Environmental Engineering and Management Journal September 2014, Vol.13, No. 9, 2145-2152
http://omicron.ch.tuiasi.ro/EEMJ/

"Gheorghe Asachi" Technical University of Iasi, Romania

FTIR ANALYSIS OF ION EXCHANGE RESINS WITH APPLICATION IN PERMANENT HARD WATER SOFTENING

Liliana Lazar[1*], Bogdan Bandrabur[2], Ramona-Elena Tataru-Fărmuş[1], Mioara Drobotă[3], Laura Bulgariu[4*], Gheorghe Gutt[5]

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

Abstract

The purpose of the present study is the comparative investigation of the calcium cations removal from aqueous solutions using two strong acid cationic resins recommended during the last years for water softening. The performances of the two resins were evaluated by the means of the cationic exchange capacity and the retention degree of the calcium cations. The evaluation of the two resins behaviour in the ion exchange process was performed by the means of the FTIR spectra recorded on the resins before and after being used in the calcium cations exchange process. By reporting to the *Purolite C100E* resin regarded as benchmark, one can state that the *Pure Resin PC002* can be considered as a viable alternative for the water softening processes, but a prior economical analysis should be performed regarding the costs reported to the usefulness and benefits.

Key words: food grade water softening, FTIR spectra, ion exchange, Purolite C100E, Pure Resin PC002, strong acid cation resin

Received: February, 2014; Revised final: August, 2014; Accepted: August, 2014

1. Introduction

Permanent water hardness is caused by the calcium and magnesium salts that do not precipitate during boiling such as chlorides, sulphates, nitrates, phosphates. The hardness of water is important parameter for industries chemical productions and food processing which can lead to problems in cooling and heating systems, steam generation, and manufacturing (Gray, 2010; Smith et al., 2008). Water softening is designed to remove hardness ions. The ion exchange method is the most common and attractive way of reducing hardness in water, because of its simplicity, effectiveness, selectivity, recovery and relatively low cost. (Gray, 2010; Hoffmann and Martinola, 1988; Smith et al., 2008; Zagorodni, 2007). The alternative methods are: electrochemical precipitation (Hasson et al., 2010; Zeppenfeld, 2011); electrodialysis (Park et al., 2007; Shaposhnik et al., 2002), electrodeionization (Fu et al., 2009), capacitive deionization (Seo et al., 2010), microfiltration (Yildiz et al., 2003), nanofiltration (Ghizellaoui et al., 2005), ultrafiltration (Kweon and Lawler, 2004), reverse osmosis (Venkatesan and Wankat, 2011), carbon nanotubes (Tofighy and Mohammadi, 2011), combination of ultrasound and

---

∗ Author to whom all correspondence should be addressed: email: lillazar@ch.tuiasi.ro; lbulg@ch.tuiasi.ro; Phone: +7 495 223 05 23 ext. 1336 ion exchange (Entezari and Tahmasbi, 2009) and microbial desalination cells (Brastad and He, 2013).

The multitude of the ion exchange processes' applications and the wide range of ion exchange resins uses (Abo-Farha et al., 2009; Bulgariu et al., 2010; Ceica et al., 2011; Hamdaoui, 2009; Phillips et al., 2008; Xiong et al., 2013), especially in the industrial field and also the expansion of these technologies in the domestic/residential field demonstrates this procedure's potential for the water treatment in order to partially or totally remove calcium and magnesium content (Coca et al., 2010; Muraviev et al., 1996; Ozmetin et al., 2009; Soliman et al., 2011; Yi et al, 2009; Yu et al., 2009). The competition increase in the ion exchange material market was a result of both products portfolio developments of the big producer companies and also of the increasing number of smaller producers, thus creating a pressure for materials price reductions (Purolite, Amberlite, Lewatite, Pure Resin etc.). The engineer involved in the selection stage of his process specific ion exchange material is now confronted with a wide range of materials and prices and the lack of scientific documentation and this can lead to wrong materials choices.

This study represents a comparative research on the performances and behaviour of the *Purolite C100E* and *Pure Resin PC002* ion exchange resins, for which there is no experimental research data available in order to scientifically explain the optimum operating parameters. These two resins are specially designed for the water hardness removal and have the particular advantage, due to high affinity for the Ca(II) and Mg(II) ions than for the other cations. The laboratory researches were performed at ambient temperature in batch mode using real ground water samples and synthetic binary solutions containing calcium cations in concentrations that correspond to moderate and hard waters.

2. Experimental

Purolite C100E is a strong acid cationic resin with polystyrene matrix cross-linked with divinylbenzene and sulphonic functional groups, specially developed for water softening processes in the food industry by an experienced and internationally well-known producer, for this reason it can be considered as one of the top choices and a comparison benchmark (www.purolite.com). *Pure Resin PC002* is produced by a smaller scale company in this field, but considering the attractive price and the technical characteristics that are almost identical to those of the *C100E* it can be regarded as an industrial alternative (www.pureresin.com).

All the experiments were conducted using the resins in the delivery form, previously swollen in ultrapure water for 24 hours. The data interpreting and analysis is always reported to the dry state of the cationic resin. The resin performances were investigated in batch mode from the point of view of the following ion exchange process specific parameters influence: resin dose, calcium cations concentration in the solution to be treated, contact time between liquid and solid phase and the associated anion (Cl^-, NO_3^- SO_4^{2-}). The groundwater samples used in the experiment can be considered as part of the hard waters group, having the following physical and chemical characteristics: pH of 7.1, conductivity value of 825 $\mu S \cdot cm^{-1}$, concentration of calcium equal to 151.02 $mg \cdot L^{-1}$ and total hardness of 23.51 German degrees.

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 delivered by Hach Company were used. The indicator used in experiments is based Murexide, specially modified to facilitate the highlighting of equivalence point, both in low and high concentrations calcium concentration range. All the experimental solutions were prepared using analytical reagents grade from Merck or Sigma Aldrich dissolved in ultrapure water.

The efficiency of water hardness removal expressed as the amount of Ca(II) cations content retained by each mass unit of ion exchange resin, q ($mg \cdot g^{-1}_{dry\text{-}resin}$) – retention capacity, calculated according to the Eq. (1) (Zagorodni, 2007). The softening process efficiency was qualitatively evaluated by using the retention degree, R (%) – removal efficiency, calculated with the Eq. (2):

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

$$R = \frac{C^0 - C}{C^0} \cdot 100 \tag{2}$$

where C^0 – cation concentration in the initial solution, ($mg \cdot L^{-1}$); C – cation concentration in the residual solution, ($mg \cdot L^{-1}$); V – the volume of solution to be softened (L); m – the amount of cationic resin in the experiment in dry state, (g).

The FTIR spectra have been recorded using a Bruker Vertex 70 spectrometer with spectral domain 400 – 4000 with a 4 cm^{-1} resolution using the KBr pellet technique, before and after water hardness removal. The analysis of the FTIR spectra was performed by examining the spectral bands that changed after the ion exchange process.

3. Results and discussion

3.1. Performance of ion exchange resins

The cationic exchange capacity of *Purolite C100E* resin was investigated in a previous study as a function of the specific parameters' influence: resin dose (1 – 12 $g_{dry\text{-}resin} \cdot L^{-1}$), contact time (0 – 24 hours), temperature (278 – 333 K), initial calcium cations concentration (40 – 200 mg·L^{-1}). For the studies performed at ambient temperature a resin dose of 8 g$_{dry\text{-}resin}$·L^{-1} and a contact time of minimum 60 minutes were selected in order to remove more than 50 % Ca(II) cations from the initial solution. It was also observed that the temperature increase only had a negligible influence on the *Purolite C100E* ion exchange resin performances (Bandrabur et al., 2012).

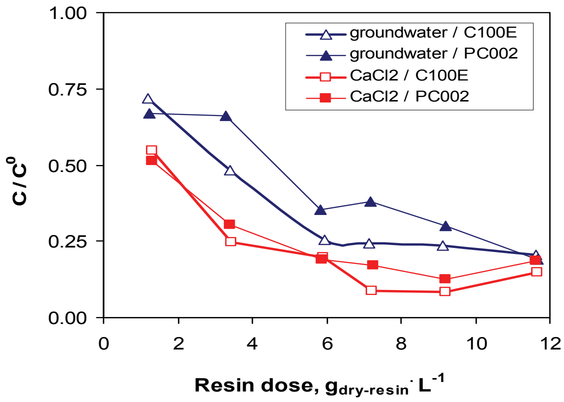

Fig. 1. Influence of resin dose on Ca(II) retention from different aqueous solution (initial pH = 7.1, 298 K, 24 hours)

Fig. 1 presents the experimental results gathered from the comparative studies of the resin dose influence on the Ca(II) cations retention performance from the artificial binary system $CaCl_2$–H_2O (113.83 mg$_{Ca(II)}$·L^{-1}), and natural ground water sources (151.02 mg$_{Ca(II)}$·L^{-1}) respectively. The contact time in this study was 24 hours, considered to be long enough to achieve the ion exchange process equilibrium. Given the same experimental conditions, for the *Pure Resin PC002* ion exchange resin a contact time of minimum 300 minutes was necessary in order to retain more than 50 % Ca(II) cations from the initial solution. The experimental results for the two cationic resins obtained while investigating the exchange capacity and retention degree of Ca(II) cations from the binary $CaCl_2$ solution and from the natural ground water samples are compared in Table 1. The study on the influence of the Ca(II) cations concentration from the initial solution in the range between 40 – 200 mg·L^{-1} revealed the increase of the cationic exchange capacity of Purolite C100E resin with the increase of the Ca(II) cations concentration, without a significant influence on the retention degree (Bandrabur et al., 2012). The values presented in table 2 resulted from the comparative investigation of the two ion exchange resins performances as a function of the initial solutions equivalent hardness.

The influence of the nature of anions on calcium removal efficiency for ion exchanger *Purolite C100E* and *Pure Resin PC002* resins used in this study was examined for synthetic calcium binary solutions with initial calcium concentration of approx. 125 mg·L^{-1} (17.5 $^{o}d_{Ca}$) and for groundwater with calcium concentration of 151.02 mg·L^{-1} (21 $^{o}d_{Ca}$) and the results obtained are illustrated in Fig. 2. The efficiency of ion exchange process depends on the ability of target ion to replace the bonded mobile ions from the ion exchanger resin structure.

This process takes place easier when the target ions are present as free ionic species, in aqueous solution. This is means that the counter-ions have also an important role in the ion exchange process, because their nature may influence the dissociation degree of the target ion salt. For this reason it is important to investigate how the counter-ions (anions, in this case) nature influences the ion exchange process.

Table 1. Influence of contact time on Ca(II) retention from different aqueous solution by *Purolite C100E* and *Pure Resin PC002* resins (8 g$_{dry\text{-}resin}$·L^{-1}, initial pH = 7.1, 298 K)

Initial solution	***Initial concentration of Ca(II) mg·L^{-1}***	***Contact time***	***Purolite C100E***		***Pure Resin PC002***	
			$q_{Ca(II)}$ mg·g^{-1}$_{dry\text{-}resin}$	***R %***	***$q_{Ca(II)}$ mg·g^{-1}$_{dry\text{-}resin}$***	***R %***
$CaCl_2 + H_2O$	153.52	2 h	13.187	69.01	4.163	28.52
		5 h	15.948	82.90	6.903	47.54
		24 h	17.842	92.18	12.041	83.10
Groundwater*	151.02	2 h	16.123	83.97	7.723	40.05
		5 h	16.629	87.44	10.062	51.99
		24 h	17.523	91.98	17.118	89.39

**Results are expressed reporting to the calcium cations*

Table 2. Influence of initial Ca(II) concentration on the performance retention from different aqueous solution by *Purolite C100E* and *Pure Resin PC002* resins (8 g$_{dry\text{-}resin}$·L^{-1}, initial pH = 7.1, 298 K, 24 hours)

Cationic resins	***Parameters***	***Initial concentration of Ca(II), mg·L^{-1}***			
		115.43	***149.98***	***186.77***	***151.02***
Purolite C100E	$q_{Ca(II)}$, mg·g^{-1}$_{dry\text{-}resin}$	12.772	17.37	20.967	17.523
	R, %	87.15	91.71	91.80	91.98
Pure Resin PC002	$q_{Ca(II)}$, mg·g^{-1}$_{dry\text{-}resin}$	12.444	12.08	20.408	17.118
	R, %	84.38	83.22	85.84	89.39
Initial solution		$CaCl_2 – H_2O$			Groundwater

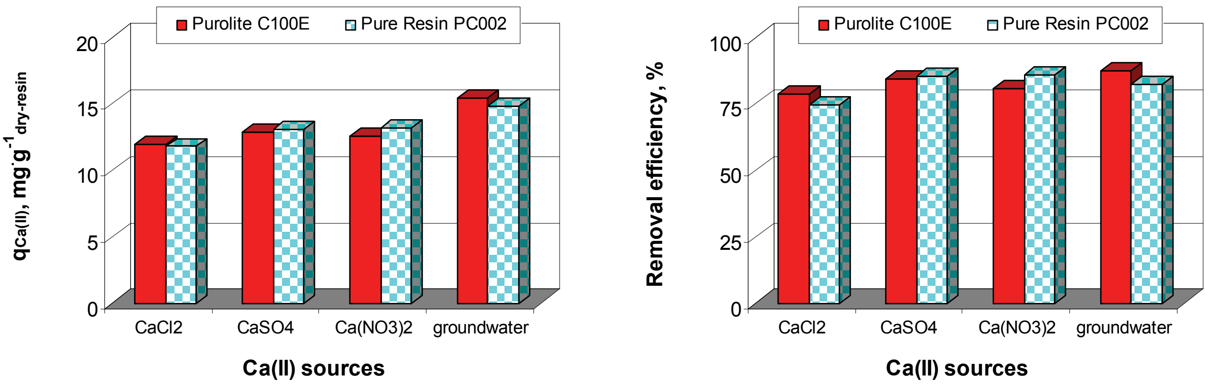

Fig. 2. Influence of the competitor anions nature on the Ca(II) retention from aqueous solution by *Purolite C100E* and *Pure Resin PC002* resins (17.5 $^{o}d_{Ca}$ for calcium solution, 21 $^{o}d_{Ca}$ for groundwater, pH = 7.1, 8 $g_{dry\text{-}resin}\cdot L^{-1}$, 298 K, 24 h)

3.2. FTIR spectra analysis

In order to evaluate the strong acid cationic resin's behavior in the ion exchange process of Ca(II) cations that produce permanent water hardness, the cation resin samples were analyzed by the means of their FTIR spectra after being used in various ion exchange systems. Figs. 3 and 4 present the FTIR absorbance spectra for the two cationic resins in the delivery form and after being used in ions exchange processes of Ca(II) ions from natural ground waters and synthetic binary solutions respectively.

According to its producer, the *Purolite C100E* cationic resin has a polystyrene crosslinked with divinylbenzene and contains sulfonic type functional groups (www.purolite.com). The FTIR peaks specific to this type of materials' chemical bonds are known in the literature (Dean, 1995; Brijmohan et al., 2005; Bekri-Abbes et al., 2008; Singare et al., 2011).

The analysis of the main absorption spectra for the *Purolite C100E* in Na^{+} delivery form as presented in Fig. 3 confirm resin structure and composition as follows: ♦ O–H simple bond that is most present in the structure due to the residual hydration water, but also present in the sulphonic group is indicated by the big absorption peak at 3446 cm^{-1}; ♦ all the bands near the 2924 cm^{-1} peak (2800 – 3000 cm^{-1} range) are characteristic for the polystyrene structure; ♦ the presence of simple C–C bonds of the din styrene ring are confirmed by the peak at 1601 cm^{-1}; ♦ the absorption bands from 1038, 1127 and 1182 cm^{-1} are clearly attributed to the stretching and asymmetric vibrations of the SO_3^- sulphonic group; ♦ the peak at 835 cm^{-1} corresponds to the C–H bond vibrations outside the benzene ring plane which is due to the divinylbenzene crosslink and the sulphonic groups.

As seen in Fig. 3, that presents the FTIR spectra for the *Purolite C100E* before and after the retention of Ca(II) cations from various calcium containing solutions ($CaCl_2$ solution – *spectrum* 1, $CaSO_4$ solution – *spectrum* 2 and $Ca(NO_4)_2$ solution – *spectrum 3*) the following aspects can be observed: ♦ the spectra's shapes are very similar, thus one can conclude that no major compositional changes occur in the materials after the retention of the calcium ions; ♦ given the 4 cm^{-1} instrumental resolution one can observe that all the peaks present in the delivery form of the *Purolite C100E* resin spectrum are also present at practically the same bandwidth values in the spectrum of the modified resin after the retention of Ca(II) ions; ♦ in the 1647, 1653 cm^{-1} wavenumber area for the synthetic chloride solutions and 1650 cm^{-1} for the sulphate solutions respectively, new peaks can be observed that are characteristic to the OH groups; ♦ in the 3450 – 3500 cm^{-1} range that is specific to the stretching vibrations of the free OH group there is a general trend for the migration of the peaks towards lower wavenumbers; the spectra for the used resin samples the absorption peaks are split (into more individual peaks), this is most obvious for spectrum 2 and 4 where the competing anion in the solution was chloride and nitrate respectively; ♦ the nature of the competing anion (Cl^-, SO_4^{2-} or NO_3^-) present in the Ca(II) solution does not exert a visible influence on the ion exchange interactions, this can be explained by the fact that calcium salts are completely dissociated and not hydrolyzed in range of pH values from the experiments.

The FTIR spectra of the *Purolite C100E* after being used in the natural ground water samples softening process can be interpreted in a similar matter as when being used in the softening of the binary synthetic solutions (Fig. 3). Still one can observe that the absorption peaks that are characteristic for both the stretching and bending vibrations of the OH group are split. But, in this spectral region, the water vapour from atmosphere can also absorbs radiations, and will generate a sharp band. The elimination of his contribution is difficult to do, and was not considered in discussion because appear in all recorded spectra.

General conclusion can be drawn from the compared analysis of all the spectra as follows: ♦ sensible peaks modifications in all the spectra for used resins are present in the wavenumbers range of 3000 – 3500 cm^{-1} and 1600 – 1700 cm^{-1} respectively, indicating the presence of free or bonded water in the interior of the resin structure; ♦ there is no modification in the peaks that are specific to the resin's structure and functional groups, this can be found at the same wavenumbers in the used resin's spectra as in the delivery form of the resin's spectra. Based on these observations one can conclude that the Ca(II) retention from the samples that were used in the experiment in contact with the resin takes place following mechanisms that do not involve new chemical reactions, but only ion exchange reactions with the participation of the functional groups which, as a result of the ion exchange process, suffer from a rearrangement of the surrounding water molecules.

The *Pure Resin PC002* resin contains sulfonic type functional groups bonded onto a micro porous acrylic gel-type crosslinked with divinylbenzene matrix. By analysing the *Pure Resin PC002* cationic resin in the delivery form FTIR spectra (Fig. 4) one can observe the similarities with the *Purolite C100E* resin. The absorption peaks confirming the *Pure Resin PC002* resin structure are present at wavenumber values as follows: ♦ wave number range between 3360 – 3590 cm^{-1} for the simple O–H bond, with the highest peak at 3457 cm^{-1} (compared to 3446 cm^{-1} for *Purolite C100E*); ♦ wave number range between 2800 – 3060 cm^{-1}, specific to the various bonds in the polystyrene structure with a peak at 2922 cm^{-1} (2924 cm^{-1} for *Purolite C100E*); ♦ the peak at 1601 cm^{-1} specific for the C–C simple bonds of the styrene ring (same as for *Purolite C100E*); ♦ the peaks at 1039, 1128 şi 1181 cm^{-1} are attributable to the sulfonic group SO_3 (1038, 1127 and 1182 cm^{-1} for *Purolite C100E*); ♦ the value of 835 cm^{-1} confirms the substitutions at the benzene ring level by the sulfonic groups and the divinylbenzene cross linking (same value as *Purolite C100E*).

The similarities observed between the FTIR spectra for the two resins in the delivery and used form can lead to similar conclusions for the cationic resin *Pure Resin PC002* as for the *Purolite C100E* behavior.

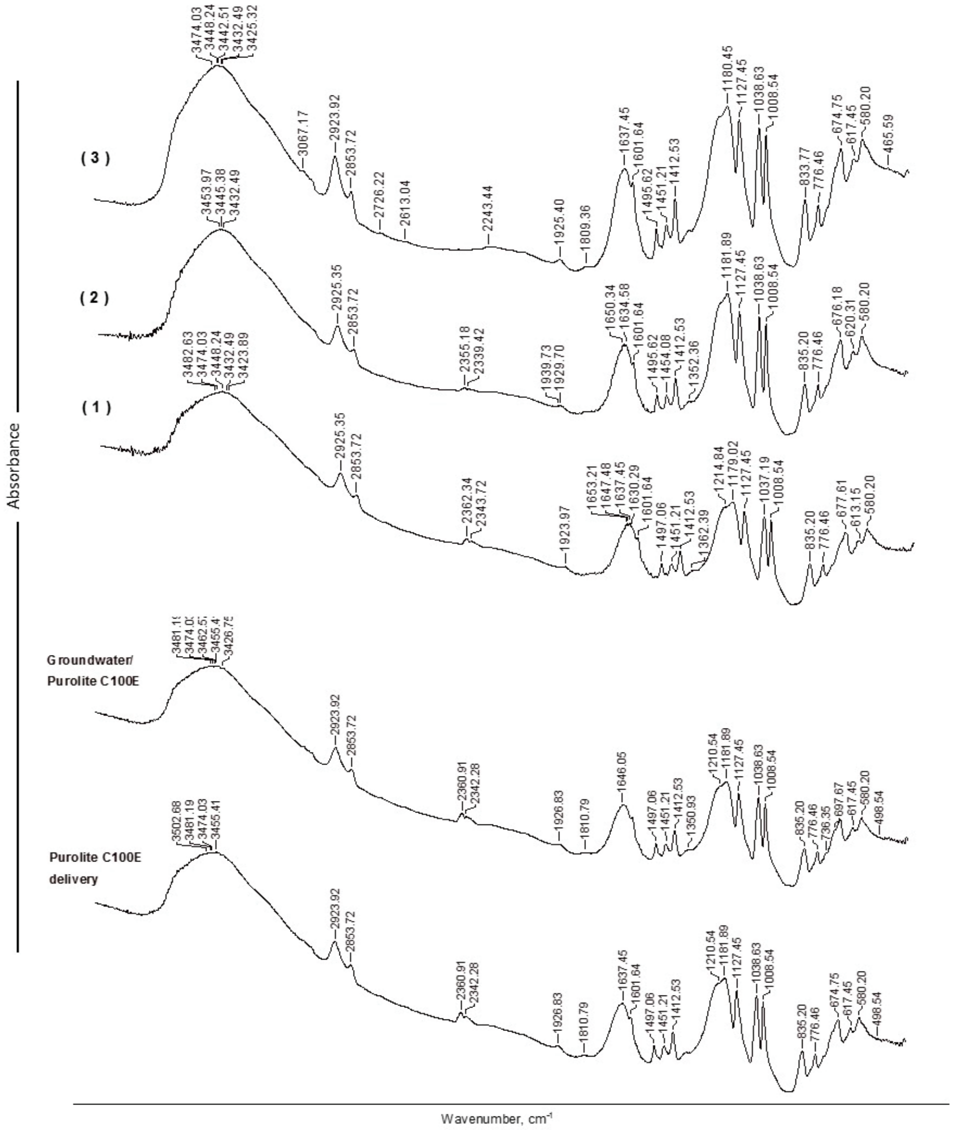

Fig. 3. FTIR spectra of *Purolite C100E* resin before and after loading with Ca(II) ions from groundwater and after the Ca(II) ions retention from binary solutions of $CaCl_2$ (1), $CaSO_4$ (2) and $Ca(NO_4)_2$ (3)

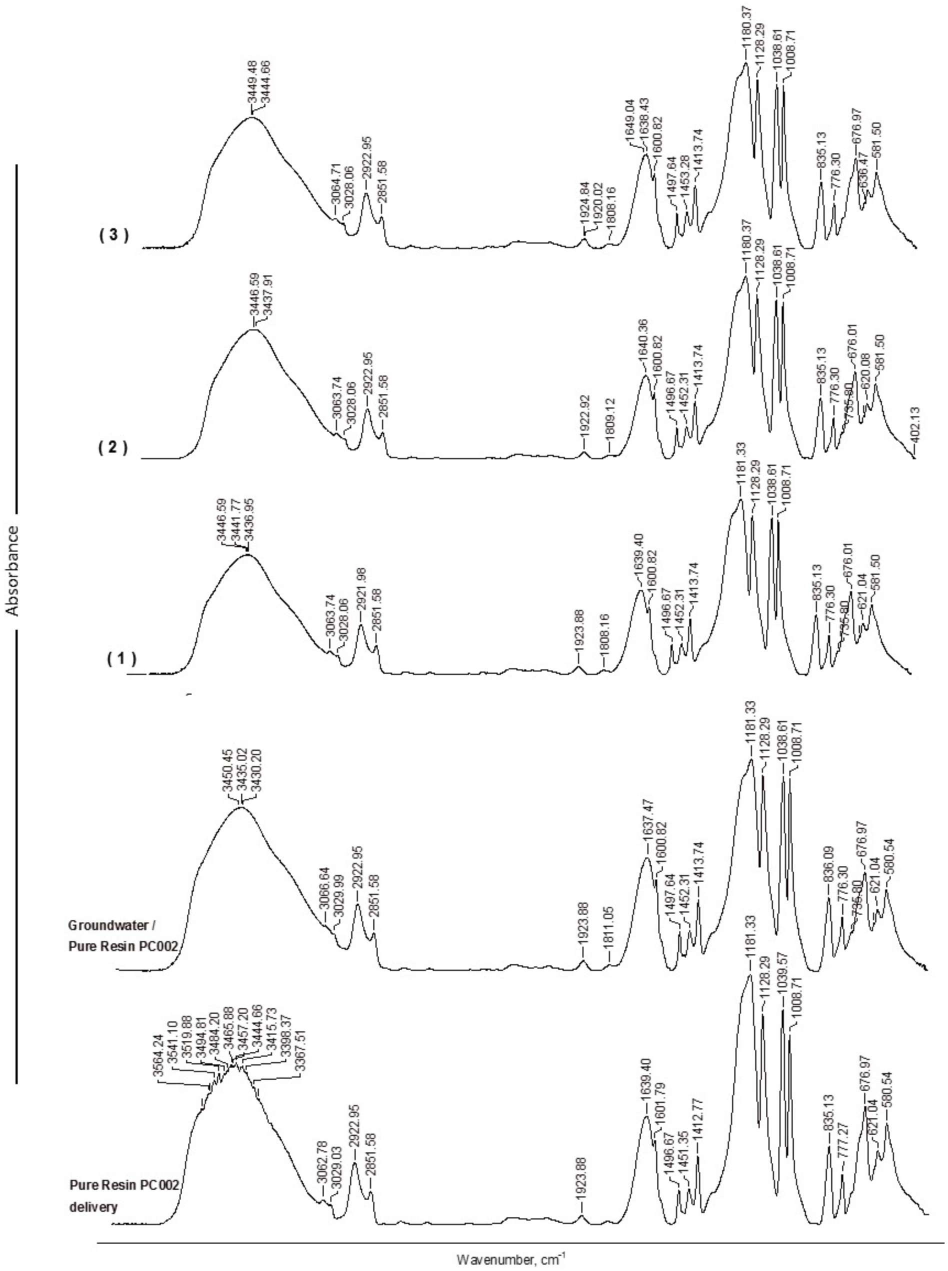

Fig. 4. FTIR spectra of *Pure Resin PC002* resin before and after loading with Ca(II) ions from groundwater and after the Ca(II) ions retention from binary solutions of $CaCl_2$ (1), $CaSO_4$ (2) and $Ca(NO_4)_2$ (3)

4. Conclusions

The practical retention capacity and the behavior of two commercially ion exchange cationite *Purolite C100E* and *Pure PC002* toward water hardness was investigated.

The cationic exchange capacity values for the two resins in the given experimental conditions and for the dose used of 8 g dry resin·L^{-1} are comparable. For 24 hours contact time, the experimental values at 298 K for this indicator for a hard water source with equivalent calcium cations concentration are, in a decreasing order, as follows: 0.87 meq·g^{-1} for *Purolite C100E* and 0.85 meq·g^{-1} for *Pure Resin PC002* (reporting to the materials dry state).

The retention degree of calcium cations is 92 % for *Purolite C100E* and 89 % for *Pure Resin PC002*. For 300 min contact time in the same given conditions the *Pure Resin PC002* presents a maximum capacity that is almost 60 % of that of the benchmark.

In order to compare the data with the ones communicated by the materials producers in the technical data sheets it was necessary to express all the values in the same unified measuring unit of gram equivalents, by this also eliminating the influence of the retained cation type. The values calculated reporting to the wet delivery form and using the average water content of the resins as communicated by their technical data sheets were found to be 1.24 eq·L^{-1} for *Purolite C100E* and 0.98 eq·L^{-1} for *Pure Resin PC002* resin.

By comparing the results to the maximum capacity of minimum 1.9 eq·L^{-1} mentioned in the data sheet for both resins we can conclude that in batch mode and the given experimental conditions we were able to reach a rate of material use of 65 % for *Purolite C100E* and 51 % for *Pure Resin PC002* resin.

The importance of the electrostatic interactions in the process of water harness removal on *Purolite C100E* and *Pure PC002* resins is evidenced by the IR spectra registered before and after the softening process. The small changes in the positions and intensities of most absorption bands, before and after water hardness removal, clearly shown that in this process are not involved coordinative or covalent interactions, and that most probable the electrostatic interactions are responsible by this.

Acknoweledgments

This research was supported by the project "Knowledge provocation and development through doctoral research PRO-DOCT", project co-funded by the European Social Fund in Romania, under the responsibility of the Managing Authority for the Sectorial Operational Programme for Human Resources (Contract no. POSDRU/88/1.5/S/52946).

References

Abo-Farha S.A., Abdel-Aal, A.Y. Ashour I.A., Garamon S.E., (2009), Removal of some heavy metal cations by synthetic resin Purolite C100, *Journal of Hazardous Materials*, **169**, 190–194.

Bandrabur B., Tataru-Fărmuș R.-E., Lazăr L., Bulgariu L., Gutt G., (2012), Use of strong acid resin Purolite C100E for removing permanent hardness of water – Factors affecting cationic exchange capacity, *Scientific study & Research – Chemistry & Chemical Engineering, Biotechnology, Food Industry*, **13**, 295-–304.

Bekri-Abbes I., Baklouti M., Bayoudh S., (2008), The removal of hardness of water using sulfonated waste plastic, *Desalination*, **222**, 81–86.

Brastad K.S., He Z., (2013), Water softening using microbial desalination cell technology, *Desalination*, **309**, 32–37.

Brijmohan S.B., Swier S., Weiss R.A., Shaw M.T., (2005), Synthesis and characterization of cross-linked sulfonated polystyrene nanoparticles, *Industrial & Engineering Chemistry Research*, **44**, 8039–8045.

Bulgariu L., Ceica A., Lazar L., Cretescu I., Balasanian I., (2010), Equilibrium and kinetics study of nitrate removal from water by Purolite A100 resin, *Revista de Chimie*, **61**, 1136–1141.

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.

Coca M., Mato S., González-Benito G., Urueña M.Á., García-Cubero M.T., (2010), Use of weak cation exchange resin Lewatit S 8528 as alternative to strong ion exchange resins for calcium salt removal, *Journal of Food Engineering*, **97**, 569–573.

Dean J.A., (1995), *Analytical Chemistry Handbook*, McGraw-Hill Inc., New York.

Entezari M.H., Tahmasbi M., (2009), Water softening by combination of ultrasound and ion exchange, *Ultrasonics Sonochemistry*, **16**, 356–360.

Fu L., Wang J., Su Y., (2009), Removal of low concentrations of hardness ions from aqueous solutions using electrodeionization process, *Separation and Purification Technology*, **68**, 390–396.

Ghizellaoui S., Chibani A., Ghizellaoui S., (2005), Use of nanofiltration for partial softening of very hard water, *Desalination*, **179***,* 315–322.

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

Hamdaoui O., (2009), Removal of copper(II) from aqueous phase by Purolite C100-MB cation exchange resin in fixed bed columns: Modeling, *Journal of Hazardous Materials*, **161**, 737–746.

Hasson D., Sidorenko G., Semiat R., (2010), Calcium carbonate hardness removal by a novel electrochemical seeds system, *Desalination*, **263**, 285–289.

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.

Kweon J.H., Lawler D.F., (2004), Fouling mechanisms in the integrated system with softening and ultrafiltration, *Water Research*, **38**, 4164–4172.

Muraviev D., Noguerol J., Valiente M., (1996), Separation and concentration of calcium and magnesium from sea water by carboxylic resins with temperature-induced selectivity, *Reactive & Functional Polymers*, **28**, 111-126.

Park J.-S., Song J.-H., Yeon K.-H., Moon S.-H., (2007), Removal of hardness ions from tap water using electromembrane processes, *Desalination*, **202**, 1–8.

Phillips D.H., Gu B., Watson D.B., Parmele C.S., (2008), Uranium removal from contaminated groundwater by synthetic resins, *Water Research*, **42** 260–268.

Özmetin C., Aydın Ö., Kocakerim M.M., Korkmaz M., Özmetin E., (2009), An empirical kinetic model for calcium removal from calcium impurity-containing saturated boric acid solution by ion exchange technology using Amberlite IR–120 resin, *Chemical Engineering Journal*, **148**, 420–424.

Shaposhnik V.A., Zubets N.N., Strygina I.P., Mill B.E., (2002), High demineralization of drinking water by electrodialysis without scaling on the membranes, *Desalination*, **145**, 329–332

Seo S.-J., Jeon H., Lee J.K., Kim G.-Y., Park D., Nojima H., Lee J., Moon S.-H., (2010), Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications, Water Research, 44(7), 2267–2275.

Singare P.U., Lokhande R.S., Madyal R.S., (2011), Thermal degradation studies of some strongly acidic cation exchange resins, *Open Journal of Physical Chemistry*, **1**, 45–54.

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

Soliman E.M., Ahmed S.A., Fadl A.A., (2011), Removal of calcium ions from aqueous solutions by sugar cane bagasse modified with carboxylic acids using microwave-assisted solvent-free synthesis, *Desalination*, **278**, 18–25.

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

Tofighy M.A., Mohammadi T., (2011), Permanent hard water softening using carbon nanotube sheets, *Desalination*, **268**, 208–213.

Venkatesan A., Wankat P.C., (2011), Simulation of ion exchange water softening pretreatment for reverse osmosis desalination of brackish water, *Desalination*, **271**, 122–131.

Yi W.T., Yan C.Y., Ma P.H., (2009), Removal of calcium and magnesium from $LiHCO_3$ solutions for preparation of high-purity Li_2CO_3 by ion-exchange resin, *Desalination*, **249**, 729–735.

Yildiz E., Nuhoglu A., Keskinler B., Akay G., Farizoglu B., (2003), Water softening in a crossflow membrane reactor, *Desalination*, **159,** 139–152.

Yu Z., Qi T., Qu J., Wang L., Chu J., (2009), Removal of Ca(II) and Mg(II) from potassium chromate solution on Amberlite IRC 748 synthetic resin by ion exchange, *Journal of Hazardous Materials*, **167**, 406–412.

Xiong C., Pi L., Chen X., Yang L., Ma C., Zheng X., (2013), Adsorption behavior of Hg^{2+} in aqueous solutions on a novel chelating cross-linked chitosan microsphere, *Carbohydrate Polymers*, **98**, 1222–1228.

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

Zeppenfeld K., (2011), Electrochemical removal of calcium and magnesium ions from aqueous solutions, *Desalination*, **277**, 99–105.

SR ISO 6058:2008, Water quality – Determination of calcium content – EDTA titrimetric method.