

Equilibrium and dynamic ion exchange studies of Cr^{3+} on zeolites NaA and NaX

Maria Angélica Simões Dornellas de Barros^{1*}, Andréia Soares Zola¹, Pedro Augusto Arroyo¹, Eduardo Falabella Sousa-Aguiar^{2,3} e Célia Regina Granhen Tavares¹

¹Departamento de Engenharia Química, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900, Maringá, Paraná, Brasil. ²Escola de Química/DPO, Universidade Federal do Rio de Janeiro, Ilha do Fundão, Cidade Universitária, 21945-970, Rio de Janeiro, Rio de Janeiro, Brasil. ³Cenpes/Petrobras, Ilha do Fundão, Quadra 7, 21949-900, Rio de Janeiro, Rio de Janeiro, Brasil. *Author for correspondence. email: angelica@deq.uem.br

ABSTRACT. In this paper, the chromium uptake in zeolites NaA and NaX was investigated in equilibrium condition and in dynamic systems at 30°C. The separation factors, obtained from the equilibrium data, were very similar to the isotherms Cr-NaA e Cr-NaX, which indicates that, in equilibrium conditions both zeolites remove similar quantities of chromium ions. For the dynamic runs, it was observed that the large size of hydrated chromium ion inhibited its exchange in all zeolite sites causing huge differences in the breakthrough curves. The dynamic data were used to estimate some mass transfer parameters such as the length of unused bed, operational ratio and dimensionless variance for various flow rates. Based on the breakthrough results, the optimal condition for column operation was 11 mL/min for zeolite NaA and 9 mL/min for zeolite NaX. Moreover, through the dynamic capacity of the column, it was concluded that the zeolite NaX has been more efficient for dynamic chromium uptake due to the larger aperture of its cages.

Key words: chromium ion-exchange, fixed-bed, zeolite, isotherm, breakthrough curve.

RESUMO. Troca iônica em equilíbrio e dinâmica de Cr^{3+} em zeólitas NaA e NaX.

Neste trabalho foi investigada a remoção de íons Cr^{3+} pelas zeólitas NaA e NaX, em condições de equilíbrio e em sistemas dinâmicos, a 30°C. Os fatores de separação, obtidos a partir dos dados em equilíbrio, mostraram-se muito próximos para as isotermas Cr-NaA e Cr-NaX, o que indica que, nestas condições, ambas as zeólitas removeram quantidades similares de cromo. Para as trocas dinâmicas foi observado que o grande tamanho do íon cromo hidratado inibiu a sua troca em todos os sítios zeolíticos, ocasionando diferenças significativas nas curvas de ruptura. Os dados dinâmicos foram usados para estimar alguns parâmetros de transferência de massa, tais como: altura da zona de transferência de massa, razão operacional e variância adimensional para várias vazões. A condição ótima de operação da coluna, em função dos resultados dinâmicos, foi a de 11 mL/min para a zeólita NaA e 9 mL/min para a NaX. Além disso, por meio dos dados de capacidade dinâmica da coluna, concluiu-se que a zeólita NaX foi mais eficiente para a remoção dinâmica de cromo devido à maior abertura de suas cavidades.

Palavras-chave: troca iônica de cromo, leito fixo, zeólita, isoterma, curva de ruptura.

Introduction

Rapid industrialization and increase in the world population have contributed to heavy metal pollution in ecosystems. Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance because of their accumulation in living organisms. They are released into the environment in different ways. Particularly, referring to chromium, sources of this element include, for example, iron and steel manufacturing,

chrome leather tanning and chrome plating. The conventional technique for the removal of Cr^{3+} is chemical precipitation (Fabiani *et al.*, 1996, Barros *et al.*, 2001a). The main limitation of this technique is its low efficiency in the removal of trace levels of the cation. The increasing contamination of bodies of water has motivated the research in new treatments that recover chromium from these diluted solutions. Among them, ion exchange processes have been applied resins and zeolites packed beds (Gomes *et al.*, 2001; Barros *et al.*, 2001b).

Zeolites are proven ion-exchange materials where the indigenous (typically sodium) charge-balancing cations are not fixed rigidly to the hydrated aluminosilicate framework and are readily exchanged with metal cations in solution. Among the various available zeolites, NaA and NaX have good selectivity about heavy metal ions (Biškup and Subotić, 2000; Barros *et al.*, 2001b). Moreover, they have high and very similar cation exchange capacity, although they are structurally different (Giannetto *et al.*, 2000). The aluminosilicate framework of zeolite 4A (NaA) includes truncated octahedron (β -cage), which encloses a cavity with a free diameter of 6.6 Å. The center of the unit cell is the supercage, which has a free diameter of 11.4 Å and an aperture close to 4 Å. The synthetic zeolite X has the biggest cavities of any known zeolites. The largest cavities, also called supercages, have a free diameter of 12.5 Å and an entrance of 7.8 Å (Giannetto *et al.*, 2000). The framework has also other cages such as sodalite and hexagonal prisms with free diameters of 6.6 and 2.2 Å, respectively. Due to its framework, it may be supposed that NaX zeolite offers less diffusion hindrance when compared to other zeolites to exchange hydrated ions such as Cr^{3+} (Barros *et al.*, 2001b).

The preference of the zeolite to the entering ion takes into account the cation exchange capacity (CEC), the channel system, the hydration radius of the out-going and the in-going ions as well as the temperature (Giannetto *et al.*, 2000). Equilibrium studies provide information about the selectivity of the zeolite. In dynamic investigations, the zeolite removes ions from solution until the exhaustion of the column. The performance of the dynamic ion exchange processes is affected by the concentration of the inlet solution (Gomes *et al.*, 2001) and the operational conditions such as particle size and flow rate (Barros *et al.*, 2001c; Inglezakis *et al.*, 2002). More concentrated solutions provide faster column saturation (Sağ and Aktay, 2001) and small particles decrease the mass transfer resistances (Barros *et al.*, 2001a). Increasing the fluid flow rates, increases the exchange system's productive capacity, but this could increase the length of the mass transfer zone because the mass transfer phenomena necessary for ion exchange may not be able to "keep up" with the higher mass transfer rates need for the high fluid flow rate (Watson, 1999). Furthermore, the flow in beds may suffer from non-idealities like flow channeling of insufficient wetting of the material. These problems may reduce the process efficiency (Watson, 1999) and that is why it is important that

the column operates as close as possible to the plug flow condition.

This study was devoted to present equilibrium and dynamic data for Cr^{3+} exchange on zeolites NaA and NaX. Selectivity deduced from equilibrium isotherms and breakthrough results were compared. Furthermore, the effect of flow rate on the dynamic exchange was investigated for upflow operation in packed beds of the zeolites NaA and NaX.

Material and methods

Materials

The starting zeolites were high crystalline aluminosilicates. NaA without binder, Advera 401, was provided by PQ Corporation. It has the unit cell composition $\text{Na}_{90}(\text{AlO}_2)_{90}(\text{SiO}_2)_{102}$ in dry basis, which corresponds to a cation exchange capacity (CEC), based on the aluminum content, of 6.47 meq/g. NaX powder has the unit cell composition $\text{Na}_{81}(\text{AlO}_2)_{81}(\text{SiO}_2)_{111}$ that corresponds to a CEC of 5.96 meq/g. In order to obtain, as far as possible, the homoionic sodium form, the zeolites, as received, were contacted four times with 1 mol/L solutions of NaCl at 60°C with a solid/liquid ratio of 1:10. The samples were then washed each time with 2 L of hot deionised water and oven-dried at 100°C. For the dynamic runs, the zeolites were pelletized, crushed, screened and collected in an average diameter size of 0.180 mm, as previously recommended as the optimal particle size for this fixed-bed system (Arroyo *et al.*, 2000; Barros *et al.*, 2001c).

The reagent-grade $\text{CrCl}_3 \cdot 9\text{H}_2\text{O}$ was mixed with deionized water to prepare the synthetic effluent. For equilibrium studies the concentration of chromium solution was 15 meq/L. The concentration of chromium in the dynamic runs was based on the natural wastewater from tanning baths after precipitation with ammonium hydroxide up to pH = 8, that is 18.0 ppm according to Barros (1996).

Equilibrium studies

The ion exchange isotherms were carried out by weighting suitable quantities of NaA and NaX powders (0.01 g up to 2.50 g) in 35-mL glass flasks containing 20 g of the salt solution and letting the system equilibrate in water bath shaker at 30°C. After 4 days of contact time between zeolite and solution, which was previously reported as enough to attain equilibrium (Custódio *et al.*, 1998), the flasks were removed from the constant-temperature bath; the solid and solution phases in equilibrium were rapidly separated by filtration. The ion-exchange studies were carried out without pH

control in order to avoid the addition of a competing exchangeable cation.

Isotherm theory

The measured equilibrium data are plotted as ion exchange isotherms reporting the equivalent fraction of the in-going cation A in the solid phase (X_{AZ}) as a function of the equivalent fraction of the same cation in solution (X_{AS}). The isotherm data were calculated by:

$$X_{AS} = \frac{C_A}{C_{oA}} \text{ and } X_{AZ} = \frac{(C_{oA} - C_A)}{CEC_{mz}} \quad (1)$$

where C_A stands for the equilibrium concentration of cation A in the solution phase; C_{oA} stands for the initial concentration of A and CEC_{mz} is the cation exchange capacity of each dried zeolite mass.

When the isotherm shows convexly upward curvature, it is because the zeolite is more selective towards the in-going cation A . Concavely upward curvature implies selectivity towards the out-going cation B .

Exchange selectivity can be quantified in terms of the separation factor α_B^A (Breck, 1974). α_B^A is defined as the quotient of the equilibrium fraction ratios of the entering ion A or the out-going ion B in the zeolite and in solution that is:

$$\alpha_B^A = \frac{X_{AZ} X_{BS}}{X_{BZ} X_{AS}} \quad (2)$$

where X_{BS} and X_{BZ} are the equivalent fractions of the out-going cation B in the solution phase and in the zeolite phase, respectively.

According to Breck (1974) the separation factor is determined when X_{AZ} reaches 0.5. If a particular entering metal cation is preferred, the isotherm shows a favorable shape and the value of the separation factor is greater than unity. The converse holds if the out-going cation is favored by the zeolite in a concavely upward isotherm (Breck, 1974).

Dynamic ion exchange studies

The laboratory unit where the fixed bed experiments were done is shown in Figure 1.

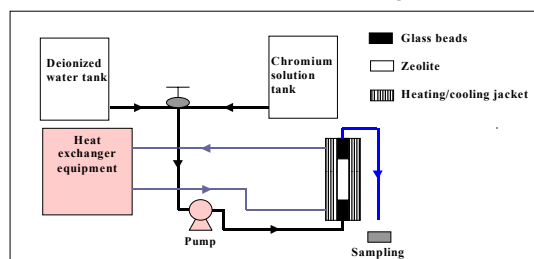


Figure 1. Dynamic ion exchange unit

The ion exchange column consisted of a clear glass tube 0.9 cm ID and 30 cm long, which contained the zeolite bed supported by glass beads. The column was connected to the heat exchanger equipment that maintained all system at 30°C. The bed was composed by 3.0 g of zeolite and the bed heights in all packed beds were about 7.5 cm for NaA and 8.8 cm for NaX. Before starting the runs, the zeolite bed was rinsed by pumping deionised water up-flow through the column. Rinsing was stopped when no air bubbles could be seen raising the column. After bed accommodation the column was completed with glass beads, and at this time the ion exchange was started by pumping solution up-flow at a constant flow rate of 7, 9 or 11 mL/min. Samples at the column outlet were collected regularly. All breakthrough curves were plotted taking into account the chromium concentration in the outlet samples as a function of the running time (C/C_o versus t).

Chromium analysis

The chromium contents were determined by atomic absorption spectrometry using a Varian SpectrAA10-Plus spectrometer. The standards employed were prepared from stock solutions and the samples were analyzed after incorporating the necessary dilutions.

Estimation of mass transfer parameters

The dimensionless time of the breakthrough curves is defined in McCabe *et al.* (2001) as:

$$\tau = \frac{u_o C_o \left(t - H_t \frac{\varepsilon}{u_o} \right)}{\rho_p (1 - \varepsilon) H_t (W_{sat} - W_o)} \quad (3)$$

where $H_t \varepsilon / u_o$ is the time to displace fluid from the bed voids (normally negligible), $u_o C_o t$ is the total solute fed to a unit cross section of bed up to time t and $\rho_p (1 - \varepsilon) H_t (W_{sat} - W_o)$ is the capacity of the bed, or the amount of the solute exchanged if the entire bed came to equilibrium with the feed, that is equal to the time equivalent to total stoichiometric capacity of the packed bed (t_i).

The time equivalent to usable capacity of the bed (t_u) and the time equivalent to total stoichiometric capacity of the packed bed (t_i) if the entire bed attains to equilibrium are provided by a mass balance in the column (Barros *et al.*, 2001a) and are easily determined by:

$$t_u = \int_0^{t_b} \left(1 - \frac{C}{C_o} \right) dt \text{ and } t_i = \int_0^{\infty} \left(1 - \frac{C}{C_o} \right) dt \quad (4)$$

where t_b is the break-point time.

According to Geankoplis (1993), t_b is defined as the time when the effluent concentration (C) reaches 5% of the influent concentration (C_o).

If the time t is considered as the time equivalent to usable capacity of the bed (t_u) up to t_b , the parameter τ may be simplified to t_u/t_i (Barros *et al.*, 2001a). The ratio t_u/t_i is the fraction of the total bed capacity or length utilized to the breakpoint (Geankoplis, 1993). Hence, the length of unused bed is:

$$H_{UNB} = \left(1 - \frac{t_u}{t_i}\right) \cdot H_i \quad (5)$$

where H_i is the total bed length.

The H_{UNB} represents the mass-transfer zone (MTZ). Small values of this parameter mean that the breakthrough curve is close to an ideal step with negligible mass-transfer resistance.

Another parameter that should be considered for a column evaluation is the average residence time (\bar{t}). From the principles of probability the average residence time of a fluid element is given according to Hill (1977) as follows:

$$\bar{t} = \int_0^{\infty} t dF(t) \quad (6)$$

where $F(t)$ is the weight fraction of the effluent with an age less than t . For breakthrough curves $F(t)$ is equivalent to C/C_o .

According to Barros *et al.* (2001a), an indirect measure of how far from the optimum operation condition the column operates is described as the operational ratio (R) as:

$$R = \left| \frac{\bar{t} - t_u}{t_u} \right| \quad (7)$$

Values of parameter R close to zero indicate that the operational conditions imposed are near the optimal region of operation (Barros *et al.*, 2001a).

With the average residence time it is also possible to evaluate the variance of the breakthrough curve (Hill, 1977), which is given by:

$$\sigma^2 = \int_0^{\infty} t^2 \left(\frac{dF(t)}{dt} \right) dt - \bar{t}^2 \quad (8)$$

The dimensionless variance should be calculate as:

$$\sigma_{\theta}^2 = \frac{\sigma^2}{\bar{t}^2} \quad (9)$$

This parameter is useful to estimate the dispersion in the packed bed. Values of $\sigma_{\theta}^2 \approx 0$ mean that the packed bed behaves close to an ideal plug flow reactor with negligible axial dispersion.

Finally, the bed performance for chromium uptake in the zeolitic sites is well evidenced through the breakthrough capacity of the column. $U_{Cr}^{t_b}$ is defined as the amount of Cr^{3+} exchanged prior to the break point ($C/C_o = 5\%$). The integration of areas under the breakthrough curve gives the amount of metal not recovered by the zeolite; based upon the difference of the quantity of metal fed to the column, this value permits the determination of the amount retained by the exchanger (Valdman *et al.*, 2001). In order to compare NaA and NaX beds, $U_{Cr}^{t_b}$ should be divided per CEC of each column

$$\left(U_{Cr}^{t_b} / CEC_{bed} \right).$$

Results and discussion

For ion exchange isotherms, all sample flasks pH was between 3.0 and 4.0, which indicated that dealumination of the zeolite or precipitation of hydroxides could be neglected and the isotherms represent only the ion exchange mechanism in the zeolite.

The ion exchange isotherms generated during the exchange of the zeolite NaA and NaX are shown in Figure 2. Both isotherms exhibited an initial steep slope, which is characteristic of favorable exchanges. It was interesting to note that in both zeolites, the isotherms failed to completion. The Cr-NaA isotherm terminated in values slightly higher than 67% of the theoretical exchange capacity, which is related to the full occupancy of the supercages (Giannetto *et al.*, 2000). The Cr-NaX isotherm did not reach 82% of the theoretical exchange capacity, which means that no chromium ions were located in the hexagonal prisms. Therefore, it may be concluded that, although the zeolites were very selective to Cr^{3+} ions, the progress of exchange was limited by the diffusion of the large hydrated cation Cr^{3+} (4.61 Å - Nightingale, 1959) through the cage apertures.

It was also noteworthy that both isotherms were almost superposed, indicating that, in spite of having different structures, the zeolites remove similar quantities of chromium ions in equilibrium conditions. In fact, the separation factors calculated

for the zeolites NaA ($\alpha_{Na(NaA)}^{Cr}=1.64$) and NaX ($\alpha_{Na(NaX)}^{Cr}=1.60$) were very similar.

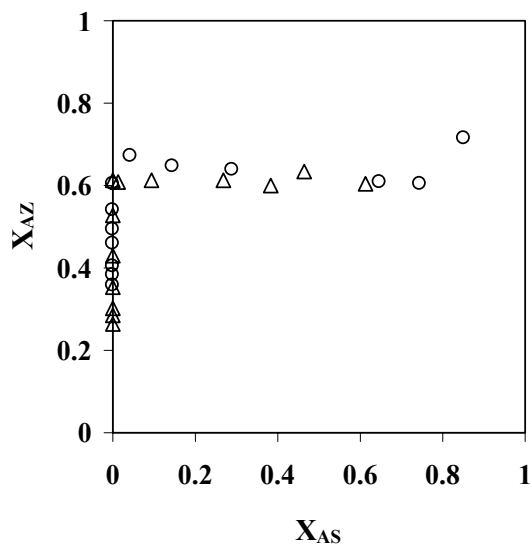


Figure 2. Chromium exchange isotherm at 30°C: (O) NaA and (Δ) NaX

Figure 3 shows the breakthrough data for NaA and NaX zeolite columns. The effect of changing flow rate from 7 up to 11 mL/min promoted a faster saturation of the zeolite bed. Moreover, increasing flow rates decreased the break-point time mainly for NaX columns as it can be seen in Table 1. It was also observed that the slope of the NaX breakthrough curves increased from 7 to 9 mL/min and remained approximately constant from 9 to 11 mL/min. For NaA bed increasing flow rates promoted steeper slopes and at 11 mL/min the breakthrough data originated almost an ideal step curve. Then, it may be supposed that at 9 mL/min for NaX beds and 11 mL/min for NaA beds occurred the minimum diffusional resistances (Helferich, 1995).

Table 1. Chromium exchange in a NaA and NaX packed columns

Zeolite	Flow rate (mL/min)	t_b (min)	H_{UNB} (cm)	R	σ_θ^2	$U_{Cr}^{t_b}/CEC_{bed}$
NaA	7	552	3.9	1.3	0.3	0.25
	9	525	1.7	1.0	0.3	0.30
	11	450	1.0	0.4	0.1	0.31
NaX	7	1402	0.8	0.1	0.0	0.70
	9	1104	0.9	0.0	0.1	0.72
	11	795	1.7	0.3	0.1	0.54

Differences in the breakthrough curves were surprising for zeolites with almost the same CEC,

very similar isotherms and very close separation factors. As NaA and NaX have distinct three-dimensional structures (Giannetto *et al.*, 2000), it may be supposed that the steric hindrance experienced by Cr^{3+} ions in order to pass through the apertures of each cage have a pronounced influence in the dynamic exchange. Therefore, far from exchange equilibrium, the zeolite three-dimensional framework may provide different intra-particle resistances, which influence the breakthrough performance. Moreover, the break point was much more influenced by the flow rate in NaX packed beds, which is a consequence of the greater accessibility of the hydrated Cr^{3+} ions to the zeolite cages (Barros *et al.*, 2001b). On the other hand, the supercage aperture of the zeolite NaA is smaller than the supercage aperture of zeolite NaX. Therefore, hydrated chromium ions have some difficulty to diffuse into the supercages of NaA. As a consequence, increasing flow rates from 7 to 11 L/min promoted small changes in the break-point time for NaA beds.

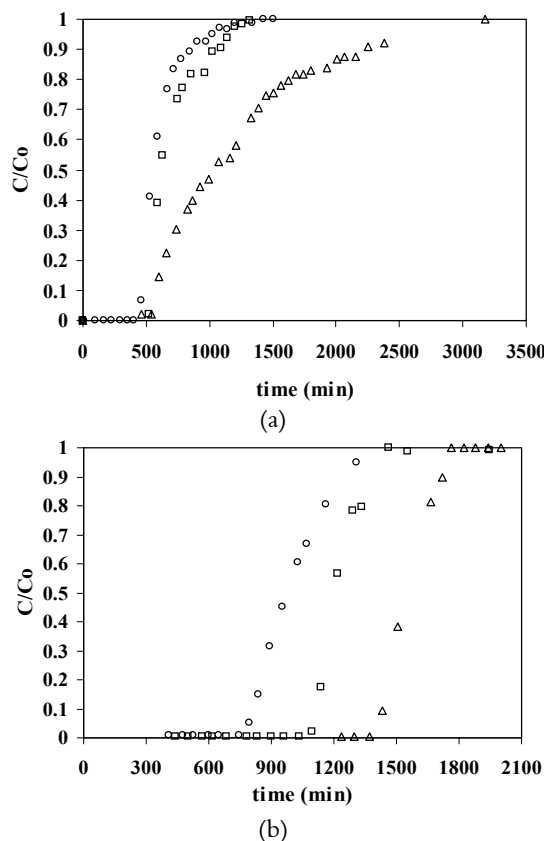


Figure 3. Breakthrough curves for the zeolites: a) NaA columns, b) NaX columns at (Δ) 7 mL/min, (\square) 9 mL/min and (O) 11 mL/min

The mass transfer parameters estimated from the breakthrough data are also given in Table 1. It was observed that H_{UNB} reached its minimum value at 11 mL/min for NaA and 9 mL/min for NaX beds. It seemed that at these flow rates occurred the maximum system's productive capacity and the sufficient exchange time for each zeolite bed, as discussed by Watson (1999), which minimizes the mass transfer resistances. In the case of NaX columns it must be emphasized that the differences between H_{UNB} values for 9 and 7 mL/min were negligible and it was possible to assure that at 9 mL/min there was a minimum mass transfer zone as well. In total agreement with the H_{UNB} values, it was observed in NaA column operated at 11 mL/min and in NaX column operated at 9 mL/min the minimum operational ratios and dimensionless variance as well as the maximum uptake of chromium ions until the break point. Furthermore, the operational ratios and the dimensionless variances for NaA packed columns were much higher than the values obtained for NaX columns. Such values indicated that the dynamic ion exchange in NaA beds did not occur as close to the optimum condition as in NaX beds with higher axial dispersions. Furthermore, NaA beds retained very low quantity of chromium ions.

Comparing the results shown for both zeolites in Table 1 it was observed that in all flow rates investigated NaX zeolite presented smaller or, at least, similar values for H_{UNB} . Lower operational ratios and dimensionless variances as well as higher chromium uptake until the break point were also observed for NaX columns. Moreover, at the saturation point, NaX bed at 9 mL/min chromium ions occupied 79% of its cation exchange capacity that means that almost all sites located in large cages of this zeolite had Cr^{3+} as balancing cations. On the other hand, the chromium uptake in the NaA bed at 11 mL/min occurred in only 36% of the sites at the saturation point. Such value is much lower than 67% of the chromium exchange capacity observed in the isotherms. Therefore, it may be concluded that although the isotherms presented similar equilibrium selectivity, the dynamic runs showed more clearly the influence of the zeolite framework. Probably the chromium ions experienced more steric problems to diffuse into the NaA cages, which could explain the low chromium uptake. Furthermore, besides the small apertures of zeolite A, a less efficiency of NaA columns was already expected since attempts to exchange with other trivalent cations were unsuccessful or partially successful (Breck, 1974; Wiers *et al.*, 1982), due to

their hindrance. Then, it was possible to assure that the best operating condition for chromium uptake in dynamic runs was NaX bed at a flow rate of 9 mL/min.

Conclusion

The findings reported herein showed that:

- Zeolites NaA and NaX have very similar favorable exchange isotherms and close affinities for chromium ions in batch equilibrium systems at 30°C;
- Concerning the dynamic runs, the optimal flow rate for NaA and NaX beds could be considered as 11 and 9 mL/min, respectively due to the better performance of the column and favorable values of the mass transfer parameters;
- NaX was proved to be more efficient for chromium uptake than NaA because the zeolite framework and mainly supercage apertures have a pronounced effect in the dynamic performance.

Acknowledgments

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Nomenclature

C	Concentration of outlet solution in the dynamic ion exchange (meq)
C_o	Initial concentration of the solution in dynamic ion exchange (meq)
C_A	Equilibrium concentration of the in-going cation A in the solution phase (meq)
C_{oA}	Initial concentration of the in-going cation A in the solution phase (meq)
CEC	Cation exchange capacity of the zeolite (meq/g)
CEC_{mz}	Cation exchange capacity of the dried mass of the zeolite (meq)
CEC_{bed}	Cation exchange capacity of the zeolite column (meq)
$F(t)$	Weight fraction of the effluent with an age less than t
H_t	Bed length (cm)
H_{UNB}	Length of unused bed (cm)
R	Operational ratio
t_b	Break-point time (min)
t_u	Time equivalent to usable capacity of the bed (min)
t_t	Time equivalent to total stoichiometric capacity of the packed-bed column (min)

\bar{t}	Average residence time (min)
u_o	Superficial velocity of fluid (cm/min)
$U_{Cr}^{t_b}$	Breakthrough capacity of the column until t_b (meq)
X_{AS}	Equivalent fraction of the in-going ion A in the fluid phase in equilibrium condition
X_{AZ}	Equivalent fraction of the in-going ion A in the solid phase in equilibrium condition
X_{BS}	Equivalent fraction of the out-going ion B in the fluid phase in equilibrium condition
X_{BZ}	Equivalent fraction of the out-going ion B in the solid phase in equilibrium condition
W_o	Initial ion exchange loading (meq of solute/g of zeolite)
W_{sat}	Ion exchange loading at equilibrium with the fluid (meq of solute/g of zeolite)
α_B^A	Separation factor
ε	External void fraction of bed
ρ_p	Particle density (g/cm ³)
σ^2	Variance (min ²)
σ_θ^2	Dimensionless variance
τ	Dimensionless time

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