

Binary and Ternary Dynamic Cation Exchange in NaA Zeolite Paper CIT02 0673

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Abstract. In this paper it was analyzed the chromium ion exchange in NaA zeolite in the presence of cations Mg^{2+} , Ca^{2+} and K^+ . Multicomponent ion exchange were studied in two groups: binary solutions (Cr/Mg, Cr/Ca and Cr/K) and ternary solutions (Cr/Mg/Ca, Cr/Mg/K and Cr/Ca/K). Mass transfer and operating parameters were obtained such as length of unused bed, overall mass transfer coefficient and dimensionless variance. It was concluded that the presence of the competing ions alters the exchange behavior and at least a binary solution must be considered in designing a packed bed to treat industrial wastewater. The presence of Ca^{2+} and Mg^{2+} ions decrease chromium uptake in a higher extension than the presence of K^+ ions.

Keywords: zeolite, NaA, dynamic ion exchange, chromium

1. Introduction

It is well known that heavy metals are very toxic elements and their discharge into receiving water causes detrimental effects on human health and on the environment. One of the most important toxic metals, chromium, finds its way to bodies of water through wastewaters from iron and steel manufacturing, chrome leather tanning, chroming plating and others anthropogenic sources. For this reason there is a constant need to remove chromium from industrial effluents. Effects of acute chromium poisoning in humans are very serious, including lung cancer (Barros et al., 2001a).

Chromium (III) salts and sulfur compounds are the main pollutants released in tannery wastewaters and in the atmosphere. The function of chromium salts in tanning processes is to form, through complexation with the polypeptide collagen components of leather, a protective layer that prevents the penetration of water in the leather pores avoiding putrefaction. As far as the chromium salts is concerned, the tanning process consumes only 60% of the chromium of the tanning bath (Fabiani et al., 1996) and the possibility of recover the residual metal represents a main goal in the processes.

Chromium removal from tanning wastewater is usually achieved by precipitation as hydroxide upon addition of lime or soda and subsequent sedimentation by the use of a coagulant. After precipitation and filtration, the residual solution still contains a chromium content considered deleterious to the environment. An alternative system of cation removal from this residual solution is represented by ion exchange, which usually allows good performances, reasonable costs and sometimes, metal recover. The main limiting condition is selectivity, but also ion exchange kinetics, cation exchange capacity and cost are unnegligible choice factors.

Among the various available cation exchangers, zeolites meet the requirements of good selectivity and acceptable capacity. The preference of the zeolite to one cation instead of another takes into account the Si/Al ratio, the exchangeable cation of the starting zeolite (co-ions), the hydration ratio of both co-ion and in-going ion as well as temperature and three dimensional channel system of zeolite framework.

Zeolite 4A is widely produced as a detergent builder, has defined chemical composition and high and constant cation-exchange capacity. The aluminosilicate framework of zeolite A includes truncated octahedron (β -cage), which encloses a cavity with a free diameter of 6.6 Å. The center of the unit cell is a large cavity (α -cage), which has a free diameter of 11.4 Å (Giannetto et al., 2000). In recent years an increasing number of studies have been made of the ion exchange properties of this zeolite with Cd^{2+} , Ca^{2+} and Mg^{2+} solutions (Biskup and Subotic, 1998; Barri and Rees, 1980; Franklin and Townsend, 1985). Attempts to exchange with trivalent cations were unsuccessful in NaA (Breck, 1974) but studies concerning chromium ion exchange in NaA are really rare and are not investigated sufficiently. In Cr-NaA exchange, a high selectivity should be expected because the cavities may accommodate many in-going ions. On the other hand, some steric problems should be evidenced because of the large Cr^{3+} hydrated ratio of 4.61Å according to Nightingale (1959).

Although some studies have exhibited high selectivity towards heavy metal ions, they also showed that the exchange behavior is hardly influenced by the presence of two or more in-going cations (Barri and Rees, 1980; Franklin and Townsend, 1985), which may compete for the same sites. As a matter of fact, multicomponent systems are

characterized by additional features besides those of single components. There are interaction effects among different species in solution and interactions between cations and sites depending on the ion exchange mechanism. Competition of different metal ion species for the sites will occur and will depend on the ionic characteristics. Individual ion exchange parameters cannot define exactly the multicomponent exchange behavior of the metal mixtures (Arroyo et al., 2000). For that reason, better accuracy may be achieved by using competitive systems containing chromium. Therefore, the study of binary and ternary ion exchange is important in order to evaluate the real selectivity towards this cation allowing the application of NaA zeolite fixed bed in tannery wastewater treatment.

Therefore, this work aims to analyze the NaA multicomponent ion exchange towards Cr^{3+} in the presence of Ca^{2+} , Mg^{2+} and K^+ , which are the main cations found in the effluents of tannery industries (Barros, 1996).

2. Experimental Section

2.1. Materials.

The starting zeolite was a very high crystalline NaA, Advera 401, provided by PQ Corporation which has the unit cell composition $Na_{90}(AlO_2)_{90}(SiO_2)_{102}$ in dry basis. In order to obtain, as far as possible, the homoionic sodium form, the zeolite, as received, was contacted four times with 1 Mol/L solutions of NaCl at 60°C. The zeolite was then washed with 2 L of hot deionised water and oven-dried at 100°C. The NaA zeolite was pelletized and subsequently screened and collected in the average diameter of 0.180 mm as this condition minimizes mass transfer resistances (Barros et al., 2001b). Finally the particle samples were fluidized to remove fines. The reagents $CrCl_3 \cdot 9H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$ and KCl were mixed with deionised water to prepare single solutions, binary (Cr/Mg, Cr/Ca, Cr/K) and ternary solutions (Cr/Ca/Mg, Cr/Ca/K, Cr/Mg/K). The concentration of chromium used was based in the natural wastewater from tanning baths after precipitation with a ammonium hydroxide up to pH = 8. According to Barros (1996) the final chromium concentration in this natural solution is approximately 18 ppm. For the other cations it was kept an equivalent ratio of 1:1.

2.2. Dynamic Ion Exchange.

A laboratory unit has been built, as schematically shown in Figure 1, in order to investigate the dynamic ion exchange mechanism.

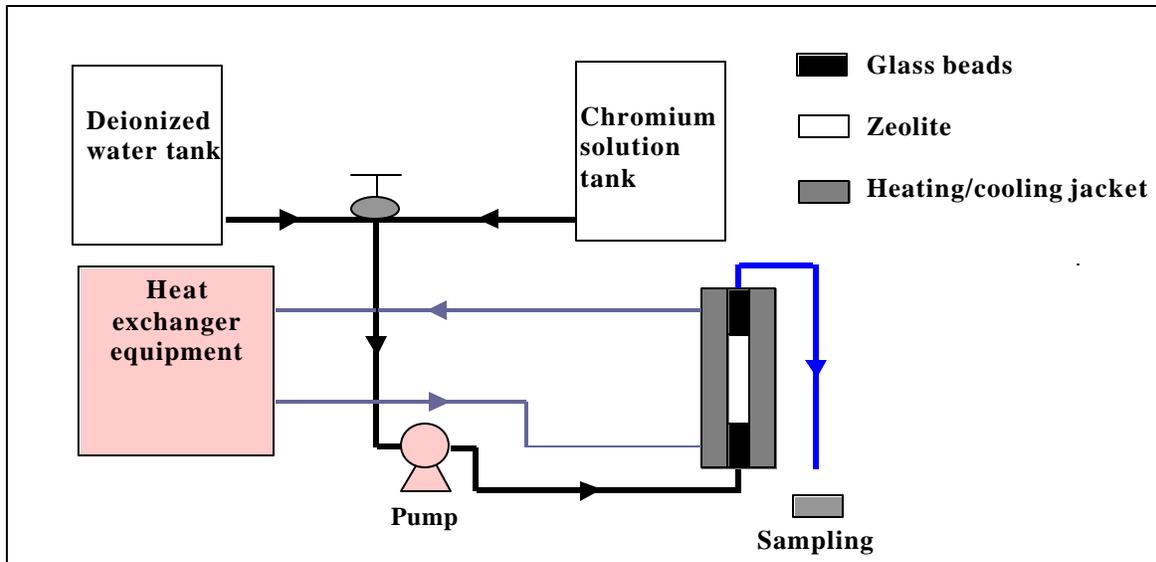


Figure 1: Flow diagram for dynamic ion exchange studies.

The ion exchange column consisted of a clear glass tube 0,9 cm ID and 30 cm long and contained the parent zeolite supported by glass beads. The column is connected to heat transfer equipment that maintains all system at 30°C. Zeolite fixed bed was composed by 3.0 g of NaA for single solutions or 0.96 g for binary and ternary solutions. The mass of 0.96 g was calculated from the breakthrough curves of single solutions using an estimation of a break-point time of 3h according to the method proposed by Geankoplis (1993). Before starting the runs, zeolite bed was rinsed by pumping deionised water up flow 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 the chromium solution also up flow. The flow rate was adjusted to 9 mL/min as this condition minimizes the mass transfer resistances for chromium ion exchange (Zola et al., 2001). Samples at the column outlet were taken

regularly and their concentrations were analyzed by the atomic absorption using a Varian SpectrAA 10 plus spectrophotometer. All breakthrough curves were plotted taking into account the chromium concentration in the outlet samples as a function of the running time (C/Co versus t).

2.3. 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 volumetric coefficient (Kca) obtained from a solute material balance in the column as proposed in McCabe et al. (1985):

$$Kca = \frac{N u_o}{Ht} \tag{1}$$

where N = overall number of transfer units, Ht = bed length and uo = superficial velocity of fluid.

As shown in McCabe et al. (1985) the overall number of transfer units may be obtained graphically by plotting C/Co versus N(τ-1). The parameter τ is the dimensionless time and it can be defined as:

$$t = \frac{u_o C_o \left(t - Ht \frac{e}{u_o} \right)}{r_p (1-e) Ht W_{sat}} \tag{2}$$

where $Ht e/u_o$ is the time to displace fluid from external voids in the bed (normally negligible), $u_o C_o t$ is the total solute fed to a unit cross section of bed up to time t and $r_p (1-e) Ht W_{sat}$ 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 tower (tt).

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

$$tu = \int_0^{t_b} \left(1 - \frac{C}{C_o} \right) dt \quad \text{and} \quad tt = \int_0^{\infty} \left(1 - \frac{C}{C_o} \right) dt \tag{3}$$

where t_b is the break-point time at C/Co=0.05.

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

$$H_{UNB} = \left(1 - \frac{tu}{tt} \right) Ht \quad \text{and} \quad \% H_{UNB} = \left(1 - \frac{tu}{tt} \right) 100 \tag{4}$$

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.

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

$$\bar{t} = \int_0^{\infty} t dF(t) \tag{5}$$

where F(t) is the weight fraction of the effluent with an age less than t, which is equivalent to C/Co for breakthrough curves.

An indirect measure of how far from the optimum operation condition the column is running is described by:

$$R = \left| \frac{\bar{t} - tu}{tu} \right| \tag{6}$$

Values of parameter R close to zero indicate that the operational conditions imposed are near the ideal condition,

that is, the optimal region of operation. Therefore, this difference may contribute to choose the best operation conditions in the column design (Barros et al., 2001b).

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

$$S^2 = \int_0^{\infty} t^2 \left(\frac{F(t)}{dt} \right) dt - \bar{t}^2 \quad (7)$$

Finally, the dimensionless variance should be calculate as:

$$\left(S_q^2 = \frac{S^2}{\bar{t}^2} \right) \quad (8)$$

The determination of this parameter is useful to estimate the dispersion in the packed bed. Values close to zero mean that the packed bed behaves close to an ideal plug flow reactor with negligible axial dispersion.

3. Results and Discussion

The preliminary stage of the investigation was devoted to the evaluation and comparison of the cations in single solutions. The respective breakthrough curves are presented in Figure 2.

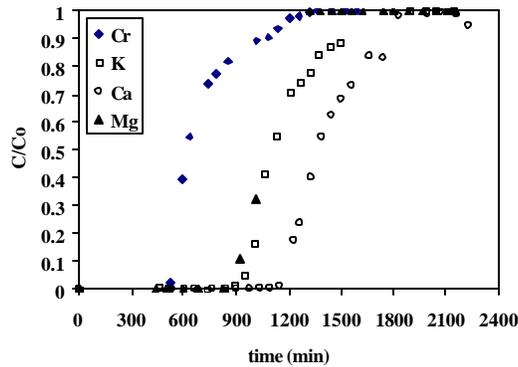


Figure 2: Breakthrough curves for Cr³⁺, Mg²⁺, Ca²⁺ and K⁺ ions

It can be seen that the breakthrough curve for chromium ions reaches to earlier than the other cations. This phenomenon could be related to the difficulty of this hydrated cation in diffusing through the apertures and accommodate in the cages. Calcium, magnesium and potassium ions are smaller and possibly the steric hindrance experienced by the chromium ions are, for these cations, less important. It was also observed in Figure 2 almost parallel concentration profiles, which could be associated to similar mass transfer resistances, mainly for Mg²⁺, Ca²⁺ and K⁺ ions.

From the breakthrough curves showed in Figure 2 and Eqns. 1 to 8 it was possible to estimate the mass transfer parameters, which are presented in Table 1.

Table 1: Mass transfer parameters estimated for single cation exchange in NaA

Exchange	%H _{UNB}	Kca (min ⁻¹)	Retention (meq _{cation} /meq _{Al})	R	S _q ²
Cr-NaA	23.3	15.8	0.255	0.989	0
Mg-NaA	17.1	22.6	0.486	0.074	0.013
Ca-NaA	17.1	22.6	0.353	0.133	0.070
K-NaA	16.9	23.3	0.252	0.367	0

In this table it is also shown the cation retention until the time equivalent to usable capacity of the bed (t_u). This estimation was done through a solute mass balance in the column until t_u. It can be seen that the %H_{UNB} of Mg²⁺, Ca²⁺ and K⁺ ions are very close and less than the numerical value obtained for chromium, which is in accordance with the parallel steepness of the breakthrough curves observed in Figure 2. Furthermore, in total agreement with these results, the overall mass transfer coefficient is lower for Cr-NaA exchange when compared to the other ion exchange curves. Concerning the removal of the in-going ion, it is observed distinct values that reflects the affinity of the zeolite towards these cations. The dynamic selectivity, based on the cation uptake until t_u, should be written as K⁺ < Cr³⁺ < Ca²⁺ < Mg²⁺. This results agree with the equilibrium selectivity obtained for batch isotherms still unpublished. These findings

made us conclude that, although dealing with different systems, that is, a continuous flow or a batch reactor, the sequences are not changed when there is no competition due to single exchanges. Concerning the ratio R it is observed that the values obtained for Mg^{2+} , Ca^{2+} and K^+ ions are lower than the value observed for chromium, which means that 9mL/min and 0.180mm are also the optimized conditions for these cations. The values of the dimensionless variance close to zero are in accordance to these findings.

Competitive breakthrough curves for binary solutions Cr-Mg, Cr-Ca and Cr-K are shown in Figure 3.

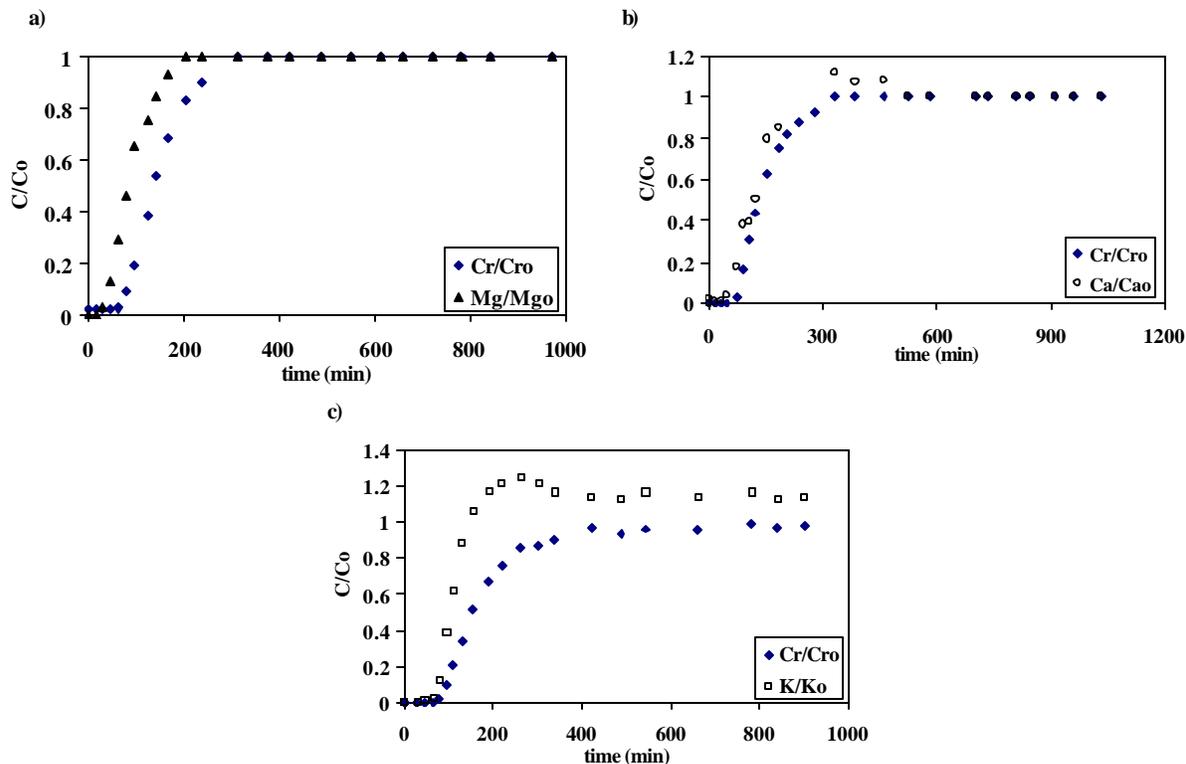


Figure 3: Competitive breakthrough curves for binary solutions: a) Cr-Mg, b) Cr-Ca and c) Cr-K

Concerning Figure 3 one can note that in the three cases studied the breakthrough curve of the competitive cation (Mg^{2+} , Ca^{2+} and K^+) reaches the breakthrough earlier than the chromium breakthrough, which is different when these results are compared to the single ion exchange shown in Figure 2. On the other hand, these findings reflect the affinity sequence obtained for equilibrium studies through batch isotherms, where Cr^{3+} ions are more selective than each competitive cation in binary solutions (Barros et al., 2002). Therefore, it is evidenced the importance of the competition of both cations to the zeolite sites. Probably the interaction of both in-going ions (Helferich, 1962) must be considered as well. It is noteworthy that some K/K_o (Fig. 3-c) points are higher than 1, which suggests a sequential ion exchange. Chromium ions, after the saturation of the available sites, are able to exchange the competitive ions already sited in the zeolite (Arroyo et al., 2000). It is also interesting to note that the closest curves are exactly Cr-Mg-NaA and Cr-Ca-NaA ion exchange. Actually this zeolite has been applied as a builder in detergents due to its high exchange selectivity for the so called “hardness ions” calcium and magnesium. Probably, when the removal of chromium is considered, the presence of these ions will promote a decrease in the zeolite selectivity towards the trivalent cation, providing a more competitive exchange than Cr-K systems.

The mass transfer data related to the breakthrough curves of binary solutions are shown in Table 2. As it could be expected, the parameters analyzed have very different values when compared to single cation exchanges presented in Table 1. Firstly one can note that approximately 50% of the height of the column is referred as unused bed ($\%H_{UNB}$). In a column design it is not good to have such high percentages because it increases the costs of the operating process. The obtained values also reflect the importance of the competition towards the zeolite sites in the packed bed. Therefore, when designing an ion exchange column to remove chromium from an industrial wastewater one must keep in mind the competitive behavior. Also concerning Table 2, the striking feature is that K_{ca} values are higher than the ones obtained for single exchanges, which, at a first glance, is incompatible with high $\%H_{UNB}$. High K_{ca} values mean negligible mass transfer resistances, which should generate a small-unused bed height. Possibly this theory is valid only for single exchange. In binary exchange, the interaction of both in-going ions may promote a less overall mass transfer resistance. According to this point of view high $\%H_{UNB}$ values may reflect the difficulty in the exchange itself, although high K_{ca} values indicate the facility in diffusing through the film and into the particle. The competition towards the sites is better evidenced considering the small amount of chromium and competitive cation retention, much less than the respective

retention in single breakthrough curves. It interesting to note that the dynamic selectivity is $Cr^{3+} \approx Mg^{2+}$, $Ca^{2+} \approx Cr^{3+}$ and $Cr^{3+} > K^+$, which is also in agreement with the selectivity provided by batch isotherms ($Cr^{3+} \gg Mg^{2+}$, $Cr^{3+} > Ca^{2+}$ and $Cr^{3+} > K^+$ - Barros et al., 2002). Differences in the magnitude order of selectivity may be explained due to distinct systems where the experiments were done. While the dynamic runs were taken under continuous flow the isotherms were construct in batch systems, providing significant differences in the diffusive features mainly in the presence of competitive in-going cations. The competition in the sites must also be considered. Results to be published demonstrate that chromium and calcium ions prefer to be exchanged in the sites located in the β -cages whereas Mg^{2+} and K^+ are supposed to be found preferentially in the α -cages. Therefore, in competitive runs chromium uptake has a higher interference in Cr-Ca systems. The ratio R presents very high values as a consequence of high discrepancies between the average residence time and the required used capacity of the column. The dimensionless variance reflects deviations from a plug flow reactor and an increase in the axial dispersion.

Table 2: Mass transfer parameters estimated for binary cation exchange in NaA

Exchange	%H _{UNB}	Kca (min ⁻¹)	Retention of Cr (meq _{cation} /meq _{Al})	Retention of C* (meq _{cation} /meq _{Al})	R**	S _q ^{2**}
Cr-Mg-NaA	51.38	29.26	0.100	0.098	1.201	0.162
Cr-Ca-NaA	46.26	31.15	0.111	0.115	1.021	0.171
Cr-K-NaA	48.66	30.90	0.149	0.104	1.587	0.602

*C=Mg²⁺, Ca²⁺, K⁺

** Related to chromium ions

Considering the ternary solution, the respective breakthrough curves are shown in Figure 4.

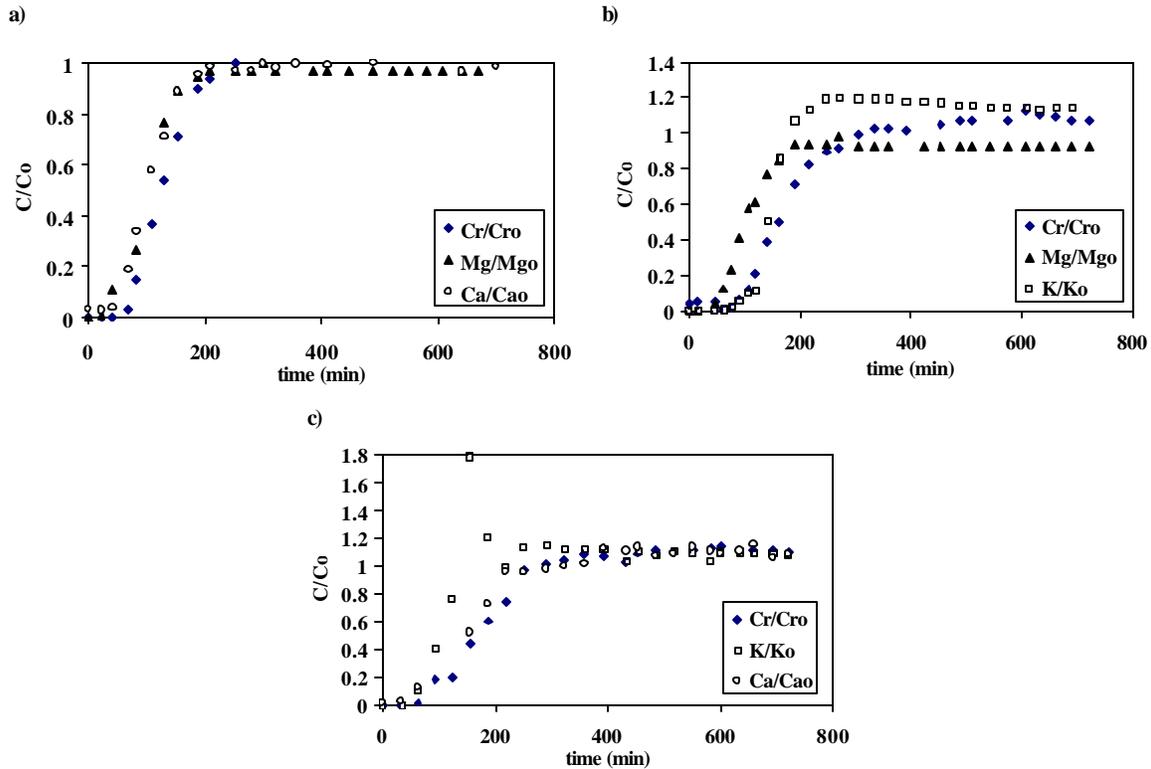


Figure 4: Competitive breakthrough curves for ternary solutions: a) Cr-M g-Ca, b) Cr-Mg-K and c) Cr-Ca-K

Concerning Figure 4 it is possible to note that in the cases analyzed the breakthrough curve of the competitive cation are more similar to the binary breakthrough curves than to the single ones, evidencing the pronounced competition to the sites. Comparing Figures 3 and 4 one can observe that the ternary system reaches tb earlier as more cations are involved in the exchange. Once again some K/Ko (Fig. 4-b and 4c) values are higher than 1, indicating the sequential exchange in the same way as it happens in the binary breakthrough curves. Probably, K⁺ is much less selective and Ca²⁺ and Mg²⁺ are as selective as Cr³⁺ ions because no Mg/Mgo or Ca/Cao points greater than 1 is evidenced.

From the available data provided by the ternary breakthrough curves, it was estimated the mass transfer parameters shown in Table 3. One can note that, concerning the %H_{UNB} values, they are also close to 50%, indicating that probably the addition of a second competitive ion does not alter significantly the competition towards the NaA sites.

In agreement with the behavior observed for %H_{UNB} and Kca in binary ion exchange, the overall mass transfer coefficient for ternary exchange has again approximately the same values. Thus, the film and particle resistances are not very different and, when designing a NaA ion exchange column, a binary breakthrough curve is sufficient to estimate even a ternary ion exchange because chromium is retained in practically the same amount. In the absence of a competition (as it is shown in Table 1) it can occupy all available sites and that is why it is much more exchanged. In a multicomponent (binary or ternary) ion exchange, Cr³⁺ ions are able to occupy specific sites, after some effort of losing part of the hydration sphere. On the other hand, the retention of the competitive cation is changed at each breakthrough curve and the removal is also different if compared to the binary runs. It may be concluded that probably these cations may compete to the same sites or the interaction of these in-going ions strongly affects the ion exchange mechanism. Considering the dynamic selectivity provided by the cation uptake one can note that Mg²⁺ < Cr³⁺ < Ca²⁺, Mg²⁺ < K⁺ < Cr³⁺ and K⁺ ≈ Ca²⁺ < Cr³⁺. These sequences do not follow the binary affinity order and are also different from the selectivity obtained for batch systems (Barros et al., 2002). Such differences may reflect the distinct diffusivities provided by continuous and batch systems, which may alter the competition mainly towards the sites located in the β-cages where Cr³⁺ and Ca²⁺ ions are preferentially exchanged. Once again the ratio R is far from the required behavior (R ~ 0) where the average residence time is close to the time equivalent to usable capacity of the bed although no huge differences are seen when it is compared to the ratio obtained for binary runs. It seems that the presence of a third cation does not alter significantly diffusion properties as already discussed. The dimensionless variance does not change as well, following the same tendency of the other parameter analyzed.

Table 3: Mass transfer parameters estimated for ternary cation exchange in NaA

Exchange	%H _{UNB}	Kca (min ⁻¹)	Retention of Cr (meq _{cation} /meq _{Al})	Retention of C [*] (meq _{cation} /meq _{Al})	Retention of C ^{**} (meq _{cation} /meq _{Al})	R ^{***}	S _q ^{2***}
Cr-Mg-Ca-NaA	43.82	31.56	0.105	0.088	0.130	0.840	0.113
Cr-Mg-K-NaA	45.60	31.60	0.136	0.111	0.123	0.926	0.290
Cr-Ca-K-NaA	58.61	24.58	0.101	0.098	0.097	1.510	0.110

*C= related to the first competitive cation (Mg²⁺ or Ca²⁺)

**C= related to the second competitive cation (Ca²⁺ or K⁺)

*** Related to chromium ions

4. Conclusion

The findings reported herein showed that NaA displays a high selectivity towards chromium ions although the presence of competitive cations may alter the behavior of single ion exchange. The presence of K⁺ ions provides a sequential ion exchange where Cr³⁺ ions are able to exchange the Na⁺ ions presented in the zeolite and the competitive cation already located in the sites. It was also shown that when designing ion exchange packed beds, the competition of the other cations presented in the effluent must be considered as they increase significantly some important parameters such the unused bed length (up to 50%) and the overall mass transfer coefficient. Probably the presence of two or three competitive cations is able to decrease the film and particle resistances due to their own interaction although they compete to the zeolite sites. On the other hand, it is supposed that, in competing conditions, the chromium ions could be exchanged just in some specific sites due to steric problems. Furthermore, chromium ion seems to be as selective as Ca²⁺, more selective than Mg²⁺ and much more selective than K⁺, in the imposed operating conditions.

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