

Removal of zinc, copper and lead by natural zeolite— a comparison of adsorption isotherms

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Abstract

An uptake of zinc (Zn), copper (Cu), and lead (Pb) from aqueous solutions by ion exchange on natural zeolitic tuff has been studied. The Croatian zeolite clinoptilolite from the Donje Jesenje deposit has been used as a natural ion exchanger. The efficiency of removal is higher for Pb and Cu than for Zn ions. Measured concentrations of Si in the liquid phase identify the detachment of the aluminosilicate structure during ion exchange in the presence of H^+ and OH^- ions. The adsorption isotherm equations; Langmuir–Freundlich, Redlich–Petersen, Toth, Dubinin–Radushkevich, modified Dubinin–Radushkevich, and Lineweaver–Burk were derived from the basic empirical equations, and used for calculation of ion exchange parameters. The best fitting of experimental results to the proposed isotherms was observed in models that assume that ionic species bind first at energetically most favorable sites, with multi-layer adsorption taking place subsequently.

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1. Introduction

The optimization of wastewater purification processes requires a development of new operations based on low cost raw materials with high pollutant-removal efficiency. Heavy metals such as zinc, lead and copper are prior toxic pollutants in industrial wastewater, and they also become common groundwater contaminants. The complexity of effluents makes the process of heavy metals removal more difficult, as well as strict limitations that have been imposed to wastewater discharge everywhere in aquatic recipients. Among the methods such as precipitation, oxidation, ultrafiltration, reverse osmosis and electro dialysis, ion exchange on natural zeolites seems to be more attractive method. Natural zeolites have been intensively studied recently because of their applicability in removing trace quantities of heavy

metal ions from aqueous solutions by utilizing the ion exchange phenomenon [1,2]. Natural zeolites are low cost aluminosilicates, with a cage-like structure suitable for ion exchange due to isomorphous replacement of Al^{3+} with Si^{4+} in the structure, giving rise to a deficiency of positive charge in the framework. This 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. Clinoptilolite is probably the most abundant zeolite in nature because of its wide geographic distribution and large size of deposits. Natural zeolites with ≈ 70 – 80% clinoptilolite content are often used in technological applications. Natural deposits of zeolitic tuff with a relatively low content of the major mineralogical component—clinoptilolite ($\approx 50\%$) indicate higher heavy metal uptake capacity due to the participation of the adsorption in the overall process. The sorption on zeolitic particles is a complex process because of their porous structure, inner and outer

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charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds, and other imperfections on the surface [3]. The most commonly used Langmuir isotherm defines the equilibrium parameters of homogeneous surfaces, monolayer adsorption and distribution of adsorption sites. It can be easily transformed into linear forms to obtain adjustable parameters by the linear regression analysis. However, the linearizing of parabolic equation does not satisfy on fitting the experimental data in a wide range of concentrations. Experimental results often show non-linear plots that can be approximated to two straight lines, and some authors have discussed disadvantages of this isotherm type [3,4]. The attempts have been made to develop models for adsorption of metal ions on heterogeneous zeolitic surfaces, particularly in the case of competitive adsorption. The Langmuir and Freundlich adsorption models are widely used because they are convenient to describe experimental results in a wide range of concentrations. The mathematical correlation of the Langmuir isotherm has provided a basis for development of other models, which include similarity of adsorption and ion exchange, Gaussian energy distribution, degree of surface heterogeneity and high solute concentrations range [3–6].

2. Experimental

The natural zeolitic tuff, examined in our work, originated from the Croatian deposit Donje Jesenje. The X-ray diffraction (XRD) of natural zeolite sample has been analyzed using a “Siemens D 500/D 501” diffractometer (CuK_α radiation, 2θ = 2–60°). The major mineralogical component is clinoptilolite (≈50%), with feldspar, calcite and quartz as main impurities, and montmorillonite, illite, and halite as components with low content. The chemical composi-

tion of the tested zeolite samples was as follows (wt%): SiO₂—55.80; Al₂O₃—13.32; CaO—5.57; K₂O—2.35; Na₂O—3.90; Fe₂O₃—1.30; MgO—0.70; loss of ignition—17.00 [7].

The ion exchange process was performed by equilibration of the natural zeolite sample with aqueous solutions of different metal ions: Zn, Cu, Pb, at various initial concentrations. Concentrations of Zn, Cu, and Pb ions in the initial solutions were prepared by dissolving the appropriate weight of the respective salt (ZnSO₄·7H₂O, CuSO₄·5H₂O, Pb(NO₃)₂) in doubly distilled water. The anions of these salts (SO₄²⁻ and NO₃⁻) in the aqueous solutions do not form any metal–anion complexes, and do not hydrolyze, so that their effect on the ion exchange process is not observed. The initial concentrations (Table 1) were checked by complexometric titration in acidic medium, using highly selective indicators; 3,3-dimetylnaphtidine was used for Zn, chromazurol-S for Cu, and methylthymol blue for Pb [8]. Prior to all experiments, the zeolite sample was milled and sieved to fraction of grain size 0.1–0.5 mm and dried at 60°C for 1 h. All ion exchange experiments were performed by the batch method, with the solid/liquid ratio 1 g zeolite/100 ml of metal ion solution in glass vessels isolated from atmospheric conditions. Suspensions were shaken in a Heidolph incubator shaker at isothermal (23°C) and constant hydrodynamic conditions (250 rpm) for 3 days until equilibrium was reached. The amount of heavy metal ions remaining in the liquid phase after equilibration has been measured in filtrates by complexometric titration using highly selective indicators [9] and checked by atomic absorption spectrometry (AAS, Varian AA375, Varian Gra-90). Concentrations of exchangeable Na, K, Ca, and Mg ions after equilibration have been measured by AAS, whereas concentrations of Si have been measured spectrophotometrically (Perkin-Elmer Lambda 201 UV/Vis Spectrophotometer) [10]. The pH value in all

Table 1
Concentrations of heavy metal ions, Si and pH in the solutions

Zn					Cu					Pb				
c _i (mmol l ⁻¹)	c _e (mmol l ⁻¹)	pH _i	pH _e	Si _e (mg l ⁻¹)	c _i (mmol l ⁻¹)	c _e (mmol l ⁻¹)	pH _i	pH _e	Si _e (mg l ⁻¹)	c _i (mmol l ⁻¹)	c _e (mmol l ⁻¹)	pH _i	pH _e	Si _e (mg l ⁻¹)
10.08	8.05	5.26	6.74	2.46	10.13	5.96	4.87	5.54	2.84	8.94	4.67	5.18	4.50	4.45
8.57	6.56	5.33	6.80	2.31	8.59	4.42	4.93	5.69	2.44	6.76	2.58	5.19	4.55	4.26
7.02	5.02	5.45	6.81	2.66	7.60	3.70	4.96	5.62	2.44	5.17	1.29	5.19	4.71	4.17
6.00	4.02	5.42	6.80	2.27	6.41	2.68	5.12	5.80	2.37	4.97	1.09	5.18	4.62	4.09
5.10	3.28	5.48	6.74	2.62	5.17	1.94	5.15	5.91	2.35	3.38	0.11	5.26	5.07	4.28
3.52	1.89	5.50	6.58	2.25	3.43	0.84	5.34	6.07	2.31	1.79	0.099	5.33	7.40	2.87
1.68	0.37	5.51	6.71	1.94	1.84	0.05	5.51	6.43	2.27	1.69	0.056	5.30	7.33	2.73
0.57	0.05	5.53	7.08	2.12	0.65	0.00	5.76	7.01	2.11	0.99	0.035	5.40	7.90	2.66
—	—	—	—	—	—	—	—	—	—	0.55	0.012	4.48	7.93	2.94

experiments was measured before and after equilibration (WTW pH-meter) at the experimental temperature of 23°C.

3. Results and discussion

3.1. The equilibrium of heavy metals uptake

The experimental results of the binding of Zn, Cu, and Pb ions on natural zeolite indicate a higher degree of ion removal at lower initial concentration area of metal ions. The plots in Fig. 1 show the uptake degree of each heavy metal ion as a function of the initial concentration. The uptake degree is defined as:

$$\alpha = \frac{c_i - c_e}{c_i} \times 100, \quad (1)$$

c_i being the initial concentration, and c_e equilibrium concentration of the particular ion. In previous experiments equilibrium was obtained after 72 h.

This method is the most efficient process of removal of heavy metal ions from wastewater containing lower pollution concentrations. The quantity of particular ionic species (Zn, Cu, and Pb) bound in dependence on the initial concentrations, shows that the removal efficiency from the liquid phase follows the sequence $Pb \geq Cu > Zn$.

The immobilization of heavy metal ions from aqueous solutions on natural zeolitic tuff is a complex process consisting of ion exchange and adsorption, likely to be accompanied by precipitation of metal ion hydroxide complexes on active sites of the particle surface [10–16]. Surface imperfections and mineralogical heterogeneity of zeolitic tuff promote the solubility of the amorphous aluminosilicate surface layers at both higher and lower pH values [11,16,17]. It was identified by determination of Si concentration in the liquid phase (Table 1). The concentration of Si was higher at lower equilibrium

pH values of the zeolitic tuff/Pb solution systems. At higher initial concentrations of Pb solutions ($c_i = 8.94\text{--}3.38\text{ mmol l}^{-1}$) the pH value decreased during the ion exchange (Table 1), due to the increased concentration and hydrolysis of Ca^{2+} ions in the solution. The type and initial concentration of metal ions do not significantly affect the phenomenon of surface solubility. Namely, solubility of aluminosilicates is a chemical property of natural zeolites, and corresponds to the detachment of framework Al–O–Si bonds according to their amphoteric behavior in the acidic or alkaline solution [13]. The surface charge remaining after the detachment of framework bonds is non-homogeneously distributed and represents active sites suitable for positive metal ionic species binding. The formation of aquametal and hydroxo-complexes species of metal ions depends on the pH value in the solution and initial metal ion concentration. It can affect the mechanism of metal ions binding by changing it from ion exchange to adsorption of monovalent hydroxo-species [11,15].

The balance of the ionic charge leaving the zeolite structure ($Na^+ + \frac{1}{2}Ca^{2+} + K^+ + \frac{1}{2}Mg^{2+}$) and the ingoing ionic charge ($\frac{1}{2}Zn^{2+}$ or $\frac{1}{2}Cu^{2+}$ or $\frac{1}{2}Pb^{2+}$) shows that the total quantity of ingoing ions is lower than the total quantity of outgoing exchangeable ions for all initial concentrations, particularly for the zeolite–lead solution system (Fig. 2).

The observed phenomenon of the nonstoichiometry of ion exchange [16] can be explained by higher hydration radius of heavy metal ions, as well as by adsorption of their positive monovalent hydroxy-species on the inner surface. These effects can block the diffusion of ions (Zn^{2+} , Cu^{2+} , Pb^{2+}) to the exchangeable site in the channels of the porous structure, and decrease the ion exchange capacity.

3.2. Testing of experimental results by adsorption isotherm equations

The equilibrium experimental results of Zn, Cu, and Pb ions exchanged have been fitted by non-linear equations of the adsorption models; Langmuir–Freundlich, Redlich–Petersen, Toth, Dubinin–Radushkevich, modified Dubinin–Radushkevich, Lineweaver–Burk (Table 2) [3].

The adjustable parameters of each isotherm were calculated using experimental results of amounts of the particular metal ion (Zn, Cu, Pb) sorbed per gram of zeolitic tuff (mmol g^{-1}), versus their equilibrium concentration in the solution (mmol l^{-1}). These isotherm equations include three adjustable parameters and cannot be estimated by ordinary linear regression or by any reliable graphical means. For this reason, the initial value of ion exchange capacity M based on the experimental results and nonlinear regression analysis

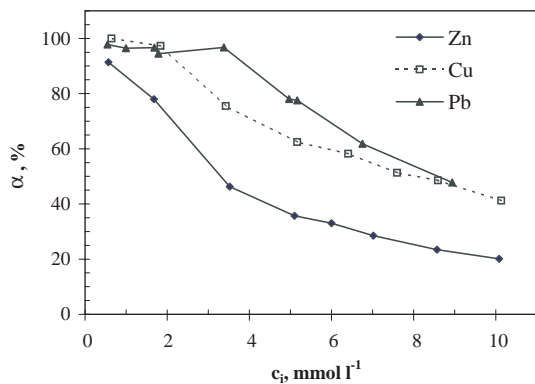


Fig. 1. The removal efficiency of Zn, Cu and Pb ions in dependence on their initial concentration.

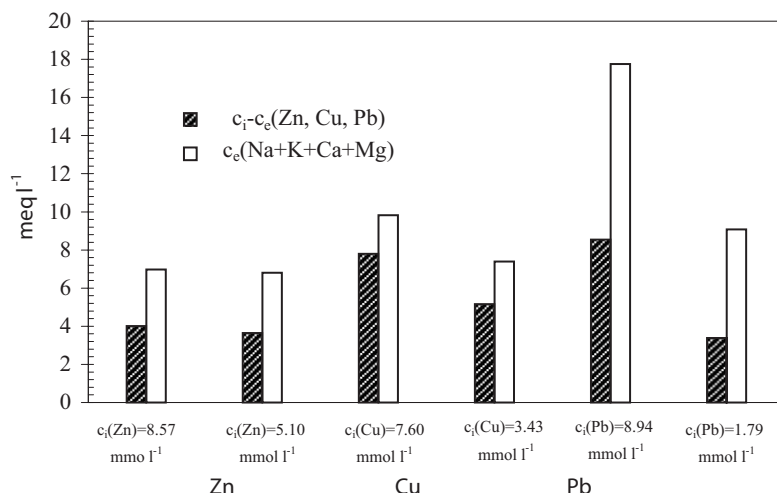


Fig. 2. The relation between outgoing and ingoing exchangeable ions for different initial concentrations of particular heavy metal ion, c_i —initial concentration, c_e —equilibrium concentration.

Table 2
The adsorption isotherm [3]

Isotherm	Isotherm symbol	Equation
Langmuir–Freundlich	LF	$F = (Kc_e)^\beta \beta M / (1 + (Kc_e)^\beta)$
Redlich–Petersen	RP	$f = Kc_e M / (1 + (Kc_e)^\beta)$
Toth	T	$f = Kc_e - \beta M / (1 + (Kc_e)^\beta)^{1/\beta}$
Dubinin–Radushkevich	DR	$\log f = -\beta(\log^2(Kc_e)) + \log M$
Modified Dubinin–Radushkevich	MDR	$\log f = -\beta(\log^2(Kc_e/1 + Kc_e)) + \log M$
Lineweaver–Burk	LB	$1/f = 1/M + 1/(MKc_e)$

Note: f = ionic species sorbed per gram of zeolitic tuff (mmol g⁻¹); c_e = equilibrium concentration of ions (mmol l⁻¹); M = maximum adsorption (mmol g⁻¹); β = degree of heterogeneity ($0 < \beta < 1$); K = constant.

has been used [18]. The parameters K , β , and the accurate value of M , were calculated from the derived isotherm equations using the MS MathCAD Professional program according to the relations:

Langmuir–Freundlich:

$$\frac{d}{dY} \left[\sum_{i=1}^n \left[f_i - \frac{(Kc_{ei})^\beta M}{1 + (Kc_{ei})^\beta} \right]^2 \right] = 0. \quad (2)$$

Redlich–Petersen:

$$\frac{d}{dY} \left[\sum_{i=1}^n \left[f_i - \frac{Kc_{ei}M}{1 + (Kc_{ei})^\beta} \right]^2 \right] = 0. \quad (3)$$

Toth:

$$\frac{d}{dY} \left[\sum_{i=1}^n \left[f_i - \frac{Kc_{ei}M}{[1 + (Kc_{ei})^\beta]^{1/\beta}} \right]^2 \right] = 0. \quad (4)$$

Dubinin–Radushkevich:

$$\frac{d}{dY} \left[\sum_{i=1}^n \left[f_i - 10^{-\beta \log(Kc_{ei}) \log(Kc_{ei}) + \log M} \right]^2 \right] = 0 \quad (5)$$

Modified Dubinin–Radushkevich:

$$\frac{d}{dY} \left[\sum_{i=1}^n \left[f_i - 10^{-\beta \log(Kc_{ei}/(1+Kc_{ei})) \log(Kc_{ei}/(1+Kc_{ei})) + \log M} \right]^2 \right] = 0. \quad (6)$$

Lineweaver–Burk:

$$\frac{d}{dY} \left[\sum_{i=1}^n \left[f_i - \frac{1}{(1/M) + (1/MKc_{ei})} \right]^2 \right] = 0. \quad (7)$$

In Eqs. (2)–(7) the symbol Y represents either K or M or β . It means that for each adsorption model, two or three equations are proposed depending on the number of adjustable parameters Y , which have been determined

according to the equations in Table 2. Using the number of experimental results for each equilibrium concentration $i = 1$ to $n = 8$, the solutions of these equations were parameters K , M , and β . The correlation coefficient (r^2) is calculated as an indicator of fitting of the experimental data to the models proposed [3,6]. The parameter M (mmol g^{-1} zeolite) in Table 3 corresponds to the experimental exchange capacity for the particular heavy metal ion.

The plots in Figs. 3–5 graphically show isotherms, as well as fitting of the experimental results to the curves of adsorption models approached.

As seen in the plots in Figs. 3–5, the sorption behavior of Zn, Cu and Pb on natural zeolitic tuff is similar, except at the value of their experimental exchange capacities. Namely, the ion exchange capacity for Cu and Pb is double than for Zn, for the same experimental conditions (Table 3). In Figs. 2–4 the Redlich–Peterson isotherm describes the sorption of Zn and Pb better than in other models, while for Cu the fitting to the experimental results is much better at higher concentration areas. The curves of Langmuir–Freundlich, Toth and Lineweaver–Burk models do not reach the experimental points, which correspond to the maximum

Table 3
Adjustable parameters and correlation coefficients calculated using experimental data

Isotherm type	Zn				Cu				Pb			
	K	β	M	r^2	K	β	M	r^2	K	β	M	r^2
LF	5.89	0.880	0.200	0.987	3.083	0.888	0.410	0.934	13.65	0.900	0.430	0.934
RP	3.422	0.999	0.211	0.981	2.100	0.970	0.410	0.933	11.00	0.990	0.431	0.947
T	3.833	0.991	0.201	0.983	3.000	0.990	0.410	0.925	13.80	0.900	0.433	0.947
LB	5.299	—	0.201	0.984	2.519	—	0.410	0.926	11.52	—	0.427	0.949
DR	0.059	0.087	0.207	0.992	0.064	0.086	0.410	0.959	0.200	0.100	0.430	0.924
MDR	1.180	0.990	0.201	0.953	0.220	0.55	0.410	0.926	2.140	0.421	0.431	0.949

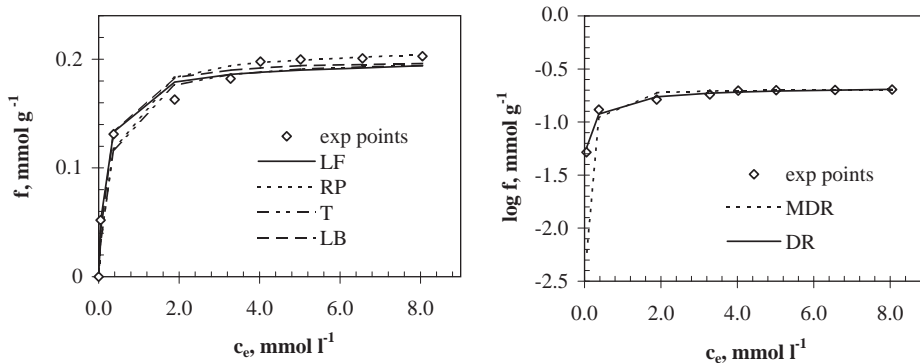


Fig. 3. Comparison of adsorption isotherms with experimental points for Zn.

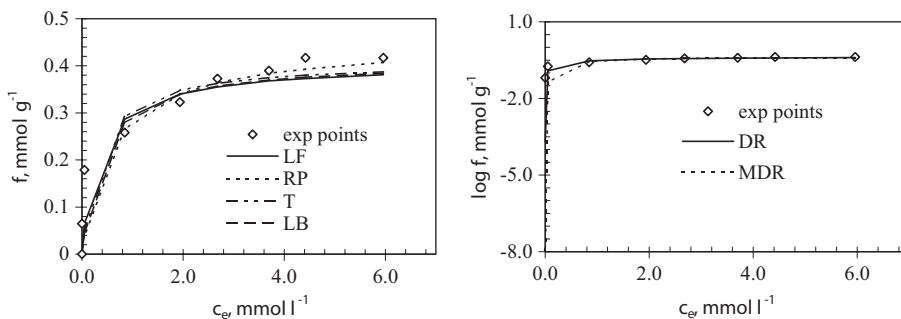


Fig. 4. Comparison of adsorption isotherms with experimental points for Cu.

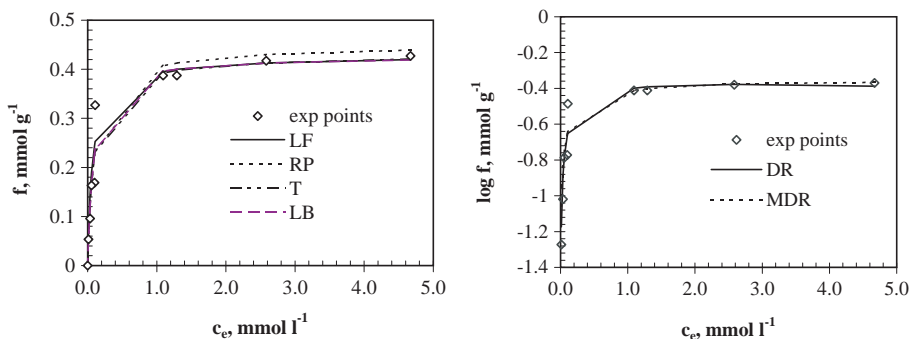


Fig. 5. Comparison of adsorption isotherms with experimental points for Pb.

exchange capacity, particularly for Cu. This can be explained by changes in surface sorption properties during the binding of ions on the inner and outer surfaces, which is more intensive at higher initial concentrations. This results in a lower number of surface sites available for ion exchange. Thus, simplified models that assume a continuous distribution of site affinities cannot show good fitting in a whole initial concentration range. As expected, the Dubinin–Radushkevich curve and its modified form give much better fit at higher concentrations. This is the case particularly for Zn and Pb, but generally the fit is better for Cu than for Zn and Pb at all concentration range. This is understandable because these models assume that ionic species bind first with the energetically most favorable sites, after which multi-layer adsorption occurs.

4. Conclusions

The possibilities of using Croatian natural zeolitic tuff with $\approx 50\%$ clinoptilolite content as a sorbent to remove Zn, Cu, and Pb ions from wastewater have been studied. The maximum exchange capacities for Cu and Pb are double than in the case of Zn, and show similar values for each particular metal ion according to models tested. Described procedure of removal of heavy metal ions is the most efficient in processes containing lower pollution concentrations [19]. The uptake of heavy metal ions from aqueous solutions on natural zeolitic tuff is a complex process consisting mainly of ion exchange and adsorption, and according to literature could be accompanied by precipitation, particularly at higher initial concentrations [13]. The metal ion hydroxo-complexes formed can be sorbed on particle surface sites of different sorption affinity. The surface charge remaining after detachment of surface framework bonds is non-homogeneously distributed over the particle, and represents a newly formed active site suitable for adsorption of ionic species [16]. Testing of the proposed isotherm equations gives evidence of the satisfying fitting of experimental points

to the empirical curves. The Redlich–Petersen, Dubinin–Radushkevich and its modified form of isotherm have shown good fitting at higher concentration areas for all examined systems. This was expected, because a degree of heterogeneity (β) is included and these equations can be used successfully at high solute concentrations [20]. The parameters K and β were calculated using the experimental data and the aforementioned program. It has been demonstrated that they have expected values for all metal ions examined. Differences in the fitting for particular models and for each metal ion are described by the square of the correlation coefficient. The comparison of r^2 for a particular model and metal ion at all ranges of examined concentrations is impossible, because of different deviations of experimental points at low and high concentration areas. The best fitting to the experimental results has been shown by the isotherms that include the coefficient of heterogeneity β .

The adsorption isotherms tested in laboratory scale can be modified to models that could predict the ions and soil interaction at expanded scale. However, the parameters calculated by these models should provide a basis for preliminary investigations of technological use of natural zeolitic tuff for heavy metal ions removal. Moreover, the improvement of its ion uptake capacity is of great interest for application in the field of wastewater treatment.

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