Acta Scientiarum

http://www.uem.br/acta
ISSN printed: 1806-2563
ISSN on-line: 1807-8664
Doi: 10.4025/actascitechnol.v36i2.18124

Evaluation of NaX and NaY packed beds for chromium uptake from multicomponent solution

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ABSTRACT. In this paper the removal of chromium from Cr/Ca/Mg/K and Cr/Ca/Mg/K/Na solutions was investigated in NaX and NaY packed beds. The breakthrough curves presented some overshooting phenomena where chromium ions displaced the previous exchanged cations. Length of unused bed, overall mass transfer coefficient, operational ratio and dimensionless variance were obtained. According to such mass transfer parameters it was concluded that the chromium uptake is influenced by the competition and interaction of the entering ions. Such influences were verified through some differences in the dynamic selectivity obtained for each system. NaY seemed to have a higher affinity towards Cr^{3+} and its sites were more efficiently used in the ion exchange process.

Keywords: zeolite, breakthrough, multicomponent, ion exchange.

Avaliação do processo de remoção do cromo em solução multicomponente em colunas de leito fixo utilizando as zeólitas NaX e NaY

RESUMO. Neste artigo, a remoção do cromo foi investigada nas seguintes soluções multicomponentes: Cr/Ca/Mg/K e Cr/Ca/Mg/K/Na utilizando as zeólitas NaX e NaY em colunas de leito fixo. As curvas de ruptura mostraram que os íons de cromo deslocaram os cátions trocadores. Os parâmetros como zona de transferência de massa, o coeficiente global de transferência de massa, a relação operacional e variância adimensional foram obtidos. De acordo com estes parâmetros de transferência de massa, concluiu-se que a adsorção de cromo foi influenciada pela competição e interação dos íons de entrada. Essas influências foram verificadas pelas diferenças da seletividade obtidas para cada sistema dinâmico. A zeólita NaY teve maior afinidade para com o Cr^{3+} e os seus sítios foram mais eficientemente ocupados no processo de troca iônica.

Palavras-chave: zeólita, curvas de ruptura, multicomponente, troca iônica.

Introduction

Rapid industrialization and the increase in the word population have contributed to heavy metal pollution in ecosystems due to their high toxicities. Heavy metals are released in the environment in a number of different ways. Particularly, referring to chromium, sources of this element may be related to iron and steel manufacturing, chrome leather tanning as well as chrome plating. The conventional technique for the removal of chromium is chemical precipitation (KU; JUNG, 2001). The main limitation of this technique is its low efficiency in the removal of trace levels of the cation. Unfortunately, removal of trace levels of chromium ions in wastewater treatment has not received a great attention in the last decades. Nevertheless, increasing contamination of bodies of water has motivated studies of new technologies in the last years. Various treatment processes have been introduced for the removal of metal ions. One of these technologies, called ion exchange, uses resins (FU; WANG, 2011) and zeolite packed beds (LIN et al., 2008, OSTROSKI et al., 2009).

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 ready exchanged with metal cations in solution. Among the various available zeolites, X and Y zeolites, mainly in the sodic form NaY and NaX, meet the requirements of good selectivity and capacity (NIBOU et al., 2010; OSTROSKI et al., 2011; RAO et al., 2006).

Zeolites Y and X are isomorphs of the mineral faujasite. The exchangeable cations can be located on various sites. Some of these sites, in the large α cages, also called supercages, and β cages, or sodalite, are easily accessible, while others are located in the dense cages, denominated hexagonal prisms. The limited dimensions of the apertures, which control access to these small cavities, are frequently given as a factor limiting the ion exchange reaction (GIANETTO et al., 2000).

The preference of the zeolite to one cation instead of another in a multicomponent system takes into account the three-dimensional zeolite framework and the nature of the counter ion (GIANETTO et al., 2000). Particularly, the theoretical cation exchange capacity (CEC) is quite significant in multicomponent exchanging processes. Competition towards the ion exchange process increases with CEC (BARROS et al., 2003). Moreover, the physical and chemical characteristics of the in-going ions such as ionic charge play an important role in the removal mechanism (GOMES et al., 2001; TOWNSEND, 1991) in batch or continuous processes. In dynamic systems, such as packed beds, the ion uptake is also influenced by the operational conditions. Inlet flow rate is one of the parameters that should be considered while investigating the process. In fact, besides the mass transfer itself; the uptake may suffer from non-idealities such as flow channeling or insufficient wetting of the exchanger. For this reason, the column should be operated under up-flow conditions (INGLESAKIS, 2005).

In single conditions, zeolites NaX and NaY exhibited remarkable selectivity for chromium cations (BARROS et al., 2004; BASALDELLA et al., 2007; GAZOLA et al., 2006). Nevertheless, in multicomponent ion exchange processes, it is supposed a lower efficiency due to competition to the sites. Moreover, little is known about the chromium exchange in competing systems (BARROS et al., 2008). Most of industrial wastewaters contain potassium, sodium, calcium and magnesium. Thus, the present work aimed to investigate the removal efficiency of chromium ions presented in the multicomponent systems Cr/Ca/Mg/K and Cr/Ca/Mg/K/Na through NaY and NaX packed beds. It must be emphasized that Na^+ is not exchanged in sodic zeolite but it is a common ion in industrial wastewater. This is the reason why the influence of such ion should be investigated as well.

Material and methods

Zeolites

The starting zeolites were high crystalline aluminosilicates. NaY had the unit cell composition $Na_{51}(AlO_2)_{51}(SiO_2)_{141}$ in dry basis and a theoretical cation exchange capacity (CEC) of 3.90 meq g^{-1}, whereas NaX zeolite had the unit cell composition $Na_{81}(AlO_2)_{81}(SiO_2)_{111}$ that corresponded to a CEC of 5.96 meq g^{-1}. In order to obtain, as far as possible, the pure homoionic sodium form, the zeolites, as received, were contacted four times with 1 Mol L^{-1} solutions of NaCl at 60ºC. The samples were then washed each time with 2 L of hot deionised water and oven-dried at 100ºC. For the dynamic runs, the zeolites were pelletized and NaX or NaY pellets were subsequently 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 (BARROS et al., 2004).

Chemicals and reagents

The reagent-grade $CrCl_3.9H_2O$, $MgCl_2.6H_2O$, $CaCl_2.2H_2O$, KCl and NaCl were mixed with deionised water to prepare the multicomponent solutions with an equal equivalent ratio of all cations (1 meq L^{-1}).

The ion concentration was determined by atomic absorption spectrophotometry. Standards were prepared from stock solutions and the samples were analyzed after incorporating the necessary dilutions. Potassium, sodium and magnesium contents were determined using an air-acetylene flame and calcium and chromium contents were determined by nitrous oxide-acetylene flame.

Ion exchange unit

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

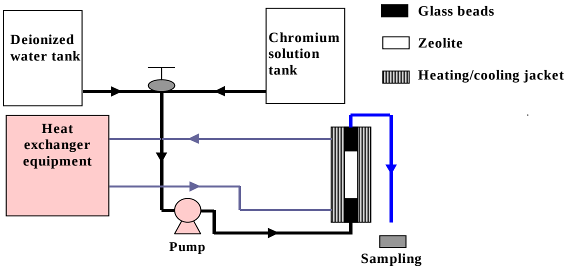


Figure 1. Flow diagram for dynamic ion exchange studies.

The column was connected to the heat-transfer equipment that maintained all system at 30ºC. In order to compare the column efficiency of both zeolites, the bed had the same cation exchange capacity of 6.2 meq g^{-1}. Then, the bed height was 5.4 cm and

3.3 cm for NaY and NaX columns, respectively. 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 inlet solution also up flow, as recommended. The flow rate was adjusted to 9 mL min.$^{-1}$ as this condition minimized the mass transfer resistances for single ion exchange of Cr^{3+} ions (BARROS et al., 2004). Samples at the column outlet were taken regularly. All breakthrough curves were plotted taking into account the cation concentration in the outlet samples as a function of running time (*C/Co* versus *t*).

Methods

In fixed-bed ion exchange, the concentration in the fluid phase and in the solid phase changes with time as well as with position in the bed. The transfer process is described by the overall volumetric coefficient (K_ca) obtained from a solute material balance in the column (McCABE et al., 1993):

$$K_c a = \frac{N.u_o}{H_t} \tag{1}$$

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 $N(\tau\text{-}1)$, where $N(\tau\text{-}1) = 1+ln(C/C_o)$ (McCABE et al., 1993). The parameter τ is the dimensionless time and it can be defined as:

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

where:
$H_t\ \varepsilon\ /\ u_0$ is the time to displace fluid from external voids in the bed (normally negligible), u_oC_ot is the total solute fed to a unit cross section of bed up to time t and $\rho_p(1\text{-}\varepsilon)H_tW_{sat}$ 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 (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 comes to equilibrium are provided by a mass balance in the column (McCABE et al., 1993) and are easily determined by:

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

where:
t_b is the break-point time.

In practice, t_b is defined as the time when the effluent concentration (C) reaches a percentage of the influent concentration (C_o) which is considerable unacceptable, e.g. 5%. In a continuous process such as industrial wastewater treatment, when the column reaches t_b, the operation is stopped and the exchanger is regenerated or replaced by a fresh one. Then, the removal capacity up to breakpoint time was investigated in this work.

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 $t_u\ /\ t_t$ (GAZOLA et al., 2006). The ratio t_u / t_t is the fraction of the total bed capacity or length utilized to the breakpoint (GEANKOPLIS, 2003). Hence, for a total bed length (H_t), the length of unused bed is then the unused fraction times the total length:

$$H_{UNB} = \left(1 - \frac{t_u}{t_t}\right).H_t \tag{4}$$

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.

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 as follows (HILL, 1977):

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

where:
F(t) is the weight fraction of the effluent with an age less than *t*. Such step function is equivalent to C/C_o for breakthrough curves (BARROS et al., 2003).

An indirect measure of how far from the optimum operation condition the column is running is described as the operational ratio (*R*) (PEREIRA et al., 2006):

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

Values of parameter *R* close to zero indicate that the operational conditions imposed are near the ideal condition. Therefore, analysis of R-values may contribute to choose the best operation conditions and to evaluate process performance.

With the average residence time it is also possible to estimate the variance of the sorption step function, that is, the breakthrough curve (PEREIRA et al., 2006):

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

Then, besides determination of non-idealities in reactors, such parameter has been used in the sorption process as well (PEREIRA et al., 2006).

The dimensionless variance should be calculated as (HILL, 1977):

$$\left(\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} \right) \qquad (8)$$

Values close to zero mean that the packed bed behaved close to an ideal plug flow reactor with negligible axial dispersion in the sorption column (PEREIRA et al., 2006).

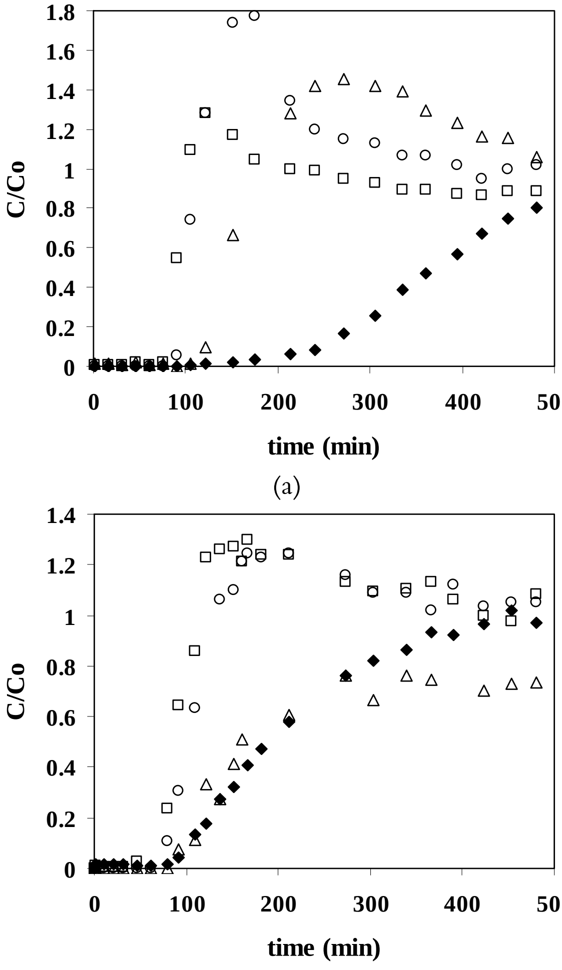
The dynamic capacity of the column, Q_i^{tb}, is defined as the amount of metal ion uptake prior to the break point (C/C_o = 5%). It can be obtained through a mass balance using the breakthrough data (McCABE et al., 1993). The effect of ionic interaction on the exchange process may be represented by the ratio of the dynamic capacity of the column in competing solutions, Q_{mix}, and the dynamic capacity in single solution, Q_o (MOHAN; CHANDER, 2001). If the chromium breakpoint time is considered, the ionic interaction factor may be written as $Q^{tb}_{Cr\,mix} / Q^{tb}_{Cr\,o}$. Then, if: $Q^{tb}_{Cr\,mix} / Q^{tb}_{Cr\,o} > 1$, the uptake is promoted by the presence of other metal ions;

$Q^{tb}_{Cr\,mix} / Q^{tb}_{Cr\,o} = 1$, no interaction exists between the in-going cations; $Q^{tb}_{Cr\,mix} / Q^{tb}_{Cr\,o} < 1$, the uptake is suppressed by the presence of other metal ions.

The ratio $Q^{t_b}_{M} / Q^{t_b}_{Cr\,mix}$, where M is the competing ion is also an important tool as it provides the dynamic selectivity. The more the ratio $Q^{t_b}_{M} / Q^{t_b}_{Cr\,mix}$ is, the lesser affinity of chromium in the packed bed.

Results and discussion

Breakthrough data of Cr/Ca/Mg/K solution is depicted in Figure 2. The overshooting process ($C_M/C_{Mo} > 1$) is clearly seen in both zeolite packed beds. The overshooting is related to a sequential ion exchange. It happens when the effluent concentration of the species possessing lower affinity rises above the inlet value (C_o) at a certain time, and this result is a direct consequence of the displacement from the zeolite of this component by a second cation, which has a higher affinity. Therefore, the overshoot peak depends on the relative affinity of the individual metals for the zeolite. As no $C_{Cr}/C_{Cro} > 1$ was evidenced, it may be concluded that in the operational conditions of 9 mL min.$^{-1}$ and d_p = 0.180 mm, chromium was preferentially removed as it replaced the competing cations already exchanged in the sites.



(a)

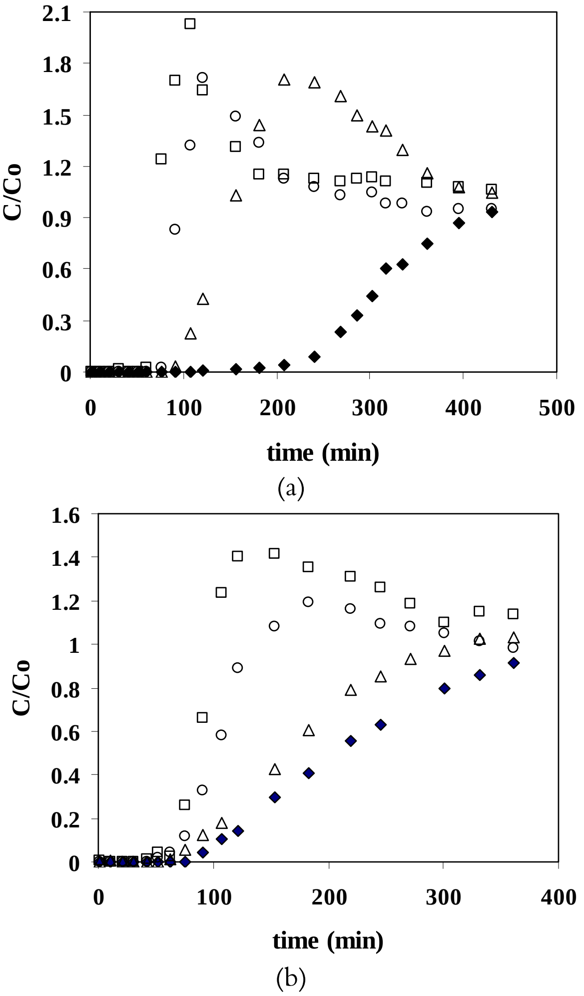
(b)

Figure 2. Breakthrough curves for competitive system Cr/Ca/Mg/K: a) NaY, b) NaX. (◆) Cr/Cr$_o$, (Δ) Ca/Ca$_o$, (O) Mg/Mg$_o$, (□) K/K$_o$.

Probably, the affinity towards the trivalent ions happened due to two main factors: the selectivity of the ion exchanger itself and the operational conditions used in the packed bed. It is known that higher charged ions are preferentially attracted to the zeolitic sites (GIANETTO et al., 2000). Thus, trivalent chromium ions were more attracted than the competing divalent and monovalent ions. Moreover, the process parameters, flow rate and average particle size, were experimentally optimized for chromium uptake (BARROS et al., 2002; 2003) and the diffusional resistances of the cations Ca^{2+}, Mg^{2+} and K^{+} were not minimized in the same way. The overshooting process was already predicted in Hsieh et al. (1977) and observed in multicomponent breakthrough curves in coconut carbon (MOHAN; CHANDER, 2001), fungus (SAĞ et al., 2000) and biomass (HAWARI; MULLIGAN, 2007). Thus, such phenomenon may be a reasonable explanation also for the chromium uptake in zeolites X and Y as well.

According to Figure 2, the chromium breakthrough curves followed the typical S-shaped curve for column operation which is related to favorable ion exchange isotherms (McCABE et al., 1993). In fact, it was already reported the favorable aspect of such process (BARROS et al., 2002, 2004; BASALDELLA et al., 2007; GAZOLA et al., 2006). Nevertheless, the chromium curves seemed to be less sharp in a competitive system than in a single solution (BARROS et al., 2003) probably due to higher diffusional resistances that implied a decrease in the mass transfer rates (McCABE et al., 1993; ZULFADHLY et al., 2001). It was also noted that the shape of the chromium breakthrough curve depended on the zeolite type (BARROS et al., 2003; 2006). The zeolite interfered in the uptake mechanism because the interaction of the entering ions with the framework oxygens played an important role in the stability of the cation in the exchange sites (BARRI; RESS, 1980). Although having the same framework, the aluminum content of NaX zeolite was 53% higher than NaY aluminum content. Then, NaX zeolite had more charge density. Consequently, it provided a higher electrostatic interaction with the in-going ions that really affected the dynamic ion exchange mechanism. Actually, the overshooting process was less pronounced in NaX breakthrough data because the ions were stronger attracted to the more dense sites.

The influence of sodium ions in the inlet solution is presented in Figure 3. Again, the overshooting behavior was less pronounced in the NaX packed bed due to a higher electrostatic attraction to the in-going ions. It was also worth to note the more pronounced overshooting process in Figure 3 of both breakthrough data when compared to the respective system with not sodium ions in solution (Figure 2). In Figure 3a the overshoot peak reached almost 2.1 in NaY packed bed while, for the same zeolite, the overshoot reached a maximum of 1.8 in Figure 2a. When NaX packed bed was considered, the overshoot peak reached 1.4 in Figure 3b. It was just a slight increment when compared to the overshoot peak of 1.3 in Figure 2b. Probably, in such case, sodium ions diminished the influence of the electrostatic attraction in NaY packed bed, and organized the exchanging process. The weaker attracted in-going ions could be homogenously distributed in the exchanging sites of the easily accessible large α and β cages. In NaX packed bed the sodium influence was less significant due to the stronger electrostatic attraction.



(a)

(b)

Figure 3. Breakthrough curves for competitive system Cr/Ca/Mg/K in the presence of sodium: a) NaY, b) NaX. (◆) Cr/Cr_o, (Δ) Ca/Ca_o, (O) Mg/Mg_o, (□) K/K_o.

It can be seen from Figures 2 and 3 that the time required for attaining the breakthrough point (C_{Cr}/C_{Cro} = 5%) was close to 100 min for NaX and 200 min for NaY packed bed, much less than in single breakthrough curves reported in Barros et al. (2003). Changes in the breakpoint time were already seen (SOUSA et al., 2010) and may be related to the diffusional process and competition. In multicomponent solution, the electrostatic attraction of the framework had a pronounced importance in the bed service time. This information should be considered when scaling-up the process.

From the breakthrough curves showed in Figures 2 and 3 and equations earlier presented it was possible to estimate the mass transfer parameters, shown in Tables 1 and 2.

In Table 1 it can be seen the length of unused bed (H_{UNB}), the overall mass transfer coefficient ($K_c a$), the operational ratio (R) and the dimensionless variance (σ_θ^2) for single chromium breakthrough curves and multicomponent ones.

Table 1. Mass transfer parameters.

Solution	Zeolite	H_{UNB}	$K_c a$(min^{-1})	R	σ_θ^2 *
*Cr	NaY	1.6	17.5	0.1	0.1
	NaX	0.9	32.3	0.0	0.1
Cr/Ca/Mg/K	NaY	2.5	10.9	0.90	0.1
	NaX	1.8	15.9	1.13	0.2
Cr/Ca/Mg/K/Na	NaY	1.7	17.4	0.50	0.0
	NaX	1.9	17.3	1.35	0.2

*Related to single chromium removal in the same operational conditions – published in Barros et al. (2003).

Table 2. Relation between the amount of each ion removed in the packed beds.

Solution	Zeolite	$Q_{Cr\,mix}^{tb} / Q_{Cr\,o}^{tb^*}$	$Q_{Ca}^{t_b} / Q_{Cr\,mix}^{t_b}$	$Q_{Mg}^{t_b} / Q_{Cr\,mix}^{t_b}$	$Q_{K}^{t_b} / Q_{Cr\,mix}^{t_b}$
Cr/Ca/Mg/K	NaY	0.7	0.8	0.3	0.5
	NaX	0.3	0.4	0.3	0.0
Cr/Ca/Mg/K/Na	NaY	0.8	1.5	1.0	1.0
	NaX	0.3	0.9	1.0	1.0

$Q_{Cr\,o}^{tb^*}$ = published in Barros et al. (2003).

Firstly one can note that the length of unused bed is strongly influenced by competing systems. From comparison with the single data (published in Barros et al., (2003)), it can be noted an increase of 50% in NaY packed beds and about 100% of NaX packed beds. This was already expected since all cations were more attracted to the denser NaX ion exchanging sites. The diffusional process was greater inhibited when cations of different types were simultaneously attracted. Nevertheless, H_{UNB} was almost the same comparing NaX packed beds and Cr/Ca/Mg/K and Cr/Ca/Mg/K/Na solutions. This was a consequence of the slightly differences in the overshoot peaks. As NaX had higher aluminum content, the influence of sodium was less pronounced, and competing ions were not easily released from the solid phase.

H_{UNB} in NaY packed beds reached a low value when the sodic multicomponent solution was considered. Indeed, this was a consequence of the better distribution of the in-going ions in the exchanging sites promoted by a decrease in the attraction forces, as seen in the more pronounced overshoot peaks of Figure 3a.

The competing systems also changed the overall mass transfer coefficient. In both zeolitic systems, $K_c a$ had a drastically decrease in multicomponent ion exchanging process in comparison to the single data. As $K_c a$ is related to the diffusional process, as expected, such values followed the tendency provided by H_{UNB}.

Competing systems had a huge increase in the operational ratio values. Such phenomenon confirmed, together with a high-unused bed, the marked competition to the ion exchange sites. The low dimensionless variance in all single and competitive solutions indicated almost negligible axial dispersion. Probably, the operational parameters such as flow rate and particle size provided similar velocity profiles in the packed bed for single or multicomponent exchanges.

Table 2 shows the quantitative values of the ionic interaction factor $\left(Q_{Cr\,mix}^{tb} / Q_{Cr\,o}^{tb} \right)$ and the dynamic selectivity provided by $Q_{M}^{t_b} / Q_{Cr\,mix}^{t_b}$. As expected, $Q_{Cr\,mix}^{tb} / Q_{Cr\,o}^{tb} < 1$, indicating that the chromium uptake was suppressed in multicomponent solutions. Moreover, the ionic interaction factor was much lower for NaX packed bed. Such value is in total agreement with the higher electrostatic interaction already discussed. The presence of sodium did not substantially affect the chromium uptake in competing systems. On the other hand, the ionic interaction fraction reached 0.7 in NaY packed bed fed with Cr/Ca/Mg/K solution and 0.8 when sodium was also added. Such fact emphasizes the influence of sodium ions in the minimization of the electrostatic forces and promotion of a better distribution of all in-going ion in the large cages.

According to the $Q_{M}^{t_b} \big/ Q_{Cr\,mix}^{t_b}$ values presented herein, it was possible to conclude that the dynamic selectivity for the multicomponent solution was: $Cr^{3+} > Ca^{2+} > K^{+} \approx Mg^{2+}$ for the NaY column and $Cr^{3+} > Ca^{2+} > Mg^{2+} > K^{+}$ for NaX column. The presence of sodium has changed the dynamic selectivity in the way that: $Ca^{2+} > Cr^{3+} > Mg^{2+} \approx K^{+}$ for NaY column and $Cr^{3+} > Ca^{2+} > Mg^{2+} \approx K^{+}$ for NaX column.

Conclusion

Chromium ions from multicomponent solutions were successfully removed in NaX and NaY packed beds. The denser sites of NaX zeolite provided less overshooting phenomena. Sodium ions in the feed solution decreased the electrostatic attraction forces mainly in NaY zeolite. Probably, with less attraction, ions could be better distributed to the ion exchanging sites located in the large cages. The length of unused bed and the operational ration increased in multicomponent solutions while the overall mass transfer coefficient decreased when compared to the single chromium dynamic removal. The operational conditions, minimized the mass transfer resistances in competing conditions as well.

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Received on August 2, 2012.
Accepted on January 10, 2013.