Removal of Cr³⁺ in fixed bed using zeolite NaY

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Abstract

In this work the chromium exchange mechanism in zeolite NaY was studied. The breakthrough data were determined in an up-flow fixed bed at 30 °C using three bed heights: 1.5, 3.0 and 4.5 cm. It was seen that the bed height influenced the maximum chromium uptake as well as the mass transfer zone due to changes in pH during the ion exchange process. Changes in pH generated different chromium species with particular difficulties in diffusing towards the exchange sites of the zeolite. The linear driving force (LDF) model for breakthrough curves fitted well to the experimental data and the estimated overall mass transfer coefficient also changed with bed height, which is a consequence of different chromium speciation in the ion exchange mechanism. The axial dispersion coefficient can be considered as an average of 8.25×10^2, 1.04×10^2 and 3.36×10^2 cm²/min for the bed heights of 1.5, 3.0 and 4.5 cm, respectively.
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1. Introduction

Aquatic contamination by heavy metals is very harmful since these elements are not degradable in the environment and may accumulate in living organisms. One of the most important heavy metal is chromium. Chromium occurs in the workplace predominantly in two valence states: hexavalent chromium [Cr^{6+}] and trivalent chromium [Cr^{3+}] [1]. Hexavalent and trivalent chromium compounds find extensive application in diverse industries. Hexavalent chromium is very toxic and commonly related to cytotoxicity and carcinogenicity [2]. On the other hand, trivalent chromium is less toxic but can be easily oxidized to the hexavalent form in the last stages of industrial wastewater treatment [3]. Therefore, it is important to minimize the Cr^{3+} residue before its oxidation. There is a wide variety of techniques available for the Cr^{3+} recovery and the most widely used is precipitation with alkalis. Nevertheless, after filtration of the sludge, the liquid phase still contains trivalent chromium. Ion exchange is one of the most effective techniques for such liquid phases. Many ion exchangers or adsorbents for chromium removal have being studied, such as carbon [4,5], resins [1] and zeolites [6,7].

Zeolites are known as very good ion exchangers due to their high cation exchange capacity. Among them, zeolite Y is one of the most promising synthetic zeolites for environmental purposes because it has an open negatively charged framework where easily exchangeable balancing cations are located [8]. Moreover, when compared to other molecular sieves, zeolite NaY seems to be more selective to Cr^{3+} ions even than its isomorphic framework, zeolite NaX, that has higher cation exchange capacity (CEC) due to differences in the cation-framework interaction [9].

Most separation and purification processes that employ sorption technology use continuous-flow columns [10]. This operating mode ensures the highest possible concentration difference driving force and dispenses a subsequent solid–liquid separation process. In such systems mass-transfer resistances are important and the overall dynamics of the system determine the efficiency of the process, rather than just the equilibrium considerations [11].

Therefore, in order to effectively design zeolite-bearing materials units, the development of mathematical models that can successfully simulate the experimental breakthrough operation is required. These models should be able to predict the dynamics of the ion-exchange process in order to facilitate the development of novel applications such as NaY packed beds for chromium removal from wastewater. The LDF model assumed that driving

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Nomenclature

C	concentration of the chromium in the bulk fluid phase (mequiv./L)
CEC	cation exchange capacity (mequiv./g)
C_{eq}	equilibrium concentration of the chromium in the bulk fluid phase (mequiv./L)
C_0	initial concentration of the chromium in the bulk fluid phase (mequiv./L)
C^F	concentration of the chromium in the inlet in the column (mequiv./L)
C_{out}^{EXP}	experimental concentration of the Cr(III) in the outlet of the column (mequiv./L)
C_{out}^{MOD}	concentration of the Cr(III) determined by the solution of the model in the outlet of the column (mequiv./L)
D_L	axial dispersion coefficient (cm²/min)
H	bed height (cm)
k_{rp}	Redlich–Peterson constant
K_S	overall mass transfer coefficient in the zeolite (min⁻¹)
m_z	dry weight of the zeolite (g)
MTZ	length of mass transfer zone (cm)
np	number of experimental data points
q	concentration of chromium exchange in the zeolite (mequiv./g)
q_{eq}	equilibrium concentration of chromium exchange in the zeolite (mequiv./g)
$q_{max\text{-}eq}$	maximum equilibrium concentration of chromium exchange in the zeolite (mequiv./g)
$\dot{Q}$	volumetric flow rate (cm³/min)
t	time (min)
t_t	saturation time (min)
t_u	break point time (min)
u	intersticial velocity (cm/min)
z	axial coordinate in the column (cm)
Z	bed height (cm)

Greek letters

α_{rp}	Redlich–Peterson constant
β	Redlich–Peterson constant
ε	column void fraction
ρ_b	fixed bed density (g/L)

Dimensionless group

Pe_b	Peclet number for the bed, Hu/D_L
St_D	Stanton number, $K_S u/H$
ξ	dimensionless axial coordinate, z/H
τ	dimensionless time coordinate, t_u/H

uses these dynamic isotherms, that means, isotherms obtained through breakthrough data. The model also predicts the axial dispersion coefficient in the bed. Therefore, this work aimed to study the mechanism of chromium uptake using zeolite NaY in a fixed bed. In order to achieve this purpose, breakthrough curves at three different bed heights (1.5, 3.0 and 4.5 cm) were investigated and the LDF model applied to the experimental data.

2. Experimental

2.1. Zeolite

The initial NaY zeolite was highly crystalline. NaY has the unit cell composition of $Na_{51}(AlO_2)_{51}(SiO_2)_{141}$ on a dry basis and a CEC of 3.90 mequiv./g. In order to obtain, as much as possible, the homoionic sodium form, the zeolite was mixed with 1 mol/L solution of NaCl four times at 60 °C at a proportion of 100 g of solid to 1 L of solution [14]. Then, each time the samples were washed with 2 L with hot deionized water and oven-dried at 100 °C. The pre-treated sample was pelletized, crushed and sieved with an average diameter of 0.180 mm previously recommended as the optimal particle size for this fixed-bed system [9].

2.2. Reagent

Reagent-grade $CrCl_3 \cdot 9H_2O$ was mixed with mixed deionized water to prepare chromium solutions from 0.27 to 2.10 mequiv./L at the pH range of 3–4.

2.3. Ion exchange unit

The column tests were carried out in a water-jacketed glass column at 30 °C with an inside diameter of 0.9 cm. The dried mass of zeolite pellets (m_z) of 0.33, 0.65 and 0.98 g filled the column generating the bed heights of 1.5, 3.0 and 4.5 cm, respectively. Deionized water was used to rinse the zeolite bed up flow in order to remove air bubbles. When the column was finally ready for the run, the flow rate was fixed to 9 cm³/min as it was previously determined as the optimal flow rate for this system [9]. Runs were started by feeding the column with the chromium solution (C_0) also in up flow. In all dynamic tests the outlet samples (C) were regularly collected until the saturation of the bed ($C/C_0 = 1$) occurred and their concentration analyzed using a Varian atomic absorption spectrophotometer. Then, the breakthrough curves were plotted (C/C_0 versus t).

2.4. Dynamic ion exchange isotherms

The breakthrough data were used to calculate the amount of Cr^{3+} ions retained in each run through the mass balance. By such balance, it can be shown that the area of the curve $(1 - C/C_0)$ is proportional to the total solute retained. Therefore, the amount of Cr^{3+} ions retained in the zeolite-packed bed may be written

force for mass transfer to be linear with respect to the metal ion concentration in adsorbent and there are equilibrium in the fluid–solid interface [12]. Equilibrium isotherms were obtained through breakthrough data in order to perform equilibrium studies using columns [13]. Therefore, the mathematical model