USE OF EXPERIMENTAL BREAKTHROUGH CURVES FOR ION EXCHANGE PROCESS OPTIMIZATION

T. DOBRE, Laura CALOTĂ, Oana C. PÂRVULESCU, G. IAVORSCHI*

Lucrarea prezintă un studiu al demineralizării totale a unei soluţii diluate de clorură de sodiu prin trecerea succesivă a acesteia prin două coloane cu strat fix de schimbători de ioni, una cu cationit puternic acid ($R_C^-H^+$), cealaltă cu anionit puternic bazic ($R_A^+HO^-$). Studiul efectuat a avut ca obiectiv utilizarea curbelor de străpungere pentru stabilirea influenţei calitative şi cantitative a factorilor procesului, respectiv viteza fictivă de curgere a soluţiei, volumul total de schimbători de ioni şi temperatura de operare, asupra răspunsurilor procesului, respectiv duratele adimensionale de străpungere şi saturare, precum şi eficienţa schimbului ionic.

The paper presents a study of the total demineralization of a dilute sodium chloride aqueous solution by ion exchange using two fixed bed columns, the former filled with a strongly acidic resin ($R_C^-H^+$) and the second with a strongly basic resin ($R_A^+HO^-$). The study aimed at the use of breakthrough curves in establishing of a qualitative and quantitative influence of the process factors, namely solution superficial velocity, total volume of the resin beds and operating temperature, on the process responses, respectively breakthrough and saturation dimensionless times and also ion exchange efficiency.

Keywords: Ion exchange; Water demineralization; Breakthrough curves; Factorial experiment.

Introduction

The ion exchange is widely used for a large number of applications that can be classified in *ion substitution*, *ion separation* and *ion removal* [1, 2].

Ion substitution refers to the applications where a valuable or toxic ion is retained from a solution and replaced by a valueless or non-toxic one.

Ion separation corresponds to the situations where the different ions from the influent of an ionic column are recovered and then eluted depending on the ion exchanger affinity for these ions.

*Prof., Ph.D. Student, Researcher, Researcher, Dept. of Chemical Engineering, University POLITEHNICA of Bucharest, Romania

Ion removal is realized using an ion exchangers system composed of a strongly acidic cationite ($R_C^-H^+$) and a strongly basic anionite ($R_A^+HO^-$) so that all ions are removed and replaced with water; *ion removal* is also called demineralization.

The development of an ion exchange application, which starts with the selection of the ion exchangers and contact proceeding among these exchangers and solution, can be done by experimental investigation or mathematical modelling. In both cases the researchers had in view to emphasize the effect of the process factors on the process response, frequently expressed by the ion exchange efficiency. The studies regarding the ion exchange in batch systems [3-6] or in fixed beds [6-12] emphasized that the ion exchange efficiency depends on many factors. Among these are: nature and concentration of the treated solution, structure, ionic form, dimensions and quantity of ion exchangers, plant type, process temperature, influent flow rate (for fixed beds), duration and rate of the stirring (for batch systems). The operating capacity usually increases for dilute solutions, small particles and great values of contact time, ion exchangers quantity and process temperature.

The mathematical model of the demineralization of a water containing Na^+ and Cl^- ions, by contacting in fixed bed of cationite and then anionite, consists of 8 partial derivates equations, which describe the dynamics of Na^+, H^+, Cl^- and OH^- ions fixed by ion exchangers, respectively in solution passing through the system [13-17]. The parameters characteristic of the shape, dimensions and porosity of ion exchangers particles, beds porosity, equilibrium of the ion exchange reactions, kinetics of the mass transfer among particles and solution, respectively axial dispersion in the treated solution, appear in these equations. If all these parameters as well as the beds height, solution flow rate and process temperature are known, the mathematical model can deliver complex data, the most important being the dynamics of NaCl concentration in the plant effluent (the breakthrough curve). When the studied case corresponds to a certain experimental plant, then the experimental and theoretic curves are identical. Because of the models complexity and parameters values incertitude, it is preferred to use the experimental breakthrough curve. The scale up of this curve, when the same ion exchangers are used and dynamic similitude is respected, emphasizes that the ion exchange process efficiency (E) and saturation degree of ion exchange zone (f) keep the same values. This observation demonstrates the practical importance of the experimental breakthrough curve.

Besides the contacting in fixed bed of strongly acidic cationite and then strongly basic anionite, the water or aqueous solutions total demineralization by ion exchange can be performed also with another techniques, for example passing the fluid through a column with mixed bed composed of a strongly acidic

cationite ($R_C^-H^+$) and a strongly basic anionite ($R_A^+HO^-$) or through four successive beds, starting with a weakly acidic exchanger bed ($R_{Cw}^-H^+$), continuing with a strongly acidic one ($R_C^-H^+$), then with a weakly basic one ($R_{Aw}^+NH_2^-$) and finishing with a strongly basic one ($R_A^+HO^-$) [1, 10, 12].

The paper aimed at the characterization of the total demineralization of a NaCl aqueous dilute solution, when this successively passes through a strongly acidic cationite and then a strongly basic anionite. Thus, the qualitative and quantitative influence of the process factors (solution superficial velocity, total volume of the resin beds and process temperature) on the parameters characteristic of the breakthrough dynamics (effluent volume at breakthrough, saturation degree of ion exchange zone, process efficiency) was established.

1. Experimental

The laboratory pilot plant consists mainly of two columns with ion exchangers fixed bed, the former with a strongly acidic resin (VIONIT CS-3) and the second with a strongly basic resin (VIONIT AT-14), each column having internal diameter $d = 0.025$ m. Each ion exchangers bed has the same porosity ($\varepsilon_0 = 0.35$), height and particles diameter ($d_P = 0.0015$ m). The NaCl solution, having Cl^- ions initial concentration $c_0 = 0.3$ g/l, is introduced with a pump on the top of cationic column. The cationic column acid effluent passes in down-flow mode through anionic column, whence completely demineralised water results.

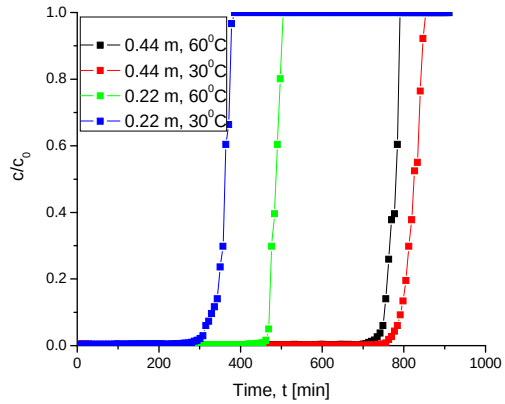
In the unexhausted zones of cationite, respectively anionite, the ion exchange reactions $R^-H^+ + Na^+Cl^- \Leftrightarrow R^-Na^+ + H^+Cl^-$, respectively $R^+HO^- + H^+Cl^- \Leftrightarrow R^+Cl^- + H_2O$, take place.

The experimental investigation used a 2^3 factorial plan, considering two levels for the process factors, respectively solution volumetric flow rate ($G_V = 15$ cm^3/min and $G_V = 35$ cm^3/min), ion exchangers beds total height ($H_S = 0.22$ m and $H_S = 0.44$ m) and process temperature ($T = 30$ ^{0}C and $T = 60$ ^{0}C). The evolution of Cl^- ions concentration in the anionic column effluent, $c(t)$, was determined on-line.

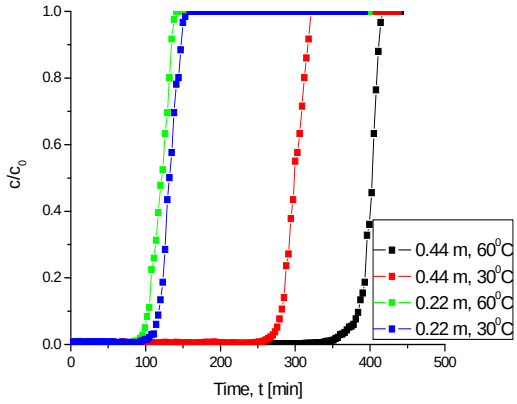
2. Results and discussion

The obtained breakthrough curves of ion exchangers mixed bed are illustrated in Fig. 1 .

The values of the breakthrough time, t_{br}, and saturation time, t_{sat}, were determined from the obtained breakthrough curves.



a



b

Fig. 1. Time variation of Cl^- ions dimensionless concentration in the plant effluent for experiences from 2^3 factorial experiment (c_0 = 0.3 g/l, a. Gv=15 cm³/min, b. Gv=35 cm³/min)

Every breakthrough curve is characterized by the factors and responses values, calculated with the following equations [18]:

$$w_f = 2.12 \cdot 10^{-8} \frac{G_V}{d^2} \tag{1}$$

$$V_S = \frac{\pi d^2}{4} H_S \tag{2}$$

$$t_{stat} = \frac{\varepsilon_0 V_S}{10^{-6} G_V} \tag{3}$$

$$V_{br} = 10^{-6} t_{br} G_V \tag{4}$$

$$\frac{V_{br}}{V_S} = \varepsilon_0 \frac{t_{br}}{t_{stat}} \tag{5}$$

$$f = \frac{1}{t_{sat} - t_{br}} \int_{t_{br}}^{t_{sat}} \left(1 - \frac{c}{c_0}\right) dt \tag{6}$$

$$H_Z = H_S \frac{t_{sat} - t_{br}}{t_{sat} - (1 - f)(t_{sat} - t_{br})} \tag{7}$$

$$E = \frac{H_S - f H_Z}{H_S} \tag{8}$$

The factors and responses values corresponding to the curves illustrated in Fig. 1 are presented in Table 1.

The process factors are: solution superficial velocity, w_f, ion exchangers total volume, V_S, and operating temperature, T. The factors coded values were determined depending on the natural values with the following relationships:

$$x_1 = \frac{w_f - 0.85 \cdot 10^{-3}}{0.35 \cdot 10^{-3}} \tag{9}$$

$$x_2 = \frac{V_S - 0.165 \cdot 10^{-3}}{0.055 \cdot 10^{-3}} \tag{10}$$

$$x_3 = \frac{T - 45}{15} \tag{11}$$

Table 1

Factors and responses values for the 2^3 factorial experiment

No.	Solution superficial velocity	Ion exchangers total volume	Temperature	Breakthrough time	Saturation time	Stationary time	Effluent volume at breakthrough	Dimensionless effluent volume at breakthrough	Saturation degree of ion exchange zone	Height of ion exchange zone	Process efficiency
	$w_f \cdot 10^3$	$V_S \cdot 10^3$	T	t_{br}	t_{sat}	t_{stat}	$V_{br} \cdot 10^3$	V_{br}/V_S	f	H_z	E
	m/s	m^3	^{0}C	min	min	min	m^3	-	-	m	-
1	0.5	0.22	60	700	791	5.04	10.50	48.61	0.85	0.052	0.90
2			30	763	854		11.45	52.99	0.69	0.048	0.92
3		0.11	60	476	504	2.52	7.14	66.11	0.47	0.013	0.97
4			30	287	385		4.31	39.86	0.76	0.060	0.79
5	1.2	0.22	60	306	417	2.16	10.71	49.58	0.85	0.122	0.76
6			30	258	321		9.03	41.81	0.67	0.092	0.85
7		0.11	60	78	138	1.08	2.73	25.28	0.72	0.109	0.64
8			30	93	147		3.26	30.14	0.74	0.089	0.69

The values $w_f = 0.85 \cdot 10^{-3}$ m/s, $V_S = 0.165 \cdot 10^{-3}$ m^3 and $T = 45$ ^{0}C represent the state of process factors within the experimental plan centre.

The dimensionless breakthrough time, y_{br}, dimensionless saturation time, y_{sat} and process efficiency, y_{ef}, were selected as response variables and calculated with the equations:

$$y_{br} = \frac{t_{br}}{t_{stat}} \tag{12}$$

$$y_{sat} = \frac{t_{sat}}{t_{stat}} \tag{13}$$

$$y_{ef} = E \tag{14}$$

Table 2 contains all the elements needed to identify the analytical relationships among the process factors and responses.

Table 2

Experimentation matrix for the 2^3 factorial experiment

No.	x_1	x_2	x_3	y_{br}	y_{sat}	y_{ef}
1	-1	1	1	138.89	156.94	0.90
2	-1	1	-1	151.39	169.44	0.92
3	-1	-1	1	188.89	200.00	0.97
4	-1	-1	-1	113.89	152.78	0.79
5	1	1	1	141.67	193.06	0.76
6	1	1	-1	119.44	148.61	0.86
7	1	-1	1	72.22	127.78	0.64
8	1	-1	-1	86.11	136.11	0.70

Processing the data from Table 2 on the basis of the procedure recommended for a factorial experiment with 2 levels [19], the correlations (15)-(17) were obtained:

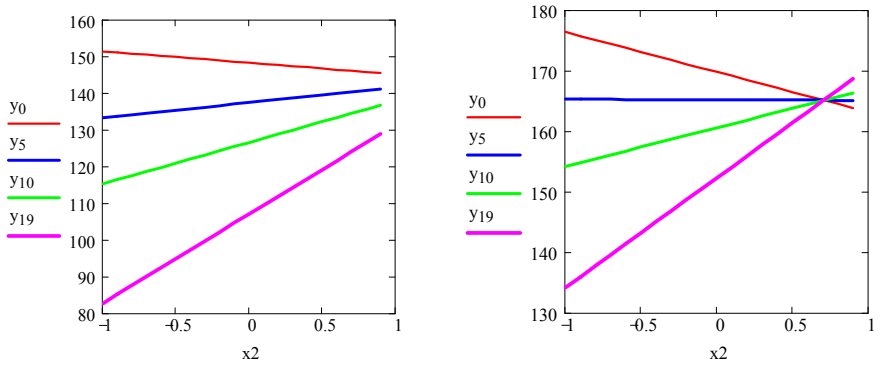
$$y_{br} = 126.56 - 21.70x_1 + 11.29x_2 + 8.86x_3 + 14.41x_1x_2 - 6.77x_1x_3 - 6.42x_2x_3 + 15.45x_1x_2x_3 \quad (15)$$

$$y_{sat} = 160.59 - 9.20x_1 + 6.42x_2 + 8.56x_3 + 13.02x_1x_2 + 0.18x_1x_3 - 0.87x_2x_3 + 14.06x_1x_2x_3 \quad (16)$$

$$y_{ef} = 0.815 - 0.080x_1 + 0.042x_2 + 0.003x_3 + 0.027x_1x_2 - 0.037x_1x_3 - 0.030x_2x_3 + 0.020x_1x_2x_3 \quad (17)$$

The obtained relationships indicate that the process responses are influenced by the factors and their interactions. It is noticed that the dimensionless breakthrough time, y_{br}, respectively demineralised water dimensionless volume at breakthrough, $\frac{V_{br}}{V_S}$, and also the process efficiency, y_{ef}, have maximum values at inferior level of x_1 (solution superficial velocity) and x_2 (ion exchangers total volume) and superior of x_3 (process temperature).

Figs. 2 – 4, illustrating the variation of selected responses versus process factors, when two factors vary between the inferior and superior level and the third take the central value, are presented to show that the obtained responses-factors dependency is a complex one, so that it can be analyzed by optimization.



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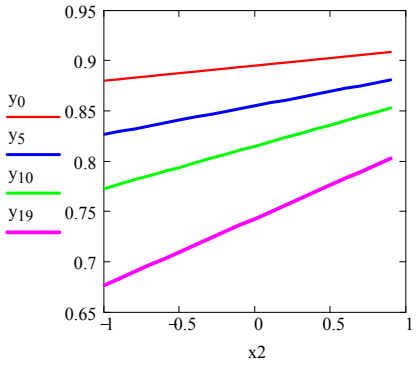

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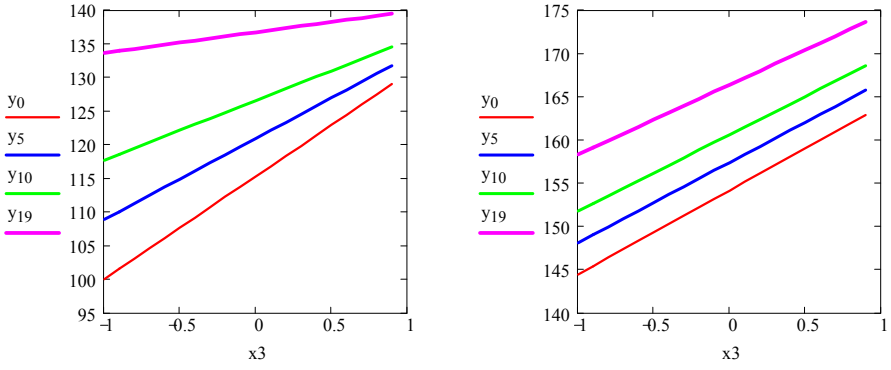
Fig. 2. Variation of y_0, y_5, y_{10}, y_{19} (a. $y = y_{str}$, b. $y = y_{sat}$, c. $y = y_{ef}$) versus solution superficial velocity ($x_1 = -1(y_0); -0.5(y_5); 0(y_{10}); 0.9(y_{19})$) and ion exchangers total volume (x_2) at process temperature within the experimental plan centre ($x_3 = 0$)



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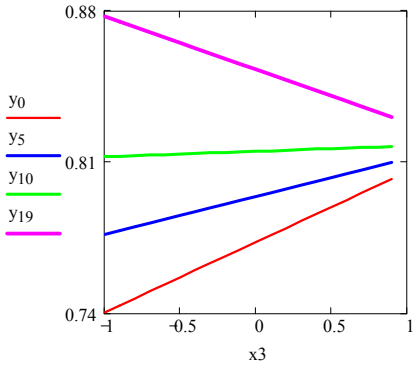

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Fig. 3. Variation of y_0, y_5, y_{10}, y_{19} (a. $y = y_{str}$, b. $y = y_{sat}$, c. $y = y_{ef}$) versus ion exchangers total volume ($x_2 = -1(y_0); -0.5(y_5); 0(y_{10}); 0.9(y_{19})$) and process temperature (x_3) at solution superficial velocity within the experimental plan centre ($x_1 = 0$)

Concerning the extension of equations (15) and (16) to another initial solution concentration, it was found that they remain unmodified when the equilibrium relationships are linear; otherwise they must be multiplied with a factor depending on the equilibrium nonlinearity. At the same time, if the initial solution concentration is modified but the equilibrium relationships among the ions from solid and liquid aren't modified, it was established that the process efficiency and saturation degree of ion exchange zone remain unchanged. The extension of relationships (15)-(17) at solutions composed of chlorides, respectively ions mixtures, is done on the basis of the relationships obtained for simple systems, like the system considered in this paper.

3. Optimization considerations

The results obtained on the basis of the breakthrough curves allow the formulation of three problems of technological optimization and one of technical-economical optimization [20].

The first problem of technological optimization consists in the finding of factors that determine the best process efficiency. The response for this problem is obtained by maximization of the function $y_{ef} = y_{ef}(x_1, x_2, x_3)$ and is expressed by factors from the relationship (18):

$$X_E = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}_E = \begin{pmatrix} -1 \\ -1 \\ +1 \end{pmatrix} \tag{18}$$

The second problem of technological optimization refers to the finding of factors that determine a maximum volume of demineralised water. The vector defined by equation (19) is the result obtained by maximization of the function $y_{br} = y_{br}(x_1, x_2, x_3)$.

$$X_B = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}_B = \begin{pmatrix} -0.207 \\ +1.029 \\ +0.775 \end{pmatrix} \tag{19}$$

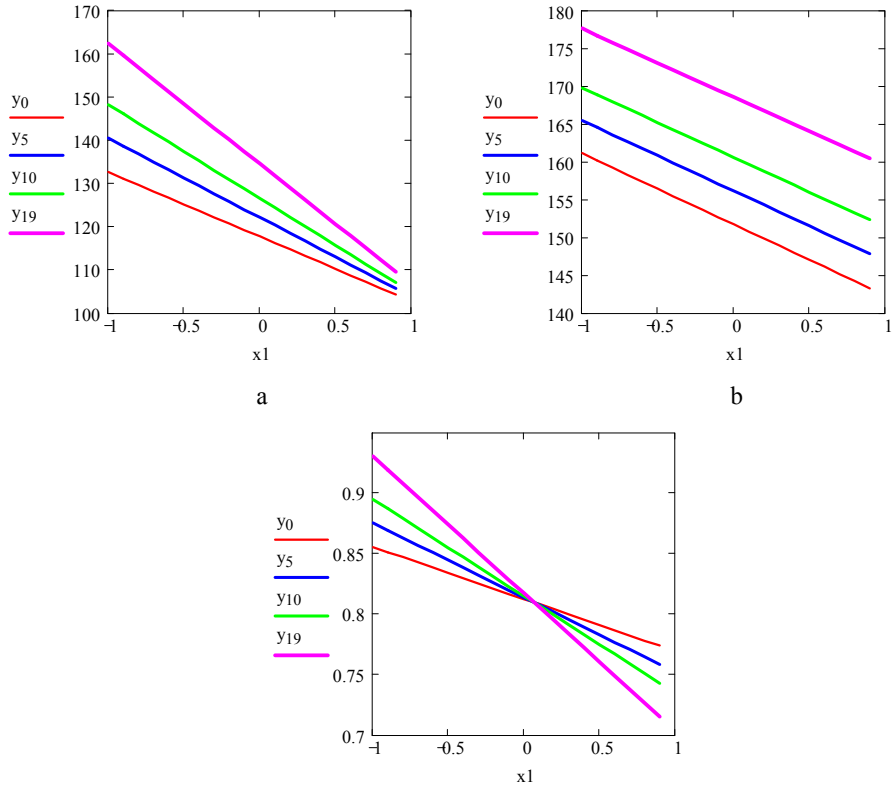

Fig. 4. Variation of y_0, y_5, y_{10}, y_{19} (a. $y = y_{str}$, b. $y = y_{sat}$, c. $y = y_{ef}$) versus solution superficial velocity (x_1) and process temperature ($x_3 = -1(y_0); -0.5(y_5); 0(y_{10}); 0.9(y_{19})$) at ion exchangers total volume within the experimental plan centre ($x_2 = 0$)

The result given by the vector defined by equation (19), very different in comparison with that recommended by the vector defined by equation (18),

imposes the third optimization problem, consisting in the finding of factors that determine a maximum volume of demineralised water for an imposed value of process efficiency. The solution of this optimization problem is obtained by maximization of an associated Lagrange function (relationship (20)), where process efficiency value, v, varies between 0.7 and 0.9.

$$L(x_1, x_2, x_3, \lambda) = 126.56 - 21.70x_1 + 11.29x_2 + 8.86x_3 + 14.41x_1x_2 - 6.77x_1x_3 - 6.42x_2x_3 + 15.45x_1x_2x_3 + \lambda(0.815 - 0.080x_1 + 0.042x_2 + 0.003x_3 + 0.027x_1x_2 - 0.037x_1x_3 - 0.030x_2x_3 + 0.020x_1x_2x_3 - v) \quad (20)$$

The evolution of dimensionless process factors versus the process efficiency value is shown in Fig. 5. It is noticed that for process efficiency values between 0.7 and 0.84 not all the parameters are within the domain for that the model was established. The results from Fig. 5, together with the restriction to have the solution (x_{1BE}, x_{2BE}, x_{3BE}) within or near to the domain [-1,1], lead to the conclusion that the best process performances are obtained for the process efficiency value of about 0.82. In this case the dimensionless superficial velocity has negative values (x_{1BE} near to –0.5), dimensionless beds height has high values (x_{2BE} a little over 1) and process temperature has values near to the value within the experimental plan centre (x_{3BE} near to 0).

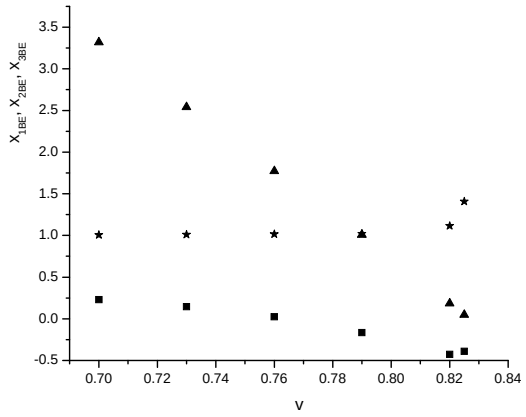

Fig. 5. Evolution of dimensionless factors when $L(x_1, x_2, x_3, \lambda)$ is maximized at different process efficiency values (■ - x_{1BE}, * - x_{2BE}, ▲ - x_{3BE})

If the demineralization optimization problem is regarded from point of view of the technical-economical considerations, then the optimization object is the plant operation benefit. Expressing the benefit as difference between the

revenue resulted from the sale of a demineralised water charge and costs corresponding to the investment, raw water pumping, heating and other current operations, the following objective function was obtained:

$$B(x_1, x_2, x_3) = my_{br}(x_1, x_2, x_3) - nx_2 y_{ef}(x_1, x_2 .x_3) - px_1 - rx_3 - s \quad (21)$$

With estimated values of constants m, n, p, r and s at the level of an industrial plant, the benefit maximization gives that x_1 and x_3 must be negative close to unit, whereas x_2 has the value close to unit. This result is in accordance with the industrial practice in water demineralization where for instance the heating over ambient temperature isn't used.

Conclusions

The following actions have been involved aiming at the development of a procedure showing how the laboratory breakthrough curves of fixed bed ion exchange can be used for the process optimization:

- removal of Na^+ and Cl^- ions from water by means of a fixed bed ion exchange plant with separated columns has been chosen as experimental support;
- an experimental analysis using a factorial plan with two levels, selecting the solution superficial velocity, beds total volume and operating temperature as natural factors and the breakthrough time, saturation time and ion exchange process efficiency as responses, has been proposed to obtain the correlations characteristic of the process;
- three technological optimization cases and also the benefit optimization have been discussed.

Acknowledgment

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Nomenclature

$B(x_1, x_2, x_3)$-benefit function defined by equation (21);
c-Cl^- ions concentration in plant effluent, g/l;
c_0-Cl^- ions concentration in plant influent, g/l;
d-columns internal diameter, m;
d_P-ion exchangers particles diameter, m;

$E = y_{ef}$ -process efficiency;

f -saturation degree of ion exchange zone;

G_V -solution volumetric flow rate, cm^3/min;

H_S -ion exchangers beds total height, m;

H_Z -height of ion exchange zone, m;

$L(x_1, x_2, x_3, \lambda)$ -Lagrange function defined by equation (20);

m, n, p, r, s -constants in equation (21);

t -time, min;

t_{br} -breakthrough time, min;

t_{sat} -saturation time, min;

t_{stat} -stationary time, min;

T -process temperature, ^0C;

v - imposed value of process efficiency;

V_{br} -effluent volume at breakthrough, m^3;

V_S -ion exchangers beds total volume, m^3;

w_f -solution superficial velocity, m/s;

x_1 -dimensionless solution superficial velocity;

x_2 -dimensionless ion exchangers beds total volume;

x_3 -dimensionless process temperature;

$x_{1BE}, x_{2BE}, x_{3BE}$ -solutions obtained by maximization of Lagrange function;

X_B -solution obtained by maximization of y_{br} function;

X_E -solution obtained by maximization of y_{ef} function;

y_{br} -dimensionless breakthrough time;

y_{sat} -dimensionless saturation time;

ε_0 -ion exchangers beds porosity;

λ -Lagrange multiplier;

$R_A{}^+HO^-$, $R_A{}^+Cl^-$ -strongly basic anionite;

$R_{Aw}{}^+NH_2{}^-$ -weakly basic anionite;

$R_C{}^-H^+$, $R_C{}^-Na^+$ -strongly acidic cationite;

$R_{Cw}{}^-H^+$ -weakly acidic cationite;

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