Kinetics and equilibrium of ion exchange of Ag$^+$ on Na-clinoptilolite

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This study investigates silver sorption by Na-clinoptilolite. Bath sorption procedure is applied in order to study the kinetics and equilibrium of Ag$^+$ uptake. Kinetic sorption data are analyzed using a pseudo-first- and pseudo-second-order model. It is found that pseudo-second-order model provides the most appropriate description of data for both studied 50 and 517 mg/L initial concentrations.The respective apparent pseudo-second-order rate constants k_2 are calculated to be 5.12 and 1.07 g/(meq min). The equilibrium data fit well to the Langmuir isotherms model from which the maximum uptake of Ag$^+$ is estimated to be $q_{m,calc}$ = 234.28 meq/g. The Freundlich model is found to be less appropriate. The total exchange capacity (TEC) is calculated from the chemical composition of the sample and the maximum exchange level (MEL) is obtained experimentally. The obtained results are compared with data on kinetics and equilibrium of Ag$^+$ sorption by clinoptilolite and other zeolites found in the literature, and discussed appropriately.

Keywords: Na-clinoptilolite; Ag$^+$ sorption; kinetics; equilibrium isotherms; ion exchange capacity.

1. INTRODUCTION

Natural zeolites are hydrated alluminosilicates of alkaline and alkaline earth metals, forming a group of minerals with microporous structure built up of spatial interaction of apex, sharing SiO$_4$ and AlO$_4$ tetrahedrons [1].

The channels in the structure are formed by sequences of tetrahedral rings, and they contain sub-lattices of cation positions and water molecules. This specificity of the zeolite structure is a basis for useful properties such as ion exchange, selective sorption, dehydration/re-hydration alteration, catalytic activity, etc [2].

Since a long time zeolites are subject of interest and of increasing investigation activity in order to use them for removal of metal cations from polluted industrial waters, municipal sewage, and radionuclide wastes [3–5].

Among the studied elements, silver is the one of special interest [6]. It is released in industrial waters during the production of a number of non-ferrous metals. Due to its toxicity, it is harmful for living organisms and should be removed. On the other hand, silver can be used as a bactericide in the inactivation and suppression of microorganisms in water disinfection. Silver supported zeolites and other materials are used in various technical and biomedical applications. [3,7,8].

Despite of the interesting potential applications, there is not much data on the interaction between the zeolites and silver in terms of kinetics and equilibrium of the sorption processes. A study of the Ag exchange equilibrium of natural and Na-modified Turkish clinoptilolite, with respect to its application in removing ions from polluted industrial waters and as a bactericide, is performed in [9,10]. IR spectra and equilibrium isotherms of Ag$^+$ - sorption on various clinoptilolite samples are presented in [11,12]. Ag$^+$ exchange kinetics of two synthetic tobermorites and their subsequent bactericide action are reported by Coleman et al. [8] as well.

This study reports the results of the research on exchange properties of Na-clinoptilolte from Eastern Rhodopes (Bulgaria) towards Ag$^+$ ions. Data on the kinetics of uptake and equilibrium state of the processes are presented and discussed.

2. MATERIALS AND METHODS

2.1. Materials and characterization

The sample of natural clinoptilolite, used in the study, was collected from the Beli Plast deposit (Eastern Rhodopes, Bulgaria). After grinding and sieving, the fraction below 75 μm (200 mesh) was separated for further use.

The chemical composition of the tested zeolite sample is (wt%): SiO$_2$ – 66.47; Al$_2$O$_3$ –10.75; Fe$_2$O$_3$ – 0.77; K$_2$O – 2.94; Na$_2$O – 0.44; CaO – 4.78; MgO

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– 1.50; TiO$_2$ – 0.11; MnO – 0.12; loss of ignition – 11.61; total 99.49%.

The X-ray powder diffraction (XRD) showed that the main mineral in the sample is clinoptilolite, 70%, the associated minerals are dolomite, 15%, and opal-cristobalite, 10%. The sample also contains traces of feldspar, ~3%, and mica, about 2%.

2. 2. Theoretical models

2.2.1. Kinetic models

Simplified kinetic models, including pseudo-first- and pseudo-second-order rate laws, were applied. These pseudo rate models are based on the assumption that the adsorption rate, dq_t/dt, is proportional to the number of sample available sorption sites.

The pseudo-first-order rate expression in integrated form for the boundary conditions, $q_t = 0$ and $q_t = q_t$ at $t = 0$ to $t = t$ [13], is linear:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)\, t \qquad (1),$$

where k_1 is the apparent pseudo-first order rate constant for the adsorption (in min^{-1}), and q_e and q_t (in meq/g) are the amounts of metal ion, adsorbed at equilibrium and time t (min), respectively.

The pseudo-second order rate model describes the adsorption processes, in which the reaction rate is proportional to the square of the available sorption site number, and is expressed as:

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)\, t \qquad (2),$$

where k_2 (g/meq min) is the rate constant for the sorption, q_e and q_t (meq/g) are the amounts of metal ions, sorbed at equilibrium and time t [14,15].

This mathematical description of the sorption is developed on the basis of the following assumptions [15]: the sorbed ions form a monolayer on the surface, the sorption is independent of the surface coverage, and there are no interactions between the sorbed ions.

The chemical equilibrium results from the mechanism of sorption which includes a mass transfer and chemical reactions. The ion transport includes surface diffusion and intraparticle diffusion depending on the diffusivity of sorbate within the particle. The chemical phenomena include hydrolysis, ion exchange or chemisorption, and precipitation. The apparent rate constant results from the adsorption and desorption rate constants. The simple kinetic models do not describe the real mechanism and the rate constants because the steps, determining the process, are experimentally uncertain.

The rate of these processes depends on the temperature, the initial metal concentrations, the pH, the used amount of adsorbent, the type of adsorbent and metal cations. The simple kinetic models are concerned only with the effect of these parameters on the overall reaction rate. In spite of these restrictions, this analysis of adsorption rates is sufficient for practical applications as a tool for prediction and comparison.

2. 2. 2. Adsorption isotherm models and MEL

The adsorption equilibrium is usually characterized by the ion exchange capacity of the material and by the equilibrium isotherms.

The adsorption equilibrium depends on the temperature and the parameters of the sorption system such as the pH, the solution composition, and the initial metal concentration, as well as on the mineral and chemical characteristics of the sorbing material. Usually, the equilibrium of the adsorption process is described in terms of adsorption isotherms. Several mathematical models, namely Langmuir, Freundlich, IAST, and Sips, have been applied to express the relationship between the sorbed amount and the equilibrium metal concentration [16], the Langmuir and Freundlich being the most frequently used.

In thermodynamic terms, the original Langmuir adsorption model for monolayer chemisorption of gases on homogenous solid surfaces is based on the assumption that the adsorption enthalpy is constant and independent on the degree of surface coverage [17]. Applied to the sorption of metal ions from solutions, this means that the binding energy per adsorbed ion remains the same during the whole adsorption process and that there is no interaction between the sorbed ions. The mathematical expression of the Langmuir model for a single metal ion uptake is:

$$C_e/q_e = 1/bq_m + C_e/q_m, \qquad (3),$$

where C_e (meq/L) and q_e (meq/g) are respectively the equilibrium Ag concentration in the aqueous phase and in the solid phase. The Langmuir parameter q_m (meq/g) represents the maximum sorbed amount and the parameter b (L/meq) is the site energy factor.

The Freundlich isotherm model is of an empirical nature and is applied to interpret the sorption on surfaces with sites of varying bonding strength. In this model, the ions occupy predominantly sites with a stronger sorption

affinity, thus provoking a decrease in the binding strength with increasing the extent of surface occupation. The linear form of Freundlich model, used to fit the Ag sorption data, is:

$$\log q_e = \log K_F + N \log C_e , \qquad (4)$$

where K_F (meq/g)/(meq/L)^N and N (dimensionless) are Freundlich parameters.

Another equilibrium parameter is the ion exchange capacity [18]. The ion exchange properties of zeolites are based on the negative charge (–1), caused by each aluminum atom in the tetrahedral structure of the clinoptilolite, balanced by the exchangeable cations. These sites determine the total exchange capacity (TEC), expressed as a number of ionogenic groups, in equivalents, per fixed amount of sorbent [19, 20].

The cation exchange capacity (meq/g) of homoionic Na-form of the zeolite is derived from the sample analysis as equal to the mmol/g of(Al+Fe) minus meq/g of ($K^+ + Ca^{2+} + Mg^{2+}$) for a pure material. Alternatively, TEC is equal to meq Na/g. When negligible mineral impurities are present in the sample, this capacity presents the total amounts of zeolite exchangeable groups and is named "ideal exchange capacity" (IEC) [18]. However, the natural samples usually contain other mineral phases. In addition, the exchangeable cations can be situated at inaccessible sites of the framework. The size of channel characteristic of each zeolite determines the incoming ions which can diffuse in the sample (ion-sieving phenomenon). For these reasons, the calculated TEC may be overestimated.

More important for practical purposes is the maximum exchange level (MEL) (expressed in meq/g) [18, 20], representing the part of the TEC which is actually available for ion exchange. MEL is determined experimentally by the "cross-exchange method" column [21] or by repeated batch experiments of ion exchange [20, 22–24]. Its value depends on the experimental conditions and on the sorbent nature and sorbed ions.

3. EXPERIMENTAL

3.1 Preparation of Na-exchanged clinoptilolite

The sodium-loaded, homoionic clinoptilolite was prepared by stirring 50 g of the natural sample and 500 ml of 1 M NaCl solution at 500 rpm. The treatment was performed in a closed bottle placed in an oven and heated at 60 °C. The NaCl solution was replaced every day by a fresh one and then analyzed. This procedure was repeated 12 times. Finally, the clinoptilolite sample was washed with distilled water in order to remove completely the occluded salt. The washing lasted until was reached a negative reaction of the Cl⁻ with the silver ions. Then the sample was dried in oven at 60 ºC.

The kinetic experiments were carried out in a bath sorption mode, using screw capped polypropylene bottles for various fixed contact times. We added 20 ml of 50 mg/L and 517 mg/L Ag⁺ solution with initial pH = 4 to series of samples, 0.1g Na-clinoptilolite each. The suspension was shacked at 20ºC on a horizontal shaker (amplitude of 20 mm and 150 oscilation.min⁻¹) and then centrifuged for 15 min at 4000 rpm. The silver concentration in the separated solutions was measured by AAS using a Perkin-Elmer 30–30 apparatus.

Cation exchange isotherms were obtained by treating 0.1 g of samples in centrifugal tubes with 20 ml of Ag⁺ aqueous solution with concentrations of 10, 25, 50, 100, 200, 300, 500, and 5000 mg/L at pH$_{initial}$ = 4.0. The reaction time was fixed equal to 90 min at 20 ºC. Further, we proceeded as described above.

The maximum exchange level of Na-clinoptilolite with Ag⁺ ions was measured using bath procedure. 20 ml of Ag⁺ solution with initial concentration 5mM and pH 4.0 were added to 0.1 g of sample. The mixture was separated every 2 days by centrifugation and decantation. A new fresh portion of Ag⁺ solution was added to a solid residue, and the treatment was repeated. The solution was analyzed for the content of Ag⁺ cations. The procedure was repeated until the concentration of Ag⁺ in the solutions from two consecutive treatments becomes the same and the deviation from the initial concentration becomes less than 4%. Totally, five treatments and 10 days were necessary in our case.

4. RESULTS AND DISCUSSION

4.1. Material characterisation

The chemical composition of Na-exchanged clinoptilolite sample is: (wt%): SiO_2 – 63.41; Al_2O_3 – 10.97; Fe_2O_3 – 0.77; K_2O – 1.26; ; Na_2O – 5.32; CaO – 1.97; MgO – 1.27; TiO_2 - 0.11; MnO - 0.12; loss of ignition – 14.78; total 99.99. The percentages of exchanged elements of natural clinoptilolite are: K – 57.14%, Ca – 58.77%, Mg – 14.4%, i.e. more than half of Ca^{2+} and K^+ ions in the clinoptilolite are readily exchanged for Na^+ ions. The content of Na in the exchanged form increases more than 10 times. The remaining Ca^{2+}, K^+ and

Mg^{2+} ions should not be available for reaction with Ag^+ under the selected experimental conditions.

4.2. Kinetics

Figure 1 shows the effectiveness of Ag^+ ions uptake by Na-clinoptilolite as a function of contact time. The effectiveness ($E\%$) was calculated by the formula:

$$E\% = 100 m_s/(VC_o),$$

where m_s is the mass of sorbed metal (mg), C_o is the initial Ag^+ concentration (in mg/L), and V (L) is the volume of solution from which the sorption occurs.

At initial concentration of 50 mg/L, the sorbed Ag^+ amount increases rapidly and reaches an equilibrium value with 94% effectiveness after 15 min. For the higher initial concentration of 517 mg/L, the effectiveness of Ag^+ uptake is lower, being after 60, 90, and 360 min equal to about 87.5%, 84.4%, and 83.5%, respectively. Akgul et al. report on 45 min equilibrium adsorption time for the Ag^+ uptake by clinoptilolite [9]. Top and Ülkü [10] have fixed a two-day duration of the adsorption in a study on the antibacterial activity of Ag^+ loaded clinoptilolite.

The initial metal ion concentrations exert infuence on the contact time, necessary to reach an equilibrium. The adsorption was very fast for the 50 mg/L concentration, and high effectiveness of sorption was reached in the first 15 min. The time to reach equilibrium was about 90 min for the higher 517 mg/L concentration.

The initial pH=4.0 increases with the increase of the contact time, changing between 6.5 and 8.6, and between 7.4 and 7.7 for both studied initial concentrations of 50 mg/L and 517 mg/L, respectively.
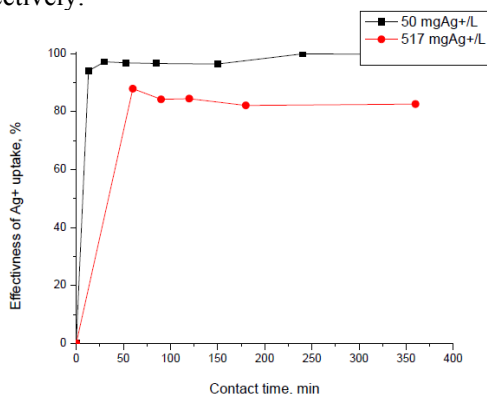

Fig. 1 Uptake of Ag^+ ions by Na-clinoptilolite as a function of the contact time (0.1000 g Na-clinoptilolite, 20 ml Ag^+ solution of 50 mg/L and 517 mg/L, pH_{init} = 4.0, t=20 ºC).

The experimental data for the Ag^+ uptake by Na-clinoptilolite were fitted to the pseudo-first- and pseudo-second-order kinetic models by least square regression analysis to check their applicability to the process. The pseudo-first- order model was shown to be non-representative because the correlation coeffcient is low, whereas a good correlation between experimental data and the pseudo-second-order reaction model was proved. The parameters of the pseudo-second-order reaction model: integrated rate equations, squares of the correlation coefficients (R^2), apparent rate constants, and experimental and calculated uptake amounts are listed in Table1. The calculated values of Ag^+ uptake, obtained from the model ($q_{e,calc}$), are in good agreement with the experimental data (the differences are 2.1 and 0.4 %). Hence, the sorption of Ag^+ ions onto Na-clinoptilolite could be a pseudo-second-order process. The determined values of k_2 rate constant increased from 1.074 to 5.162 when the initial silver concentration decreased from 517 to 50 mg/L, as reported also by other authors [15].

Table 1. Kinetic parameters for the Ag^+ uptake by Na-clinoptilolite, pseudo-second-order rate model.

Ag (mg/L)	Integrated rate equation	R^2	k_2 (g/(meq min)	$q_{e,exp}$ (meq/g)	$q_{e,calc}$ (meq/g)
50	$t/q_t = 10.77t + 22.42$	0.9998	5.16	0.091 (± 0.002)	0.093
517	$t/q_t = 1.25t + 1.46$	0.9995	1.07	0.801 (± 0.012)	0.798

During the last 20 years, numerous sorption systems have been investigated, and particularly for application of simple kinetic model to describe the process [25]. However, in the studies, concerning Ag^+ sorption by diverse materials, the kinetics of the processes has almost not been examined. To date, no studies for the application of kinetic models for description of Ag^+ uptake by natural and modified clinoptilolite and other zeolites were found. Data on the uptake of Ag^+ conforming to the pseudo-second-order kinetic model with k_2 = 0.033 g/mmol min has been reported in the investigations on the use of the chitosan, the Ag^+ loaded biosorbent, as a bactericide [26], and in the study for the uptake of Ag^+ ions by two tobermorites - k_2 is 0.067 and 0.079 g/(mmol min), respectively [8]. The pseudo-second-order rate constant for the uptake of Ag^+ by Na-clinoptilolite at initial concentration 517 $mgAg^+/L$ (~ 5mM), determined in the present study, is about 16 times grater than the silver uptake in the above cited investigations [8] and 32 times faster that the sorption on modified

chitosan [26]. The rate constant for initial concentration 50 mgAg$^+$/L is almost five times greater than for 517 mg/L. These results suppose that the rate limiting step depends not only on the concentration of sorbed ions, but on the concentration of active sites and the bonding mechanism - especially on the transfer phenomena and accessibility of the active sites.

4.2. Adsorption isotherms

The silver sorption isotherms for the initial Ag$^+$ concentrations 10 to 5000 mgAg$^+$/L are presented in Figure 2.

The applicability of the Langmuir and Freundlich models to silver sorption by Na-clinoptilolite was tested by fitting the experimental data to the theoretical models by least squares regression analysis. The obtained equations, experimental and calculated values of maximum uptake, the constants and the corresponding squares of correlation coefficients (R^2) are listed in Table 2. The experimental equilibrium data correlate well with the Langmuir isotherm model for the interval

of concentrations 10 to 500 and 10 to 5000 mgAg$^+$/L. The Freundlich model was found to be comparatively less appropriate for both studied intervals of concentrations.
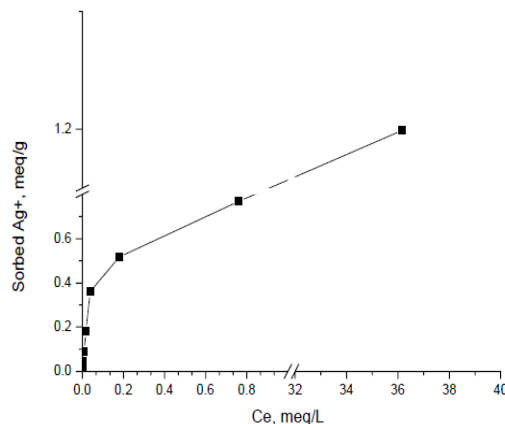

Fig. 2. Sorption isotherm of Ag$^+$ ions uptake by Na-clinoptilolite (0.1 g of zeolite, 20 ml Ag$^+$ solution, pH$_{init}$ = 4.0, t = 20°C).

Table 2. Langmuir and Freundlich sorption equations and parameters for Ag sorption by Na-clinoptilolite

Langmuir model equation	Initial concentrations range (mg/L)	R^2	b (L/meq)	$q_{m,calc}$ (meq/g)	$q_{m,calc}$ (mg/g)
$C_e/q_e = 1.229C_e + 0.067$	10 - 500	0.9925	18.234	0.813	87.76
$C_e/q_e = 0.831C_e + 0.124$	10-5000	0.9999	6.703	1.204	129.86
Freundlich model equation		R^2	K_F (meq/g)/(meq/L)^N	N	
$\log q_e = 0.533 \log C_e + 0.060$	10 - 500	0.9776	1.149	0.533	
$\log q_e = 0.487 \log C_e - 0.037$	10 -5000	0.9610	0.632	0.386	

To date only a small number of studies on the equilibrium of Ag$^+$ uptake by clinoptilolite could be found in the literature. In [9] the sorption isotherm of Ag$^+$ by clinoptilolite is presented and a good correlation with both Langmuir and Freundlich models is reported. The maximum adsorption capacity, calculated according to the Langmuir model is 38.91 mgAg$^+$/g for experimental conditions: 0.05 g of sample, 25 ml of solution, and highest initial concentration 150 mg Ag+/L. The amounts of Ag$^+$ sorbed by a composite material containing clinoptilolite [12] have been determined as 4.36, 27.85, and 183.78 mg/g, for initial AgNO$_3$ concentrations of 50, 500, and 5000 mg/L, respectively, solid to liquid ratio 1:100 (w/v) and 24 h of treatment. The experimental data for the sorption isotherm have showed a better fitting with the Freundlich model. The capacities of a series of clinoptilolites of different origin for silver are within the range 59.75 − 85.32 mgAg$^+$/g [11], and the capacities of two tobermorites are 0.958 and 0.993 meq/g [8]. In a recent study [26] using

modified chitosan for Ag$^+$ sorption a good correlation with the Langmuir model has been reported with high maximum adsorption capacity 2.1 meqAg$^+$/g. The result for the maximal Ag$^+$ uptake of 87.76 mg/g and 129.8 mg/g by Na - clinoptilolite in our work are in the range of the reported values, although it is difficult to compare these values, because they are obtained at very different conditions.

4.3. Cation exchange capacity

The sample of natural clinoptilolite, used in this study, is not pure - it contains some amounts of other minerals, mainly dolomite. That is why it is not appropriate to calculate the total cation exchange capacity (TEC) of Na-clinoptilolite from the contents of framework and extra-framework cations, as described in Section 2.2. The value, obtained on the basis of Na content (in meq/g) is 1.72.

The maximum exchange level for Ag$^+$ sorption by Na-clinoptilolite, measured by repeated bath

ion-exchange experiments is 1.43 meq/g or 83.1% from the calculated TEC, due to failure of complete replacement of Na^+ for Ag^+. During these treatments the initial pH 4.0 changed in the interval 8.7 − 7.5 with a trend to decrease with the number of treatments.

The maximum uptake calculated from the Langmuir isotherms model represents 84.2% of the measured maximum exchange level. This discrepancy is due to different extent of replacement of exchangeable extra-framework cations and can be explained by the difference in experimental conditions. MEL is determined under conditions of repeated refreshing of high concentrated sorbate solution after each equilibrium state. Moreover, during the intense and long shaking, typical mechanical and structural changes in the sorbent could take place and influence the ions uptake.

The results, obtained from the kinetics and equilibrium studies in the investigation of sorption systems are useful for comparison of sorption properties of sorbents, the cations uptake effectiveness, and estimation of performance, although the theoretical base of modeling and the real process mechanisms are disputable.

5. CONCLUSION

Sodium exchanged form of natural clinoptilolite from Beli plast deposit was studied for Ag^+ sorption. Batch studies show that a simple model of pseudo-second-order kinetic equation can adequately describe the Ag+ uptake with the rate constant k_2 being more faster than the ones reported in the literature for other materials. The isotherm equilibrium data fit well to the Langmuir and Freundlich models. The calculated maximum uptake values are 87.76 and 234.28 $mgAg^+$/g at initial concentrations up to 500 and 5000 $mgAg^+$/L. The calculated value of TEC is found to be 1.72 meq/g and the measured MEL is 1.43 meq/g. The obtained results show that Na-exchanged clinoptilolite has excellent adsorptive characteristics represented by a high sorption capacity and fast sorption process and is very effective for the sorption of Ag^+ from aqueous solutions.

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КИНЕТИКА И РАВНОВЕСИЕ НА ЙОННИЯ ОБМЕН НА Ag⁺ ВЪРХУ КЛИНОПТИОЛИТ

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(Резюме)

Изследвана е сорбцията на сребро от Na-клиноптилолит. Експериментите за изучаване на кинетиката и равновесието на извличането на среброто от разтвора са извършени в статични условия. Данните от изследване на кинетиката са анализирани чрез прилагане на модела на реакции от псевдо-първи и псевдо-втори порядък. Намерено е, че моделът на реакции от псевдо-втори порядък дава по-добро описание на данните за двете изследвани изходни концентрации на сребро – 50 и 517 mg/L със скоростни константи k_2 съответно 5.12 и 1.07 g/(meq min). Данните за равновесието на сорбцията се описват по-добре с модела на изотермите на Langmuir, откъдето е намерено максималното извличане на сребро $q_{m,calc}$ = 234.28 meq/g. Общият обменен капацитет (TEC) е изчислен на базата на химическия състав на изходния клиноптилолит. Максималното обменено количество за изследвания йон Ag⁺ (MEL) е намерено експериментално. Получените резултати са сравнени с данните за кинетиката и равновесието на сорбцията на Ag⁺ от клиноптилолит и други зеолити, намерени в литературата и са съответно дискутирани.