

APPLICATION OF A STRONG ACID RESIN AS ION EXCHANGE MATERIAL FOR WATER SOFTENING – EQUILIBRIUM AND THERMODYNAMIC ANALYSIS

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Abstract: The adsorption equilibrium isotherm of calcium from aqueous solution onto *Purolite C100E* synthetic ion exchange resin have been studied and modelled. The batch method has been employed, using Ca^{2+} concentration in calcium chloride solution ranging from 42 to 176 $\text{mg}\cdot\text{L}^{-1}$ at pH 7.1. The suitability of the Langmuir and Freundlich adsorption isotherm was investigated for calcium chloride solutions – ion exchange resin system. The temperature effect on the calcium removal onto resin was also investigated, and various thermodynamic parameters (ΔG , ΔH and ΔS) have been calculated. These parameters indicate the spontaneous and endothermic nature of the ion exchange process.

Keywords: adsorption isotherms, ion exchange, *Purolite C100E* resin, thermodynamics, water softening

INTRODUCTION

Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions coming in contact with them [1-3]. Strong acid cation (SAC) resins have been developed as a major option for water softening process for the domestic or food industry specific applications [3-5]. These resins are insoluble polymers prepared by the copolymerization of styrene and divinyl benzene and have sulfonic acid groups ($-\text{SO}_3\text{H}$) introduced into most of the benzene rings [3, 6-9].

Water softening using SAC resin in sodium form ($\text{R}-\text{SO}_3\text{Na}$) is possible because of the material selectivity for the ion exchange reactions between Na^+ ions and Ca^{2+} or Mg^{2+} ions [5]. The calcium and magnesium ions dissolved in water are bound by the resin exchanging the equivalent amount of sodium ions, which are released from the resin to the water, so that the total dissolved solids content of the water remains unchanged as does the pH and the anionic content. These exchanges take place without any physical alteration to the resin. Strong acid cation exchangers operate over a very wide pH range because the sulphonate group, being strongly acidic ($-\text{SO}_3^-$) is ionized throughout the pH range (1 to 14) [3, 5, 10].

Among the commercially available products *Purolite C100E* is one of the best options considering its food grade water softening applications [6]. The literature lacks sufficient experimental research that scientifically explains the behaviour and the performance of the new commercial resins and also investigations on the equilibrium, thermodynamic and kinetics of its use in the water softening process [10-16]. These studies for a chosen ion exchange process under various experimental conditions are quite important and are always studied at the beginning of the research [2, 17-19].

Nowadays there are many approaches that can be used to describe the ion-exchange equilibrium [13, 15, 20, 21]. The equilibrium of ion exchange process is normally represented by the adsorption isotherm curves [19, 21]. Adsorption isotherms describe the interaction between adsorbates (hard water) and adsorbent (ion exchange resin) and are crucial to the practical design and operation of water softening system [3, 4, 21]. Over the years, a wide variety of equilibrium isotherm models (Freundlich, Langmuir, Dubinin-Radushkevich, Temkin etc.) have been formulated in terms of three fundamental approaches (kinetic consideration, thermodynamics, trend in the isotherm modelling) [21].

In the present paper, strong acid cation *Purolite C100E* resin in Na^+ form was examined for its sorption properties towards Ca^{2+} from calcium chloride solution using batch adsorption method and optimum conditions. The main objective of study was to investigate the equilibrium process and also to evaluate the thermodynamics parameters from the ion exchange measurements. Two linear models were used to describe the experimental adsorption isotherms: Langmuir and Freundlich. The adsorption isotherm is an invaluable curve describing the phenomenon governing the retention or mobility of a substance from the aqueous porous media to a solid-phase at a constant temperature and pH. In a previous study it has been shown that calcium ions removal from various types of water and synthetic solutions on *Purolite C100E* resin depends on the experimental parameters such as: initial solution concentration, resin dose, temperature, and contact time [22, 23].

MATERIALS AND METHODS

Commercially available *Purolite C100E* resin is a strong acid cation exchanger gel resin with polystyrene and divinylbenzene (DVB) copolymerised matrix and sulphonic acid type functional groups [7]. This resin is delivered by the Purolite Co. producer company in regenerable sodium form. The physical properties and specification reported by the supplier are shown in Table 1.

Table 1. Characteristics of the *Purolite C100E* cation exchange resin [7]

| Characteristics | Values |
|------------------------------|--|
| Application | Food grade water softening - Potable water |
| Polymer matrix structure | Gel polystyrene crosslinked with DVB |
| Physical form and appearance | Amber, clear spherical beads |
| Functional group | R-SO ₃ H |
| Ionic form as shipped | Na ⁺ |
| Total capacity (min.) | 1.9 eq/L (Na ⁺ form) |
| Particle size range | 0.3 – 1.2 mm / < 0.3 mm (max.) 1 % |
| Moisture retention | 46 – 50 % (Na ⁺ form) |
| Shipping weight | 800 – 840 g·L ⁻¹ |
| Specific gravity | 1.27 (moist Na ⁺ form) |
| pH range, operating | 1 – 14 |
| Maximum temperature limit | 393 K |

All the experiments were conducted using the resin in the delivery form, previously swollen in ultrapure water for 24 hours. The data interpreting and analysis is always reported to the dry cationic resin state.

The experimental investigation of the *Purolite C100E* resin performance in the Ca²⁺ ions removal process was performed in batch mode at a constant temperature, using binary synthetic calcium chloride solutions at different initial Ca²⁺ concentration (42 to 176 mg·L⁻¹). The optimum parameters were selected based on that preliminary studies results and were maintained in all experiments for the Ca²⁺ retention on this resin: initial solution pH of natural water value (about 7), resin dose of 8 g·L⁻¹ (dry resin) [22, 23]. The pH value correction for the aqueous solutions used in the experiments was performed by using a buffer sodium acetate 0.1M solution. The experiments were conducted in batch mode and the contact time was around 24 hours, so that equilibrium was reached. Erlenmeyer flasks were used for the 50 mL solution and the pre swollen cationic resin dose contact according to the desired experiment. All flasks were kept under agitation at a constant speed of 100 rpm using an orbital shaker. All the experimental solutions were prepared using analytical reagents grade from Merck or Sigma Aldrich dissolved in ultrapure water.

The initial and final Ca²⁺ ions concentration analysis was performed using the EDTA method (SR ISO 6058:2008 [24]). An automatic titrator and specific titration end-point indicators for water hardness analysis delivered by Hach Company were used (CalVER®).

Adsorption isotherms establish the relationship between the equilibrium concentration and the amount of calcium retained by the unit mass of ion exchange resin at a constant temperature [19, 20]. The equilibrium cationic exchange capacity of *Purolite C100E*

resin was calculated using eqn. (1):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where: q_e is the equilibrium retention capacity, in $\text{mg} \cdot \text{g}^{-1}$ dry resin; C_0 – the initial concentration of calcium ions, in $\text{mg} \cdot \text{L}^{-1}$; C_e – the equilibrium concentrations of calcium cations, in $\text{mg} \cdot \text{L}^{-1}$; V – the volume of solution to be softened, in L; m – the amount of cationic resin in the experiment in dry state, in g reported.

RESULTS AND DISCUSSION

Equilibrium isotherm

Similar to the adsorption process, equilibrium for the ion exchange process by synthetic resin (the ratio between the adsorbed amount and the amount remaining in the solution) is established when an adsorbate containing phase has been in contact with the liquid phase for sufficient time for its adsorbate concentration in the bulk solution to be in a dynamic balance with the interface concentration [1, 3, 17].

The quantity of calcium that could be taken up by a strong acid *Purolite C100E* resin is a function of both the concentration of calcium and temperature. The isotherms for the calcium ions retention on *Purolite C100E* resin at different temperatures (298, 313 and 333 K) are shown in Figure 1 presenting the Ca^{2+} ions equilibrium cationic exchange capacity as function of the amount of Ca^{2+} ions left in equilibrium solution (C_e , $\text{mg} \cdot \text{L}^{-1}$). It can be seen that temperature increase positively influences the amount of calcium retained on *Purolite C100E*. This can be easily explained because higher temperatures increase the attraction forces between the positive charged functional groups of the resin and Ca^{2+} ions thus improving the exchange process.

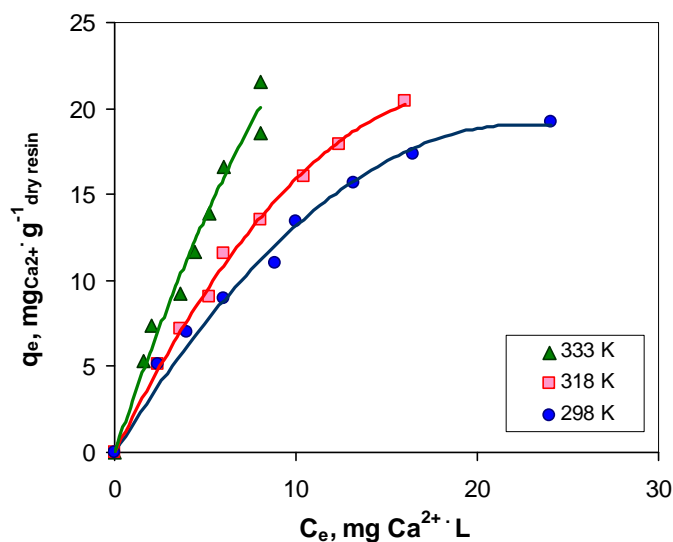


Figure 1. Equilibrium isotherms for calcium retention onto *Purolite C100E* resin ($8 \text{ g dry resin} \cdot \text{L}^{-1}$, $\text{pH} = 7.1$, $\text{time} = 24 \text{ h}$)

From Figure 1 can be concluded that for all the studied temperatures the retention equilibrium occurs rapidly at lower calcium concentration and for higher equilibrium concentrations the values become relatively constant. For calcium initial concentration of $150 \text{ mg}\cdot\text{L}^{-1}$ (equivalent to a calcium hardness of $21^\circ\text{d}_{\text{Ca}}$ [23]), the equilibrium cationic exchange capacity values for various temperatures are respectively: $17.311 \text{ mg}\cdot\text{g}^{-1}$ for 298 K, $17.925 \text{ mg}\cdot\text{g}^{-1}$ for 313 K and $18.534 \text{ mg}\cdot\text{g}^{-1}$ for 333 K without presenting significant differences with temperature. This illustrates that since the temperature increase does not significantly improve the efficiency of calcium removal process the use of high temperature is not necessary, by also being economically non-feasible.

Adsorption isotherms are very powerful tools for the analysis of the retention process by ion exchange resin [20]. For the equilibrium data comparison two adsorption isotherms models that are widely used were employed: Langmuir and Freundlich. Other isotherms proposed in the literature [19, 21] are not suitable for this liquid – solid system.

Langmuir model considers only superficial monolayer adsorption, considering a homogenous surface containing a limited number of ion exchange centers represented by the functional groups, but it covers a wide range of concentrations [21, 25]. This model assumes that adsorption forces are similar to the ones in the chemical interactions and it can be used to evaluate the maximum retention capacity (q_{max} , $\text{mg}\cdot\text{g}^{-1}$ dry resin), reached after the complete saturation of the resin surface. Langmuir isotherm model can be expressed by the following eqn. (2) and eqn. (3):

$$q_e = q_{\text{max}} \frac{K_L C_e}{1 + K_L C_e} \quad (2)$$

$$\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_L} \cdot \frac{1}{C_e} \quad (3)$$

where: q_e represents the maximum amount of calcium ions per weight unit of cationic resin to cover a complete monolayer covering the surface bonding sites ($\text{mg}\cdot\text{g}^{-1}$ dry resin), q_{max} represents the practical limiting retention capacity when the surface is fully covered with calcium ions and is used for the comparison of retention performance, in experiments where the cationic resin did not reach its saturation ($\text{mg}\cdot\text{g}^{-1}$ dry resin), C_e is the calcium concentration at the equilibrium ($\text{mg}\cdot\text{L}^{-1}$) and K_L ($\text{L}\cdot\text{mg}^{-1}$) is the Langmuir isotherm constant which is related to the affinity of the binding sites [2].

The simple Langmuir isotherm equation valid for the adsorption of a single component on a single-site surface is frequently applied to ion exchange reactions. If this equation does not generate a single straight line then a multi-site surface is assumed and additional terms of the equation are used for analysis [21, 25].

The linear representation of the Langmuir model (eqn. 3) for the calcium ions retention on *Purolite C100E* resin is shown in Figure 2 for different studied temperature values. From the linear trendline of the $1/q_e$ vs. $1/C_e$ plots slope and intercept the of q_{max} and K_L constants values were calculated as presented in Table 2 together with the linear regression coefficients. According to the Langmuir isotherm, the maximum calcium retention capacity values for *Purolite C100E* resin increase with temperature. The experimental results for the 298 K temperature indicate the maximum calcium retention capacity (q_{max}) of $25.773 \text{ mg}\cdot\text{g}^{-1}$ dry resin and energy of adsorption value K_L of $0.0998 \text{ L}\cdot\text{mg}^{-1}$.

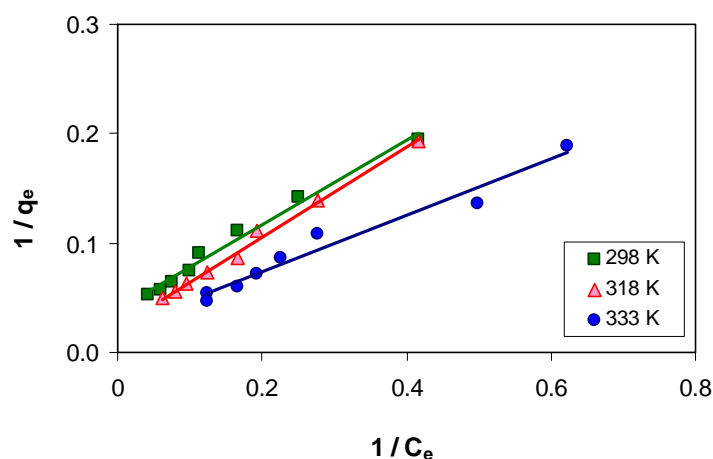


Figure 2. Linearized forms of Langmuir isotherm for removal of calcium ion from CaCl_2 solution onto Purolite C100E resin

The Freundlich model takes into consideration also the surface heterogeneity of the cationic exchange resin [19, 21] and it can be used to estimate the adsorption intensity of calcium towards the resin, defined by the following eqn. (4):

$$q_e = K_f \cdot C_e^{(1/n)} \quad (4)$$

where: K_f represents the Freundlich constant that is an indicator of the retention capacity ($\text{mg} \cdot \text{g}^{-1}$) and n is a constant related to the affinity of calcium ions for the resin. These constants for the given system can be calculated from the linear form of eqn. (4):

$$\lg q_e = \lg K_f + \frac{1}{n} \lg C_e \quad (5)$$

where: q_e is the calcium ion retention at equilibrium ($\text{mg} \cdot \text{g}^{-1}$ dry resin) and C_e – equilibrium concentration ($\text{mg} \cdot \text{L}^{-1}$).

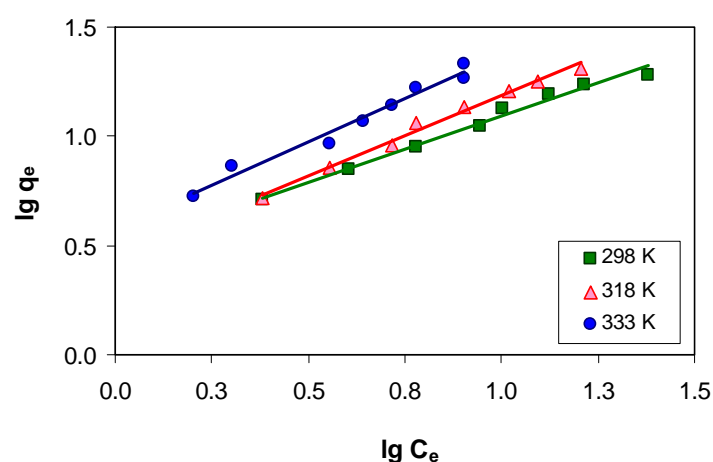


Figure 3. Linearized forms of Freundlich isotherm for removal of calcium ion from CaCl_2 solution onto Purolite C100E resin

Figure 3 shows the linear representation of Freundlich model for calcium ions retention

on *Purolite C100E* resin at different temperature values. The linear regression coefficients (R^2) of the $\lg q_e$ function of $\lg C_e$ are very close to 1, confirming the Freundlich adsorption isotherm. K_f and n , the Freundlich model constants, can be determined from the intercept and the slope of the straight line respectively and are presented in Table 2.

Table 2 presents all the calculated results of the Langmuir and Freundlich isotherm parameters and also the correlation coefficients R^2 . It can be seen that the Langmuir equation better describe the cationic exchange on *Purolite C100E* resin on the entire concentration range in the study compared to Freundlich. The isotherm models parameters can be further construed providing understandings on adsorption mechanism, surface properties and affinity of the ion exchanger resin.

Table 2. Langmuir and Freundlich isotherm parameters for removal of calcium ions from CaCl_2 solution onto *Purolite C100E* resin

| Type isotherms | Isotherm parameters | Temperature, K | | |
|----------------|--|----------------|--------|--------|
| | | 298 | 313 | 333 |
| Langmuir | q_{\max} , $\text{mg}\cdot\text{g}^{-1}$ dry resin | 25.773 | 43.103 | 34.364 |
| | K_L , $\text{L}\cdot\text{mg}^{-1}$ | 0.0998 | 0.0560 | 0.1711 |
| | R^2 | 0.9845 | 0.9939 | 0.9725 |
| Freundlich | K_F , $\text{mg}\cdot\text{g}^{-1}$ | 3.7506 | 2.7996 | 3.0782 |
| | n | 1.2545 | 1.3552 | 1.6518 |
| | R^2 | 0.9715 | 0.9888 | 0.9850 |

From the Langmuir isotherm a dimensionless constant can be calculated, that is used to predict if an adsorption system is “favourable” ($R_L < 1$) or “unfavourable” ($R_L > 1$) [13]. This equilibrium parameter also called separation factor, R_L is defined by eqn. (6):

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (6)$$

where: C_0 is the initial calcium ion concentration ($\text{mg}\cdot\text{L}^{-1}$) and K_L is the retention equilibrium constant from the Langmuir equation ($\text{L}\cdot\text{mg}^{-1}$).

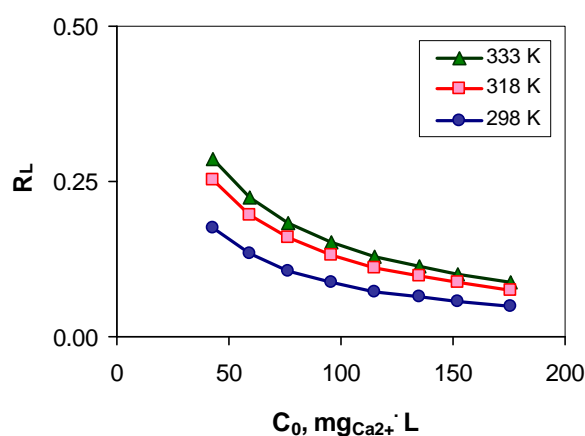


Figure 4. R_L constant variation with initial calcium concentration

The calculated R_L values for the calcium ions retention on *Purolite C100E* resin at all the temperature values in the study are below 0.3 (Figure 4). A decrease of R_L values with the increase of initial concentration can be observed for all the studied temperatures. Based on the Langmuir equation calculated values can be concluded that *Purolite C100E* resin shows favourable monolayer adsorption onto homogeneous surfaces.

Thermodynamic parameters

Based on the experimental and calculated data the thermodynamic parameters were also evaluated for the ion exchange process. The process driving force and also the fundamental spontaneity criteria in the system is the free Gibbs energy change (ΔG). For a given temperature if ΔG value is negative than the processes occurs spontaneously [13, 17, 19]. The free energy of the retention process can be calculated from the Langmuir constant (K_L) using eqn. (7):

$$\Delta G = -RT \cdot \ln K_L \quad (7)$$

where: T is the temperature (K) and R is the universal gas constant, ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). In order to evaluate the other thermodynamic parameters, such as enthalpy change (ΔH) and entropy change (ΔS) it is necessary to use eqn. (9), which is the linear form of the eqn. (8), plotting the $\ln K_L$ as a function of T^{-1} :

$$\Delta G = \Delta H - T \cdot \Delta S \quad (8)$$

$$\ln K_L = \left(\frac{\Delta S}{R} \right) - \left(\frac{\Delta H}{R} \right) \frac{1}{T} \quad (9)$$

The thermodynamic study of the equilibrium experimental results shows that ΔG values were negative at all temperatures investigated. For the experimental condition in the temperature range of 298 to 313 K, the thermodynamic constants of ion exchange phenomena values are: $\Delta H = 22.733 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S = 9.545 \cdot 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The ΔH positive values indicate that the ion exchange process of calcium ions onto the strong acid cationic *Purolite C100E* resin is endothermic. The positive values of ΔS indicate the affinity of the cationic exchange resin for calcium ions, which would cause increase in the entropy, during the adsorption process. The negative value of ΔG confirms the spontaneity of the calcium retention on the *Purolite C100E* resin. The free energy of the ion exchange reaction is calculated according to the eqn. (10):

$$\Delta G = -22.733 + 9.545 \cdot 10^{-3} \cdot T, \text{ kJ} \cdot \text{mol}^{-1} \quad (10)$$

CONCLUSIONS

Calcium removal from calcium chloride solutions equilibrium and thermodynamic were investigated using the strong acid cation exchange *Purolite C100E* resin in the batch method, for the following experimental conditions: temperature range 278 – 333 K, initial calcium concentrations between 42 and 176 $\text{mg} \cdot \text{L}^{-1}$, pH solution equal to 7.1 and constant resin dose amount of 8 g dry resin $\cdot \text{L}^{-1}$.

The strong acid cation resin – aqueous solution equilibrium experimental curves $q_e - C_e$

(equilibrium cationic exchange capacity vs. equilibrium concentration of Ca^{2+} in CaCl_2 solution), so called adsorption isotherms have been confronted with two linear isotherm equations such as Langmuir and Freundlich, and the constant of these models have been identified. Based on the linear regression coefficients (R^2) and on the theoretical value of the retention capacity the best-fit model was demonstrated. It is obvious from the experimental data that the retention of calcium ions is fitted well to the Langmuir isotherm model than that of the Freundlich isotherm models and the adsorption coefficients agree well with the conditions supporting favourable adsorption. The values of maximum retention capacity (q_{\max} , $\text{mg}\cdot\text{g}^{-1}$) of *Purolite C100E* resin (Table 2), calculated from Langmuir isotherm equation, increase with the increase of temperature, the highest value of $43.103 \text{ mg}\cdot\text{g}^{-1}$ being obtained at 313 K vs. $25.773 \text{ mg}\cdot\text{g}^{-1}$ at 298 K. The values of thermodynamic parameters ΔG and ΔH indicate that the cationic exchange process is spontaneous and endothermic for all studied temperatures. This is also supported by the increase in value of cationic exchange capacity. The positive values of ΔS reflect the affinity of Ca^{2+} for resin, and show the increasing randomness at the resin – calcium chloride solution interface during adsorption of Ca^{2+} on *Purolite C100E* resin.

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