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Modeling hydrogen fluoride adsorption by sodium fluoride

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ABSTRACT

In the current study, hydrogen fluoride (HF) adsorption onto the sodium fluoride pellets is modeled. For this purpose a two-dimensional, non-isothermal model was developed and the governing equations were solved numerically. The contributions of diffusion transport in axial and radial directions also were considered in mathematical formulations. The model results of effluent concentration and breakthrough curves of HF were compared with the experimental data obtained in a lab-scale adsorption unit, reported in our previous work [1]. The results indicate while the feed gas velocity decreases, the HF adsorption capacity on NaF is significantly enhanced and there is a delay in breakthrough time. The adsorption capacity of HF on NaF decreases slightly when inlet HF concentration increases. Moreover, the model results were compared with the obtained results from a one-dimension model. This comparison indicates that one-dimensional model can well predict the HF dynamic adsorption behavior for lab-scale fixed beds. Comparing the experimental breakthrough curves of HF adsorption on NaF pellets with the model results shows the ability and accuracy of the model with maximum 7.82% errors.

1. Introduction

The hydrogen fluoride (HF) separation from fluorine (F_2) is an essential process in the uranium conversion industry. In this industry, fluorine is produced based on the electrolysis of potassium anhydride difluoride. The produced fluorine containing significant amounts of hydrogen fluoride need to be upgraded in order to meet the process quality for producing high quality uranium hexafluoride. As mentioned in our previous paper [1], adsorption process is a common and also the best method for separating hydrogen fluoride from fluorine gas. Besides, it is a fact that due to the particular applications and also the economical considerations there is not enough and validated data about purifying process of hazardous fluorine in the literature. After all, as the first part of a comprehensive study, HF adsorption by sodium fluoride (NaF) pellets has been studied experimentally in a lab-scale fixed-bed adsorption column and the results, including the adsorption isotherms and the experimental breakthrough curves were presented in our previous work [1]. A brief discussion of the experimental method and the obtained results is presented in the next part of this paper. The current paper focuses on modeling HF adsorption by sodium fluoride pellets in a fixed-bed column.

Modeling or experimental studies about the adsorption beds and different kind of adsorbents have been performed for a long time and are still one of the greatest interests for the investigators. Some items like decreasing the computational time, calculating and predicting the accurately effective parameters such as diffusion coefficients in particles have been studied widely in recent years (1947–2008).

Due to the importance of the subject, there have been many attempts to find analytic solutions for the breakthrough curves for mono disperse sorbents in fixed beds. Hougen and Marshal developed some methods to calculate the time–position temperature–concentration conditions in both gas and solid during dilute gases adsorption following through the granular beds [2].

Thomas developed a mathematical description of single solute chromatography for two mechanisms of adsorption considered as a kinetic process [3]. Thomas found a closed form solution in the form of a series for solid diffusions in chromatography [4]. Rosen and Winsche introduced the concept of admittance while studying the kinetics of chromatography [5]. Rosen presented a solution for the case, what he called it a general problem of the transient behavior of a linear fixed-bed system where the rate of adsorption is determined by the combined effect of a liquid film and solid diffusion into spherical particles [6]. Babcock, Green and Perry made a theoretical study about the longitudinal dispersion mechanism during the steady flow of a fluid through unconsolidated spherical beads [7]. Rasmuson and Neretnieks provided an exact solution of a model for

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Nomenclature

a	heat transfer area (m^2/m^3)
B_0	constant of Langmuir equation
C_A	concentration of HF (mol/m^3)
C_{pg}	specific heat capacity of gas (mol/m^3)
C_A^*	equilibrium concentration of HF in gas phase in equilibrium with adsorbed HF in solid (mol/m^3)
d_p	particle diameter (m)
De	effective diffusivity (m^2/s)
D_l	axial dispersion coefficient (m^2/s)
D_r	redial dispersion coefficient (m^2/s)
D_k	Knodsen's diffusivity (m^2/s)
D_m	molecular diffusivity in gas phase (m^2/s)
D_t	bed diameter (m)
h_i	heat convection transfer coefficient (w/m °C)
h_w	overall heat transfer coefficient between gas and environment(w/m °C)
ΔH	adsorption energy (J/mol)
K_{cext}	external mass transfer coefficient (m/s)
k_{cint}	internal mass transfer coefficient (m/s)
$H_{s,A}$	mass transfer coefficient from gas to solid (m/s)
L	bed length (m)
M	gas molecular weight (g/mol)
$N_A.a$	rate of mass trsansfer from gas to solid (mol/m^3 s)
P_t	gas pressure (Pa)
q	adsorbed concentration for unit mass of solid (g HF/g NaF)
q_m	maximum capacity of adsorption HF on NaF pellets (g HF/g NaF)
r	redial of element (m)
re	radius of pore particle (m)
R	redial of bed (m)
Rg	constant of gas
Re	particle Reynolds number
Sc	Schmit number
t	time (s)
t_e	equilibrium time (s)
T_{feed}	feed temperature (K)
T_g	gas temperature (K)
T_∞	environmental temperature (K)
u_s	superficial velocity (m/s)
z	length of element (m)

Greek letters

ε_b	bed voidage fraction
ρ	gas density
ρ_s	solid density
M	gas viscosity
λ_l	thermal axial dispersion coefficient (w/m^2 °C)
λ_r	thermal redial dispersion coefficient (w/m^2 °C)
T	pore tortuosity factor

diffusion in particles and longitudinal dispersion in packed beds [8]. Raghavan and Ruthven numerically simulated a fixed-bed adsorption column by the method of orthogonal collection [9]. Rasmuson numerically evaluated the results were previously reported by Rasmuson and Neretnieks [10]. Costa and Rodrigues suggested a model for phenol adsorption in a fixed bed of a polymeric adsorbent and presented a numerical solution of their model equation using the method of lines with double orthogonal collection in finite elements [11]. Cen and Yang reported an analytical solution for adsorber breakthrough curves with bidisperse sorbents (zeolites) [12]. Brian and Zwiebel reproduced Raghavan and Ruthven's results by applying the method of lines [13]. Kumar and Golden investigated TSA process in order to remove the low-concentration impurities [14]. Sun and Quere simulated PSA process numerically via using finite difference method [15].

Xiu presented a model for breakthrough curves calculations in a fixed bed of active carbon fiber and provided an exact solution and an approximate solution using the parabolic approximation technique [16]. Xiu et al. used the quasi-lognormal distribution (O-LND) approximation method to predict breakthrough curves in fixed-bed adsorbers for a linear adsorption system with axial dispersion, external film diffusion resistance and intra particle diffusion resistance for slab-, cylindrical-, and spherical particle geometries [17]. Shams proposed a desorption model for situ volatilization of volatile organic compounds (VOCs) to remediate vadose zone contaminated soils [18]. Susu presented a mathematical model for aromatics adsorption and sulfur compounds in a fixed bed of kerosene deodorization and numerically solved by fourth-order Runge–Kutta method [19]. Chahbani and Tondeur studied mass transfer kinetics in pressure swing adsorption [20]. They also studied pressure drop in fixed adsorption beds [21]. Chern and Chien presented an isothermal mathematical model for obtaining the breakthrough curves for nitrophenol adsorption in fixed bed by activated carbon [22]. Cheng et al. reported a new model for proposing to describe the removal of volatile organic compounds (VOCs) by adsorption on activated carbon fibers in a fixed bed [23].

Cruz et al. studied the simulation and optimization of cyclic adsorption process [24]. Afterwards, Chang et al. performed numerical simulation of PSA adsorption process with CO_2 highly adsorbent [25]. Delgado et al. presented a model for adsorption of methane/nitrogen mixture on silicate pellets in a fixed bed [26]. Schinder et al. studied adsorption of chrounium ions in activated carbon [27]. Xiuo et al. experimentally and theoretically studied on hydrogen sulfide adsorption on impregnated activated carbon under anaerobic conditions [28].

The aim of this study is establishing a mathematical model to predict the breakthrough curves of HF adsorption on NaF pellet in a fixed-bed column. The accuracy of the model predictions is assessed by comparing the model results with the obtained experimental data presented in our previous work [1]. For this aim, a two-dimension model which accounts for non-isothermal operation and nonlinear adsorption in a fixed-bed packed with porous adsorbent coupled with axial dispersion is developed and numerically solved. Beside, there is a comparison carried out between the results of one and two-dimensional models.

2. Experiments and results

In this section, a brief discussion is presented on experiments, isotherm study and the obtained results. The details of experimental study may be found in [1].

A scheme of the setup for the fixed-bed adsorption experiments is shown in Fig. 1. The physical dimensions, characteristics and properties of experimental setup, NaF pellets and gas mixtures are summarized in Tables 1 and 2.

In order to obtain the adsorption isotherm, the sodium fluoride pellets were weighted and carefully packed into the column. Then the height of the packed bed was measured. The mixture of nitrogen gas and HF was entered into the bed with a constant flow rate. Water was passed through the shell as the cooling fluid. The outlet concentration was recorded continuously by a UV–IR analyzer. Furthermore, the inlet and outlet temperatures of the gas flow and the cooling fluid were measured by the existing thermocouples. The