CHEMIJA. 2015. Vol. 26. No. 2. P. 69–78
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Adsorption of potassium ions on natural zeolite: kinetic and equilibrium studies

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Experimental data show that the adsorption of potassium on clinoptilolite after 7-hour relatively fast start eventually becomes diffusion-controlled and slows down. The rate and capacity of adsorption does not depend on the type of solution used – KNO_3 or KCl, but favours higher temperatures. It was found that potassium adsorption is similar to chemisorption and this assumption was confirmed by both equilibrium and kinetic modeling. The applicability of Langmuir and Dubinin–Radushkevich models indicated a non-uniform nature of the clinoptilolite surface and suggested the formation of an adsorbate monolayer, which was used to calculate the clinoptilolite active surface area. The kinetic modeling showed that the pseudo-second order kinetic model was the most suitable for the obtained experimental data, which once more confirmed the chemical nature of potassium adsorption. Despite diffusion-limited potassium adsorption, the release of potassium proceeds at much higher rate in the presence of counter ions and equilibrium can be reached about 10 times faster.

Key words: clinoptilolite, potassium, ion exchange, fertilizers

INTRODUCTION

With increasing demand for food due to population growth, chemists, engineers and agronomy researchers are constantly looking for new ways to increase crop yields, minimize fertilizer production costs and eliminate their negative impact on the environment and humans [1–3]. Some of the materials, suitable for this purpose, are natural zeolites, which are eco-friendly, non-toxic and inert substances. Due to their unique structure, which determines high ion exchange, good adsorptive properties, resistance to high temperatures, aggressive media and effects of ionizing radiation, zeolites are widely used in many industrial, agricultural, domestic and environmental fields [4–6]. Natural zeolites are natural volcanic minerals – tectosilicates, which are porous hydrated alkali or alkaline earth metal aluminosilicates with multiple three-dimensional crystalline structures [7]. These structures consist of $[(Si, Al)O_4]^{4-}$ groups where the negative charge is usually neutralized by alkali or alkaline earth metal cations. Cations are connected via weak ionic bonds and can be easily replaced without changing the structure of aluminosilicate. The cation exchange capacity of zeolite is directly proportional to the number of aluminum atoms that are present in a tetrahedral structure – usually it varies from 2 to 5 meq/g [8].

Clinoptilolite $[(Na, K, Ca)_{2-3}Al_3(Al, Si)_2Si_{13}O_{36} \cdot 12H_2O]$ is aluminosilicate of the heulandite family, which $[(Si, Al)O_4]^{4-}$ tetrahedra (Fig. 1) bind over all four apexes with the formation of a honeycomb-like three-dimensional framework [9]. Clinoptilolite has the Si/Al molar ratio of about 5, so there are a lot of negatively charged cavities, which constitute up to 34% of the zeolite volume and determines its relatively low density. Open cavities and channels, with a diameter ranging from 2.5 to 9 Å, enable the diffusion of water molecules that form the medium for cation exchange [12]. Depending on the formation conditions, zeolite can contain various combinations of metal cations and so it can be named clinoptilolite-K, clinoptilolite-Ca or clinoptilolite-Na. In some cases such cations as Mg^{2+}, Ba^{2+}, Fe^{2+} and Sr^{2+} can also be present in the structure of clinoptilolite [9]. It is known that clinoptilolite's selectivity for the cations can be arranged in the following order: $Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{2+} > Al^{3+} > Mg^{2+} > Li^+$, which under certain conditions may change. One of the most important

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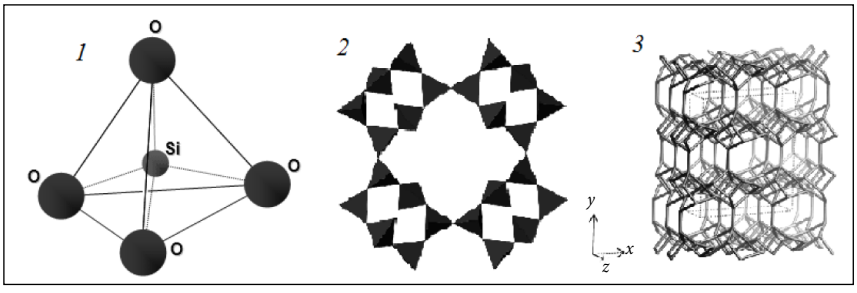

Fig. 1. Natural clinoptilolite $[SiO_4]^{4-}$ tetrahedron (*1*) and its clusters (*2*) [10]; framework of tetrahedra (*3*) [11]

properties – clinoptilolite's maximum theoretical cation exchange capacity is 2.16 meq/g and depends on the size and concentration of adsorbed cations, anion presence in the solution, temperature, pressure, pH, and structural properties of zeolite [13–15].

Due to high abundance, natural zeolites are easily available so it is beneficial to carry out researches in order to find new areas of their application and utilization of their advantageous properties. One of such areas is the use of potassium-saturated natural zeolite as a source of potassium for plants. Potassium is one of the major plant nutrients, crucial for their productivity. In this case, it is beneficial to utilize the ion exchange process since potassium can be assimilated and transmitted through plants only in the form of K^+ [16–18]. A review of existing data suggests that natural zeolites can be used in agriculture not only by means of improving the soil quality but also as a special fertilizer obtained via adsorption of potassium ions.

EXPERIMENTAL

Materials

The natural zeolite was supplied by CSC Elega and it mainly consists of clinoptilolite (ca. 70%). As a potassium source, the analytically pure salts were used: KNO_3, KCl and K_2SO_4. Prior to experimental runs zeolite was crushed with a disk mill and fractioned by employing a sieve shaker Retsch AS 200 with the corresponding Retsch sieves.

Adsorbent characterization

Simultaneous thermal analysis (STA), X-ray diffraction analysis (XRD) and Fourier transform infrared spectroscopy (FTIR) methods were employed in order to identify possible changes in the content and structure of the tested natural zeolite. STA was performed under the flow of air using a Netzsch STA 409 Luxx instrument, XRD analysis was performed with a DRON-6 powder X-ray diffractometer using Ni-filtered Cu K_α radiation, FTIR spectroscopy was carried out by using a Perkin Elmer FT-IR Spectrum GX spectrometer. A complexonometric titration method was used to determine concentrations of calcium and magnesium and for a quantitative analysis of sodium and potassium flame atomic emission spectroscopy (FAES) was performed by using a Jenway PFP-7 flame photometer. Other components were determined by atomic absorption spectroscopy (AAS) using a Perkin Elmer AAnalyst 200 instrument.

Adsorption and desorption tests

The clinoptilolite adsorption capacity for potassium was determined in static conditions. The examined fractions of zeolite were immersed in solutions (zeolite/solution rato 1:50) of every potassium-containing compound and stored at constant temperature by using a heating circulator. All samples were periodically stirred and after the selected amount of time filtered and analyzed. The potassium uptake as well as the loss of zeolite lattice elements due to desorption was calculated by increase or decrease of their respective concentration in the liquid phase:

$$q = \frac{(C_0 - C_1) \cdot V}{m}, \tag{1}$$

where q is the amount of adsorbed/desorbed cation, mg/g; C_0 and C_1 are the initial and final concentrations of cation, mg/mL; V is the volume of the solution, mL; m is the mass of clinoptilolite, g.

Desorption of potassium from potassium-saturated zeolite was investigated in static conditions using NaCl solution (5 mg/mL Na^+) with the zeolite/solution ratio 1:50. The samples were stored at room temperature (ca. 20 °C), periodically stirred and after the selected amount of time filtered and analyzed.

RESULTS AND DISCUSSION

Potassium adsorption dependence on the affinity of the solution

Our selected natural zeolite mainly consists of clinoptilolite with some impurities of quartz, which is also inert and not harmful for plants. Clinoptilolite itself contains a number of displaceables – free cations which can be replaced via adsorption process. Out of several elements sodium, potassium, calcium and magnesium represent the largest fraction of loosely held cations with the total content of 5.91%. The latter three are primary and secondary nutrients for plants which desorption could be beneficial as it would subsequently promote flowering and fruiting. On the contrary,

the ion exchange of microelements would be negligible because of their small amounts, although some elements such as Fe, Mn and Zn could be also useful for plants.

According to our previously collected data, different potassium containing solutions should have an impact on cation exchange between the solution and zeolite. Therefore, potassium ion adsorption using the selected aqueous solutions of potassium sulphate, potassium nitrate and potassium chloride (2, 15, 25 and 35 mg/mL of K^+) was investigated under the same experimental conditions. During experimental runs with potassium sulphate, consequently desorbed calcium and magnesium resulted in precipitation of poorly soluble magnesium and calcium sulphates. In this case, the process became complicated and imprecise so potassium adsorption using K_2SO_4 solution has not been studied in more detail. The selection of a suitable particle fraction of clinoptilolite was made in earlier works and it showed that during the first 7 hours of potassium uptake it is inversely proportional to the particle size of zeolite. But this phenomenon becomes less and less noticeable as the difference between adsorption rates on different fractions diminishes after 20 hours from the start of the experiment. This suggested that at first potassium ions adsorb in the pores that are near the clinoptilolite-solution boundary and further adsorption takes place in pores that are located deeper in zeolite and the overall process becomes diffusion-controlled. So for further studies the fraction of 1–2 mm particle size was used because of more exceptional adsorption rates. The pH measurements were made to determine the acidity of prepared solutions, which could damage the frame of aluminosilicate and undermine his adsorptive properties. The measured pH values appeared to be above 4 and varied between 5.79 and 6.0, so solutions were suitable for adsorption studies. Initial adsorption experiments with clinoptilolite showed that potassium adsorption is a quite slow process, so in order to achieve the ion exchange equilibrium, potassium ion adsorption was conducted at room temperature (20 °C) in the course of 408 hours.

As the experimental data in Table 1 show, the potassium uptake increases with the increase of both KNO_3 and KCl solution concentration. Also it can be noted that at higher K^+ concentrations, particularly the ones exceeding 15 mg/mL, the adsorbed amount of potassium increases only slightly. After 408 hours, the largest amounts of adsorbed potassium were 26 mg/g for KNO_3 solution and 26.2 mg/g for KCl solution, so it is reasonable to assume that different types of solutions as a potassium source have no crucial influence on the process of ion exchange. This assumption is also confirmed by molar equivalents of desorbed calcium, sodium and magnesium, which are proportional to the adsorbed amount of potassium. Therefore, the adsorbed equivalent of potassium is approximately equal to the sum of equivalents of all desorbed ions. These results suggest that adsorption of potassium goes by ion exchange and is mostly influenced by potassium exchange with calcium and sodium.

In order to investigate the possible changes in the structure or formation of new phases in clinoptilolite itself, X-ray diffraction analysis, FTIR absorption spectrometry as well as simultaneous thermal analysis of potassium saturated zeolite were performed. The XRD pattern (Fig. 2) of potassium-saturated zeolite from KNO_3 solution is almost identical to the pattern of parent zeolite. Most peaks can be attributed to clinoptilolite and quartz and their intensities vary very slightly. This shows that during the adsorption only cation exchange took place, the zeolite structure remained intact, and no new phases were formed. On the contrary, potassium-rich zeolite, saturated in KCl solution, revealed a new intense peak in the XRD pattern alongside those related to clinoptilolite and quartz. The peak at 28.01° diffraction angle corresponding to the 0.318 nm interplanar spacing can be attributed to potassium chloride.

The FTIR absorption spectrum of KNO_3 potassium-saturated zeolite showed a new narrow absorption band at 1 384 cm^{-1} wave, which can be explained by the vibrations of NO_3^- remaining in the pores of zeolite. The IR spectrum of zeolite saturated in KCl solution (not shown) did not reveal any difference as compared to the parent clinoptilolite and contains usual bands that are attributable to Si(Al)–O, Si–O–Al, Si–O, O–Si–O, Si–O–Si as well as H–O–H vibrations.

STA showed no changes in the thermal characteristics of zeolite after potassium adsorption. TG curves (not shown) of KCl and KNO_3 potassium saturated zeolite are almost identical to the non-saturated zeolite – with the increase of temperature clinoptilolite gradually loses water. While the DSC curve of KCl saturated clinoptilolite showed no new thermal effects, the one attributed to KNO_3 saturated clinoptilolite revealed a new peak at 295 °C, which indicated an exothermic process. This might be associated with a small amount of potassium nitrate, which decomposes to nitrite during the exothermic reaction.

Table 1. **Clinoptilolite adsorbed and desorbed amounts of respected ions in KCl/KNO_3 solutions**

Cation	Initial concentration of potassium, mg/mL									
	2		5		15		25		35	
	KNO_3	KCl	KNO_3	KCl	KNO_3	KCl	KNO_3	KCl	KNO_3	KCl
Ads. K^+, mg/g	8.716	8.889	20.094	18.897	25.530	25.968	25.921	26.110	26.000	26.200
Des. Ca^{2+}, mg/g	2.996	3.073	6.812	6.787	8.733	8.656	8.831	9.040	8.835	9.015
Des. Na^+, mg/g	1.525	1.543	3.128	2.904	4.167	4.033	4.216	4.092	4.178	4.173
Des. Mg^{2+}, mg/g	0.258	0.258	0.485	0.486	0.641	0.683	0.683	0.714	0.698	0.714

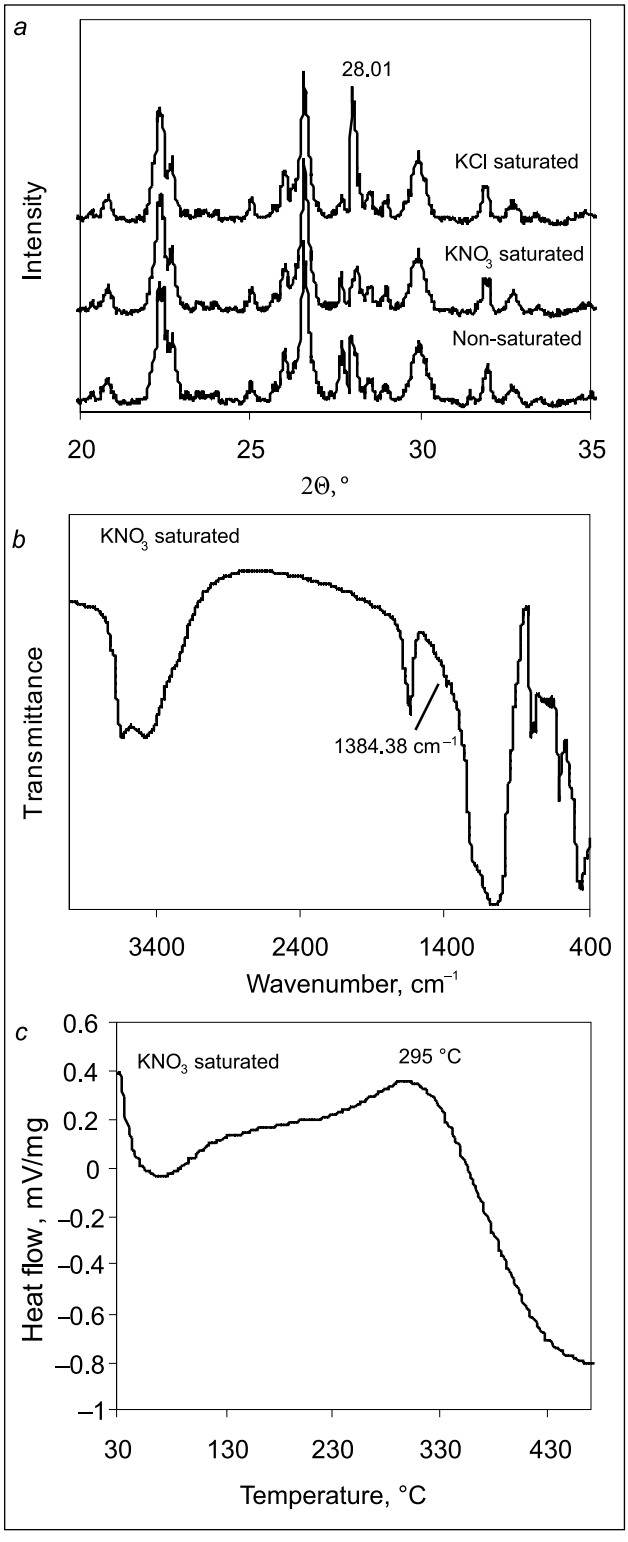

Fig. 2. XRD (*a*), FTIR (*b*) and DSC (*c*) analyses curves of non-saturated and saturated clinoptilolite

According to the results, it can be assumed that the type of solution does not affect the adsorption of potassium ions and in the course of the experiments no new compounds were found either. However, the solution of KNO_3 was chosen for further experiments because chlorine ions, remaining in zeolite's pores, can be harmful for chloride-sensitive plants and it is important that the use of produced special fertilizers would not be limited by any containing components.

Temperature effect on potassium ion adsorption

The use of zeolite to produce special potassium fertilizers is limited mostly by low adsorption rate of potassium ions, which is determined by slow exchange with calcium ions that are present in clinoptilolite. Therefore, it was necessary to investigate the potassium adsorption dependence on the temperature. Experiments were carried out at temperatures of 15, 40 and 65 °C using different KNO_3 solutions containing 2, 5, 15, 25 and 35 mg/mL of potassium. Since previous studies have showed that ion exchange is the most intense during the first 7 hours, the adsorbed amount of potassium was measured only after this point.

Adsorption curves in Fig. 3 show that adsorption takes place in favour of higher temperatures when potassium ion concentration is higher than 2 mg/ml. For example, at temperature of 15 °C and after 7 hours, zeolite adsorbed only 13.4 mg/g of potassium from the solution with the highest concentration, as compared to 19.4 and 28.8 mg/g of adsorbed potassium at 40 and 65 °C, respectively. Kinetic curves also indicate that the optimal concentration of potassium in the solution is 15 mg/g because further increase of concentration is not very advantageous for adsorption as it changes the uptake of K^+ very little. In this case subsequent studies were carried out using only one solution containing 15 mg/g of potassium.

When analyzing kinetic curves in Fig. 4 it is clearly visible that the potassium ion adsorption is much faster at elevated temperatures. At the beginning, the influence of temperature is not eminent and zeolite adsorbs similar amounts of potassium, but after 15 minutes the adsorption rate increases greatly at higher temperatures. After 7 hours of adsorption at 15 °C clinoptilolite adsorbed

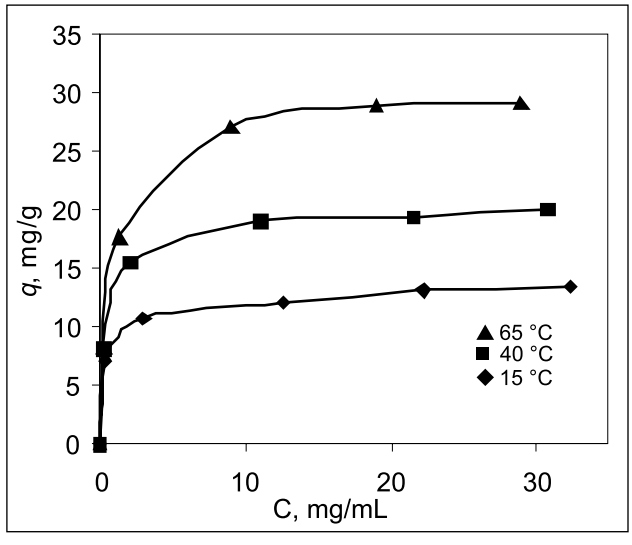

Fig. 3. Potassium uptake dependence on temperature after 7 hours

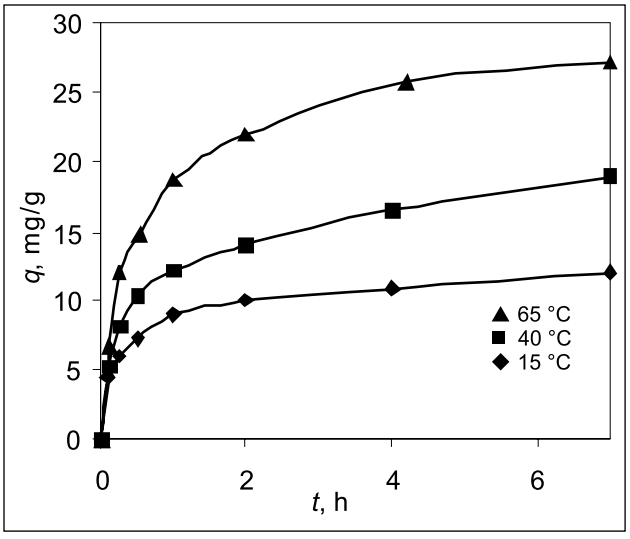

Fig. 4. Kinetic data of potassium uptake when the initial K^+ concentration in liquid phase is 15 mg/mL

12 mg/g of potassium as compared to 27 mg/g of potassium ions at 65 °C. Due to higher adsorption rate, cation adsorption equilibrium can be reached much faster at higher temperatures.

Temperature influence on the adsorption process is more evident when analyzing the desorption results of displaced ions. Similarly to potassium adsorption, calcium desorption occurs more rapidly at higher temperatures and after 7 hours clinoptilolite releases 5.245 and 10.135 mg/g of calcium at 40 °C and 65 °C, respectively, while at 15 °C it releases only 1.880 mg/g. Because of higher calcium content, adsorption rate of potassium ions is mainly limited by slow exchange between potassium and calcium ions. In this case, the increased calcium desorption rate leads to a faster K^+ ion adsorption at higher temperatures.

Desorption of magnesium and sodium also proceeds much faster at higher temperatures, but it has a lesser influence on the adsorption of potassium ions because of their relatively lower content. Depending on temperature (15–65 °C), zeolite releases between 0.228 and 0.860 mg/g of magnesium and between 4.150 and 4.200 mg/g of sodium. It is interesting that sodium ion desorption is fast even at lower temperatures and ion exchange equilibrium can be reached much faster as compared to magnesium and calcium ions. The ion exchange equilibrium between sodium and potassium can be reached after 2 hours from the start of experiment and, as results show, the total amounts of desorbed sodium are very similar despite different experimental conditions. Therefore, the equilibrium between sodium and potassium ions is independent of temperature and should have lower impact on the adsorption of potassium ions.

When summarizing the results, it can be concluded that adsorption of potassium ions on clinoptilolite is very similar to chemisorption by nature because the aforementioned exchange takes place faster at higher temperatures and adsorbed amounts of potassium also increase. In general, potassium ion adsorption dependence on temperature is an important factor that needs to be evaluated in order to establish conditions for the production of potassium fertilizers.

Potassium ion adsorption equilibrium parameters

As it was mentioned before, adsorption of potassium ions from KNO_3 solution on natural clinoptilolite is a relatively slow process, so it takes time to achieve the cation exchange equilibrium. In order to reach adsorption equilibrium and to obtain the adsorption isotherm, an additional adsorption experiment was carried out at room temperature (20 °C) with the maximum adsorption time – more than 1 000 hours. Zeolite's particle size fraction of 1–2 mm as well as KNO_3 solutions of different potassium concentrations (2, 5, 15, 25, 35 and 45 mg/mL of K^+) were used to investigate the adsorption of potassium with the accompanying desorption of calcium, sodium and magnesium. The results of potassium ion adsorption are shown in Fig. 5.

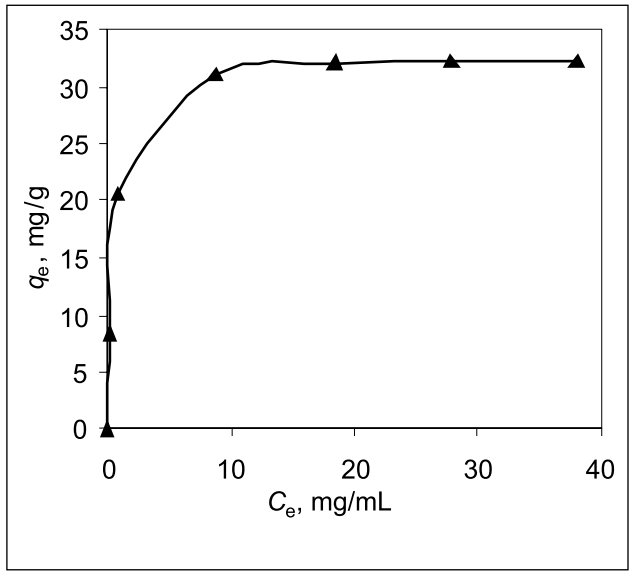

Fig. 5. Isotherm of potassium adsorption on clinoptilolite at 20 °C

The form of the potassium ion adsorption isotherm is typical for chemical adsorption. Almost maximum amount of adsorbed potassium ions at room temperature, 32 mg/g, was already achieved using the KNO_3 solution containing 15 mg/mL of K^+, so further increase of potassium concentration in the solution practically does not affect the clinoptilolite's uptake of potassium.

In order to describe the obtained potassium ion adsorption isotherm, several two-parameter adsorption models were applied: Langmuir, Freundlich, Dubinin–Radushkevich, Temkin and Elovich. Probably the most used one, Langmuir model, is based on the assumption that each active site of the homogenous surface is occupied by only one molecule, which energy of adsorption is constant and independent of surface coverage [19]:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e}, \quad (2)$$

where q_e and C_e are equilibrium solid (mol/g) and liquid (mol/L) phase concentrations; q_m and K_L are Langmuir equation constants that are related to the maximum adsorption capacity (mol/g) and the equilibrium constant of adsorption, respectively.

The Freundlich adsorption model [20] is also frequently used and, contrarily to the Langmuir model, is based on the assumption that adsorption takes place on the heterogeneous surface with non-uniform distribution of adsorption energy, which tends to decrease logarithmically with increasing the coverage

$$q_e = K_F C_e^{\frac{1}{n}}, \quad (3)$$

where K_F and n are Freundlich equation constants indicating the capacity (when C_e is equal to unity) and intensity of adsorption process.

The Dubinin–Radushkevich model [21] is based on the potential energies theory and adsorption on the heterogeneous surface:

$$q_e = q_m \exp\left[-\frac{\left(RT\ln(1+1/C_e)\right)^2}{2E^2}\right], \quad (4)$$

where q_m and E are the maximum adsorption capacity (mol/g) and energy of adsorption (J/mol), R is the gas constant (J/mol · K) and T is the absolute temperature (K).

The Temkin model [22] follows similar assumptions as the Freundlich model, but states that the energy of adsorption decreases linearly, rather than logarithmically, and it is evenly distributed:

$$q_e = \frac{RT}{\Delta Q}\ln\left(K_T C_e\right), \quad (5)$$

where ΔQ and K_T are Temkin equation constants related to the heat of adsorption (J/mol) and the equilibrium constant.

The Elovich model [23] describes adsorption with the formation of a multilayer of adsorbate, which produces an exponentially increasing number of new adsorption sites:

$$\frac{q_e}{q_m} = K_E C_e \exp\left(-\frac{q_e}{q_m}\right), \quad (6)$$

where q_m and K_E are the maximum adsorption capacity (mol/g) and equilibrium constant.

The applicability of the mentioned models was determined by the linearization of the corresponding equations and estimating their coefficients of determination when using the experimental data. Linear forms of all model equations were used to determine their parameters as well. Straight lines were obtained by plotting the model corresponding variables, which allowed determining constants graphically by calculating slopes and intercepts of every analyzed line.

As results in Table 2 show, the applicability of all models differs greatly. Only two of them, Langmuir and Dubinin–Radushkevich, have coefficients of determination higher than 0.95. It is worth to mention that the Langmuir model appeared to be the most accurate since it gave the highest coefficient of determination $R^2 = 1$ and similar results were obtained by other authors [24–26]. Altogether, isotherm models can be arranged into the following sequence by the best fitting: Langmuir > Dubinin–Radushkevich > Temkin > Elovich > Freundlich.

The obtained fit of Langmuir and Dubinin–Radushkevich models indicates that the adsorption of potassium on clinoptilolite is a complex process because it proceeds with the formation of a monolayer of adsorbate on possible homogenous and heterogeneous surfaces. Furthermore, the inapplicability of Temkin, Elovich and Freundlich models rules out any possibility of multilayered adsorption. The maximum amount of adsorbed potassium ions, associated with saturation of the adsorbent and formation of the adsorbate monolayer, was determined graphically and for the Langmuir model it is $q_m = 8.394 \cdot 10^{-4}$ mol/g or

Table 2. **Different adsorption model parameters for potassium adsorption on clinoptilolite**

Adsorption model	Linear form of equation	Equation parameters		
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{q_m K_L}$	q_m, mol/g	K_L, L/mol	R^2
		$8.394 \cdot 10^{-4}$	76.873	1
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$	K_F, $mol^{0.77} \cdot L^{0.23}/g$	n	R^2
		$9.591 \cdot 10^{-4}$	4.286	0.843
Dubinin–Radushkevich	$\ln q_e = \ln q_m - \frac{\left(RT\ln(1+1/C_e)\right)^2}{2E^2}$	q_m, mol/g	E, J/mol	R^2
		$8.922 \cdot 10^{-4}$	$7.877 \cdot 10^3$	0.956
Temkin	$q_e = \frac{RT}{\Delta Q}\ln C_e + \frac{RT}{\Delta Q}\ln K_T$	ΔQ, J/mol	K_T, L/mol	R^2
		$2.436 \cdot 10^7$	$8.103 \cdot 10^3$	0.925
Elovich	$\ln\frac{q_e}{C_e} = \ln K_E q_m - \frac{1}{q_m}q_e$	q_m, mol/g	K_E, L/mol	R^2
		$1.666 \cdot 10^{-4}$	$1.425 \cdot 10^3$	0.844

32.7 mg/g of potassium ions. This value coincides well with the one determined by the fitted Dubinin–Radushkevich model – $q_m = 8.922 \cdot 10^{-4}$ mol/g or 34.8 mg/g. This confirms the fitness of both models and while the maximum adsorption capacity, determined by the Dubinin–Radushkevich model, is very close to the experimental results, q_m determined by the Langmuir model is practically equal. While the calculated q_m value is smaller than the theoretical adsorption capacity of clinoptilolite, it is very similar to the results obtained by other authors [25–28]. The adsorption constant K_L, which describes the ratio of potassium adsorption and desorption rate constants, was found to be $K_L = 76.87$ at room temperature. The Langmuir constant shows that the potassium ion adsorption rate is significantly higher than the desorption rate and clinoptilolite has high affinity for potassium. The nature of adsorption can also be described by the dimensionless separation factor R_L [29]:

$$R_L = \frac{1}{1 + K_L C_0}. \quad (7)$$

Values of the separation factor points out the type of isotherm: unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($1 > R_L > 0$) or irreversible ($R_L = 0$). For the potassium adsorption on clinoptilolite, the values of the separation factor vary between 0.014 and 0.202, depending on the initial concentration, which strongly suggests the favourable adsorption. This is also confirmed by the Freundlich adsorption intensity constant n, which greater-than-unity value indicates favourable adsorption.

The Dubinin–Radushkevich parameter E stands for the energy of adsorption which is equal to the amount of energy (in joules) needed to adsorb 1 mole of substance, counting all the way from the bulk of solution to the active site of the surface. The calculated value of potassium adsorption energy is $E = 7877$ J/mol, which has a very similar value to the one obtained during lead adsorption on clinoptilolite [27]. It also indicates that lower amount of energy is needed to adsorb potassium as compared to lead and it may be associated with a smaller size of potassium ion. Furthermore, the value of adsorption energy falls within the boundary which is used to distinguish chemisorption (between 8 and 16 kJ/mol) and physisorption (less than 8 kJ/mol) processes. Since other ion-exchange studies suggest likewise, we can state that potassium adsorption may be close to chemisorption by nature, whereas it can also be confirmed by the previous similar assumption made due to the increasing extent of adsorption with the increase of temperature.

Having in mind the monolayered adsorption of potassium and determined amount of adsorbed potassium, we can calculate an active specific surface area of the 1–2 mm zeolite fraction. It can be assumed that the potassium ion is adsorbed by clinoptilolite in a hydrated form, which average radius is 331 pm. In this case one hydrated potassium ion should take $S_0 = 3.44 \cdot 10^{-19}$ m^2 of the zeolite surface and the whole monolayer of potassium ions should take:

$$S = q_m N_A S_0 = 8.394 \cdot 10^{-4} \cdot 6.022 \cdot 10^{23} \cdot 3.44 \cdot 10^{-19} = 174\,\mathrm{m^2/g}. \quad (8)$$

The calculated active surface area of zeolite is relatively large and it determines good adsorptive properties of clinoptilolite. As it was mentioned before, adsorption of potassium ions is always followed by desorption of clinoptilolite components: calcium, sodium and magnesium ions, which results are presented in Table 3.

Table 3. **Desorbed amounts of Ca, Mg and Na at equilibrium**

Cation	Initial concentration of potassium, mg/mL				
	2	5	15	25	35
	Desorbed amounts of cation, mg/g				
Ca^{2+}	3.124	7.504	10.654	10.756	10.859
Na^{+}	1.505	2.765	3.933	4.051	4.112
Mg^{2+}	0.273	0.668	0.991	1.088	1.133

It is evident that desorption of all investigated elements occurred and calcium can be characterized by the largest released amounts, while magnesium by the smallest amounts. In order to confirm the cation exchange process between zeolite and the solution as well as to determine the amounts of components present in potassium-saturated clinoptilolite, a chemical composition analysis was carried out which showed that clinoptilolite contains (excluding Al and Si) 5.39% potassium, 0.41% calcium, 1.06% sodium, 0.53% magnesium, 0.56% iron, 0.023% manganese and 0.0044% zinc. All the determined elements were recalculated as their corresponding oxides and results show that at room temperature our investigated zeolite can be saturated with 6.5% of K_2O. Although the potassium content is not very high, it would be sufficient enough for soils, characterized by light granulometric composition, which in particular lacks potassium.

Kinetic modeling of potassium adsorption

In order to obtain more data about the adsorption process, kinetics experiments were conducted at room temperature. For these studies, the same 1–2 mm fraction of zeolite and KNO_3 solutions containing 2, 5, 15, 25, 35 mg/mL of potassium ions were used. The time dependence of potassium ion adsorption, with different concentrations of potassium in the solution, is presented in Fig. 6.

As curves in Fig. 6 show, higher potassium concentration in the solution results not only in higher potassium uptake by clinoptilolite but also in faster adsorption overall. But this is evident only during the first 7 hours from the start of adsorption. From that point on, the adsorption rate decreases greatly and remains almost constant till the end of adsorption. It is interesting that after relatively fast adsorption during the first 7 hours, the potassium uptake by zeolite reaches about 50% (with 2 mg/mL K^+ solution ca. 80%) of the amount adsorbed after 408 hours of adsorption. This clearly shows the decreased rate of adsorption, which basically does not depend on the concentration of potassium in

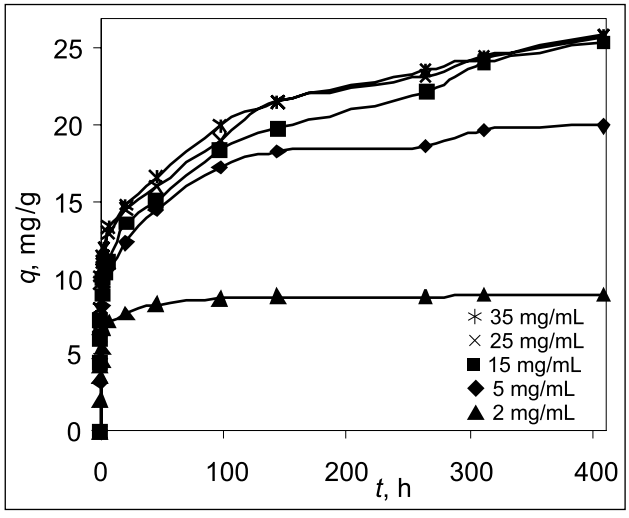

Fig. 6. Kinetic curves of potassium adsorption on clinoptilolite depending on the initial concentration of potassium

the solution and may occur due to diffusion as a limiting step. In this case, the search for the most suitable kinetic model was needed to depict and understand the mechanism of adsorption on clinoptilolite. Four different models were applied to the experimental data: pseudo-first, pseudo-second, Vermeulen and Elovich. The main difference between the first/second order and pseudo-first/pseudo-second order kinetic models is that the latter is based on the assumption that the adsorption rate of the substance does not depend on its concentration in the solution, but rather depends on the number of active sites on the adsorbent surface. Relatively recently proposed, pseudo-first and pseudo-second order kinetic models are now widely used to depict adsorption and ion exchange processes of various substances (dyes, metal ions) on various adsorbents (activated carbon, peat, zeolites, ash, wood, sawdust) [30, 31]. The pseudo-first order model suggests that the adsorption rate is directly proportional to the number of active adsorption sites:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right), \tag{9}$$

where k_1 is the pseudo-first order rate constant (1/min), q_e and q_t are adsorbed amounts of potassium (mol/g) at the equilibrium and at any time t (min).

The driving force (q_e–q_t) is proportional to the fraction of active sites which are unoccupied by adsorbate molecules. The pseudo-second order kinetic model is based on the assumption that the adsorption rate depends on the number of adsorption sites powered by two:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2, \tag{10}$$

where k_2 is the pseudo-second order rate constant (g/mol · min).

The Elovich kinetic model [30, 31] is usually used for activated sorption which is associated with chemisorption on heterogeneous surfaces. It is especially suitable for adsorption processes where the adsorption rate decreases in time due to increase of adsorbent surface coverage:

$$\frac{dq_t}{dt} = \alpha \exp\left[-\beta q_t\right], \tag{11}$$

where α and β are Elovich equation constants related to the initial adsorption rate (mol/g · min) and the activation energy of chemisorption.

The Vermeulen model [32] advantage is that it can be used to determine the rate-limiting step associated with diffusion. It is beneficiary, since the adsorption rate on zeolites is usually limited either by film or particle diffusion:

$$\frac{q_t}{q_e} = \sqrt{1 - \exp\left(-K_V t\right)}, \tag{12}$$

where K_V is the equation constant which depends on the particle size and diffusion coefficient.

All models were fitted to the experimental data using a linear regression analysis as it was performed for modeling of adsorption isotherms. For this, linear forms of each corresponding model were used, which, when presented in special plots, should yield straight lines. Furthermore, the slopes and intercepts of the obtained straight lines were used to calculate kinetic parameters of each model.

As the results in Table 4 show, only the pseudo-second order fitted the experimental kinetic data with the coefficient of determination higher than 0.95, which is not unusual, because this model is one of the most frequently used for adsorption and ion exchange processes, especially if chemisorption is involved. Although it is peculiar that exactly the pseudo-second, but not the pseudo-first order kinetic model agreed with our experimental data better, because namely the latter one fits better when the initial concentration of adsorbent in the solution is relatively high [33]. But nevertheless, the results of modeling showed that there was a slight decrease in the value of determination coefficient when the initial concentration of potassium increases, which indicates that the applicability of the model indeed may be limited by higher concentrations of potassium.

It is also interesting to point out that contrary to first- and second-order classic kinetic models, the pseudo-second order kinetic model rate constant decreases with increasing the initial concentration of adsorbent [25, 27, 34, 35]. Adsorption of potassium on clinoptilolite is not an exception and the pseudo-second order rate constant decreases from 40.352 to 2.313 g/mol · min when the initial concentration of potassium increases from 2 to 35 mg/mL. It basically confirms the assumption, which the pseudo-second order kinetic model is based on. The multiplication of the rate constant k_2 and q_e powered by two gives the value of h, the initial adsorption

Table 4. **Different kinetic model parameters for potassium adsorption on clinoptilolite**

Kinetic model	Linear form of equation	Equation parameters		
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	k_1, min^{-1}		R^2
		$1.224 \cdot 10^{-4}$–$2.794 \cdot 10^{-4}$		0.905–0.970
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	k_2, g/mol · min		R^2
		2.313–40.352		0.988–0.999
Elovich	$q_t = \frac{1}{\beta} \ln \alpha\beta + \frac{1}{\beta} \ln t$	α, mol/g · min	β, γ/mol	R^2
		$3.045 \cdot 10^{-5}$–$1.488 \cdot 10^{-4}$	$16.631 \cdot 10^{3}$–$49.019 \cdot 10^{3}$	0.939–0.987
Vermeulen	$-\ln\left(1 - \left(\frac{q_t}{q_e}\right)\right) = K_V t$	K_V, min^{-1}		R^2
		$1.018 \cdot 10^{-4}$–$2.636 \cdot 10^{-4}$		0.924–0.988

rate, which in our case ranges between $2.143 \cdot 10^{-6}$ and $9.261 \cdot 10^{-7}$ mol/g·min. While the pseudo-first order and Elovich kinetic model did not fit our data satisfactorily and could be rejected as not applicable, the Vermeulen kinetic model was tried for a fitting in a narrower range of the obtained kinetic results. As it turned out, our kinetic curves obeyed the Vermeulen kinetic model quite reasonably when applying it from the seventh hour of the adsorption up until 144th hour. Its coefficients of determination were in the range between 0.983 and 0.999, which is more than acceptable. Since the suitability of the Vermeulen model points out that the limiting step in such adsorption is indeed particle diffusion, it confirmed our previously proposed hypothesis which was based on the evidently decreased adsorption rate after seven hours of adsorption. The Vermeulen model implies that despite higher initial concentration of potassium and high active surface area of clinoptilolite, the diffusion of potassium ions becomes very complicated when the zeolite surface becomes covered with potassium-occupied adsorption sites which were more easily accessible.

Desorption of potassium ions

Beside adsorption, the possibility to use potassium-saturated zeolite as special fertilizers should be evaluated by potassium ion desorption from clinoptilolite into the soil solution because plants are able to uptake potassium only from the soil.

After the adsorption stage, some of potassium, present in zeolite pores, is in the KNO_3 form which will be released into the soil solution due to diffusion. In addition, zeolite is saturated with relatively high-concentration KNO_3 solutions, while ionic concentration in the soil does not exceed 5 mg/mL of any salt. The change in ionic equilibrium conditions will result in the desorption of potassium untill the new equilibrium will be reached. The intensity and rate of ion exchange between zeolite and soil is directly proportional to the concentration of cations in the soil solution and inversely proportional to the potassium concentration.

The ionic composition of the soil depends on its type and many other parameters so likewise desorption of potassium from zeolite in various soils will take place differently. For the simulation of soil in laboratory conditions, the solution containing 5 mg/mL of sodium chloride at room temperature (20 °C) was used. Studies were conducted using the 1–2 mm fraction of zeolite, which was saturated with 53.9 mg/g of potassium (1 000 hours at 65 °C with the initial potassium concentration of 45 mg/mL).

Desorption of potassium ions is relatively fast in the NaCl solution with regeneration time and the equilibrium can be reached after approximately 70 hours. After 98 hours zeolite is able to desorb up to 17.850 mg/g of potassium with simultaneous adsorption of sodium up to 11.7 mg/g. The change of sodium concentration in the simulated soil solution indicates that namely ion exchange takes place. The similar parallel experiment confirmed the nature of potassium release from zeolite. In this case, distilled water was used as the soil solution and after 98 hours only 1.8 mg/g of potassium was released from zeolite. It confirms once more that desorption of potassium from clinoptilolite occurs manly due to the ion exchange. Even though after 98 hours of desorption in the NaCl solution zeolite still contains 35.8 mg/g of potassium, we can predict that in real conditions the extent of desorption will be much higher. This could occur mainly due to more diverse composition of the soil solution which contains not only sodium but various other cations as well: calcium, magnesium, ammonium etc. Our experiments showed that various cations participate in the ion exchange differently. In addition, the soil volume is constantly shifting thus preventing the system from reaching the ion exchange equilibrium, and it will result in significantly higher amounts of desorbed potassium.

CONCLUSIONS

Despite slight acidity, the utilized KCl and KNO_3 solutions do not change the crystal structure of clinoptilolite and its composition. The adsorbed amounts of potassium ions are directly dependent on the concentration of potassium in the liquid phase, although the use of concentrations higher than 15 mg/mL is not recommended, because the increase of potassium uptake becomes negligible. Adsorption of potassium takes place via ion exchange with calcium, sodium and magnesium ions that are present in the clinoptilolite lattice. The adsorption rate and capacity are positively affected by the increased

temperature, which suggested that ion exchange may be similar to chemisorption. This hypothesis was confirmed both by the adsorption equilibrium and kinetic modeling. Adsorption equilibrium data agreed best with Langmuir and Dubinin–Radushkevich isotherm models, which also pointed out that the adsorption of potassium results in the formation of a monolayer over adsorption sites. The applicability of a pseudo-second order kinetic model proved once more the chemisorption present and the fit of the Vermeulen model confirmed that after 7 hours of adsorption diffusion becomes the rate-limiting step. The potassium-saturated clinoptilolite (6.5% of K_2O) can be used as a potassium source for soil fertilization because saturated clinoptilolite can easily desorb potassium into the soil solution via ion exchange.

Received 19 February 2015
Accepted 13 April 2015

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KALIO JONŲ ADSORBCIJA GAMTINIU CEOLITU: KINETIKA IR PUSIAUSVYRA

Santrauka

Atliktų eksperimentų rezultatai rodo, kad po 7 val. greitos kalio adsorbcijos gamtiniu ceolitu procesas sulėtėja, o limituojančia stadija tampa difuzija. Adsorbcijos procesas nepriklauso nuo naudojamo kalio junginio – KNO_3 ar KCl, tačiau vyksta intensyviau didėjant temperatūrai. Nustatyta, kad kalio adsorbcija klinoptilolitu yra artima chemosorbcijos procesui. Tai patvirtina tiek kinetiniai, tiek pusiausvyros skaičiavimai. Iš visų skaičiavimams taikytų adsorbcijos pusiausvyros modelių geriausiai tiko Langmuir ir Dubinin-Radushkevich modeliai, jie patvirtino netolygų adsorbento paviršių ir galimą adsorbato monosluoksnio susiformavimą adsorbcijos metu. Pastarasis buvo panaudotas adsorbento savitajam paviršiui nustatyti. Kinetiniai skaičiavimai parodė, kad pseudoantrojo laipsnio modelis geriausiai aprašo gautus rezultatus ir dar kartą patvirtino, kad kalio adsorbcija yra chemosorbcinis procesas. Nepaisant adsorbcijos metu vyraujančios limituojančiosios difuzijos, kalio desorbcija vyksta sparčiau esant pakaitinių jonų, o pusiausvyra pasiekiama 10 kartų greičiau.