (2012) 233–239.

[3] S. Jevtić, I. Arčon, A. Rečnik, B. Babić, M. Mazaj, J. Pavlović, D. Matijaševic, M. Nikšić, N. Rajić, The iron (III)-modified natural zeolitic tuff as an adsorbent and carrier for selenium oxyanions, Microporous Mesoporous Mater. 197 (2014) 92–100.

[4] N. Rajic, Dj. Stojakovic, S. Jevtic, N. Zabukovec Logar, M. Mazaj, V. Kaucic, Removal of aqueous manganese using the natural zeolitic tuff from the Vranjska Banja deposit in Serbia, J. Hazard. Mater. 172 (2009) 1450–1457.

[5] N. Rajic, Dj. Stojakovic, M. Jovanovic, N. Zabukovec Logar, M. Mazaj, V. Kaucic, Removal of nickel(II) ions from aqueous solutions using the natural clinoptilolite and preparation of nano-NiO on the exhausted clinoptilolite, Appl. Surf. Sci. 257 (2010) 1524–1532.

[6] Dj. Stojakovic, J. Hrenovic, M. Mazaj, N. Rajic: On the zinc sorption by the Serbian natural clinoptilolite and the disinfecting ability and phosphate affinity of the exhausted sorbent, J. Hazard. Mater. 185 (2011) 408–415.

[7] M. Jovanovic, N. Rajic, B. Obradovic, Novel kinetic model of the removal of divalent heavy metal ions from aqueous solutions by natural clinoptilolite, J. Hazard. Mater. 233–234 (2012) 57–64.

[8] S. Babel, T. Agustiono Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review, J. Hazard. Mater. 97 (2003) 219–243.

[9] S.E. Bailey, T.J. Olin, R. Mark Bricka, D. Dean Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (2009) 2469–2479.

[10] E. Padilla-Ortega, R. Leyva-Ramos, J.V. Flores-Cano, Binary adsorption of heavy metals from aqueous solution onto natural clays, Chem. Eng. J. 225 (2013) 535–546.

[11] I. Nuić, M. Trgo, J. Perić, N. Vukojević Medvidović: Analysis of breakthrough curves of Pb and Zn sorption from binary solutions on natural clinoptilolite, Microporous Mesoporous Mater. 167 (2013) 55–61.

[12] S. Kocaoba, Y. Orhan, T. Akyüz, Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite, Desalination 214 (2007) 1–10.

[13] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry—Principles of Structure and Reactivity, fourth ed., HarperCollins College Publishers, Hinsdale, IL, 1993, pp. 14–115.

[14] O. Oter, H. Akcay, Use of natural clinoptilolite to improve water quality: Sorption and selectivity studies of lead(II), copper(II), zinc(II), and nickel(II), Water Environ. Res. 79 (2007) 329–335.

[15] N. Gupta, S.S. Amritphale, N. Chandra, Removal of Zn(II) from aqueous solution by using hybrid precursor of silicon and carbon, Bioresour. Technol. 101 (2010) 3355–3362.

[16] Y.S. Ho, J.F. Porter, G. McKay, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems, Water Air Soil Pollut. 141 (2002) 1–33.

[17] B. Alyüz, S. Veli, Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, J. Hazard. Mater. 167 (2009) 482–488.