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Chromium uptake from tricomponent solution in zeolite fixed bed

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Abstract Removal of Cr^{3+}, Ca^{2+}, Mg^{2+} and K^{+} in equilibrium isotherms and in tricomponent solutions (Cr/Ca/K, Cr/Ca/Mg and Cr/Mg/K) were investigated in NaX and NaY packed beds at 30°C. The equilibrium selectivity was obtained as $Cr^{+3} > Mg^{2+} > Ca^{2+} \approx K^{+}$ for zeolite NaY and $Ca^{2+} \gg Cr^{3+} > Mg^{2+} \approx K^{+}$ for zeolite NaX. The breakthrough curves showed sequential ion exchange where chromium ions are able to replace the competing cations. Some mass transfer parameters, such as length of unused bed and overall mass transfer coefficient, were investigated. Chromium retention was also investigated through a mass balance. Based on the breakthrough results, it was concluded that chromium-uptake mechanism was hardly influenced by the competition and interaction between the entering ions. NaY showed a higher affinity towards Cr^{3+} for both equilibrium and dynamic systems and its sites were more efficiently used in the ion exchange process. Chromium was less retained in NaX due to the high selectivity towards calcium ions.

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1 Introduction

Chromium is commonly found in two stable oxidation states in the environment, Cr(III) and Cr(VI). Cr(III) is a cation and forms stable complexes with negatively charged compounds. Cr(VI) is very water-soluble and forms strong divalent anionic oxidants. The reduction of Cr(VI) to Cr(III) usually occurs in nature, but under certain conditions, such as in the presence of large quantities of Mn oxide, oxidation of Cr(III) to Cr(VI) may also occur. Cr(VI) is highly toxic, mutagenic, carcinogenic, and in cells induces the formation of reactive oxygen species that damage cellular membranes (Barros and Sousa-Aguiar, 2001). Therefore, the spontaneous oxidation process in the nature is responsible for upsurge of research in alternative removal technologies for Cr(III) ions that are widely applied in industry.

During the past decades, various different treatments have been investigated, including adsorption and ion exchange. For the ion exchange phenomenon, zeolites deserve a special attention due to their selectivity to some cations.

Among the various available zeolites, synthetic faujasites Y and X meet the requirements of good selectivity and capacity (Giannetto et al., 2000). Unfortunately there is a lack of information about ion exchange process in these zeolites when environmental purposes are considered.

While information of the uptake of chromium species by zeolites has been expanding (Barros et al., 2001, 2004; Pansini et al., 1991) relatively little is known about removal of metal ions from multicomponent systems (Arroyo et al., 2000), mainly in zeolites X and Y. Our incomplete understanding of chromium in multicomponent systems precludes us from taking full advantage of zeolite properties for tertiary treatment. Single ion exchange cannot predict the multicomponent behavior of the metal mixtures (Arroyo et al., 2000; Barros et al., 2003a) but it provides information about the affinity of the zeolite for the entering ions. Monocomponent equilibrium isotherms, for example, give information about the separation factor (α_B^A). Higher α_A^B values are associated with more selective zeolites (Breck, 1974). The equilibrium selectivity can be obtained from α_A^B values. It gives us an idea about the dynamic selectivity. Therefore, in a competitive system, the zeolite with a higher separation factor is supposed to retain the entering cation more efficiently when a continuous system is operated with low diffusional resistances.

Monovalent ions, such as K^+, and also divalent ones, such as Ca^{2+} and Mg^{2+}, commonly occur in a lot of wastewaters that have chromium ions Thus, the affinity of each cation for NaY and NaX can be evaluated. The goals of the present work were to investigate the ability of such zeolites to remove Cr^{3+} from ternary solutions Cr/Ca/K, Cr/Ca/Mg and Cr/Mg/K through fixed bed columns and to compare the influence on each competing cation on the ion exchange mechanism.

2 Experimental section

2.1 Zeolites

The starting zeolites were highly crystalline aluminosilicates. NaY has the unit cell composition $Na_{51}(AlO_2)_{51}(SiO_2)_{141}$ (dry basis) and a cation exchange capacity (CEC) of 3.90 meq/g, whereas NaX zeolite has the unit cell composition $Na_{81}(AlO_2)_{81}(SiO_2)_{111}$ that corresponds to a cation exchange capacity of 5.96 meq/g. In order to obtain, as far as possible, the homoionic sodium form, zeolites, as received, were contacted four times with 1 Mol/L solutions of NaCl at 60°C with a ratio of zeolite to solution of 1:10. Samples were then washed each time with 2 L of hot deionised water and oven-dried at 100°C (Barros et al., 2003b). For dynamic runs, zeolites NaY and NaX were pelletized, screened and collected in an average diameter size of 0.180 mm. This particle size was previously chosen for this fixed bed system among the average sizes from 0.180 mm to 0.995 mm (Barros et al., 2001). At 0.180 mm the breakthrough curves presented the narrowest mass transfer zone (H_{UNB}).

2.2 Equilibrium studies

The ion exchange isotherms for monocomponent solutions were carried out weighting suitable quantities of NaY and NaX powders (0.01 up to 2.50 g) in 35-mL glass flasks containing 20 g of the salt solution and letting the system equilibrate in a 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 (Barros et al., 2003a), 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.

2.3 Chemicals and reagents

Reagent-grade $CrCl_3{\cdot}9H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}2H_2O$ and KCl were mixed with deionised water to prepare the monocomponent solutions for the isotherms or the ternary solutions for the dynamic runs. The concentration of chromium for 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 (Barros et al., 2001). The concentration of the competing ions Mg^{2+}, Ca^{2+} and K^+ were 12.6 ppm, 20.8 ppm and 40.1 ppm, respectively, corresponding to a equivalent ratio of 1:1:1.

2.4 Isotherm theory

The measured equilibrium data were 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:

$$X_{AS} = \frac{C_A}{C_{OA}} \quad \text{and} \quad X_{AZ} = \frac{C_{OA} - C_A}{\text{CEC}_{mz}} \tag{1}$$

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_A^B (Breck, 1974) that can be defined as the quotient of the equilibrium fraction ratios of the entering ion A or the out-going B in the zeolite and in solution that is:

$$\alpha_A^B = \frac{X_{AZ} X_{BS}}{X_{BZ} X_{AS}} \tag{2}$$

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

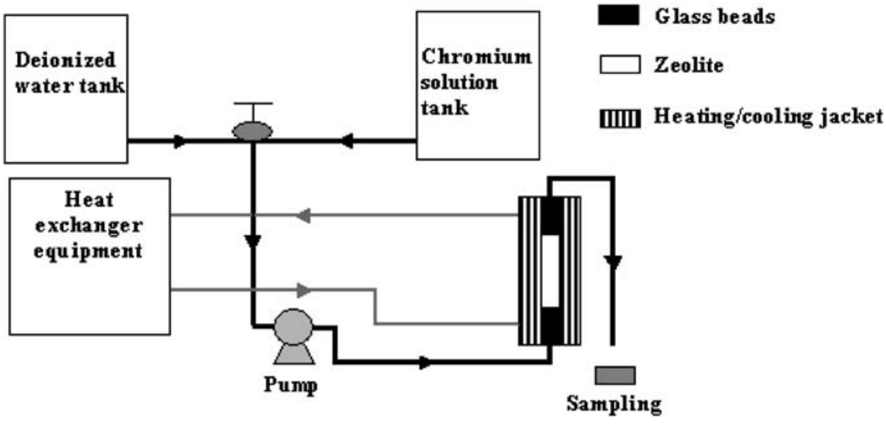
The equilibrium selectivity is expressed through the separation factor when X_{AZ} reaches 0.5 (Breck, 1974). If the zeolite exhibits a preference for the entering ion A($\alpha_A^B > 1$) and the isotherms lies above the diagonal. For non-favorable isotherms, i.e., in which the isotherm lies below the diagonal, α_A^B is less than unity.

2.5 Ion exchange unit

A laboratory unit where the fixed bed experiments were performed is shown in Fig. 1.

The ion exchange column consisted of a clear glass tube 0.9 cm ID and 30 cm long and contained the zeolite bed supported by glass beads. The column was connected to a heat exchanger equipment that maintained all system at 30°C. The bed was composed by 1.60 g of NaY or 1.04 g of NaX. Such differences in mass content provided the same cation exchange capacity based on the aluminum content of each zeolite. Therefore, it is possible evaluate and compare both systems. The bed height in all NaY packed beds was about 5.7 cm while the bed height in NaX ones was about 3.3 cm. Before starting a run, the bed was rinsed by pumping deionised water upwards through the column. The service was stopped when no air bubbles could be seen. After bed accommodation the column was completed with glass beads and at this time the ion exchange started by pumping solution also up-flow. The pump was adjusted to 9 mL/min, as this flow rate minimizes the mass transfer resistances over the range of 4 to 15 mL/min for single Cr^{3+} exchange, i.e, it yields the smallest length of mass transfer zone (MTZ)—Barros et al. (2001). Therefore, the operating conditions of 0.180 mm and 9 mL/min were also used in the multicomponent runs in order to favor Cr^{3+} uptake. Samples at the column outlet were collected regularly. All breakthrough curves were plotted taking into account the cation concentration in the outlet samples as a function of the running time (C/C_o versus t).

Fig. 1 Flow diagram for dynamic ion exchange studies



The exchanging ions concentration was determined by atomic absorption spectrophotometry using a Varian spectrometer.

2.6 Estimation of mass transfer parameters

In fixed-bed ion exchange, the concentration in the fluid phase and the solid phase change with time as well as with position in the bed. The transfer process is described by the overall mass transfer coefficient ($K_c a$) obtained from a solute material balance in the column considering irreversible isotherms (McCabe et al., 2001):

$$K_c a = \frac{u_o N}{H_t} \tag{3}$$

where $N =$ overall number of transfer units, $H_t =$ bed length and $u_o =$ superficial velocity of fluid.

The overall number of transfer units may be obtained graphically by plotting C/C_o versus $N(\tau - 1)$, where $N(\tau - 1) = 1 + \ln(C/C_o)$ (McCabe et al., 2001). The parameter τ is the dimensionless time defined as:

$$\tau = \frac{u_o C_o \left(t - H_t \frac{\varepsilon}{u_o}\right)}{\rho_P (1 - \varepsilon) H_t W_{\mathrm{sat}}} \tag{4}$$

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 $\rho_p(1 - \varepsilon) H_t W_{\mathrm{sat}}$ is the capacity of the bed, or the amount of the solute exchanged if the entire bed came to equilibrium with the feed, which is equal to the time equivalent to total stoichiometric capacity of the packed-bed tower (t_t).

The time equivalent to the usable capacity of the bed (t_u) and the time equivalent to the total stoichiometric capacity of the packed-bed tower (t_t), assuming the entire bed attains equilibrium, are provided by a mass balance in the column (Geankopolis, 1993) and are easily determined by:

$$t_u = \int_0^{t_b} \left(1 - \frac{C}{C_o}\right) dt \quad \text{and} \quad t_t = \int_0^{\infty} \left(1 - \frac{C}{C_o}\right) dt \tag{5}$$

where t_b is the break-point time.

In practice, 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 the usable capacity of the bed (t_u) up to t_b, the parameter τ may be simplified to t_u/t_t (Barros et al., 2003b). The ratio t_u/t_t is the fraction of the total bed capacity or length utilized to the breakpoint (Geankoplis, 1993). Hence, for a total bed length (H_t), the length of unused bed is:

$$H_{\mathrm{UNB}} = \left(1 - \frac{t_u}{t_t}\right) \cdot H_t. \tag{6}$$

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. Then, minimum H_{UNB} quantities are required in optimized operational conditions.

The dynamic capacity of the column, $U_i^{t_b}$, is defined as the amount of metal ion retained 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 the column, this value permits the determination of the amount retained by the exchanger (Valdman et al., 2001). Therefore, the dynamic capacity provides information on the dynamic selectivity of the cations in a competitive system.

The effect of ionic interactions on the exchange process may be represented by the ratio of the uptake capacity for one metal in presence of the other metal ions, $U_{i-\mathrm{mix}}^{t_b}$, to the uptake capacity for the same metal when it is present alone in the solution, $U_{i-\mathrm{single}}^{t_b}$ (Mohan and Chander, 2001). Thus if

$U_{i\text{-mix}}^{t_b}/U_{i\text{-single}}^{t_b} > 1$, the uptake is promoted by the presence of other metal ions;

$U_{i\text{-mix}}^{t_b}/U_{i\text{-single}}^{t_b} = 1$, no interaction exists between the in-going cations;

$U_{i\text{-mix}}^{t_b}/U_{i\text{-single}}^{t_b} < 1$ uptake is suppressed by the presence of other metal ions.

Therefore, the evaluation of the removal ratio ($U_{i\text{-mix}}^{t_b}/U_{i\text{-single}}^{t_b}$) at the time equivalent to usable capacity of the bed (t_u) for chromium ions may be useful to investigate the influence of one cation on the uptake of another.

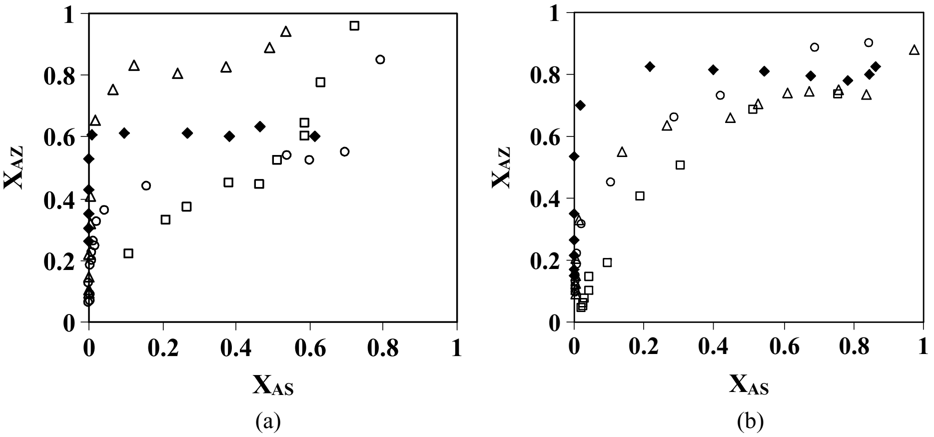


Fig. 2 Isotherms for (a) NaX zeolite, (b) NaY zeolite. (♦) Cr, (△) Ca, (○) Mg, (☐) K

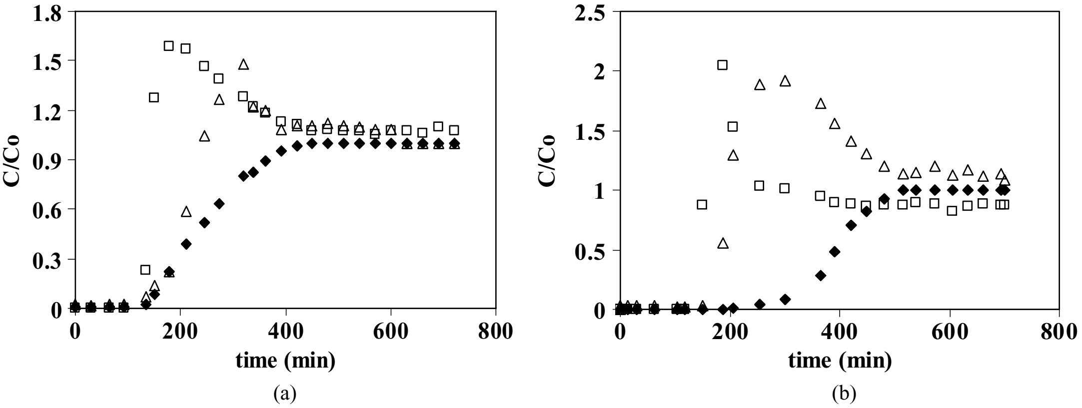


Fig. 3 Breakthrough curves for competitive system Cr/Ca/K: (a) NaX, (b) NaY. (♦) Cr/Cro, (△) Ca/Cao, (☐) K/Ko

3 Results and discussion

The first part of this work was devoted to the analysis of ion exchange mechanism in equilibrium conditions. For this purpose, the isotherms for monocomponent solutions were determined and presented in Fig. 2. It is seen that both zeolites have selectivity to the in-going ions Cr^{3+}, Ca^{2+}, Mg^{2+} and K^{+}. The separation factors were estimated as $\alpha_{Cr}^{Na} = 4.3$, $\alpha_{Ca}^{Na} = 2.2$, $\alpha_{Mg}^{Na} = 3.4$, $\alpha_{K}^{Na} = 2.1$ for NaY and $\alpha_{Cr}^{Na} = 1.7$, $\alpha_{Ca}^{Na} = 8.7$, $\alpha_{Mg}^{Na} = 1.1$, $\alpha_{K}^{Na} = 1.0$ for NaX at 30°C. Thus, the equilibrium selectivity can be written as $Cr^{+3} > Mg^{2+} > Ca^{2+} \approx K^{+}$ for zeolite NaY and $Ca^{2+} \gg Cr^{3+} > Mg^{2+} \approx K^{+}$ for zeolite NaX. Moreover, as chromium isotherms have a pronounced plateau, they can be considered as irreversible, which permits the estimation of K_{ca} for the dynamic runs.

Breakthrough curves generated during the exchange of the zeolites NaY and NaX are shown in Figs. 3 to 5. It is interesting to note that all curvatures are different when the same multicomponent solution is used in both zeolites. It can be seen from these Figures that the time required for attaining the breakthrough point ($Cr/Cr_o = 5\%$) is $t_b < 200$ min for NaX and $200 < t_b < 400$ min for NaY. It indicates the influence of the zeolite and also of the competing ion M (M $= Ca^{2+}$, Mg^{2+} or K^{+}) on chromium uptake. Although the zeolites are isomorphs, high site density, provided by a high aluminum content in the NaX may alter the interaction of each in-going cation with the framework, which is in agreement with different separation factors. Moreover, chromium exchange in multicomponent systems is very different when compared to the single ones (Barros et al., 2001), which emphasizes the

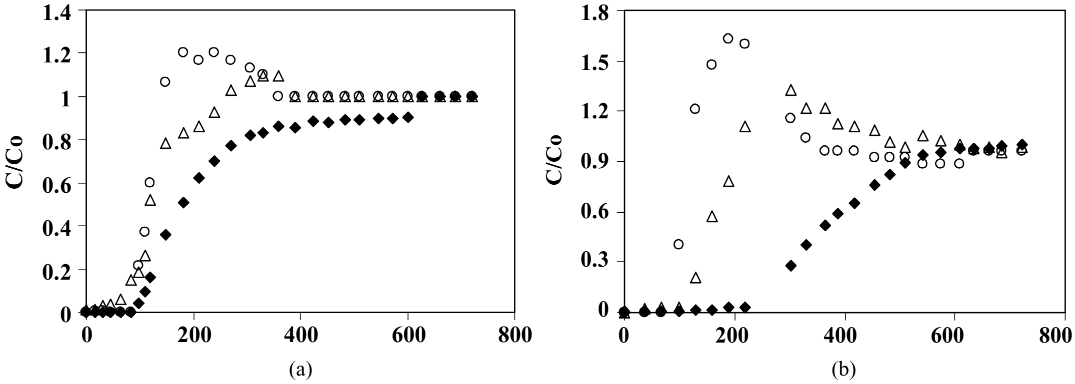


Fig. 4 Breakthrough curves for competitive system Cr/Ca/Mg: (a) NaX, (b) NaY. (◆) Cr/Cro, (△) Ca/Cao, (○) Mg/Mgo

influence of the competing cations. In fact, even for binary ion exchanges such as Cr/Ca, Cr/Mg and Cr/K the influence of the competing ion was pronounced (Barros et al., 2003b).

It may also be seen in all runs that the breakthrough curves for the competing cations generally show C_M/C_{Mo}($M = Ca^{2+}$, Mg^{2+} or K^+) values higher than one. Initially, all metal ions are exchanged on unsaturated sites. As the exchange proceeds, the competing cations are released at different running times with continued feed of the multicomponent solution. As $Cr/Cr_o > 1$ is not observed it may be concluded that, in the operating conditions applied to the column, chromium is preferentially removed relative to the other cations. It replaces the competing cations already exchanged in the sites, promoting, therefore, a sequential ion exchange. It is noteworthy that in all cases, C_M/C_{Mo} for NaY runs are higher than for NaX runs, which indicates that NaY is more selective to chromium. The sequential exchange was already observed in multicomponent breakthrough curves in coconut carbon (Mohan and Chander, 2001), fungus (Sağ et al., 2000), zeolite A (Arroyo et al., 2000) and even in NaY and NaX systems for binary solutions (Barros et al., 2003b). Therefore, such phenomenon is a reasonable explanation also for the chromium uptake from ternary solutions in zeolites X and Y. Its extension depends on the nature of the competing cations and on the selectivity of the zeolite.

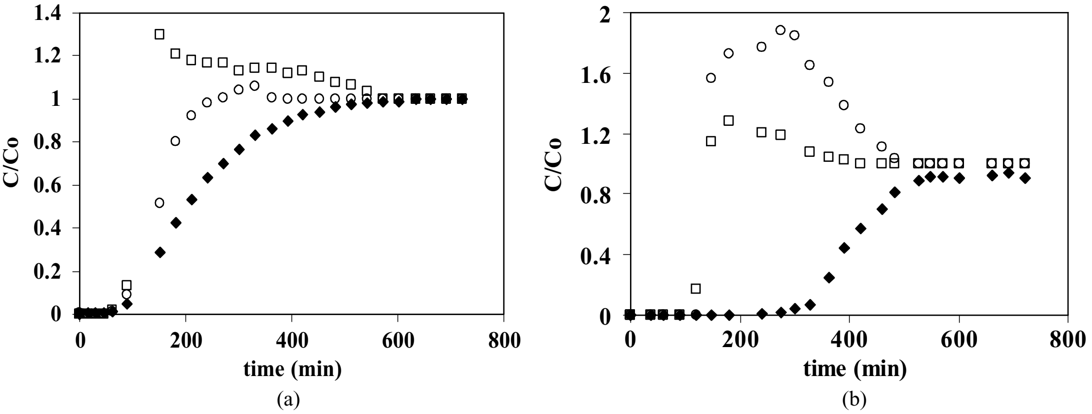
Considering the Cr/Ca/K ion exchange, shown in Fig. 3(a), it is possible to observe that the break-point time for chromium ions in the NaX packed bed is practically the same for the other cations. Therefore, the operational conditions for Cr^{3+} may be also close to the best conditions for the competing ions. On the other hand, the Cr/Ca/K-NaY breakthrough curve (Fig. 3(b)) has a different shape, evidencing the influence of the zeolite on the uptake mechanism. Considering the sequential ion exchange in Fig. 3(a) and (b), it is noted that potassium ions are released earlier from the zeolitic phase, followed by calcium ions. Possibly the determining factor in this ion exchange mechanism is the charge of the ion.

Figure 4 presents the breakthrough curves for the Cr/Ca/Mg system. In both NaY and NaX beds, magnesium ions are released earlier than calcium. It seems that Mg^{2+} ions have a poor dynamic affinity, mainly in NaY packed beds as it has been released in the beginning of the first hour of the run, followed by calcium ions. It may be supposed that when the competing ions have the same charge, the one with smaller ionic radius is released earlier.

In Fig. 5(a), where the Cr/Mg/K exchange is shown for NaX packed beds, it is observed that K^+ ions are released before than Mg^{2+} ions due to the valence effect already discussed. In NaY packed bed (Fig. 5(b)) it is the opposite: magnesium is released earlier than potassium again due to a weak affinity of the zeolite to Mg^{2+}. In fact, this ion is more easily exchanged in the six-membered oxygen sites located in the hexagonal prisms of NaY (Barros et al., 2004). Therefore, Mg^{2+} cations are weakly exchanged in the large cages and are easily displaced in a competitive condition.

In Table 1 the mass transfer parameters were estimated from the breakthrough data of the competitive systems.

In Table 1, the length of unused bed and the overall mass transfer coefficient for both zeolites are presented. Firstly, one can note that H_{UNB} is slightly greater



(a) (b)

Fig. 5 Breakthrough curves for competitive system Cr/Mg/K: (a) NaX, (b) NaY. (♦) Cr/Cro, (○) Mg/Mgo, (□) K/Ko

for NaY columns probably due to the different ion exchange mechanism when in contact with a multicomponent feed solution. Also it is worthwhile noting that the tricomponent dynamic runs have unused bed lengths for chromium ions that are higher than the ones observed for chromium ions in single breakthrough curves, that is, 1.6 cm for NaY and 0.9 cm for NaX zeolites and an average of 1.4 cm for binary solutions for NaY and 1.2 cm for NaX zeolites (Barros et al., 2003b). Thus, an increase in the species of competing cations decreases the efficiency in the chromium uptake mainly for NaX packed beds, as the effect of increasing H_{UNB} is more pronounced in this zeolite.

Also in Table 1 it is observed that the overall mass transfer coefficients for NaY runs are close to the ones obtained for single exchange, that is 17.5 min^{-1} (Barros et al., 2001). On the other hand, $K_c a$ for NaX breakthrough curves decreased significantly. For single chromium exchange it reached 32.3 min^{-1} (Barros et al., 2003b). Therefore, it seems that when ternary ion exchange is considered, competition and also interaction of the in-going cations interfere, in a greater extent, in the diffusion through the film and into the particle of NaX zeolite.

Table 1 Mass transfer parameters for the dynamic runs

Zeolite	Solution	$H_{\text{UNB}}{}^{a}$ (cm)	$K_c a^{a}$ (min^{-1})
NaX	Cr/Ca/K	1.3	21.7
	Cr/Ca/Mg	1.4	19.7
	Cr/Mg/K	1.6	17.3
NaY	Cr/Ca/K	1.9	15.3
	Cr/Ca/Mg	2.2	13.2
	Cr/Mg/K	1.4	20.7

[a] Related to chromium ions.

The competition towards the sites is better evidenced when the uptake of the ions are analyzed. Considering the data provided by Table 2, one can note that up to the chromium break-point time (t_b^{Cr}), the amount of metal ion fed into the column (C_o^{ion}) is the same as it should be due to the initial equivalent ratio of 1:1:1.Some small numeric differences are due to experimental procedures and are negligible. However, the amount retained in the column ($U_{\text{Cr-mix}}^{t_b}$, $U_{M1\text{-mix}}^{t_b}$ and $U_{M2\text{-mix}}^{t_b}$) and the percentage of competing cations retained up to t_b^{Cr} are clearly distinct and show the selectivity of zeolite NaY for chromium ions. This is in accordance to the removal ratio, ($U_{\text{Cr-mix}}^{t_b}/U_{\text{Cr-single}}^{t_b}$), as it changed due to the dynamic selectivity of each cation exchanger. Then, it can be seen that NaY packed column retained more chromium than the NaX columns. These results were already expected since the break-point time for NaY breakthrough curves are higher than for NaX and the zeolite saturation is delayed. Table 2 also presents the percentage of competing cations retained up to t_b^{Cr}. It can be seen that for zeolite NaY such percentage is lower, which is in agreement with the breakthrough curves (Figs. 3 to 5), where t_b^{Cr} is very different when compared to the break point time of the competing cations.

If the Cr/Ca/K system is considered, it can be observed that the dynamic selectivity sequence is $\text{Cr}^{3+} > \text{Ca}^{2+} > \text{K}^{+}$ for both zeolites investigated, although the values are very close to each other, mainly for the NaX column. In the competitive system there is a strong interaction and competition towards the sites, which inhibits a selective removal of chromium. The dynamic

Table 2 Cation uptake data for the ternary breakthrough curves

Zeolite	Solution	C_o^{Cr} (meq)	C_o^{M1} (meq)	C_o^{M2} (meq)	$U_{\mathrm{Cr\text{-}mix}}^{t_b}$ (meq)	$U_{M1\text{-mix}}^{t_b}$ (meq)	$U_{M2\text{-mix}}^{t_b}$ (meq)
NaX	Cr/Ca/K	1.30	1.33	1.28	1.30	1.29	1.22
	Cr/Ca/Mg	1.04	0.96	0.95	1.04	0.96	0.85
	Cr/Mg/K	0.87	0.83	0.80	0.87	0.75	0.75
NaY	Cr/Ca/K	2.35	2.41	2.32	2.35	1.34	0.83
	Cr/Ca/Mg	2.30	2.07	2.08	2.03	1.56	0.45
	Cr/Mg/K	3.06	2.92	2.80	3.06	$4.8.10^{-3}$	0.82

C_o^{Cr} = Amount of meq of chromium ions fed into the column up to the chromium break point time.
C_o^{Mi} = Amount of me0q of competing cation fed into the column up to the chromium break point time. 1: the first competing cation; 2: the second competing cation.
$U_{\mathrm{Cr\text{-}mix}}^{t_b}$ = chromium uptake until the chromium break point time (t_b^{Cr}).
$U_{Mi\text{-mix}}^{t_b}$ = competing cation (Mg^{2+}, Ca^{2+}, K^{+}) uptake until the chromium break point time (t_b). 1: the first competing cation; 2: the second competing cation.

Table 3 Percentage of competing cations retained up to chromium break point time and chromium removal ratio

Zeolite	Solution	% M_1 retained up to t_b^{Cr}	% M_2 retained up to t_b^{Cr}	$(U_{\mathrm{Cr\text{-}mix}}^{t_b}/U_{\mathrm{Cr\text{-}single}}^{t_b})$
NaX	Cr/Ca/K	97	95	0.51
	Cr/Ca/Mg	100	90	0.41
	Cr/Mg/K	90	94	0.34
NaY	Cr/Ca/K	56	36	0.79
	Cr/Ca/Mg	75	22	0.68
	Cr/Mg/K	0	29	1.03

affinity order for Cr/Ca/Mg breakthrough curves is $\mathrm{Cr}^{3+} > \mathrm{Ca}^{2+} > \mathrm{Mg}^{2+}$ for NaX and NaY. Although both zeolite columns provide the same dynamic affinity, NaY seems to be more selective to chromium, which can be seen through the values of $U_i^{t_b}$. Cr/Mg/K breakthrough curves yield the sequence order: $\mathrm{Cr}^{3+} > \mathrm{Mg}^{2+} \approx \mathrm{K}^{+}$ for NaX and $\mathrm{Cr}^{3+} > \mathrm{K}^{+} > \mathrm{Mg}^{2+}$ for NaY, which indicates that in both cases chromium ions are again preferentially retained, and the numerical values indicate that NaY is a more efficient system. Finally, it is observed that there is a small magnesium uptake in the NaY packed beds until chromium break-point time. This may reflect the preference of Mg^{2+} ions for the NaY hexagonal prisms as already mentioned.

It is noteworthy to compare the sequence of equilibrium selectivity provided by the separation factor with the dynamic selectivity. In both cases chromium is preferable for zeolite NaY. This happens because the operating conditions were optimized for chromium removal. On the other hand, there is no agreement between the equilibrium selectivity and the dynamic selectivity for the zeolite NaX. It happens exactly because the operating parameters favor the uptake of chromium ions, while zeolite NaX is more selective to calcium ions.

Results presented in Table 3 emphasize the affinity of zeolite NaY to chromium ions. In this table it can be seen that the percentage of competing ions retained up to chromium break point time is lower for zeolite NaY, which is in agreement with the breakthrough curves (Figs. 3 to 5), where t_b^{Cr} is very different when compared to the break point time of the competing cations.

Table 3 also shows quantitatively the effect of ionic interactions on the exchange process through the removal ratio $(U_{i\text{-mix}}^{t_b}/U_{i\text{-single}}^{t_b})$ for chromium ions. The removal ratio clearly shows the influence on the competing cation as chromium uptake is suppressed since $(U_{i\text{-mix}}^{t_b}/U_{i\text{-single}}^{t_b}) < 1$. Due to the higher affinity of NaY to Cr^{3+} ions, the influence on the competing cations, as it could be expected, is lower in this zeolite. Then, it can be seen that NaY packed column retains more chromium than the NaX columns. These results were already expected since the break-point time for NaY breakthrough curves are higher than for NaX and the zeolite saturation is delayed. Also concerning the removal ratio, the Cr/Mg/K-NaY system deserves special attention because this parameter is equal to unity. It must be emphasized that the greatest difference between the breakthrough curves of the competing cations and chromium ion occurs exactly in this system (Fig. 5(b)). It seems, in this case, that the high selectivity of suchzeolite to Cr^{3+} ions and the poor dynamic affinity to Mg^{2+} ions are responsible for such striking ion exchange mechanism.

Considering the total amount of cation removal at the end of the runs, it is observed that only 66% of the cation exchange capacity of NaX is used, which means that the packed column still has available sites, some of them located at the large cages. On the other hand, 75% of the sites in NaY have the entering ions, which indicates the occupancy of all sites located in the large cages. Thus, zeolite NaY is more efficiently used in ion exchange columns than NaX.

4 Conclusions

The findings reported herein showed that:

(i) The equilibrium selectivity can be assumed as $Cr^{+3} > Mg^{2+} > Ca^{2+} \approx K^{+}$ for zeolite NaY and $Ca^{2+} \gg Cr^{3+} > Mg^{2+} \approx K^{+}$ for zeolite NaX. This sequence may be not observed in dynamic runs if the operational conditions do not favor the removal of the cation of interest;

(ii) The dynamic runs present some C_M/C_{Mo} values higher than one, due to sequential ion exchange where chromium ions are able to replace the competing cations already exchanged in the sites. The extension of such a phenomenon depends on the nature of the competing cation and on the selectivity of the zeolite;

(iii) Longer mass transfer zones and lower overall mass transfer coefficients in ternary solutions were obtained when compared to single chromium breakthrough curves or binary ones, due to the competition of the entering ions to the zeolitic sites. Therefore, when designing ion exchange packed beds, a multicomponent solution should be considered for industrial effluent treatment;

(iv) The interactions between the entering ions, as well as with the zeolite structure, are important since they influence the chromium uptake and the dynamic selectivity;

(v) Considering all the results, NaY zeolite removes more efficiently Cr^{3+} presented in the ternary solutions investigated. NaY is able to retain more efficiently chromium ions with less influence of the competing cations calcium, magnesium and potassium.

Nomenclature

A	Entering cation
B	Out-going cation
C	Concentration of solution (meq/L)
C_A	Equilibrium concentration of cation A in the solution phase (meq/L)
CEC_{mz}	Cation exchange capacity of each dried zeolite mass (meq)
C_o	Initial concentration of solution (meq/L)
C_{oA}	Initial concentration of cation A in the solution phase (meq/L)
C/C_o	Concentration in the fluid relative to that in the feed
H_t	Bed length (cm)
H_{UNB}	Length of unused bed (cm)
$K_c a$	Overall mass transfer coefficient (min^{-1})
M	Competing cation Mg^{2+}, Ca^{2+} and K^{+}
N	Overall number of transfer units
U_i^{tb}	Dynamic capacity of the column of the in-going cation *i* (meq)
$(U^{t_b}_{i-\mathrm{mix}}/U^{t_b}_{i-\mathrm{single}})$	Removal 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 tower (min)
uo	Superficial velocity of fluid (cm/min)
W_{sat}	Ion exchange loading at equilibrium with the fluid (meq/g)
X_{iS}	Equivalent fraction of cation *i* in solution
X_{iz}	Equivalent fraction of cation *i* in the solid phase
α_A^B	Separation factor. A is the entering ion, B is the out-going ion
δ	Film thickness (cm)
ε	External void fraction of bed
ρ_p	Particle density ($\mathrm{g/cm^3}$)
τ	Dimensionless time

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