ORIGINAL RESEARCH PAPER

USE OF STRONG ACID RESIN *PUROLITE C100E* FOR REMOVING PERMANENT HARDNESS OF WATER – FACTORS AFFECTING CATIONIC EXCHANGE CAPACITY

Bogdan Bandrabur[1], Ramona-Elena Tataru-Fărmuş[2], Liliana Lazăr[2*], Laura Bulgariu[2], Gheorghe Gutt[1]

[1]*"Stefan cel Mare" University of Suceava, Faculty of Food Engineering, 13 University Street, 720229 - Suceava, Romania*
[2]*"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 73 Prof. dr. doc. D. Mangeron Street, 700050 - Iasi, Romania*

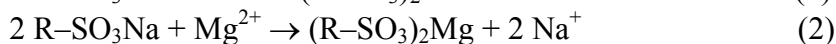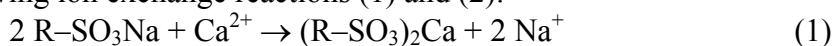*Corresponding author: lillazar@ch.tuiasi.ro

Abstract: This paper experimentally investigates the performance and capacity of *Purolite C100E* commercial resin recommended for water softening applications in the food industry. The practical ion exchange capacity and the softening process efficiency are studied in batch mode as a function of the sorption specific process factors. Optimum operation conditions were determined as initial pH 7.1, resin dose 8 g dry resin·L^{-1}, temperature 25 ^{o}C, contact time of 360 min, and in those conditions the retention capacity for the Ca^{2+} ions is 17.18 mg·g^{-1} that corresponds to a removal efficiency equal to 85.7%.

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INTRODUCTION

Water is a primary raw material for the food industry and it requires quality conditions similar with the ones specific for drinking water [1]. Based on the fabrication process where water is used, a certain limit for the water hardness is required. Permanent water hardness is caused by the calcium and magnesium salts that do not precipitate during boiling (chlorides, sulphates, nitrates, phosphates) [1, 2].

One of the industrial level applied methods for the Ca^{2+} and Mg^{2+} cations content reduction is the ionic exchange using polymeric strong acid cation resins (SAC) or weak acid resins (WAC) [3 – 6]. The classical water softening process for the domestic or food industry specific applications imply the use of strong acid resins in sodium form (RSO_3Na) that present a selectivity for the ion exchange reactions between Na^+ ions and Ca^{2+} or Mg^{2+} cations. [1, 3, 6]. The cationic exchange process that takes place at the interface between the resin and the solution containing Ca^{2+} and Mg^{2+} ions can be described by the following ion exchange reactions (1) and (2):

$$2\ R–SO_3Na + Ca^{2+} \rightarrow (R–SO_3)_2Ca + 2\ Na^+ \qquad (1)$$
$$2\ R–SO_3Na + Mg^{2+} \rightarrow (R–SO_3)_2Mg + 2\ Na^+ \qquad (2)$$

The depleted resin regeneration after one technological cycle is simple and low cost due to the use of sodium chloride solution (0.5 to 3.0 M) as regeneration agent [3, 4, 6].

Nowadays there are many polymeric ion exchange resins recommended for the water softening processes in the food industry. These materials' data sheets from the producers the total (theoretical) ion exchange capacity is presented for the resin delivery form [7 – 10]. The usable (practical) ion exchange capacity is influenced by the specific conditions of the sorption process: the nature and concentration of the exchange ions, the ratio between resin quantity and the solution volume (resin dose), initial solution pH, ions concentration in the treated solution, temperature, contact time between solid and liquid phase, aqueous solution nature etc. [11 – 13]. Knowing the kinetic parameters' influence on the total cationic exchange capacity allows the softening process equilibrium analysis, thermodynamic and kinetic analysis based on the sorption in ion exchanger materials process specific models [11 – 14].

The literature lacks sufficient experimental research that scientifically explains the behaviour and the performance of the new commercial resins and also investigations on the kinetics and thermodynamics of the water softening process [4, 5, 14 – 18].

This paper presents the study on the practical cationic exchange capacity of the commercially available *Purolite C100E* resin in batch mode as function of the water softening ion exchange process' specific experimental factors. In the experiment both natural water and binary synthetic solutions containing ions Ca^{2+} and Mg^{2+} respectively were used.

MATERIALS AND METHODS

Commercially available *Purolite C100E* resin is a strong acid cation exchanger gel resin with polystyrene and divinylbenzene copolymerised matrix and sulphonic acid type functional groups ($–SO_3H$). The resin was delivered by the Purolite Co. producer company in regenerable sodium form. The characteristics of *Purolite C100E* total ion exchange capacity is reported in the technical data sheet 1.9 eq/L minimum [19].

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 removal of Ca^{2+} and Mg^{2+} cations process was performed in batch mode at a constant temperature, using ground water with a 24.3 ^{o}dH (German degrees) hardness and binary synthetic solutions containing calcium or magnesium ions. 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 constant agitation speed 100 rpm using an orbital shaker. The *p*H value correction for the aqueous solutions used in the experiments was performed by using a buffer sodium acetate 0.1M solution. All the experimental solutions were prepared using analytical reagents grade from Merck or Sigma Aldrich dissolved in ultrapure water.

The initial and final Ca^{2+} and Mg^{2+} cations concentration analysis respectively was performed using the EDTA method (SR ISO 6058:2008 [20]) and SR ISO 6059:2008 respectively [21]). An automatic titrator and specific titration end-point indicators for water hardness analysis delivered by Hach Company were used (CalVER® and, ManVER®).

Water hardness for both natural water and artificial aqueous solutions was expressed as function of cations concentration using the following equivalences [2]:

$$1 \ ^o\text{dH} = 10 \text{ mg CaO·L}^{-1} = 7.14 \text{ mg Ca}^{2+}·\text{L}^{-1} \ (1 \ ^o\text{d}_{Ca})$$
$$1 \ ^o\text{dH} = 7.14 \text{ mg MgO·L}^{-1} = 3.34 \text{ mg Mg}^{2+}·\text{L}^{-1} \ (1 \ ^o\text{d}_{Mg})$$

The softening process efficiency was qualitatively evaluated by using the retention degree, *R* (in %), calculated according to the eqn. (3):

$$R = \frac{C^0 - C}{C^0} \cdot 100 \tag{3}$$

The cationic exchange capacity (retention capacity), *q* (in mg/g dry resin) was evaluated by the amount of Ca^{2+} respectively Mg^{2+} cations content retained by each mass unit of ion exchange resin calculated with the eqn. (4):

$$q = \frac{\left(C^0 - C\right) \cdot V}{m} \tag{4}$$

where C^0 – cation concentration in the initial solution, in mg·L^{-1}; *C* – cation concentration in the residual solution, in mg·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

The *Purolite C100E* resin performance was investigated from the point of view of the following sorption process specific parameters' influence: resin dose (1 – 10 g dry resin·L^{-1}), initial solution *p*H (5.5 – 7.5), Ca^{2+} ions concentration in the solution to be treated (40 – 180 mg·L^{-1}), contact time (0 – 24 hours), temperature (5 – 60 ^{o}C), and aqueous solution nature (CaCl$_2$, CaSO$_4$, CaNO$_3$ and groundwater). The groundwater samples used in the experiment can be considered as part of the hard waters group, having the following physico-chemical characteristics: *p*H of 7 – 7.2,

conductivity value of 825 $\mu S \cdot cm^{-1}$, 145.10 mg $Ca^{2+} \cdot L^{-1}$ and 17.25 mg $Mg^{2+} \cdot L^{-1}$ (equivalent to a calcium hardness of 20.3 $^o d_{Ca}$ and magnesium hardness of 4 $^o d_{Mg}$, respectively). In order to compare the experimental results for the ground water softening process the equivalent Ca^{2+} hardness values were employed, considering that permanent water hardness is mostly generated by this ion.

Effect of initial solution *p*H on the cationic exchange capacity

The initial solution *p*H is an important parameter influencing the sorption process at the water − ion exchange resin interfaces. The *p*H value determines on one hand the dissociation degree of the resin's functional groups and the electrical charges of the resin surface and on the other hand the concentration and ionic state of the exchange species in the solution.

Considering the *p*H values where calcium and magnesium ions can start to precipitate, to determine the optimum *p*H for the maximum removal of Ca^{2+} or Mg^{2+}, the equilibrium sorption of this ion was investigated over initial *p*H range of 5 − 8.5. The initial solution *p*H influence on the resin performance was investigated for synthetic $CaCl_2$ solution and $MgCl_2$, respectively, keeping constant the initial concentration, the temperature, the contact time and the resin dose. The effect of initial solution *p*H on the removal of Ca^{2+} and Mg^{2+} by the *Purolite C100E* resins was shown in Figure 1.
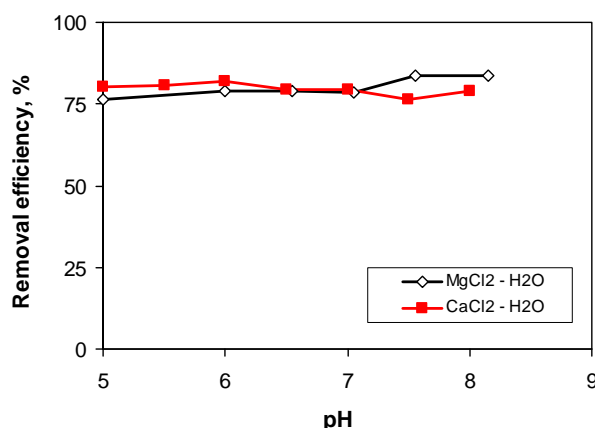

Figure 1. *Effect of initial solution pH on Ca^{2+} and Mg^{2+} removal efficiency by Purolite C100E resin (153.52 mg $Ca^{2+} \cdot L^{-1}$, 73.55 mg $Mg^{2+} \cdot L^{-1}$, 8 g dry resin $\cdot L^{-1}$, 25 $^o C$, 24 h)*

The experimental data shows that initial solution *p*H does not significantly influence the cationic exchange capacity of *Purolite C100E* resin. This argument is also explained in the literature by the fact that generally sulphonic type cationic resins' functional group is ionised among almost the whole *p*H range and thus they can work at almost any *p*H value. Consequently, the ion exchange capacity of strong acid resins does not depend on the solution *p*H [11]. In the following experimental research the typical groundwater *p*H value was chosen for the working solutions. For the groundwater sample treated at it's natural *p*H 7.1 value a Ca^{2+} ions retention capacity of 15.85 mg $\cdot g^{-1}$ and a removal efficiency of 87.30% were achieved.

Effect of resin dose on the cationic exchange capacity

The ratio between the resin amount and solution volume to be treated (resin dose) is decisive for a good softening process. This factor's influence on the *Purolite C100E* resin performance was investigated for the softening process of synthetic $CaCl_2$ and $MgCl_2$ solutions (with initial concentration 153.52 mg $Ca^{2+} \cdot L^{-1}$ and 73.55 mg $Mg^{2+} \cdot L^{-1}$ respectively) and for groundwater, maintaining constant the following factors: pH, temperature and contact time. The resin dose varied from 1 to 10 g dry resin$\cdot L^{-1}$ and equilibrated for 24 hours.

Figure 2 shows the Ca^{2+} removal form $CaCl_2$ solution and groundwater as a function of resin dose. The same resin dosage was observed in our previous study on magnesium removal form $MgCl_2$ solutions. The experimental data indicate that independent on the Ca^{2+} or Mg^{2+} to be removed in the presence of *Purolite C100E* resin the retention degree increases with the increase of resin dose and the cationic exchange capacity decreases with resin dose increase.
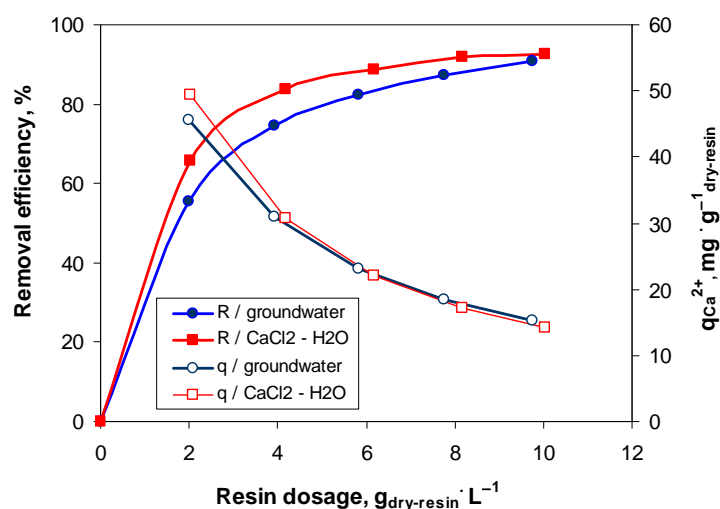

Figure 2. *Effect of resin dose on the cationic exchange capacity of Purolite C100E resin (153.52 mg $Ca^{2+} \cdot L^{-1}$, pH 7.1, 25 ^oC, 24 h)*

As seen in Figure 2, optimum resin dose can be proposed between 7 – 8 g dry resin$\cdot L^{-1}$. For resin doses higher than 8 g dry resin$\cdot L^{-1}$ this trends decrease in intensity because the saturation of the resin in the exchange ion is reached. The decrease in ion exchange density can be attributed to the fact that some of the ion exchanger remains unsaturated during the adsorption process, whereas the number of available ion-exchange sites increases with the increasing of resin dosage and results in an increase in removal efficiency [11].

Effect of initial calcium concentration on the cationic exchange capacity

The concentration of the solution to be treated can have a more complicated effect on the ion exchange process selectivity. The study on this factor's influence on the *Purolite C100E* resin performance was performed for the calcium removal on synthetic $CaCl_2$ solutions at different initial calcium concentration (42 – 176 mg $Ca^{2+} \cdot L^{-1}$) maintaining

constant solution pH, resin dose, contact time and temperature. The effect of initial calcium concentration on the equilibrium sorption of Ca^{2+} by ion exchange resins was shown in Figure 3.
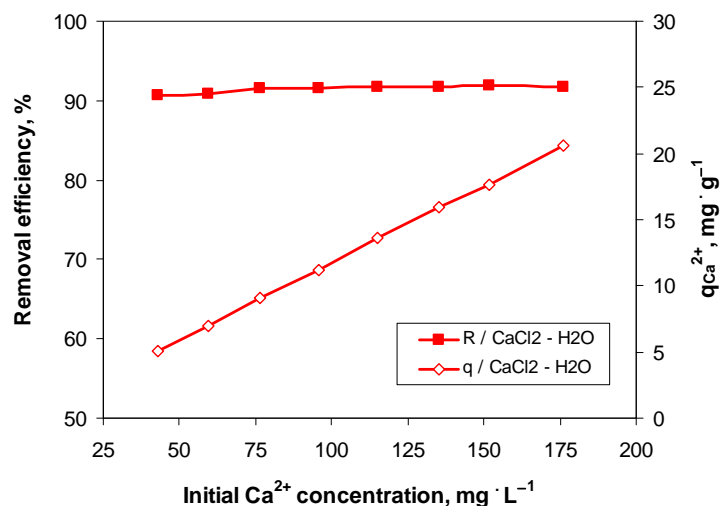

Figure 3. Effect of initial Ca^{2+} concentration on the cationic exchange capacity of Purolite C100E resin (pH 7.1, 8 g dry resin·L^{-1}, 25 ^{o}C, 24 h)

The cationic exchange capacity of *Purolite C100E* resin increases with the increase of calcium ions concentration. This behaviour can be explained by the swelling effect of the resin with Ca^{2+} ions followed by the decrease of resin affinity for this ion (the effect of solution's ion strength) with the increase of solution concentration [11]. The ratio of number of moles of Ca^{2+} in solution to the available surface area at higher calcium concentration is higher so the available binding sites become less, explaining why the Ca^{2+} ions removal is relatively independent on the initial concentration.

Effect of temperature on the cationic exchange capacity

Softening process operation temperature is limited only by the thermal stability of the resin. The influence of the temperature on the resin performance study was performed for the softening process of the artificial $CaCl_2$ solutions (153.52 mg Ca^{2+}·L^{-1}) and groundwater samples by keeping constant: pH, resin dose and contact time.
The cationic exchange capacity of *Purolite C100E* resin increases slightly with the increase of temperature (Figure 4). Considering the insignificant temperature influence above ambient temperature values on the removal efficiency of Ca^{2+} ions and the potential costs for increasing the temperature the process operation at higher temperatures than 25 ^{o}C, where the retention capacity of Ca^{2+} ions is equal to 18.34 mg·g^{-1} and the removal efficiency after 24 hours is better than 90.82% is not recommended.
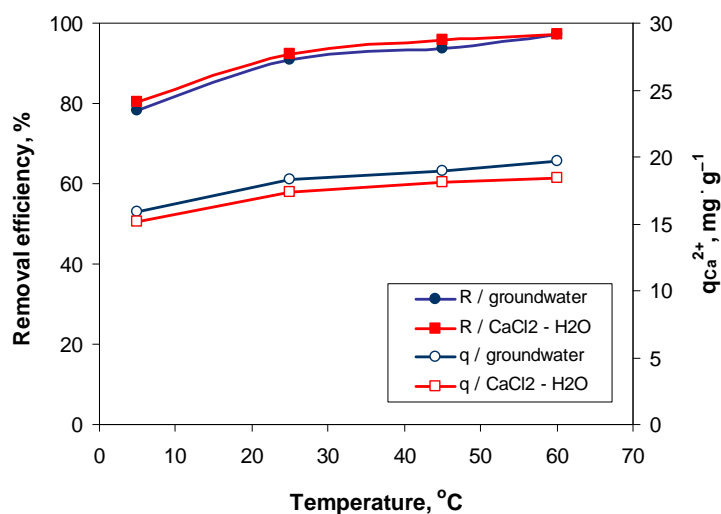
Figure 4. *Effect of temperature on the cationic exchange capacity of Purolite C100E resin (pH 7.1, 8 g dry resin·L^{-1}, 24 h)*

Effect of contact time influence on the cationic exchange capacity

The study on the contact time between the two phases influence on the resin performance was performed for the synthetic $CaCl_2$ solution and groundwater samples softening process by keeping constant the initial calcium concentration, the sample *p*H, the resin dose and the temperature. The results were given in Figure 5. The cationic exchange capacity of *Purolite C100E* resin is positively influenced by the increase of the contact time between the two phases, until the resin saturation degree for the exchange ion is reached.
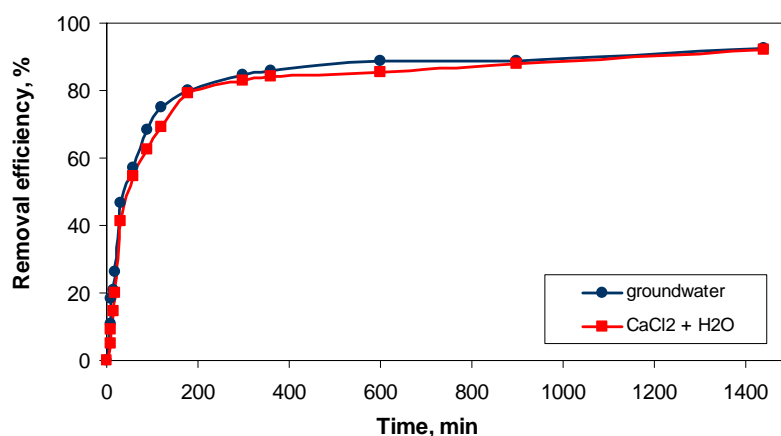

Figure 5. *Effect of contact time on removal of Ca^{2+} by Purolite C100E resin (pH 7.1, 8 g dry resin·L^{-1}, 25 ^{o}C)*

As shown in Figure 5, removal efficiency, as a function of contact time, was noted to occur in two phases. The first phase involved rapid Ca^{2+} removal during the first 60 min of solution – ion exchange resin contact, which was followed by a slow phase of Ca^{2+} removal spread over a significantly longer period of time until the equilibrium was

reached. Time required for attaining equilibrium for the Ca^{2+} removal was 360 min a further increase in contact time had a negligible effect on the cationic exchange capacity. The rapid removal of Ca^{2+} ions from groundwater during the first 60 min of contact time accounted for 57.2% (11.53 $mg \cdot g^{-1}$) and better than 85.7% (17.18 $mg \cdot g^{-1}$) after 6 hours. The maximum removal at 24 hours was 92.35% (18.51 $mg \cdot g^{-1}$). Yu *et al.* [16] have used Amberlite IRC 748 resin as Na^+ form to treat the potassium chromate solution containing Ca^{2+}. They found the equilibrium exchange capacity is 19.06 $mg \cdot g^{-1}$ at 480 min.

The two-phase softening process, the first being rapid and the second slower, has been extensively reported in literature. The rapid phase is probably due to the abundant availability of active site on the ion exchange resin, whereas with the gradual occupancy of the site, sorption becomes less efficient during the slower phase. The curves of calcium removal versus time are single, smooth and continuously leading to saturation, suggesting the possible monolayer coverage of Ca^{2+} ions on the surface ion exchange resin.

Effect of the nature of anions on the cationic exchange capacity

The efficiency of ion exchange process depends by the ability of target ion to replace the bonded mobile ions on ion exchanger resin structure. This process takes place easier when the target ion is present as free ionic specie, in aqueous solution. This is means that the counter-ions have the same an important role in the ion exchange process, because their nature may influence the degree of dissociation of the target ion salt. From this reason, it is important to see how the nature of counter-ions (anions, in this case) influenced the ion exchange process.

The influence of the nature of anions on calcium removal efficiency for ion exchanger *Purolite C100E* resin, used in this study, was examined for synthetic calcium solutions with initial calcium concentration of 125 $mg \cdot L^{-1}$ (17 $^o d_{Ca}$) and for groundwater with initial calcium concentration of 145 $mg \cdot L^{-1}$ (21 $^o d_{Ca}$) and the obtained results are illustrated in Figure 6.

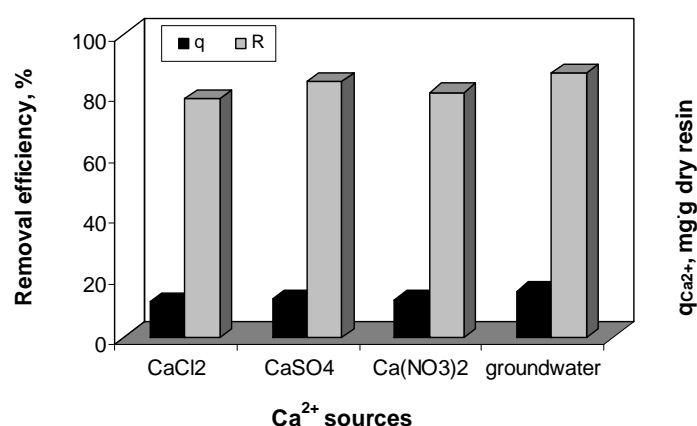**Figure 6.** *Effect of the nature of anions on calcium removal efficiency by Purolite C100E resin (17 $^o d_{Ca}$ for calcium solution, 21 $^o d_{Ca}$ for groundwater, pH 7.1, 8 g dry resin $\cdot L^{-1}$, 25 $^o C$, 24 h)*

It can be observed that the nature of anions has an insignificant influence on cation exchange capacity of *Purolite C100E* resin in case of synthetic calcium solutions. In this case a calcium retention capacity of cca. 12.45 mg·g^{-1} and removal efficiency of approx. 81 % (± 3%) was achieved regardless of the Ca^{2+} sources. Some differences appears and these are more evident at high calcium concentrations, such as groundwater with 145 mg·L^{-1}. For the groundwater sample treated at it's natural pH 7.1 value a Ca^{2+} ions retention capacity of 15.85 mg·g^{-1} and a removal efficiency of 87.3% were achieved.

CONCLUSIONS

The investigation of commercially available *Purolite C100E* resin conducted in batch mode through the variation of the softening process by ion exchange specific experimental factors (initial solution pH, resin dose, initial calcium concentration, temperature, contact time, nature of counter-ions) allows the following conclusions to be observed:

- Commercial resin *Purolite C100E* presents a remarkable performance in the water softening process at ambient temperature for the entire range of most natural waters pH values. The cation exchange capacity is independent of initial solution pH.
- The retention degree of Ca^{2+} ions is not significantly influenced by the temperature increase, but depends on the resin dose, initial solution concentration and contact time between resin and treated water sample. Use of high temperature not being economically profitable.
- For the ambient temperature an optimal dose of de 8 g dry resin·L^{-1} was observed, a minimum contact time of 60 min is required for a calcium removal efficiency of 57.2%, corresponding to a calcium exchange capacity of more than 11.53 mg·g^{-1} or minimum 15 hours to achieve a retention degree of more than 90% and a Ca^{2+} ions retention capacity more than 16.67 mg·g^{-1}.
- The competitor anions that correspond to calcium salts that can be present dissolved in hard water (Cl$^-$, NO$_3^-$, SO$_4^{2-}$) do not influence in a significant degree the Ca^{2+} cations exchange capacity.

ACKNOWLEDGMENTS

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