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CATIONIC EXCHANGE CAPACITY OF *PURE PC200FD* RESIN IN FOOD INDUSTRY WATER SOFTENING PROCESS

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Abstract: *The present paper represents a preliminary study regarding the ion exchange capacity of the Pure PC200FD weak acid macroporous cationic food grade resin in the water softening processes in the food industry. The ion exchange capacity was experimentally investigated in batch mode as a function of the resin dose, initial solution concentration, contact time, temperature and competitor anions corresponding to the dissolved salts that induce water hardness. More than 50 % efficiency of the cationic exchange in the presence of Pure PC200FD resin was achieved in the following conditions: resin dose equal to 8 g dry resin/L, temperature of 298 K, over 250 minutes contact time. Considering the ion exchange capacity of the strong acid food grade Purolite C100E resin as a comparison benchmark it was concluded after the experiments that weak acid Pure PC200FD resin represents a reliable alternative for water softening.*

Keywords: *cationic exchanger, food water softening, sorption, strong acid resin, weak acid resin*

1. Introduction

Water used as raw material or heat transfer agent in the technological processes specific to the food industry requires certain quality conditions to be fulfilled. The permanent water hardness induced by the calcium and magnesium dissolved salts (chlorides, sulphates, nitrates, phosphate) [1, 2] presents a special importance.

The reduction of Ca^{2+} and Mg^{2+} ions concentrations from the water sources (softening) can be achieved using ion exchanger materials such as synthetic polymeric cationic resins in R–Na or R–H form [3-7]. The ion exchange capacity of the polymeric resin can be influenced by the type of the functional group contained, that can be sulphonic groups ($–SO_3H$) - strong acid cation (SAC) or carboxylic groups (–COOH) - weak acid cation (WAC) [3-8]. The conventional water softening process consists of the exchange reaction between Na^+ or H^+ ions and Ca^{2+} or Mg^{2+} cations [3, 5]. Exhausted resins regeneration can be realised using sodium chloride solutions (for the Na^+ form) or hydrochloric acid (for the H^+ form) respectively [6, 7]. In the food industrial and domestic applications the resins that do not imply acid solutions regeneration are preferred [6, 8].

Nowadays various polymeric resins for water softening in the food industry are commercially available [9-12]. Even so, the last year's specialty literature lacks scientific research referring to both the behaviour and the performance of commercial ion exchange resins in the softening process [13-18].

In this paper a preliminary study is performed on the cationic exchange capacity of the polymeric resin with weak acid functional groups sold under the brand name *Pure PC200FD* [12]. The amounts of the Ca^{2+} ion removal were investigated in batch stirred mode as an influence of sorption process specific parameters: resin to solution ratio (dose), initial Ca^{2+} ions concentration, solid – liquid phase contact time, temperature, and aqueous solution nature. The cationic exchange capacity *Pure PC200FD* resin is regarded compared to that of the strong acid cationic exchanger *Purolite C100E* [9].

2. Experimental

2.1. Material and methods

Weak acid cation exchanger *Pure PC200FD* from Pure Co. Ltd. [12] is a delivered in form of macroporous spherical gel resin beads with acrylic crosslinked with divenylbenzene matrix containing carboxyl type functional groups, in H^+ form and is not regenerable. This material is similar to *Purolite C107E* resin which can be regenerated [9, 12]. Strong acid cationic exchanger *Purolite C100E* from Purolite Co. [9] is a conventional gel polystyrene sulphonate ion exchanger delivered in Na^+ form and is regenerable.

Laboratory research was conducted employing the cationic exchanger resins in the delivery form, previously swollen in ultrapure water for 24 hours. Experimental data interpreting and presentation was reported to the dry mass of the cationic resin.

Ion exchange capacity of both resins were investigated using surface water samples with total hardness of 24.5 ^{o}dH (German degrees [2]) and binary solutions containing Ca^{2+} ions. The laboratory research was performed in batch stirred mode [5, 17] at constant temperature using Erlenmeyer flasks containing 50 mL solution in which the wet resin dose was introduced according to the experimental requirements. All the flasks were kept under constant agitation at 50 rpm on an orbital shacker. The all experiments were conducted at a pH 7.1, value corresponding to common natural water samples. The synthetic solutions pH value correction was performed with a sodium acetate buffer solution 0.1 M. All the experimental solutions were prepared by dissolving in ultrapure water the p.a. grade Merck or Sigma Aldrich chemicals.

2.2. Analytical methods

The Ca^{2+} and Mg^{2+} ions concentrations respectively quantitative analysis were performed by the aid of EDTA volumetric methods (SR ISO 6058:2008 [19], and SR ISO 6059:2008 respectively [20]). An automatic titrator and specific titration indicators for water hardness analysis from a German supplier (CalVER® and ManVER® respectively) were used.

The cationic exchange capacity was evaluated based on the amount of cations retained by the resin, *q* (expressed in mg/g dry resin) – *retention capacity*, calculated according to the Eq. (1) [7, 17]:

$$q = \left(C^0 - C\right)\frac{V}{m} \qquad (1)$$

where: C^0 is the cation concentration in the initial solution, in mg/L; *C* – the cation concentration in the residual solution, in mg/L; *m* – the amount of cationic resin on the experiment, in g dry resin; *V* – volume of the solution in the experiment, in L.

In order to quantitatively express the calcium removal yield was calculated the sorption effectiveness percent, *R* (%) – *removal efficiency*, according to the Eq. (2) [7, 17]:

$$R = \frac{C^0 - C}{C^0}\cdot 100 \qquad (2)$$

Water hardness for the natural water and the synthetic solutions was expressed based on the Ca^{2+} ions concentration according to the equivalence rel. (3) [2]:

$$1\ ^{o}dH = 10\ mg\ CaO/L = 7.14\ mg\ Ca^{2+}/L\ (1\ ^{o}d_{Ca}) \quad (3)$$

3. Results and Discussion

3.1. Resin dose influence

Figures 1 and 2 present the cationic exchange capacity of *PC200FD* resin as function of the resin amount that comes in contact with a $CaCl_2$ solution and surface water respectively, for a 24 hours time.

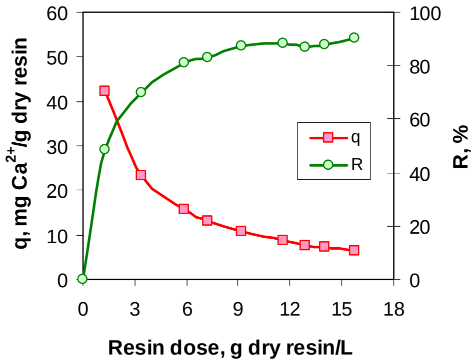

Figure 1. Influence of resin dose on the cationic exchange capacity of *Pure PC200FD* resin (114 mg Ca^{2+}/L_{CaCl2}; pH = 7.1; 298 K; 24 hours).

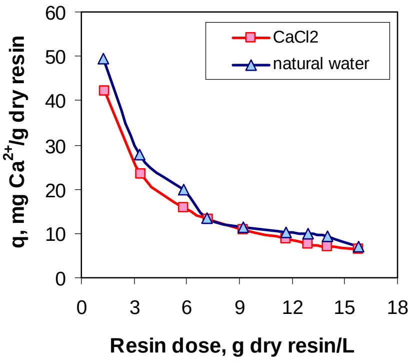

Figure 2. Comparative effect of resin dose on the cationic exchange capacity of *Pure PC200FD* resin (114 mg Ca^{2+}/L_{CaCl2}; 151 mg Ca^{2+}/L_{water}; pH = 7.1; 298 K; 24 hours).

The softening process efficiency (*R*) in the binary system $[CaCl_2 – H_2O]_{aq}$, increases with the increase of resin dose. The amount of Ca^{2+} retained on each mass unit of ion exchanger resin (*q*) decreases with the increase of the dose, indicating a decrease of the resin efficiency (Figure 1). This trend was expected due to saturation level attained during a sorption proces.

The same influence is valid for surface water as shown in Figure 2; the cationic exchange capacity variation for the same resin dose can be explained by the different concentration of Ca^{2+} cations in the initial solutions.

Following this study a dry resin dose of 8 g for 1 L of solution was chosen for further research, so that the softening process efficiency will be higher than 85 %.

3.2. Initial concentration influence

The cationic exchange capacity of *Pure PC200FD* resin is influenced by the concentration of Ca^{2+} cations in the initial solutions (Figure 3). Regardless of the contact time between the two phases a slight diminishing of the softening process efficiency is revealed in Figure 4 for concentrations higher than 150 mg Ca^{2+}/L, corresponding to water hardness values higher than 21 $^{o}d_{Ca}$ (hard waters [2]).

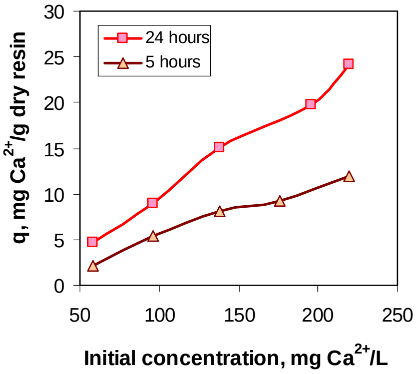

Figure 3. Influence of initial Ca^{2+} concentration on the cationic exchange capacity of *Pure PC200FD* resin (pH = 7.1; 8 g dry resin/L; 298 K).

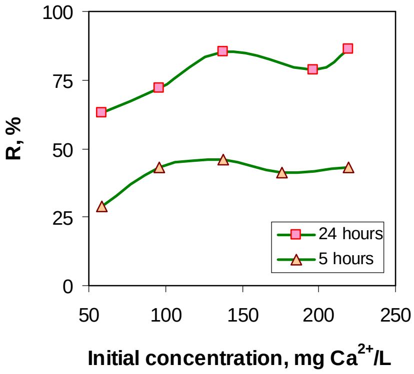

Figure 4. Influence of initial concentration of solution on the hardness removal efficiency onto *Pure PC200FD* resin
(pH = 7.1; 8 g dry resin/L; 298 K).

At higer calcium concentration, the ratio of number of moles of Ca^{2+} in solution to the available surface area is higer and the available sites for binding is less and hence metal removal is relatively independent on the initial concentration.

3.3. Contact time influence

The cationic exchange capacity of *Pure PC200FD* is positively influenced by the increase of contact time between the two phases (Figure 5), until the resin saturation degree for the exchange ion is reached. The softening process efficiency is approx. 40 % after the first 180 min and more than 70 % after 15 hours. In order to achieve process efficiency higher than 50 % more than 5 h contact time is required.

3.4. Temperature influence

The cationic exchange capacity of *Pure PC200FD* resin increases with temperature (Figure 6) because the random motion of Ca^{2+} was accelerated which meanwhile promoted the sorption process.

Considering that the temperature increase over the ambient temperature values has just slight influence on the cationic exchange capacity it makes no sense to operate the process at higher temperatures than 298 K, where softening process efficiency is higher than 80 % after 24 h.

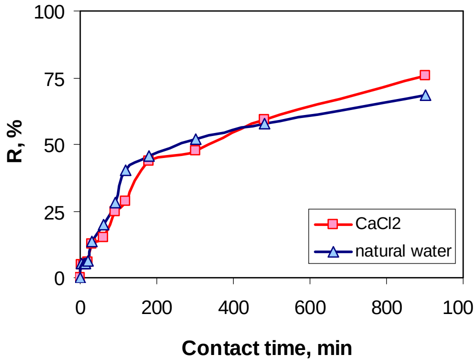

Figure 5. Influence of contact time on the hardness removal efficiency onto *Pure PC200FD* resin
(114 mg Ca^{2+}/L_{CaCl2}; 151 mg Ca^{2+}/L_{water}; pH = 7.1; 8 g dry resin/L; 298 K).

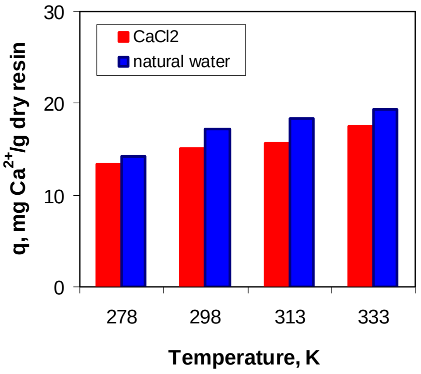

Figure 6. Influence of initial temperature on the cationic exchange capacity of *Pure PC200FD* resin
(138 mg Ca^{2+}/L_{CaCl2}; 151 mg Ca^{2+}/L_{water}; pH = 7.1; 8 g dry resin/L; 24 hours).

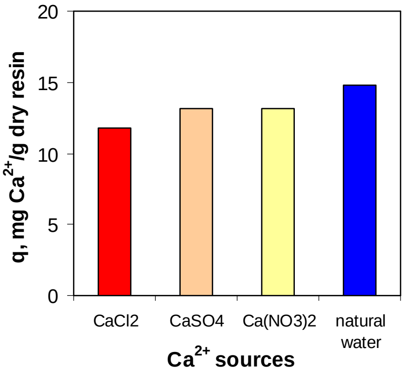

Figure 7. Influence of competitor anions form aqueous solution on the cationic exchange capacity of *Pure PC200FD* resin
(125 mg $Ca^{2+}/L_{aq.sol.}$; 151 mg Ca^{2+}/L_{water}; pH = 7.1; 8 g dry resin/L; 24 hours; 298 K).

3.5. Competitor anions influence

The cationic exchange capacity of *Pure PC200FD* is not significantly influenced by the competitor anions that correspond to the calcium salts inducing water hardness (Figure 7). A process efficiency of approx. 80 % (± 5 %) was achieved regardless of the Ca^{2+} cation sources.

3.6. Pure PC200FD resin performance versus Purolite C100E

Considering as a benchmark the strong acid cationic resin *Purolite C100E* the cationic exchange capacity [21, 22] of weak acid *Pure PC200FD* resin was investigated for various concentrations of $CaCl_2$ solution corresponding to moderate and hard waters respectively (Figure 8).

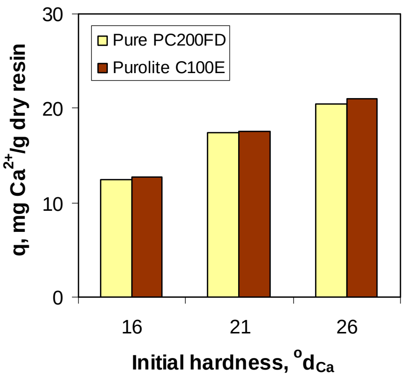

Figure 8. Cationic exchange capacity in the softening process of the polymeric resins (1 $^{o}d_{Ca}$ = 7.14 mg Ca^{2+}/L, pH = 7.1; 8 g dry resin/L; 24 hours, 298 K).

Comparable results for the cationic exchange capacity can be attributed to both resins in the delivery form. *Pure PC200FD* resin is delivered and used in the experiments in H^+ form, whilst *Purolite C100E* resin is delivered and used in Na^+ form. It is known that H^+ form resins are more efficient than Na^+ [6, 7], the later being preferred in food industry because they are regenerated using NaCl solutions.

The fact that the producer company of *PC200FD* resin specifies that this is not regenerable can be a consequence of its use in H^+ form. Usually this H^+ form resins are regenerated with HCl or H_2SO_4, which is not so desirable for the food industry specific processes.

Still weak acid cation resin *Pure PC200FD* represents a viable alternative for the water softening process, if the beneficiary has implemented a certain waste management programme to cope with the waste represented by the depleted resin.

4. Conclusion

The preliminary investigation of the cationic exchange capacity of the *Pure PC200FD* resin in the water softening depending on various specific parameters of sorption process leads to the following conclusions:

(1) Appreciable Ca^{2+} cations retention efficiencies can be achieved for the following conditions: (*i*) resin dose equal to 8 g/L (reported to the dry resin state), (*ii*) 25 °C working temperature; (*iii*) more than 200 min contact time in order to eliminate more than 50 % of the initial hardness.

(2) Cationic exchange capacity increases with the increase of Ca^{2+} ions concentration in the initial solution and the increase of water hardness respectively.

(3) 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 retention capacity.

(4) For similar operating conditions the cationic exchange capacity of weak acid *Pure PC200FD* resin is comparable to that of the strong acid *Purolite C100E* resin; this performance can be assigned to the ionic form in which the two commercial cationic resins are delivered and used.

Because weak acid cation exchanger *Pure PC200FD* cannot be regenerated the industrial beneficiary that uses it should also consider besides the technological performance the additional costs required by the storage, depositing and elimination of the depleted resin. It is advisable to perform an economical analysis for the use of this resin in the water softening equipment by comparison with a regenerable resin such as the strong acid cationite *Purolite C100E.*

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