

BINARY ION EXCHANGE OF METAL IONS IN Y AND X ZEOLITES

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Abstract - The ion exchange of Na for Cr/K, Cr/Mg and Cr/Ca in Y and X zeolites was studied using breakthrough curves. It was observed that Cr³⁺ ions were able to remove some competitive ions that had already been exchanged at the zeolitic sites, producing a sequential ion exchange. Some mass transfer parameters such as length of unused bed, overall mass transfer coefficient, operational ratio and dimensionless variance were studied. Chromium uptake was influenced much more by the competing ion in the NaX zeolite columns. The dimensionless variance indicated that Cr/K solution produced a greater axial dispersion than the Cr/Mg and Cr/Ca systems, probably due to some interaction between Cr³⁺ and K⁺ ions. The order of dynamic selectivity, provided by the cation uptake, was Cr³⁺ > Ca²⁺, Cr³⁺ > Mg²⁺ and Cr³⁺ > K⁺ for NaY zeolite and Ca²⁺ ≈ Cr³⁺, Mg²⁺ > Cr³⁺ and Cr³⁺ > K⁺ for NaX zeolite. Due to the more favorable mass transfer parameters and higher affinity for Cr³⁺, it was concluded that NaY zeolite was more efficient at chromium uptake in competitive systems.

Keywords: zeolite, multicomponent ion exchange, breakthrough curve, chromium.

INTRODUCTION

The use of zeolites in the control of pollution, including of effluents polluted with heavy metal ions, has recently increased (Chen et al., 1990; Pansini et al., 1991; Custódio et al., 1998; Biškup and Subotić, 1998 and 2000; Barros et al., 2001a). Zeolites are an appropriate material for removing heavy metal ions from wastewater because of their relatively low price coupled with the harmlessness of their exchangeable ions. One of the most pollutive heavy metals is chromium, which finds its way into bodies of water through wastewaters from iron and steel manufacturing, chrome leather tanning and other industrial sources. Due to its toxic effects on the environment, there is a constant need to remove chromium ions from industrial effluents (Barros et

al., 2001a). Removal of chromium from wastewater is most often accomplished by precipitating its hydrous oxides (Fabiani et al., 1996); however, application of this method becomes costly at lower concentrations of this cation. Therefore, the use of zeolites as ion exchangers is an attractive means of Cr³⁺ removal from wastewater, both in terms of removal ability and cost effectiveness.

Of the various zeolites available, synthetic faujasites meet the requirements of good selectivity and cation exchange capacity. Y and X zeolites, isomorphs of the mineral faujasite, have an open, negatively charged framework (Giannetto et al., 2000). The exchangeable cations can be located at various sites. Some of these sites, located in α and β cages, are easily accessible, whereas others, located in hexagonal prisms, have balancing cations which are exchanged under extremely

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favorable conditions. The limited dimensions of the apertures, which control access to these small cavities, are frequently given as a limiting factor of the ion exchange reaction (Giannetto et al., 2000).

While knowledge of the uptake of chromium species by zeolites is increasing (Tagami et al., 2001; Custódio et al., 1998; Barros et al., 2001b; Pansini et al., 1991), relatively little is known about the combined effects of two or more metals and simultaneous removal of metal ions by multicomponent ion exchange (Arroyo et al., 2000). Single-ion exchange cannot define exactly the multicomponent behavior of the metal mixtures (Arroyo et al., 2000; Barros et al., 2001c). For this reason, better accuracy can be achieved for using competitive breakthrough curves. Competition between different metal species for exchangeable sites depends on their ionic characteristics. The preference of the zeolite for one cation rather than another in a multicomponent system depends on the Si/Al ratio, the exchangeable cation of the starting zeolite (co-ions), the hydration ratio of the co-ion and the in-going ions as well as temperature and the three-dimensional zeolite framework. Therefore, these features should be analyzed for a better understanding of the multicomponent ion exchange mechanism.

In a lot of wastewater containing chromium ions, the monovalent K^+ ion and also divalent ones such as Ca^{2+} and Mg^{2+} are commonly found. Thus, the affinity of each cation for NaY and NaX zeolites should be evaluated. The goals of the present work were to study the ability of these zeolites to remove Cr^{3+} from Cr/K, Cr/Ca and Cr/Mg binary solutions through fixed-bed columns and to compare the influence of each competitive cation in the ion exchange mechanism.

EXPERIMENTAL SECTION

Zeolites

The initial NaY and NaX zeolites were highly crystalline. NaY has the unit cell composition of $Na_{51}(AlO_2)_{51}(SiO_2)_{141}$ on a dry basis and a cation exchange capacity (CEC) of 3.90 meq/g, whereas NaX zeolite has a unit cell composition of $Na_{81}(AlO_2)_{81}(SiO_2)_{111}$, which corresponds to a cation exchange capacity of 5.96 meq/g. In order to obtain, as much as possible, the homoionic sodium form, the zeolites, as received, were mixed with a 1 mol/L solution of NaCl four times at 60°C. Then, each time the samples were washed with 2 L of hot deionised water and oven-dried at 100°C. For the dynamic runs, the zeolites were pelletized and NaY or NaX pellets with the average diameter size of 0.180 mm

previously the recommended as the optimal particle size for this fixed-bed system were subsequently screened and collected (Barros et al., 2001b).

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 deionized water to prepare chromium solution as well as binary solutions with a constant equivalent 1:1 metal/metal ratio. The concentration used was based on the natural wastewater from tanning baths after precipitation of chromium with ammonium hydroxide up to pH = 8, which is 18 ppm of chromium (Barros et al., 2001b).

Ion Exchange Unit

The laboratory unit shown in Figure 1 was built in order to study the dynamic ion-exchange mechanism.

The ion-exchange column consisted of a clear glass tube 0.9 cm ID and 30 cm long, which contained the parent zeolite on a bed of glass beads. The column was connected to heat exchanger equipment that maintained the entire system at 30°C. For the single chromium runs the column was filled with 3.00 g of NaY or NaX. For the binary runs, the zeolite fixed bed was composed of 1.60 g of NaY or 1.04 g of NaX. These differences in mass contents for the competitive systems provided the same cation exchange capacity making possible the evaluation and comparison of both zeolites. The bed heights for the single runs were 10.1 cm for the NaY bed and 9.0 cm for the NaX bed. For the binary runs, the average bed height in all NaY runs was about 5.7 cm, whereas the bed height in the NaX runs was about 3.3 cm. Before starting the runs, the zeolite bed was rinsed by pumping deionized water up through the column. Rinsing was stopped when no air bubbles could be seen rising in the column. After accommodation of the bed the rest of the column was filled with glass beads, and then the ion exchange was started by continuous upward pumping of the chromium solution. The flow rate was adjusted to 9 mL/min as this condition minimizes the mass transfer resistances for chromium ion exchange (Barros et al., 2001b). Samples were taken at the column outlet at regular intervals. All breakthrough curves were plotted, taking into account the cation concentration in the outlet samples as a function of running time (C/C_0 versus t).

The amount of ion exchanged was determined by atomic absorption spectrometry using a Varian SpectrAA10-Plus spectrometer. The standards employed were prepared from stock solutions, and the samples from both zeolitic systems were analyzed after the necessary dilutions.

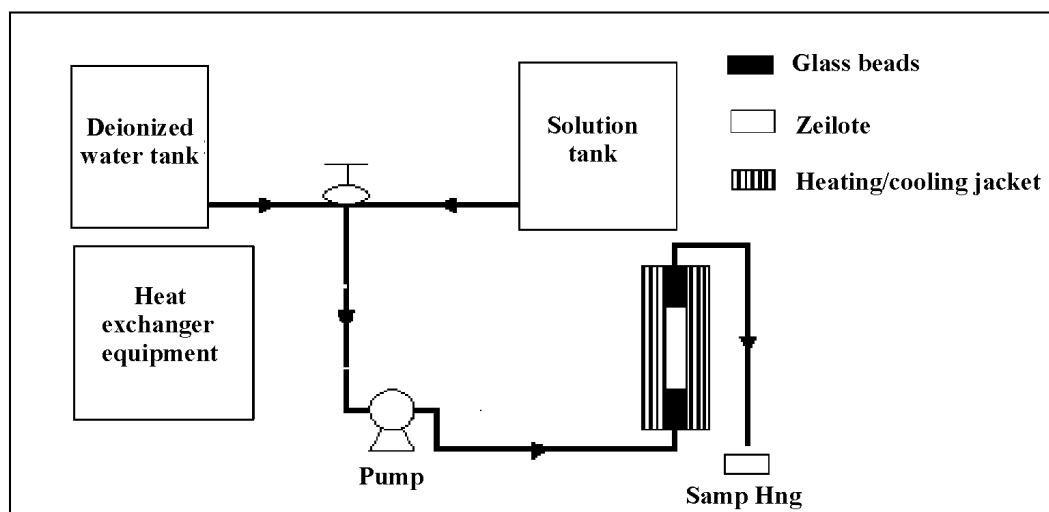


Figure 1: Flow diagram for dynamic ion exchange studies.

Methods

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

$$K_c a = \frac{N \cdot u_o}{H_t} \quad (1)$$

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

In fact, Eq. 1 can be used for modeling the breakthrough curves, once the chromium isotherms in zeolites NaX and NaY can be considered irreversible (Tagami et al., 2001; Barros et al., 2001c).

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). Parameter τ is dimensionless time defined as

$$\tau = \frac{u_o C_o \left(t - H_t \frac{\varepsilon}{u_o} \right)}{\rho_p (1 - \varepsilon) H_t W_{sat}} \quad (2)$$

The term $H_t \varepsilon / u_o$ in Eq. 3 is the time required to displace fluid from external voids in the bed, which

is normally negligible. The product $u_o C_o t$ is the total amount of metal fed per unit cross section of the bed up to time t and $\rho_p (1 - \varepsilon) H_t W_{sat}$ is the capacity of the bed, which is equal to the time equivalent to total stoichiometric capacity of the packed-bed tower (t_t).

The time equivalent to usable capacity of the bed (t_u) and the time equivalent to total stoichiometric capacity of the packed-bed tower (t_t) if the entire bed reaches equilibrium are provided by a mass balance in the column (Barros et al., 2001a), and they are easily determined by

$$t_u = \int_0^{t_b} \left(1 - \frac{C}{C_o} \right) dt \quad (3)$$

$$t_t = \int_0^{\infty} \left(1 - \frac{C}{C_o} \right) dt \quad (4)$$

where t_b is the breakpoint time.

In practice, t_b is defined as the time at which the effluent concentration (C) reaches 5% of the influent concentration (C_o).

If time t is assumed to be the time equivalent to the usable capacity of the bed (t_u) up to t_b , parameter τ may be simplified to t_u/t_t (Barros et al., 2001a). The t_u/t_t ratio is the fraction of total bed capacity or length utilized to the breakpoint (Geankoplis, 1993). Hence, the length of unused bed (H_{UNB}) is the unused fraction times the total length (H_t)

$$H_{\text{UNB}} = \left(1 - \frac{t_u}{t_t} \right) H_t \quad (5)$$

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 in evaluation of a column is the average residence time

(\bar{t}) of the fluid in the column. Based on 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 of an age less than t , which is equivalent to C/C_0 for breakthrough curves.

According to Barros et al. (2001a), an indirect measure of how far from the optimum operational condition the column operates is expressed by 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 ideal condition, i.e., the optimal region of operation. Therefore, this difference may contribute to the choice of best operational conditions in the column design (Barros et al., 2001b).

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

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

Finally, the dimensionless variance should be calculated as

$$\sigma_0^2 = \frac{\sigma^2}{\bar{t}^2} \quad (9)$$

Determination of this parameter is useful to estimate the axial dispersion in the packed bed.

Values of dimensionless variance close to zero mean that the behavior of the packed bed is close to that of an ideal plug-flow reactor with negligible axial dispersion.

Finally, the competition for zeolitic sites is well evidenced by the dynamic capacity of the column. Thus, the term U_M^{tb} is defined as the amount of metal ion adsorbed at t_b prior to the breakpoint ($C/C_0 = 0.05$). Integration of areas under the breakthrough curve gives the amount of metal not recovered by the zeolite; based upon the difference in the quantity of metal fed into the column, this value permits determination of the amount retained by the exchanger (Valdman et al., 2001). In order to compare systems with different cation exchange capacities, as in the case of single and competitive systems, U_M^{tb} was divided by the value of CEC for each column.

RESULTS AND DISCUSSION

Figure 2 shows the chromium breakthrough results for the NaY and NaX zeolite columns. Both curves can be considered to be step curves, indicating minimum mass transfer resistances, as already discussed in Barros et al. (2001b). Moreover, it was observed that the breakpoint for the NaY zeolite packed bed occurred earlier, but as both zeolite columns had the same mass contents but not the same cation exchange capacity, it was not possible to draw any conclusions based on column efficiency, only on the breakthrough curves. Quantitative results from data presented shown in Table 1 will be discussed later.

The binary-ion-exchange breakthrough curves generated during the ion exchange of the parent NaY and NaX zeolites are shown in Figures 3 to 5. Different curvature profiles can be seen as a consequence of the affinity of the zeolites for each in-going cation in a competitive system. It can be seen from these figures that the removal of chromium was qualitatively almost the same. The only difference was in the time required to attain the breakthrough point ($Cr/Cr_0 = 0.05$) where $180 \leq t_b < 400$ min, which indicates the influence of the zeolite and also of the competitive Mg^{2+} , Ca^{2+} or K^+ ion. It was observed that in all breakthrough curves for NaY zeolite packed beds, the competing cations started exiting the column earlier than the chromium ions, which indicates that this zeolite has a more dynamic affinity for the trivalent cation. On the other hand, only potassium was released much

earlier from the NaX zeolite column. Therefore, it was possible to be assured that the NaX zeolite preferred the chromium to the potassium cations. For the Cr/Mg-NaX and Cr/Ca-NaX ion exchange systems, saturation of the competing cations and chromium cations started almost simultaneously. Therefore, it was not possible to draw conclusions about the dynamic selectivity only based on the breakthrough curves.

Despite the fact that the NaX and NaY zeolite beds had the same exchangeable sites, it can be observed that the influence of the nature of the zeolite on the different ion exchange mechanisms could be due to the different Si/Al ratios. Although NaX and NaY zeolites are isomorphs, dense sites produced by high aluminum contents in the framework, may alter the interaction of each in-going cation with the zeolitic framework (Rupp, 1996). Therefore, the order of selectivity of NaX, which has a high CEC, was expected to show some differences from the NaY affinity.

The competing in-going ions can alter the ion-exchange mechanism as they may interact with chromium ions, and more importantly to consider that they can be exchanged at the available sites, decreasing chromium uptake. It was interesting to note that in all breakthrough curves, except for those of the Mg/Cr-NaX system (Fig. 3-b), some C/C_0 higher than 1 was observed, which suggests a sequential ion exchange. When the available sites were saturated, chromium ions seemed to displace the competing cations already located in the zeolite, releasing them to the fluid phase. This phenomenon had already been observed in NaA zeolite (Arroyo et al., 2000), coconut carbon (Mohan and Chander, 2001), fungus (Sağ et al., 2000) and even fibrous ion exchangers (Soldatov et al., 1999). Therefore, this sequential ion exchange is also a reasonable explanation for the chromium uptake in X and Y zeolites. The sequential ion exchange probably occurred due to two main factors: the selectivity of the ion exchanger itself and the operational conditions used in the packed bed. Depending on the cation-framework interaction, which takes into account the charge and the hydration energy of the cation and also the CEC of the zeolite, it may prefer one cation over another. Thus, the process parameters were optimized for chromium uptake (Barros et al., 2001b) and the diffusional resistances of the Ca^{2+} , Mg^{2+} and K^+ cations may not be minimized in the same way. The sequential ion exchange observed in the breakthrough curves led us to conclude that all sites available to the competing cation were also available to chromium ions. Finally,

Figures 3-a, 4-a and 5-a show a more pronounced sequential ion exchange for NaY breakthrough curves than for the respective NaX breakthrough curves shown in Figures 3-b, 4-b and 5-b. Therefore, it may be concluded that NaY zeolite has a greater affinity for chromium in competitive systems.

The mass transfer parameters estimated from the breakthrough data are given in Table 1. This table also contains values for the $U_M^{\text{th}}/\text{CEC}$ ratio up to the chromium breakpoint.

Comparing the performance of the NaY and NaX zeolite columns, it can be observed from Table 1 that the length of unused bed as well as the overall mass transfer coefficient for the NaX zeolite columns was more favorable than for NaY zeolite beds in single or competitive systems. The dimensionless variance for both systems generated similar values, which shows that axial dispersion was not strongly affected by the nature of the zeolite or the in-going ions. On the other hand, the operational ratio and mainly the dynamic selectivity show that inclusion of a competing cation altered the exchange mechanism, mainly for the NaX zeolite columns.

It may be observed that there are only small differences in the length of unused bed for the single and competitive breakthrough curves for NaY zeolite columns. For NaX columns $H_{\text{UNB}} = 0.9$ cm was observed for the single chromium breakthrough curve and values approximately 30% higher were observed for competitive systems. Therefore, it may be assumed that the chromium breakthrough was more strongly affected by the presence of a competing cation in NaX zeolite columns. In column design for ion exchange large changes in H_{UNB} values are not recommended because this increases the operating costs. Nevertheless, the values obtained reflected the competition for zeolite sites, which cannot be avoided. The striking feature of Table 1 is that some K_c values for competitive systems are higher than the ones obtained for single exchanges in NaY zeolite columns and lower in NaX zeolite columns. Therefore, it may be assumed that interaction of both in-going ions may alter in different ways the cation diffusion through the film and into the particle of NaY or NaX zeolites. The parameter R for both zeolite columns is greater for competitive systems than for single runs, which clearly indicates the influence of a competitive cation in the ion exchange mechanism. The dimensionless variance (σ_0^2) becomes slightly different for single and competitive runs. This feature emphasizes changes in the uptake mechanism of chromium ions. It is interesting to note that the

operational ratio and the dimensionless variance are higher for Cr/K systems in both zeolite columns. Potassium ions are much smaller than trivalent chromium cations (Nightingale, 1959), which may favor some interaction between them. In fact, the addition of calcium or magnesium to a chromium solution does not significantly alter the velocity profile, as could be expected due to their similar hydration radii (Nightingale, 1959) and hydration energy (Rupp, 1996). The amount of chromium retained in NaY zeolites (U_{Cr}^{tb}/CEC) in competitive

systems is slightly smaller than in single ion-exchange systems. On the other hand, a large decrease in chromium uptake was observed in NaX zeolite. The dynamic selectivity for NaY zeolite should be written as $Cr^{3+} > Mg^{2+}$, $Cr^{3+} > Ca^{2+}$ and $Cr^{3+} > K^+$. For the NaX zeolite systems, it was observed that the sequence of dynamic selectivity up to the chromium breakpoint is $Ca^{2+} \approx Cr^{3+}$, $Mg^{2+} > Cr^{3+}$ and $Cr^{3+} > K^+$. Therefore, it may be concluded that NaX zeolite is not as selective for chromium ions as the zeolite NaY.

Table 1: Mass transfer parameters for the dynamic runs

Ion exchange system	H_{UNB}^* (cm)	K_{ca}^* (min^{-1})	R^*	σ_{θ}^{2*}	U_{Cr}^{tb}/CEC	U_M^{tb}/CEC
Cr-NaY	1.6	17.5	0.1	0.13	0.69	-
Cr/Mg-NaY	1.8	19.6	0.4	0.03	0.54	0.22
Cr/Ca-NaY	1.3	26.1	0.4	0.05	0.51	0.24
Cr/K-NaY	1.6	21.8	0.2	0.20	0.66	0.23
Cr-NaX	0.9	32.3	0.0	0.12	0.71	-
Cr/Mg-NaX	1.1	31.2	0.7	0.02	0.27	0.32
Cr/Ca-NaX	1.1	32.0	0.5	0.08	0.31	0.32
Cr/K-NaX	1.3	27.6	0.8	0.10	0.41	0.35

U_{Cr}^{tb}/CEC = ratio of chromium uptake up to the chromium breakpoint time (t_b) and the cation exchange capacity of the column

U_M^{tb}/CEC = ratio of the competing cation (Mg^{2+} , Ca^{2+} , K^+) uptake up to the chromium breakpoint time (t_b) and the cation exchange capacity of the column

*Related to chromium ions

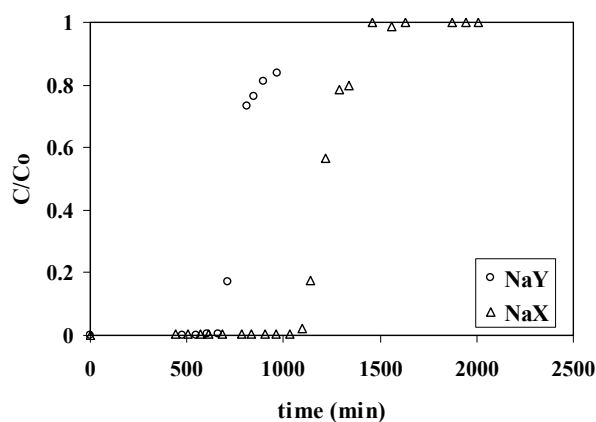
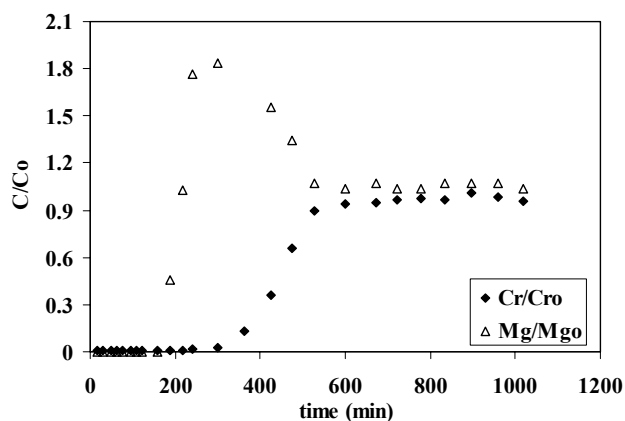
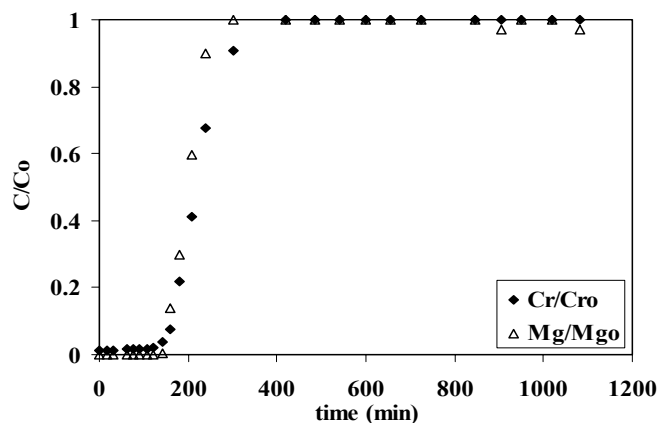


Figure 2: Single breakthrough curves for chromium exchange

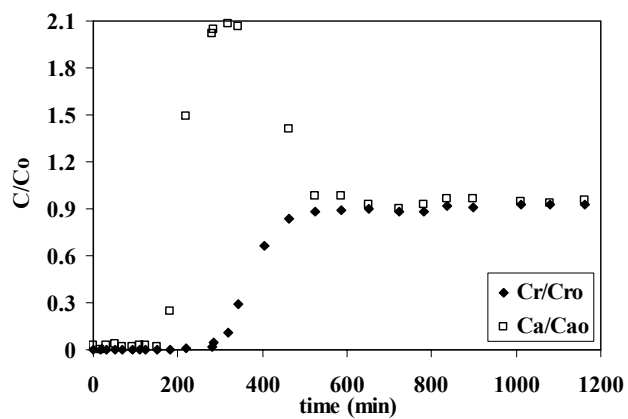


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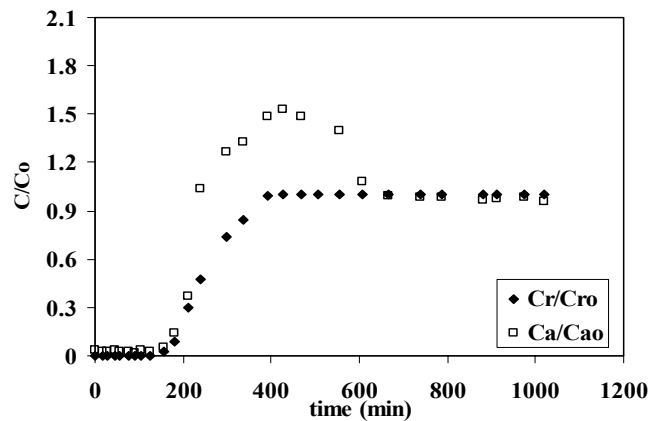


b)

Figure 3: Breakthrough curves for the Cr-Mg competitive system: a) NaY, b) NaX

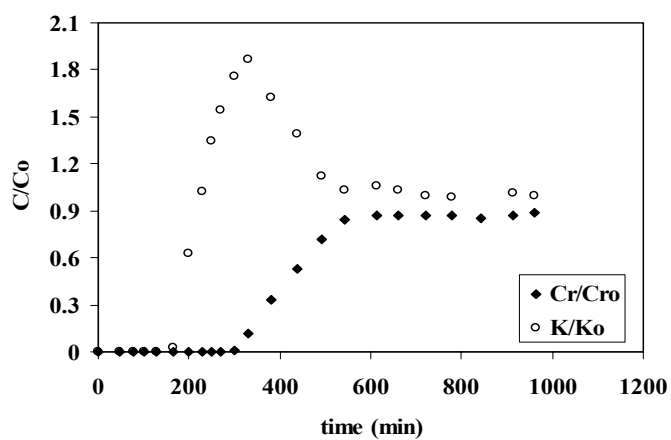


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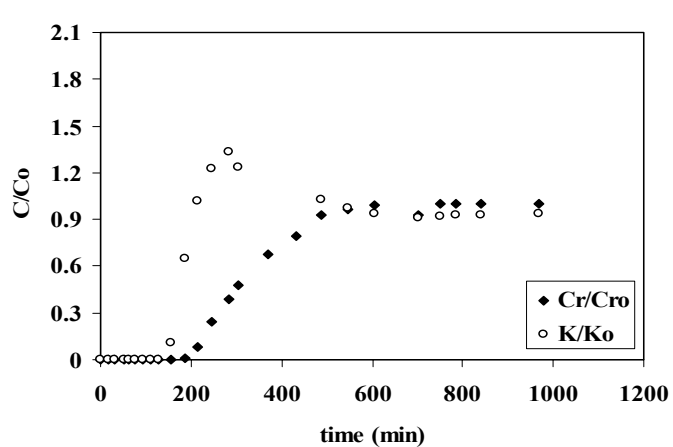


b)

Figure 4: Breakthrough curves for the Cr-Ca competitive system: a) NaY, b) NaX



a)



b)

Figure 5: Breakthrough curves for the Cr-K competitive system: a) NaY, b) NaX

CONCLUSIONS

In this work, trivalent chromium uptake by NaY and NaX zeolites in binary systems was studied. It was demonstrated that the breakthrough curves for competitive cations generally show C/C_0 values higher than one, due to a sequential ion exchange where chromium ions were able to replace the competing cation already exchanged at the sites. Extension of this phenomenon depended on the nature of the competitive cation and also on the selectivity of the zeolite.

For single runs NaY or NaX zeolite could be used as it retained the same amount of chromium ions with negligible values of operational ratio and dimensionless variance. Differences in length of unused bed and overall mass transfer coefficient did not contradict earlier conclusions.

For competitive runs, the length of unused bed and the operational ratio were influenced much more by competitive systems for NaX zeolite, and neither the overall mass transfer coefficient nor the dimensionless variance was strongly affected. The presence of potassium ions interfered more in the axial dispersion of the fluid than the presence of calcium or magnesium, probably due to some interaction with chromium ions. Chromium uptake decreased significantly in competitive systems in NaX zeolite beds, but only small differences were observed in NaY zeolite. The order of dynamic selectivity for NaY was $Cr^{3+} > Mg^{2+}$, $Cr^{3+} > Ca^{2+}$ and $Cr^{3+} > K^+$ and for NaX it was $Ca^{2+} \approx Cr^{3+}$, $Mg^{2+} > Cr^{3+}$ and $Cr^{3+} > K^+$. Therefore, NaY zeolite was more efficient for chromium uptake when the competing Mg^{2+} , Ca^{2+} or K^+ cation was present.

NOMENCLATURE

CEC	Cation exchange capacity (meq/g)
C/C_0	Concentration in the fluid relative to that in the feed
C_0	Initial concentration of the fluid (g / L)
F(t)	Weight fraction of the effluent of an age less than t
H_t	Bed length (cm)
H_{UNB}	Length of unused bed (cm)
K_{ca}	Overall volumetric coefficient (min^{-1})
N	Overall number of transfer units
R	Operational ratio
t_b	Breakpoint 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)
\bar{t}	Average residence time (min)
U_{Cr}^{tb}	Chromium uptake up to the chromium breakpoint time (meq)
U_M^{tb}	Competing ion uptake up to the chromium breakpoint time (meq)
u_o	Superficial velocity of fluid (cm/min)
W_{sat}	Ion exchange loading at equilibrium with the fluid (g metal / g zeolite)
ϵ	External void fraction of the bed
ρ_p	Particle density (g / cm^3)
τ	Dimensionless time
σ^2	Variance (min^2)
σ_θ^2	Dimensionless variance

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