"Gheorghe Asachi" Technical University of Iasi, Romania

EQUILIBRIUM PERFORMANCES OF *CRYSTAL-RIGHT^{TM} CR100* ZEOLITE USED IN WATER SOFTENING PROCESS

Liliana Lazar[1]*, **Bogdan Bandrabur[2], Ramona-Elena Tataru-Fărmuş[1],**
Mioara Drobota[3], Silviu-Gabriel Stroe[4], Gheorghe Gutt[4]

[1]*"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection,*
Department of Chemical Engineering, 73 Prof. dr. docent Dimitrie Mangeron Str., 700050 Iasi, Romania
[2]*Hach Lange SRL, 3 Căminului Str., 021741 Bucharest, Romania*
[3]*"Petru Poni" Institute of Macromolecular Chemistry, Department of Polymer Materials Physics,*
41A Gr. Ghica Voda Alley, 700487 Iasi, Romania
[4]*"Stefan cel Mare" University of Suceava, Faculty of Food Engineering, 13 University Str., 720229 Suceava, Romania*

Abstract

The present work investigates the performance of *Cristal-Right^{TM} CR100* zeolite based on the equilibrium and thermodynamics water softening process. The commercial zeolite was characterized by scanning electron microscopy combined with energy dispersive X-ray spectroscopy and FT-IR spectroscopy. The equilibrium performances of zeolite were evaluated by the sorption capacity of calcium cations from calcium chloride solutions varying the calcium concentrations corresponding to moderate, hard and very hard waters. Experiments were carried in batch mode out as a function of temperature (278, 298, 318 and 338 K) and in fixed optimum conditions for soption process (pH, zeolite dose and contact time). Equilibrium sorption data were analysed using Langmuir, Freundlich and Dubinin-Radushkevich isotherm models to obtain the characteristic parameters of each model. Sorption equilibrium data fitted very well to the Langmuir model that confirmed the monolayer sorption with high correlation coefficients. According to the evaluation using the Langmuir isotherm, the maximum sorption capacities of calcium cations onto *Cristal-Right^{TM} CR100* zeolite were 31.45 mg/g for 298 K. The thermodynamic parameters values indicate the spontaneous and endothermic nature of the sorption process by ambient temperature. The sorption energy fell in the range of physisorption.

Key words: isotherms, permanent hard water softening, sodium-zeolite, sorption capacity, thermodynamics

1. Introduction

Water with a high level of hardness caused by calcium (Ca^{2+}) and magnesium (Mg^{2+}) cations is an important operational costs increase factor in most of its application fields (Gray, 2010; Ştefanache et al., 2015). Most of the water sources require treatment processes before being used as a raw material or as technological water. Water softening is a treatment process where the calcium and magnesium cations are removed from water. The most widespread industrial scale method employed for partly or total removing of permanent hard water caused by calcium and magnesium salts that do not precipitate is based on the ion exchange procedure (Smith et al., 2008; Zagorodni, 2007). The ion exchange materials used consisting of polymeric resins (Bandrabur et al., 2012; Hoffmann and Martinola, 1988; Lazar et al., 2014) and zeolites (Shoumkova, 2011; Wang and Peng, 2010).
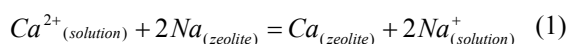
Zeolite both as natural and as produced synthetic are widely used nowadays in various water and treatment processes due to low cost, high ion exchange and adsorption potential, selectivity, high surface area distributed throughout pores with several diameters (Zagorodni, 2007). This advantage in

---

economic aspect of zeolite has been reported in several works that was investigated and applied to remove cation contaminants in water and wastewater, such as:

(1) *water softening* – removal of permanent hard water for drinking or industrial water preparation (Arrigo et al., 2007; Cinar and Beler-Baykal, 2005; Coker and Rees, 2005; Qin et al., 2010a, 2010b; Sivasankar and Ramachandramoorthy, 2011; Xue et al., 2014; Zhao et al., 2009);

(2) *water purification* – removal of *heavy metal cations*: Fe^{3+} (Al-Anber and Al-Anber, 2008); Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+} (Doula, 2009; Ibrahim at al., 2010; Jamil et al., 2010; Nibou at al., 2010; Ören and Kaya, 2006), As^{3+}, As^{5+} (Baskan and Pala, 2011; Noroozifar et al., 2014), Ce^+ (Shahwan et al., 2005). Zeolites used for water softening process are mostly charged with sodium (Na^+) or potassium (K^+) cations that will be exchanged with Ca^{2+} and Mg^{2+} cations from the raw hard water passing through the crystalline structure (Loiola et al., 2012; Lührs et al., 2012; Shoumkova, 2011; Wang and Peng, 2010). For example, sodium-zeolite removes Ca^{2+} cations from water by exchange with sodium as illustrated by Eq. (1).

$$Ca^{2+}_{(solution)} + 2Na_{(zeolite)} = Ca_{(zeolite)} + 2Na^+_{(solution)} \quad (1)$$

Zeolite softening will also remove other soluble cation species such as iron and manganese present in the raw water and will mechanically retain small suspended solids. When zeolite for water softening is saturated with Ca^{2+}, Mg^{2+}, Fe^{3+}, Mg^{2+} cations, it may be backwashed with a sodium chloride solution to remove the calcium and used again (Zagorodni, 2007). Typically, the operating cycle of an ion exchanger consists of three stages: (I) cations removal, (II) column regenerations and (III) column washing (Górka et al., 2008).

The ion exchange process in zeolites is influenced by several factors such as concentration and nature of cations and anions in the initial aqueous solution, initial pH value of solution, the ratio zeolite mas/ solution volume (dose), temperature, phase contact time and crystal structure of the zeolite (Al-Anber and Al-Anber, 2008; Jamil et al., 2010; Nibou at al., 2010; Ören and Kaya, 2006). Optimal design of the process operating in dinamic process requires preliminary knowledge on both the ion exchange equilibrium and kinetics models (Górka et al., 2008; Zhao et al., 2009).

Sorption equilibrium analysis is fundamental in supplying the essential information required for understanding of phenomena at the solid-liquid interface and design of the sorption process. In this perspective, equilibrium relationships between zeolite (sorbent) and calcium cations from aqueous solution (sorbate) are describe by sorption isotherms obtained in batch system at fixed temperature (Foo and Hameed, 2010). The quantity of a solute adsorbed can be given conventionally in terms of

moles of volume (for adsorption) or ion-equivalents (for ion exchange) per unit mass of volume of zeolite (Douglas et al., 2008).

The present work consists in experimental studying the performances at equilibrium of a commercial *Cristal-Right*[TM] *CR100* zeolite recommended for water softening. Equilibrium studies in sorption process gave the capacity of the zeolite. Accordingly, the objectives of the work are: (1) study of the equilibrium isotherms on the calcium cations from calcium chloride solution sorption onto zeolite and (2) evaluation of the application of sorption isotherms and analysing of the sorption mechanism. The equilibrium isotherm for sorption of calcium cations on zeolite is evaluated using Langmuir, Freundlich and Dubinin-Radushkevich models. The thermodynamic parameters were also determined from the temperature dependence.

2. Experimental

2.1. Materials and characteristics

Cristal-Right[TM] *CR100* is a modified natural zeolite produced by *Mineral Right*[®] *Inc.* company (USA), relatively recently introduced in the Romanian market, delivered in the form of aluminosilicate crystals and which has ion exchange properties due to its sodium cations content. It is recommended for the use in the domestic and industrial water softening at the same time with the retention of ammonia, iron, manganese cations removal, and the rise of the pH of some low acidic waters. In addition, *Crystal-Right*[TM] *CR100* zeolite is impervious to chlorine and so it can be used with self-chlorinating, automated sanitizing systems.

The particles with average diameters 0.85 mm were tested (Gruett, 2003). The structural and morphological characteristics of the *Crystal-Right*[TM] *CR100* zeolite in delivery form are examined through scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX) and Fourier transforms infrared spectroscopy (FT-IR). SEM micrographs of the zeolite were recorded on a 30 kV VEGA Tescan microscope. Fig. 1 showed the SEM image of zeolite particle from a 30 keV with 150X magnification.

The nonuniform macro crystals distribution from the dimensional and shape point of view and the irregular surface confirm the natural origins of the material. The surface elemental analysis recorded with Quanta 200 instrument indicates that the material is a sodium alumina-silicate type with a molar ratio Si : Al = 3.2 (Table 1). The FT-IR spectra of zeolite was obtained at room temperature, were performed on a Bruker Vertex 70 spectrometer with $400 - 4000$ cm[-1] spectral range and a 4 cm^{-1} resolution in transmition technique using the KBr pellet and the Opus 5 FTIR Software. In Fig. 2 is presented the FT-IR spectra of *Crystal-Right*[TM] *CR100* zeolite in delivery form.

Table 1. *Crystal-Right^{TM} CR100* zeolite surface elemental analysis for the delivery form from the SEM-EDX analysis results

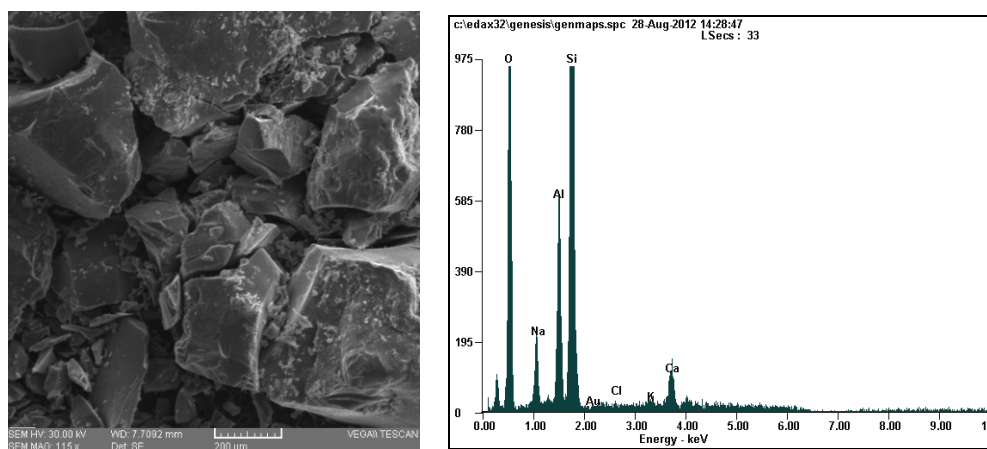| Element	Si	Al	O	Na	Ca	K	Au	Cl
Value (%, w/w)	30.25	9.27	52.02	5.13	2.43	0.66	0.44	0.29

Fig. 1. SEM image and EDX spectra for the *Crystal Right^{TM} CR100* zeolite in the delivery form
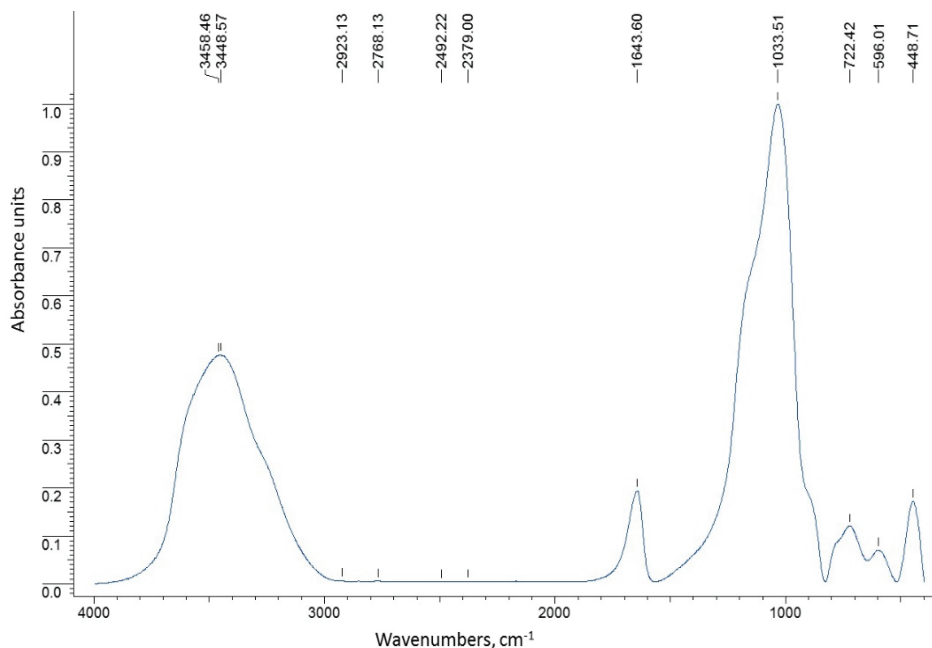

Fig. 2. FT-IR spectra of *Crystal-Right^{TM} CR100* commercial zeolite

According with literature (Breck, 1974; Korkuna et al., 2006; Qin et al., 2010a; Loiola et al., 2012; Sivasankar and Ramachandramoorthy, 2011), the bands at 1200 – 450 cm^{-1} are known to be assigned to Si–O–Al, Si–O–Si, Si–O, and Al–O species. The most well pronounced band in the spectrum is the one present at 1033 cm^{-1}, being attributed to the asymmetric vibrations of the SiO$_4$ tetrahedral structure or to the Si–O bonds.

We can detect a small peak at 1643 cm^{-1} together with the 3448 cm^{-1} peak which is a harmonic (overtone) attributed characteristic the HO bonds. This evolution is due to the formation of hydrogen bonds, which confirm some molecules of water are kept in the cages and channels inside the zeolite

structure. The peaks at 596 and 722 cm^{-1} are of Al–OH translation type. The peak at 448 cm^{-1} is attributed to Al–O type bonds.

2.2. Batch sorption experiments

All the experiments were realised using the *Cristal-Right^{TM} CR100* zeolite in the delivery form, according to the instructions provided by their producers. The data interpreting and analysis is always reported to the dry state of the zeolite. The equilibrium sorption capacity of the zeolite of the calcium cations used to express the zeolite performance was evaluated in batch technique at contact time equal with 24 hours, from the point of

view of the following sorption process specific experimental factors: temperature and concentration of calcium cations in the aqueous solutions to be treated. Sorption results show that a 24 hours equilibrium-period was sufficient to establish steady state or equilibrium.

The experiments for equilibrium sorption of calcium cations from calcium chloride solution were performed at constant zeolite amount of 8 g/L and various initial calcium concentrations between 44.5 to 230.5 mg Ca^{2+}/L, corresponding to moderate hard and hard waters. The optimum zeolite dose equal with 8 g/L was selected based on the preliminary studies and was maintained in all experiments. During all the experiments at constant pH 6.75, the value was adjusted as it was varying more than ±0.1 unit by small addition of 0.1 M NaOH aqueous solution. Erlenmeyer flasks were used for the 50 mL $CaCl_2$ solution and the zeolite dose. All flasks were kept under agitation at a constant speed of 100 rpm. The effect of temperature on the calcium cations sorption was investigated at different value of temperature: 278, 298, 313 and 338 K with ±1 K. The initial and final calcium cations concentrations analysis was performed using the EDTA method (SR ISO 6058, 2008). An automatic titrator and specific titration end-point indicators for water hardness analysis from Hach Company were used. The indicator used in experiments is based on Murexide, specially modified to facilitate the highlighting of equivalence point, both in low and high concentrations calcium range. All the experimental solutions were prepared using analytical grade reagents from Merck or Sigma Aldrich dissolved in ultrapure water.

The performance of the sorbent usually means its uptake capacity (Volesky, 2003). The amount of calcium cations sorbed at equilibrium by the zeolite (equilibrium sorption capacity in mg/g – q_e) was calculated according to Eq. (2).

$$q_e = \frac{(C_0 - C_e) \cdot V_{sol}}{m_{zeo}} \tag{2}$$

The softening process efficiency was qualitatively evaluated by using the calcium sorption degree, *R* (%), calculated with the Eq. (3), where C_0 is the initial calcium concentration of $CaCl_2$ solution (mg/L); C_e is the equilibrium calcium concentration (mg/L); V_{sol} is the volume of solution to be softened (L); m_{zeo} is the weight of the zeolite used in the experiment in dry state, (g).

$$R = \frac{C_0 - C_e}{C_0} \tag{3}$$

2.2. Equilibrium isotherms

The equilibrium performances of the *Cristal-Right^{TM} CR100* zeolite for sorption of calcium cations were investigated using the isotherm (equilibrium

sorption capacity versus equilibrium concentration of calcium cations in calcium chloride solution). The most common isotherms frequently used in literature for sorption equilibrium are the Langmuir, Freundlich and Dubinin-Radushkevich models (Foo and Hammed, 2010; Volesky, 2003).

The experimental data were fitted to the Langmuir, Freundlich and Dubinin-Radushkevich isotherms calculated by linear regression to obtain the characteristic parameters of each model.

The Langmuir isotherm model is based on the monolayer sorption onto homogeneous surface. This model assumed that adsorption forces are similar to the forces in chemical interactions, and can be used to estimate the maximum sorption capacity (q_{max}, mg/g), upon complete saturation of the adsorbent surface. The empirical Freundlich model which indicates the surface heterogeneity of the adsorbent, was chosen to estimate the sorption intensity of the adsorbate towards adsorbent. The Dubinin-Radushkevich isotherm model, which is based on the Polanyi theory, is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential. It is used to estimate the apparent free energy of adsorption as well as to make a difference between physical and chemical adsorption process (Douglas et al., 2008; Foo and Hammed, 2010; Volesky, 2003).

Langmuir, Freundlich and Dubinin-Radushkevich isotherm models can be expressed by Eqs. (4-6), respectively, where q_e represents a maximum amount of the calcium cations at the equilibrium per unit weight of the zeolite to from a complete monolayer on the surface bound at high (mg/g, or mol/g); q_{max} is the practical limiting sorption capacity when the surface is fully covered with calcium and assists in the comparison of sorption performance, particularly in cases where the zeolite did not reach its full saturation in experiments (mg/g or mol/g); C_e is the equilibrium calcium concentration (mg/L); K_L is the Langmuir isotherm constant (L/mg) related to the affinity of the binding sites; K_F is the Freundlich constant is an indicator of the sorption capacity (mg/g); *n* represents a constant that characterizes the affinity of the calcium for the zeolite; β is a constant related to the sorption energy (mol^2/J^2); ε is the Polanyi potential, calculated according to Eq. (7) (where *R* is the universal gas constant, (8.314 J/mol K) and *T* is temperature (K)).

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \quad (mg/g) \tag{4}$$

$$q_e = K_F (C_e)^{1/n} \quad (mg/g) \tag{5}$$

$$q_e = q_{max} \cdot \exp\left(-\beta \cdot \varepsilon^2\right) \quad (mol/g) \tag{6}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{7}$$

For determining the best-fitting isotherms the linear regression is frequently used. The linear least-squares method with linearly transformed isotherm equations has also been widely applied to confirm experimental data and isotherms using coefficients of determination (Douglas et al., 2008; Foo and Hammed, 2010; Volesky, 2003). The linearized forms of Langmuir, Freundlich and Dubinin-Radushkevich nonlinear equations are given by Eqs. (8 – 10).

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}K_L} \cdot \frac{1}{C_e} \qquad (8)$$

$$\lg q_e = \lg K_F + \frac{1}{n} \lg C_e \qquad (9)$$

$$\ln q_e = \ln q_{max} - \beta \cdot \varepsilon^2 \qquad (10)$$

3. Results and discussion

3.1. Effect of initial calcium concentration and temperature on the sorption capacity of calcium cations

The equilibrium sorption process is a function of temperature and calcium concentration of initial solution. Equilibrium sorption capacity of calcium cations on *Crystal-Right^{TM} CR100* zeolite were investigated out by varying the initial concentration of the calcium from 44.5 to 230.5 mg/L at different sorption temperatures of 278, 298, 318 and 333 K. The experimental data showed that the equilibrium sorption capacity of zeolite increased with the increase of temperature and initial calcium cations concentration (Fig. 3), thereby indicating the process to be endothermic.
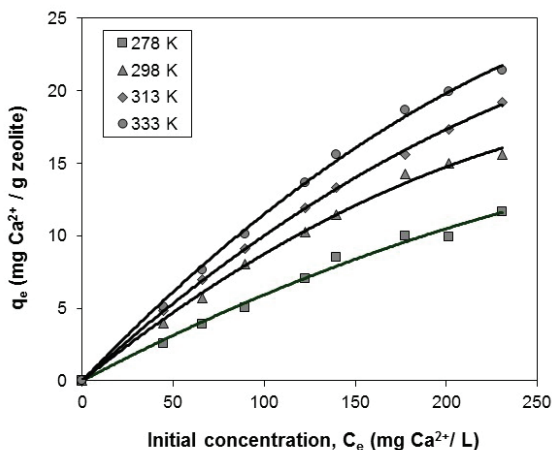

Fig. 3. Effect of initial concentration on the sorption equilibrium onto *Crystal-Right^{TM} CR100* zeolite at different temperatures (pH = 6.75, m$_{zeo}$ = 8 g/L, time = 24 hours)

This behaviour is explained in literature by the migration of calcium cations from the external surface to the internal micro-phase of the zeolite

within a given contact time and at higher initial concentration (Bulgariu et al., 2012; Ceica et al., 2011; Sepehr et al., 2013).

The calcium cations could exchange with sodium cations not only on the surface of the zeolite but also on the internal surface of the zeolite. This suggests that zeolite has strong calcium sorption ability at higher temperature. At higher temperature, calcium cations are moving faster and cations become smaller because solvation is reduced. This reduction effect allows cations to diffuse in the inner part of the pore system of the zeolite. Increasing the temperature may produce a selling effect within the internal structure of zeolite enabling calcium cations to penetrate further.

3.2. Calcium sorption isotherms

The sorption isotherms of calcium cations on *Crystal-Right^{TM} CR100* zeolite were plotted between the equilibrium sorption capacity (q_e, mg/g) and the amount of calcium cations left in equilibrium solution, C_e (mg/L) at different temperature (Fig. 4). As can be seen from Fig. 4 the isotherms are regular, positive, and concave to the concentration axis. The temperature increase was observed to occur in two stages. The sorption equilibrium occurs rapidly at lower calcium concentration, for all studied temperatures and becomes relatively constant at higher concentrations. On the basis of these considerations, the studied resin could be efficiently used at ambient temperature, avoiding the high temperatures, which are not economically justified.

The performances of the *Crystal-Right^{TM} CR100* zeolite at the equilibrium and isotherm parameters were evaluated using Langmuir, Freundlich and Dubinin–Radushkevich models.
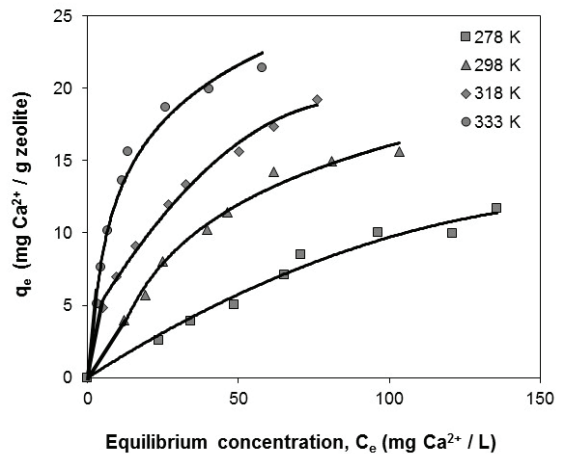

Fig. 4. Effect of temperature on the calcium sorption isotherm on *Crystal-Right^{TM} CR100* zeolite (pH = 6.75, m$_{zeo}$ = 8 g/L, 298 K; time = 24 hours)

These isotherms are useful tools for describing the distribution of calcium cations (sorbate species) between the zeolite and the batching calcium chloride solution. The Langmuir, Freundlich and Dubinin–Radushkevich isotherms for the

sorption of calcium cations of calcium chloride solution are illustrated in Fig. 5.

The straight lines obtained for the three isotherms indicate that the sorption of both cations fit with the three investigated isotherms models. The value of three isotherm parameters and the correlation coefficient were calculated from the slope and the intercept of the linear plots: $1/q_e$ vs. $1/C_e$ (for Langmuir model – Fig. 5a), lg q_e vs lg C_e, (for Freundlich model– Fig. 5b) and ln q_e vs. ε^2 (for Dubinin–Radushkevich model – Fig. 5c).

(a) Langmuir
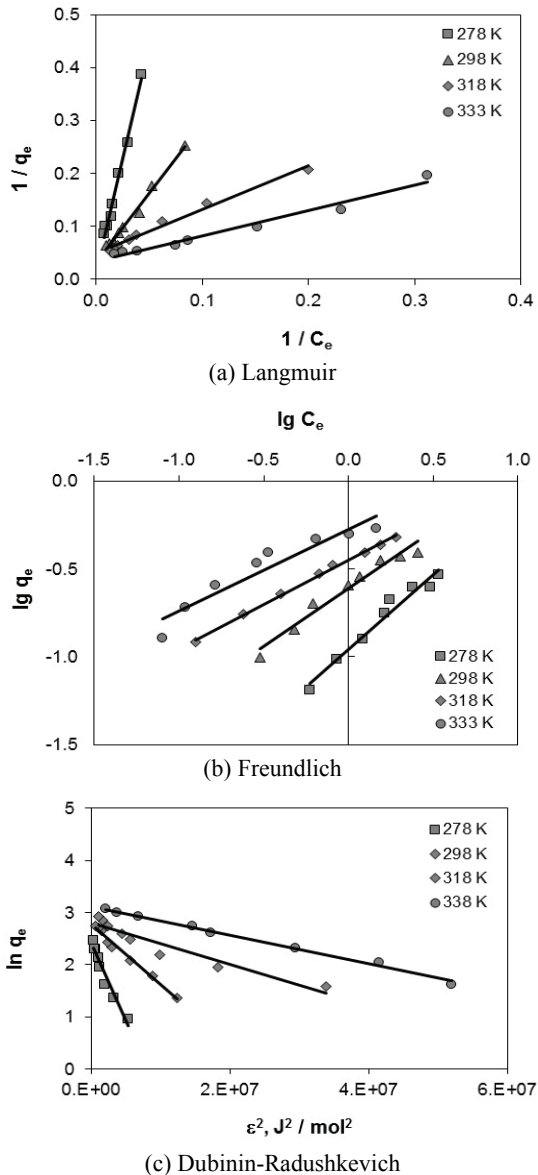

(b) Freundlich

(c) Dubinin-Radushkevich

Fig. 5. The linearized Langmuir (a), Freundlich (b) and Dubinin-Radushkevich (c) isotherm of calcium onto *Crystal-Right^{TM} CR100* zeolite at different temperatures (pH = 6.75; m_{zeo} = 8 g/L; time = 24 hours)

The corresponding Langmuir, Freundlich and Dubinin–Radushkevich parameters along with correlation coefficients are given in Table 2. The best-fit equilibrium model was established based on the linear regression correlation coefficients (R^2). The Langmuir model fitted the data (R^2 = 0.97 –

0.99) beter than the Freundlich model (R^2 = 0.90 – 0.99) and Dubinin–Radushkevich model (R^2 = 0.94 – 0.96).

The simple Langmuir isotherm equation for adsorption of a single adsorbate on a single-site surface is still frequently applied to sorption process. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (Foo and Hammed, 2010; Volesky, 2003), that is used to predict if an sorption system is favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The separation factor, R_L is calculed by Eq. (11), where C_0 is initial concentration (mg/L), K_L is Langmuir constant (L/mg).

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{11}$$

For the temperature range studied, all R_L values obtained using Eq. (11) are given in Fig. 6. The R_L value indicate that sorption of calcium cations onto *Crystal-Right^{TM} CR100* zeolite is more favourable for the higher initial calcium ion concentrations than for the lower ones.

A plot of lg q_e in function of lg C_e, yielding a straight line, indicated the confirmation of the Freundlich sorption isotherm. Although the Langmuir and Freundlich constants q_{max} and K_F have different meanings, they led to the same conclusion about the correlation of the experimental data with the sorption model. The Langmuir isotherm assumes sorption free energy independent of both the surface coverage and the formation of monolayer whereas the solid surface reaches saturation while the Freundlich isotherm does not predict saturation of the solid surface by the sorbate, and therefore, the surface coverage being mathematically unlimited.
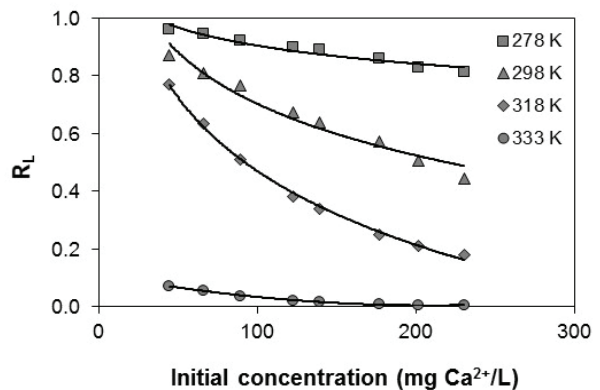

Fig. 6. Plot of dimensionless constant separation factor R_L against initial calcium ion concentration (pH = 6.75; m_{zeo} = 8 g/L; time = 24 hours)

For example, the experimental results for 298 K of Langmuir model indicate the monolayer sorption capacity value q_{max} of 31.447 mg/g zeolite and constant related to the energy of sorption value K_L of 0.0121 L/mg, whereas the Freundlich model indicate the relative sorption capacity K_F of 1.5361 mg/g with the sorption intensity n of 1.5361.

Table 2. Isotherm sorption parameters for removal of calcium cations from aqueous solution onto *Crystal-Right™ CR100 zeolite* (pH = 6.75; m_{zeo} = 8 g/L; time = 24 hours)

Isotherm	Parameters	Temperature, K			
		278	298	318	338
Langmuir	q_{max}, mg/g	68.0272	31.447	20.284	30.303
	K_L, L/mg	0.00171	0.0121	0.0598	0.0687
	R^2	0.9883	0.9906	0.9840	0.9730
	S_o, m²/g	31.534	14.5772	9.399	14.014
Freundlich	K_f, mg/g	0.1099	0.2442	0.3475	0.5320
	n	1.1724	1.5361	2.0597	2.1542
	R^2	0.9654	0.9487	0.9894	0.9058
Dubinin–Radushkevich	q_{max}, mg/g	11.003	15.991	16.425	22.594
	β, mol²/kJ²	$2.98 \cdot 10^{+3}$	0.1166	0.0400	0.0276
	E, kJ/mol	0.0130	2.0712	3.5338	4.2530
	R^2	0.9559	0.9633	0.9401	0.9581

However, the value of sorption intensity of calcium cations on zeolite surface is greater than 1.0 at temperatures above 298 K, indicating that calcium ion is favourable adsorbed by zeolite, even at higher calcium concentration.

Fig. 7 shows plots comparing the experimental data with theoretical Langmuir isotherm and empirical Freundlich isotherm. The equation shows an excellent fit with the experimental data for the Langmuir isotherm. Assumption of a value for the surface area covered per molecule (plateau on each isotherm) could allow computation of the active specific surface area of the sorbent using Avogadro's number (Volesky, 2003).
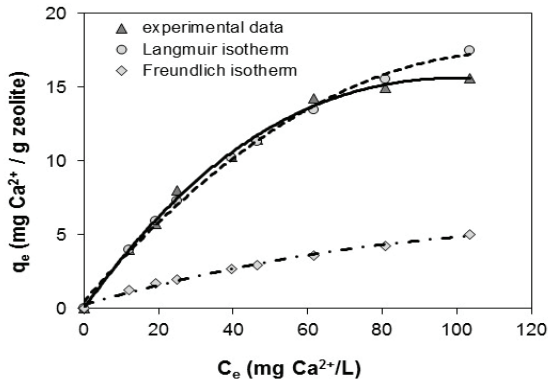

Fig. 7. Isotherm of calcium cations sorbed on *Crystal-Right™ CR100* zeolite (pH = 6.75; m_{zeo} = 8 g/L; time = 24 hours, temperature = 298 K)

For the ultimate sorptive capacity (q_{max}) when the zeolite surface is fully covered with calcium cations (corresponds to monolayer coverage), can be calculated the specific surface area occupied by calcium cations (S_0 in m²/g zeolite) using Eq. (12), where q_{max} is monolayer sorption capacity (g/g); N is Avogadro number ($6,023 \cdot 10^{23}$); A is cross sectional area of calcium ion (m²); M is molecular weight of calcium ion (g/mol). For calcium ion, the molecular weight is 40 g/mol and the cross sectional area have been determined to 3.08 Å² (radius is 0.99 Å, Cruceanu et al., 1986) in a close packed monolayer.

The results are shown in Table 2. The magnitude of sorption energy (E) determined in the Dubinin-Radushkevich equation can be related to the nature of the sorption mechanism in this system (Foo and Hammed, 2010).

$$S = q_{max} \frac{N \cdot A}{M} = q_{max} \frac{N \cdot \left(\pi r_{Ca}^2\right)}{M} \quad (12)$$

The mean free energy of sorption (E), is defined as the free energy change when one mole of ion is transferred to the surface of the solid from infinity in the solution, and was calculated from the constant rated to the sorption energy value (β) using the Eq. (13):

$$E = \left(-2\beta\right)^{-1/2} \quad (13)$$

According with literature (Cruceanu et al., 1986; Zagorodni, 2007) the magnitude of E gives the information about the type of sorption process: physical (< 8 kJ/mol), ion exchange (8 – 16 kJ/mol) and chemical (> 16 kJ/mol). For present experimental data, the values of mean free energy, E, of calcium sorption decrease in the range 0.1166 to 0.0276 kJ/mol with increasing temperature from 298 K to 333 K. These values indicate that the physical forces may affect the sorption mechanism and calcium cations sorption of *Crystal-Right™ CR100* zeolite could be considered physicsorption in nature.

3.3. Thermodynamic parameters

Based on the sorption constant K_L in the Langmuir isotherm (Volesky, 2003), thermodynamic parameters (ΔG^0 – free Gibbs energy, ΔH^0 – standard enthalpy and ΔS^0 – standard entropy) changes were also calculated using Eqs. (14 – 16), where R is the gas constant and T is the absolute temperature. The plot of $ln\ K_L$ vs. $1/T$ gives the straight line from wich ΔH^0 and ΔS^0 was calculed from the slope and intercept of the linearised form.

$$\Delta G^0 = -RT \cdot \ln K_L \qquad (14)$$

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T} \qquad (15)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \qquad (16)$$

Table 3 shows the values of thermodynamic parameters of calcium cations sorption onto *Crystal-Right^{TM} CR100* zeolite.

Table 3. Thermodynamic parameters of calcium sorption onto *Crystal-Right^{TM} CR100* zeolite (pH = 6.75; m_{zeo} = 8 g/L; time = 24 hours)

Temperature, K	ΔG^0, kJ/mol	ΔH^0, kJ/mol	ΔS^0, J/mol.K
278	1.986	54.184	187.764
298	−1.770		
318	−5.525		
333	−8.341		

As seen that of low temperature below 278 K the sorption process of calcium cations is not spontaneous. For range of temperature 298 – 333 K, the sorption is spontaneous with the negative values of ΔG^0. It was also observed that with increase in temperature ΔG^0 became more negative, which justify that sorption is favoured by an increasing temperature. The positive value of ΔH^0 for the sorption of calcium cations on zeolite indicates that the process is endothermic in nature. The positive ΔS^0 value corresponds to an increase disorder at the zeolite – calcium solution interface during the sorption of calcium cations. The positive value of the ΔS^0 indicates the partial dehydratation of the calcium cations before sorption, thus increasing the spontaneity.

The sorption increases randomness at the zeolite/solution interface with some structural changes in the zeolite and calcium cations and an affinity of the zeolite.

4. Conclusions

In this study were investigated of the performances of *Crystal-Right^{TM} CR100* zeolite to calcium cations form calcium chloride solution at equilibrium at temperatures of 278, 298, 318 and 338 K. The equilibrium sorption study is important for an estimation of the practical sorption capacity and optimization of the design of water softening process. The *Crystal-Right^{TM} CR100* zeolite presents a good equilibrium sorption capacity for calcium cations for the experimental conditions.

The equilibrium sorption study increased with initial calcium cations concentration of solution and temperature increased. For example, at initial concentration of calcium cations equal with 139.478 mg/L (equivalent with 19 degree German), the experimental equilibrium sorption capacity are respectively: 8.492 mg/g for 278 K (R = 49.43 %), 11.426 mg/g for 298 K (R = 66.67 %), 13.323 mg/g for 318 K (R = 76.72 %) and 15.607 mg/g for 333 K (R = 90.34 %).

The equilibrium and thermodinamic studies show that the sorption of calcium cations is feasible at ambient temperature when the process is endothermic ($\Delta H^0 > 0$) and is spontaneous ($\Delta G^0 < 0$). The equilibrium $q_e - C_e$ data have been analysed against Langmuir, Freundlich and Dubinin-Radushkevich models and the characteristic parameters for each isotherm have been determined. The results from this study indicated that the sorption described by the theoretical Langmuir isotherm.

The correlation coefficients for fitting the Langmuir model were significantly better than the coeficients for Freundlich or Dubinin-Radushkevich models. The energy of activation for calcium sorption to zeolite is lower and takes place predominantly by physical sorption mechanism. This finding suggests a better orientation of calcium cations to zeolite surface.

References

Al-Anber M., Al-Anber Z.A., (2008), Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron, *Desalination*, **225**, 70–81.

Arrigo I., Catalfamo P., Cavallari L., Di Pasquale S., (2007), Use of zeolitized pumice waste as a water softening agent, *Journal of Hazardous Materials*, **147**, 513–517.

Baskan M.B., Pala A., (2011), Removal of arsenic from drinking water using modified natural zeolite, *Desalination*, **281**, 396–403.

Bandrabur B., Lazăr L., Tataru-Fărmuş R.-E., Bulgariu L., Gutt G., (2012), Permanent hard water softening using different cation exchange resins, *Bulletin of the Polytechnic Institute of Iasi, Section Chemistry and Chemical Engineering*, **58**, 141–150.

Breck D.W., (1974), *Zeolite Molecular Sieves – Structure Chemistry and Use*, Wiley Interscience, New York.

Bulgariu L., Ceica A., Lazar L., Creţescu I., Balasanian I., (2012), Equilibrium and kinetics study of nitrate removal from water by Purolite A520-E resin, *Environmental Engineering and Management Journal*, **11**, 37-45.

Ceica A., Bulgariu L., Lazar L., Cretescu I., Balasanian I., (2011), Influence of parameters to nitrate removal from water by Purolite A-520E, *Environmental Engineering and Management Journal,* **10**, 1553–1559.

Cinar S., Beler-Baykal B., (2005), Ion exchange with natural zeolites: an alternative for water softening?, *Water Science and Technology*, **51**, 71–77.

Coker E.N., Rees L.V.C., (2005), Kinetics of ion exchange in quasi-crystalline aluminosilicate zeolite precursors,

Microporous and Mesoporous Materials, **84**, 171–178.

Cruceanu M., Popovici E., Balba N., Naum N., Vladescu L., Russu R., Vasile A., (1986), *Zeolite Molecular Sieves*, Scientific and Enyclopedic Publishing House, Bucharest, Romania.

Douglas LeVan M., Carta G., Yon C.M., (2008), *Adsorption and Ion Exchange*, In: *Perry's Chemical Engineers'Handbook*, 8th Edition, Perry R.H., Green D.N. (Eds.), McGraw-Hill Companies, Inc., New York, 16:1 – 16:16.

Doula M.K., (2009), Simultaneous removal of Cu, Mn and Zn from drinking water with the use of clinoptilolite and its Fe-modified form, *Water Research*, **43**, 3659–3672.

Foo K.Y., Hameed B.H., (2010), Insights into the modeling of adsorption isotherm systems – Review, *Chemical Engineering Journal*, **156**, 2-10.

Górka A., Bochenek R., Warchoł J., Kaczmarski K., Antos D., (2008), Ion exchange kinetics in removal of small ions. Effect of salt concentration on inter- and intraparticle diffusion, *Chemical Engineering Science*, **63**, 637–650.

Gray N.F., (2010), *Water Technology an Introduction for Environmental Scientists and Engineers*, Second Edition, Elsevier.

Gruett K., (2003), *The art of zeolite application. Acomplete guide to zeolite use for a host of water treatment problems*, Water Technology, Appliying Crystal-Right – Water Right, Inc., 1–5.

Hoffmann H., Martinola F., (1988), Selective resins and special processes for softening water and solutions; A review, *Reactive Polymers, Ion Exchangers*, Sorbents, **7**, 263–272.

Ibrahim H.S., Jamil T.S., Hegazy E.Z., (2010), Application of zeolite prepared from Egyptian kaolin for the removal of heavy metals: II. Isotherm models, *Journal of Hazardous Materials*, **182**, 842–847.

Jamil T.S., Ibrahim H.S., Abd El-Maksoud I.H., El-Wakeel S.T., (2010), Application of zeolite prepared from Egyptian kaolin for removal of heavy metals: I. Optimum conditions, *Desalination*, **258**, 34–40.

Korkuna O., Leboda R., Skubiszewska-Zieba J., Vrublevsy`ka T., Gun`ko V.M., Ryczkowski J., (2006), Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite, *Microporous and Mesoporous Materials*, **87**, 243-254.

Lazar L., Bandrabur B., Tataru-Fărmuş R.-E., Drobotă M., Bulgariu L., Gutt G., (2014), FTIR analysis of ion exchange resins with application in permanent hard water softening, *Environmental Engineering and Management Journal*, **13**, 2145–2152.

Loiola A.R., Andrade J.C.R.A., Sasaki J.M., Da Silva L.R.D., (2012), Structural analysis of zeolite NaA synthesized by a cost-effective hydrothermal method using kaolin and its use as water softener, *Journal of Colloid and Interface Science*, **367**, 34–39.

Lührs H., Derr J., Fischer R.X., (2012), K and Ca exchange behavior of zeolite A, *Microporous and Mesoporous Materials*, **151**, 457–465.

Nibou D., Mekatel H., Amokrane S., Barkat M., Trari M., (2010), Adsorption of Zn^{2+} ions onto NaA and NaX zeolites: Kinetic, equilibrium and thermodynamic studies, *Journal of Hazardous Materials*, **173**, 637–646.

Noroozifar M., Khorasani-Motlagh M., Naderpour H., (2014), Modified nanocrystalline natural zeolite for adsorption of arsenate from wastewater: Isotherm and kinetic studies, *Microporous and Mesoporous Materials*, **197**, 101–108.

Ören A.H., Kaya A., (2006), Factors affecting adsorption characteristics of Zn^{2+} on two natural zeolites, *Journal of Hazardous Materials*, **131**, 59–65.

Qin C., Wang R., Ma W., (2010a), Characteristics of calcium adsorption by Ca–Selectivity zeolite in fixed-pH and in a range of pH, *Chemical Engineering Journal*, **156**, 540–545.

Qin C., Wang R., Ma W., (2010b), Adsorption kinetic studies of calcium ions onto Ca–Selective zeolite, *Desalination*, **259**, 156–160.

Sepehr M.N., Zarrabi M., Kazemian H., Amrane A., Yaghmaian K., Ghaffari H.R., (2013), Removal of hardness agents, calcium and magnesium, by natural and alkaline modified pumice stones in single and binary system, *Applied Surface Science*, **274**, 295-305.

Shahwan T., Akar D., Eroğlu A.E., (2005), Physicochemical characterization of the retardation of aqueous Cs^+ ions by natural kaolinite and clinoptilolite minerals, *Journal of Colloid and Interface Science*, **285**, 9–17.

Shoumkova A., (2011), Zeolites for water and wastewater treatment: An overview, *Research Bulletin of the Australian Institute of High Energetic Materials, Special Issue on Global Fresh Water Shortage*, **2**, 10–70.

Sivasankar V., Ramachandramoorthy T., (2011), Water softening behaviour of sand materials – Mimicking natural zeolites in some locations of Rameswaram Island, India, *Chemical Engineering Journal*, **171**, 24–32.

Smith R., Kim J.K., Kleme J., (2008), *Handbook of Water and Energy Management in Food Processing*, Hardcover, Woodhead Publishing Ltd.

SR ISO 6058, (2008), Water quality – Determination of calcium content – EDTA titrimetric method, ASRO, Bucharest, Romania.

Ştefanache A., Mihăilescu E., Stan C., (2015), Forecasting the presence of Ca^{2+} and Mg^{2+} cations in mineral waters. A model based on fuzzy logic, *Environmental Engineering and Management Journal*, **14**, 223-232.

Volesky B., (2003), *Sorption and Biosorption*, Bv Sorbex, Inc., Canada.

Wang S., Peng Y., (2010), Natural zeolites as effective adsorbents in water and wastewater treatment, *Chemical Engineering Journal*, **156**, 11–24.

Xue Z., Li Z., Ma J., Bai X., Kang Y., Hao W., Li R., (2014), Effective removal of Mg^{2+} and Ca^{2+} ions by mesoporous LTA zeolite, *Desalination*, **341**, 10–18.

Zagorodni A.-A., (2007), *Ion Exchange Materials: Properties and Applications*, Elsevier Science, Oxford, UK.

Zhao H., Vance G.F., Urynowicz M.A., Gregory R.W., (2009), Integrated treatment process using a natural wyoming clinoptilolite for remediating produced waters from coal bed natural gas operations, *Applied Clay Science*, **42**, 379–385.