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THE VARIATION OF THE IONIC CALCIUM ADSORPTION COEFFICIENT ON A RESIN WITH SULPHONIC GROUPS

VARIAȚIA COEFICIENTULUI DE ADSORBȚIE A CALCIULUI IONIC PE CATIONIT CU GRUPĂRI SULFONICE

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Abstract. *Determination of the adsorption coefficient is essential for all retention processes of ionic species on surfaces, to determine the process efficiency and influence of the various factors on the adsorption. Calcium ions are present in significant quantities in many natural waters, causing high values of hardness, implicitly restricting the possibilities of using these waters. Decreasing the content of ionic calcium from aqueous solutions can be done by retaining them on cation exchangers, so in the present paper we chose a sulphonic resin - Dowex 50 - to study the calcium adsorption from aqueous solutions of different concentrations. We determined both the values of the adsorption coefficient over time for each concentration in the dynamic process as well as the correlation between the amount of ion in the initial solution and that retained on the surface of the adsorbent, depending on the amount of resin used.*
Key words: ionic calcium, adsorption, softening, water

Rezumat. *Determinarea coeficientului de adsorbție este esențială în cazul tuturor proceselor de reținere a unor specii ionice pe suprafețe, pentru a stabili eficacitatea procesului şi influența diferiților factori asupra adsorbției. Ionii de calciu sunt prezenți în cantități însemnate în multe ape naturale, determinând valori mari ale durității, implicit restricționând posibilitățile de utilizare ale acestor ape. Scăderea conținutului în calciu ionic din soluții apoase se poate face prin reținere pe schimbători de cationi, de aceea am ales în prezenta lucrare o răşină cu grupări sulfonice, Dowex 50 pentru studiul adsorbției calciului din soluții apoase de diferite concentrații. S-au determinat atât valorile coeficientului de adsorbție în timp, pentru fiecare concentrație, în procedeu dinamic cât şi corelația dintre cantitatea de ion aflat în soluția inițială şi cea reținută pe suprafața adsorbantului, în funcție de cantitatea de răşină folosită.*
Cuvinte cheie: calciu ionic, adsorbție, dedurizare, apă

INTRODUCTION

Ion exchange materials are insoluble substances containing loosely held ions and are able to exchange those with other ions, as calcium or magnesium, in solutions coming in contact with them (Bandrabur *et al*, 2012).

Strong acid cation (SAC) resins proved to be an option for water softening process for the domestic or food industry specific applications (Zagorodni, 2007).

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A group of Chinese researchers synthesized a Ca-selective zeolite characterized by SEM, XRD and FT-IR and used it as adsorbent for calcium in an ion exchange and hydroxyl complex adsorption mechanism. It indicated that the zeolite has potential application value in zero discharge of seawater desalination (Qin *et al*, 2010).

MATERIAL AND METHOD

The chosen adsorbent material was a strong acid changing resin with sulphonic groups, Dowex 50, added in three different doses – 0.5; 1.0 and 1.5 g per 50 ml sample solution. The tested ionic calcium solutions contained calcium chloride prepared in situ from calcium carbonate and hydrochloric acid, with the following initial concentrations: 1.672 mg Ca^{2+}/mL; 2.376 mg Ca^{2+}/mL; 3.28 mg Ca^{2+}/mL. We adsorption was conducted in dynamic conditions, under continuous magnetic stirring took samples of 1 mL solution at specific intervals, considering that the resin is rapidly adsorbing calcium and the surface tends to be quickly covered.

We calculated the decrease in calcium levels for the analysed solutions and the adsorption coefficients variation in time and after that, traced the correlation between these coefficients and the initial calcium concentration for all three resin quantities added as adsorbent in the process.

RESULTS AND DISCUSSIONS

The considered adsorbent retained calcium ions from the aqueous solutions, tending to equilibrium in a very short time, therefore we tested and calculated the adsorption coefficient at 0.5, 1, 2 and 5 minutes after we added the adsorbent in the solution. Table 1 and figure 1 present the variation of the adsorption coefficient in time for the initial concentration of 1.672 mg Ca/mL depending on the amount of added adsorbent.

Table 1

Variation of the adsorption coefficient in time for the initial concentration of 1.672 mg Ca/mL

Time (min)	C (mg Ca/mL)	mg adsorbed Ca	γ(mg ads Ca /g Dowex)
0.5 g Dowex			
0	1.672	0	0
0.5	1.436	0.236	0.450897975
1	1.26	0.412	0.787160871
2	1.044	0.628	1.199847153
5	0.984	0.688	1.314482232
1.0 g Dowex			
0	1.672	0	0
0.5	1.332	0.34	0.315340382
1	0.924	0.748	0.693748841
2	0.708	0.964	0.89408273
5	0.512	1.16	1.075867186
1.5 g Dowex			
0	1.672	0	0
0.5	1.084	0.588	0.383186706
1	0.928	0.744	0.484848485
2	0.456	1.216	0.792440534
5	0.288	1.384	0.90192245

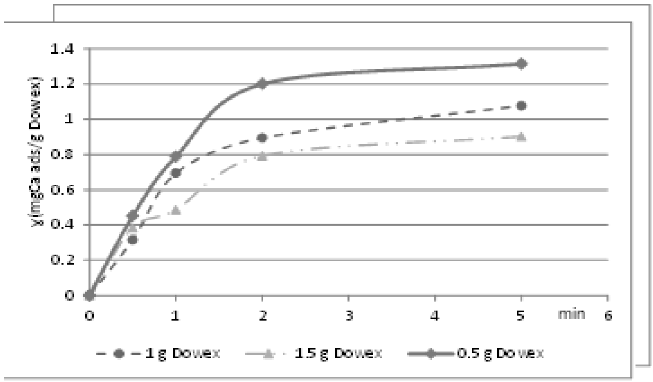

Fig. 1 Variation of adsorption coefficient at 1.672 mg Ca/mL in time depending on the amount of adsorbent

Table 2 and figure 2 present the variation of the adsorption coefficient in time for the initial concentration of 2.376 mg Ca/mL depending on the amount of added adsorbent.

Table 2

Variation of the adsorption coefficient in time for the initial concentration of 2.376 mg Ca/mL

Time (min)	C (mg Ca/mL)	mg adsorbed Ca	γ(mg ads Ca /g Dowex)
0.5 g Dowex			
0	2.376	0	0
0.5	2.152	0.224	0.43956044
1	1.984	0.392	0.769230769
2	1.732	0.644	1.263736264
5	1.632	0.744	1.459968603
1.0 g Dowex			
0	2.376	0	0
0.5	1.952	0.424	0.420176395
1	1.756	0.62	0.614408879
2	1.412	0.964	0.955306709
5	1.236	1.14	1.129719552
1.5 g Dowex			
0	2.376	0	0
0.5	1.812	0.564	0.375424349
1	1.496	0.88	0.585768488
2	1.068	1.308	0.87066498
5	0.816	1.56	1.038407775

Fig. 2 Variation of adsorption coefficient at 2.376 mg Ca/mL in time depending on the amount of adsorbent

Table 3 and figure 3 present the variation of the adsorption coefficient in time for the initial concentration of 3.28 mg Ca/mL depending on the amount of added adsorbent.

Table 3

Variation of the adsorption coefficient in time for the initial concentration of 3.28 mg Ca/mL

Time (min)	C (mg Ca/mL)	mg adsorbed Ca	γ (mg ads Ca /g Dowex)
0.5 g Dowex			
0	3.28	0	0
0.5	2.804	0.476	0.911877395
1	2.628	0.652	1.249042146
2	2.536	0.744	1.425287356
5	2.488	0.792	1.517241379
1.0 g Dowex			
0	3.28	0	0
0.5	2.72	0.56	0.543161979
1	2.4	0.88	0.853540252
2	2.136	1.144	1.109602328
5	2.1	1.18	1.144519884
1.5 g Dowex			
0	3.28	0	0
0.5	2.48	0.8	0.523457436
1	2.24	1.04	0.680494667
2	1.78	1.5	0.981482693
5	1.588	1.692	1.107112478

For each quantity of adsorbent we determined the correlation between the adsorption coefficients and the initial concentrations (fig 4, fig. 5, fig. 6).

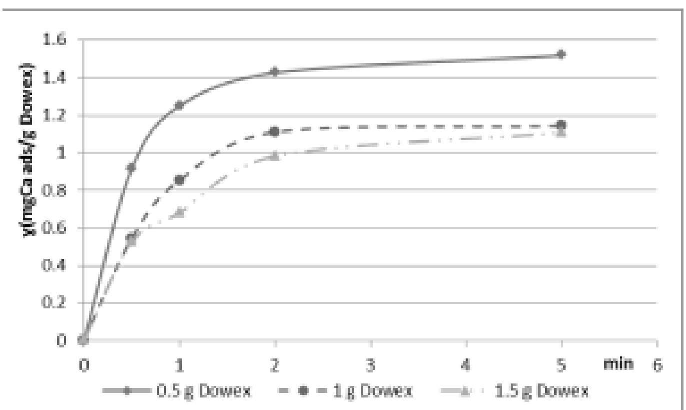

Fig. 3 Variation of adsorption coefficient at 3.28 mg Ca/mL in time depending on the amount of adsorbent

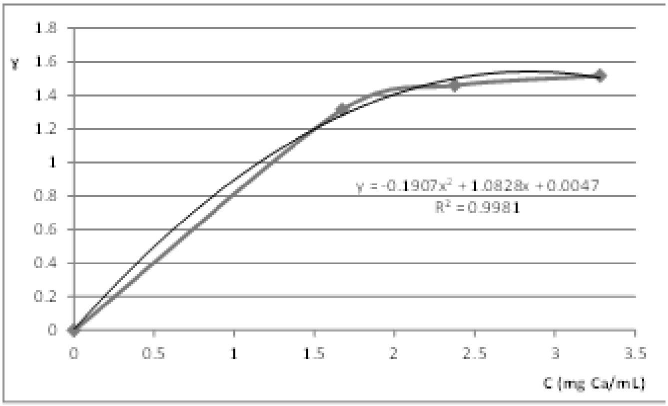

Fig. 4 Correlation adsorption coefficient - calcium concentration for 0.5 g Dowex

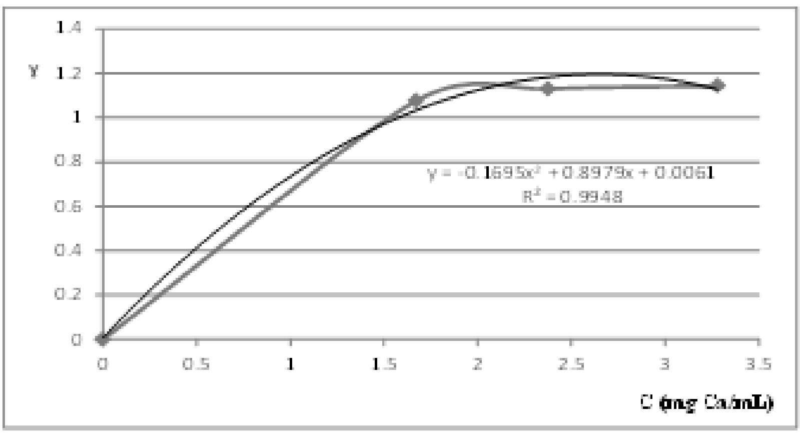

Fig. 5 Correlation adsorption coefficient - calcium concentration for 1.0 g Dowex

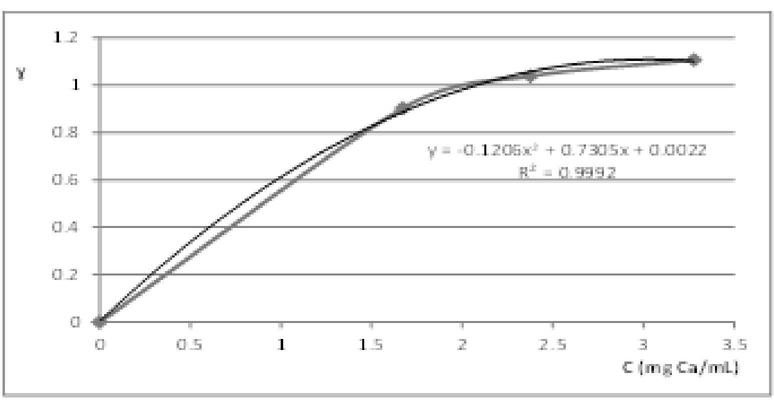

Fig. 6 Correlation adsorption coefficient - calcium concentration for 1.5 g Dowex

CONCLUSIONS

1. Dowex 50 is very efficient as adsorbent material for calcium ions from aqueous solutions, including natural water with an elevated hardness degree;

2. The adsorption procedure, in dynamic conditions, proved to be very simple and quick;

3. The sorption equilibrium installs in a short time after mixing the adsorbent in the tested solution;

4. Considering we tested solutions with an equivalent of 200 or more German degrees of hardness (1 Gd=10mg CaO/L), using small quantities of adsorbent for natural water would soften them quickly, being easily removed afterwards by simple filtration.

REFERENCES

1. Bandrabur B., Tataru-Fărmuş R.E., Lazãr L., Gutt Gh., 2012 - *Application of a strong acid resin as ion exchange material for water softening – equilibrium and thermodynamic analysis*, Scientific Study & Research, Chemistry & Chemical Engineering, Biotechnology, Food Industry, ISSN 1582-540X, 13 (4), pp. 361 – 370;

2. Qin C., Wang R., Ma W., 2010 - *Characteristics of calcium adsorption by Ca-Selectivity zeolite in fixed-pH and in a range of pH*, Chemical Engineering Journal, 156(3), 540–545;

3. Zagorodni, A.-A., 2007 - Ion Exchange Materials: Properties and Applications, Elsevier, ISBN 978-008-044-5526.