EQUILIBRIUM PERFORMANCES OF CRYSTAL-RIGHT™ CR100
ZEOLITE USED IN WATER SOFTENING PROCESS

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Abstract

The present work investigates the performance of Cristal-Right™ 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 sorption 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™ 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

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1. Introduction

Water with a high level of hardness caused by calcium (Ca²⁺) and magnesium (Mg²⁺) cations is an important operational costs increase factor in most of its application fields (Gray, 2010; Ștefanache 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 totally 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
The 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 Ramachandranmooorthy, 2011; Xue et al., 2014; Zhao et al., 2009);

2. Water purification – removal of heavy metal cations: Fe³⁺ (Al-Anber and Al-Anber, 2008); Cu²⁺, Zn²⁺, Mn²⁺, Ni²⁺, Cd²⁺, Pb²⁺ (Doula, 2009; Ibrahim et al., 2010; Jamil et al., 2010; Nibou et al., 2010; Ören and Kaya, 2006), As⁵⁺, As³⁺ (Baskan and Pala, 2011; Noroozifar et al., 2014), Ce⁺ (Shahwan et al., 2005).

Zeolites used for water softening process are mostly Zn²⁺, Mn²⁺, Ni²⁺, Cd²⁺, Pb²⁺ (Doula, 2009; Ibrahim at al., 2009; Shoumkova, 2011; Wang and Peng, 2010). For example, sodium-zeolite removes Ca²⁺ cations from the raw hard water passing through the crystalline structure (Louiola et al., 2012; Lührs et al., 2012; Shoumkova, 2011; Wang and Peng, 2010). For example, sodium-zeolite removes Ca²⁺ cations from water by exchange with sodium as illustrated by Eq. (1).

\[ \text{Ca}^{2+}(\text{solution}) + 2\text{Na}_i(\text{zeolite}) = \text{Ca}_i(\text{zeolite}) + 2\text{Na}^{+}(\text{solution}) \] (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 Ca²⁺, Mg²⁺, Fe³⁺, Mg²⁺ 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 mass/ solution volume (dose), temperature, phase contact time and crystal structure of the zeolite (Al-Anber and Al-Anber, 2008; Jamil et al., 2010; Nibou et 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™ 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™ 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, Cristal-Right™ 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 Cristal-Right™ 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 transmission technique using the KBr pellet and the Opus 5 FTIR Software. In Fig. 2 is presented the FT-IR spectra of Cristal-Right™ CR100 zeolite in delivery form.

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Value (%, w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>30.25</td>
</tr>
<tr>
<td>Al</td>
<td>9.27</td>
</tr>
<tr>
<td>O</td>
<td>52.02</td>
</tr>
<tr>
<td>Na</td>
<td>5.13</td>
</tr>
<tr>
<td>Ca</td>
<td>2.43</td>
</tr>
<tr>
<td>K</td>
<td>0.66</td>
</tr>
<tr>
<td>Au</td>
<td>0.44</td>
</tr>
<tr>
<td>Cl</td>
<td>0.29</td>
</tr>
</tbody>
</table>

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 SiO₄ 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™ 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 by the zeolite (equilibrium sorption capacity in mg/g – q\(_e\)) was calculated according to Eq. (2).

\[
q_e = \frac{(C_0 - C_e) \cdot V_{sol}}{m_{zeo}}
\] (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).

\[
R = \frac{C_0 - C_e}{C_0} \times 100\%
\] (3)

2.2. Equilibrium isotherms

The equilibrium performances of the Cristal-Right\textsuperscript{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/mol) 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; \(\beta\) is a constant related to the sorption energy (mol/J/mol); \(\varepsilon\) 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)).

\[
q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \quad \text{ (mg/g)}
\] (4)

\[
q_e = K_F (C_e)^{1/n} \quad \text{ (mg/g)}
\] (5)

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

\[
\varepsilon = R T \ln \left(1 + \frac{1}{C_e}\right)
\] (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).

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_L} \cdot C_e
\]  

(8)

\[
\lg q_e = \lg K_F + \frac{1}{n} \lg C_e
\]  

(9)

\[
\ln q_e = \ln q_{\text{max}} - \beta \cdot e^2
\]  

(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™ 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™ CR100 zeolite at different temperatures (pH = 6.75, mzeo = 8 g/L, time = 24 hours)](image)

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™ 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™ 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™ CR100 zeolite (pH = 6.75, mzeo = 8 g/L, 298 K; time = 24 hours)](image)

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. \(\varepsilon^2\) (for Dubinin–Radushkevich model – Fig. 5c).

![Fig. 5. The linearized Langmuir (a), Freundlich (b) and Dubinin-Radushkevich (c) isotherm of calcium onto Crystal-Right™ CR100 zeolite at different temperatures (pH = 6.75; mzeo = 8 g/L; time = 24 hours)](image)

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 \((R^2 = 0.97 – 0.99)\) better 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 calculated by Eq. (11), where \(C_0\) is initial concentration \((\text{mg/L})\), \(K_L\) is Langmuir constant \((\text{L/mg})\).

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

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™ 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 \(q_{\text{max}}\) 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; mzeo = 8 g/L; time = 24 hours)](image)

For example, the experimental results for 298 K of Langmuir model indicate the monolayer sorption capacity value \(q_{\text{max}}\) 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; mzeo = 8 g/L; time = 24 hours)

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Temperature, K</th>
<th>278</th>
<th>298</th>
<th>318</th>
<th>338</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
<td></td>
<td>68.0272</td>
<td>31.447</td>
<td>20.284</td>
<td>30.303</td>
</tr>
<tr>
<td></td>
<td>q_{max}, mg/g</td>
<td></td>
<td>0.00171</td>
<td>0.0121</td>
<td>0.0598</td>
<td>0.0687</td>
</tr>
<tr>
<td></td>
<td>K_{L}, L/mg</td>
<td></td>
<td>0.9883</td>
<td>0.9906</td>
<td>0.9840</td>
<td>0.9730</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td></td>
<td>0.9564</td>
<td>0.9847</td>
<td>0.9894</td>
<td>0.9058</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
<td></td>
<td>11.003</td>
<td>15.991</td>
<td>16.425</td>
<td>22.594</td>
</tr>
<tr>
<td></td>
<td>K_{f}, mg/g</td>
<td></td>
<td>0.1099</td>
<td>0.2442</td>
<td>0.3475</td>
<td>0.5320</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td></td>
<td>1.1724</td>
<td>1.5361</td>
<td>2.0597</td>
<td>2.1542</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td></td>
<td>0.9654</td>
<td>0.9487</td>
<td>0.9894</td>
<td>0.9058</td>
</tr>
<tr>
<td><strong>Dubinin-Radushkevich</strong></td>
<td></td>
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<td>11.003</td>
<td>15.991</td>
<td>16.425</td>
<td>22.594</td>
</tr>
<tr>
<td></td>
<td>q_{max}, mg/g</td>
<td></td>
<td>2.98·10^{-3}</td>
<td>0.1166</td>
<td>0.0400</td>
<td>0.0276</td>
</tr>
<tr>
<td></td>
<td>E, kJ/mol</td>
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<td>0.0130</td>
<td>2.0712</td>
<td>3.5338</td>
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</tr>
<tr>
<td></td>
<td>R^2</td>
<td></td>
<td>0.9559</td>
<td>0.9633</td>
<td>0.9401</td>
<td>0.9581</td>
</tr>
</tbody>
</table>

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. Isotherm of calcium cations sorbed on Crystal-Right™ CR100 zeolite (pH = 6.75; mzeo = 8 g/L; time = 24 hours, temperature = 298 K)](image)

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 m^2/g zeolite) using Eq. (12), where q_{max} is monolayer sorption capacity (g/g); N is Avogadro number (6,023·10^{23}); A is cross sectional area of calcium ion (m^2); 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 Å^2 (radius is 0.99 Å, Cruceanu et al., 1986) in a close packed monolayer.

\[
S = \frac{q_{max}}{M} = \frac{N}{M} \left( \frac{\pi A^2}{4} \right) \tag{12}
\]

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 (\beta) using the Eq. (13):

\[
E = (-2\beta)^{-1/2} \tag{13}
\]

Based on the sorption constant K_{L} in the Langmuir isotherm (Volesky, 2003), thermodynamic parameters (\Delta G^0 – free Gibbs energy, \Delta H^0 – standard enthalpy and \Delta S^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 \Delta H^0 and \Delta S^0 was calculated from the slope and intercept of the linearised form.

3.3. Thermodynamic parameters

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 Hammedd, 2010).

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 (\beta) using the Eq. (13):
the process is endothermic in nature. The positive sorption of calcium cations on zeolite indicates that 
ΔG° is endothermic (ΔG° > 0) and is spontaneous (ΔG° < 0).

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

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

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>ΔG°, kJ/mol</th>
<th>ΔH°, kJ/mol</th>
<th>ΔS°, J/mol.K</th>
</tr>
</thead>
<tbody>
<tr>
<td>278</td>
<td>–1.986</td>
<td>54.184</td>
<td>187.764</td>
</tr>
<tr>
<td>298</td>
<td>–1.770</td>
<td></td>
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</tr>
<tr>
<td>318</td>
<td>–5.525</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>–8.341</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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°. It was also observed that with increase in temperature ΔG° became more negative, which justify that sorption is favoured by an increasing temperature. The positive value of ΔH° for the sorption of calcium cations on zeolite indicates that the process is endothermic in nature. The positive ΔS° value corresponds to an increase disorder at the zeolite – solution interface during the sorption of calcium cations. The positive value of the ΔS° 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™ 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™ 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 thermodynamic studies show that the sorption of calcium cations is feasible at ambient temperature when the process is endothermic (ΔH° > 0) and is spontaneous (ΔG° < 0). The equilibrium qe – Ceq 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 coefficients 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.

Acknowledgments

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