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Alberto A. Pinto · David Zilberman
Editors

Modeling, Dynamics, Optimization and Bioeconomics III

DGS IV, Madrid, Spain, June 2016, and Bioeconomy VIII, Berkeley, USA, April 2015—Selected Contributions

Springer

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Foreword

> *L'esprit n'use de sa faculté créatrice que quand l'expérience lui en impose la nécessité.*
>
> Henri Poincaré

The tremendous challenges that are faced by humanity as the 21st century unfolds itself require a multidisciplinary approach. Now, more than ever before, the need for exploring our creative capacities to solve relevant problems for society is crucial for our very survival. However, this can only be done by a cross-cultural and multidisciplinary networking effort.

Having a group of scientists from different areas networking and exchanging experiences in a vibrant environment requires the correct environment. One can safely say that such environment came about in the two opportunities connected to the present volume of papers, namely in Berkeley, at the University of California, during the month of March 2014, and in Madrid, at the Universidad Nacional de Educatión a Distancia (UNED), during the month of June 2016.

In the first occasion, during the Seventh Berkeley Bioeconomy Conference, the ideal environment of the San Francisco Bay Area, with its sunny days and foggy afternoons, conjoined with the highly inquisitive and revolutionary tradition of the Cal Berkeley Campus had as its central theme "Biofuels as part of a sustainable strategy". In this occasion, an array of leading experts under the coordination of David Zilberman tackled topics ranging from global biofuel investments to the future of Brazilian biofuels, passing through extreme weather, biotechnology and agricultural productivity. In the present volume, the paper "Simulation and Advanced Control of the Continuous Biodiesel Production Process" by Brásio et al. and "Myopia of Governments and Optimality of Irreversible Pollution Accumulation" by Policardo are good examples of a quantitative follow-up of the conference themes. The paper by Mendes et al. deals with modelling by differential equations the kinetic separation of hexane isomers when they flow through a packed bed containing the micro-porous Metal-Organic Framework (MOF) ZIF-8 adsorbent. It is shown that a proper combination of two characteristic times can lead to very different dynamics of fixed bed adsorbers wherein a limiting case can give rise to a spontaneous breakthrough curve of solutes.

In the second occasion, in the quiet Madrileño Summer and under the auspices of the UNED, we had the "4th International Conference on Dynamics, Games and Science" with the key topic being decision models in a complex economy. Here, under the warm hospitality of our Spanish colleagues, I was pleased to witness a broad plethora of distinguished speakers discussing topics ranging from human decisions, from a game theoretical viewpoint, to the simulation of energy demand and efficiency and passing through swarms of interacting agents in random environments. The remaining papers that can be found in the present volume are in a certain sense a written testimony of such diversity and effusiveness of interactions. For instance, the article by dos Santos et al. studies the influence of human mobility of dengue's transmission in the state of Rio de Janeiro from a statistical viewpoint. Still within the area of statistics, but from a broad theoretical perspective, the chapter by Casaca discusses prior information in Bayesian linear multivariate regression. The work of Nassif et al. presents a mathematical model for the tick life cycle based on the McKendrick partial differential equation. The article of Balsa et al. proposes a two-phase acceleration technique for the solution of symmetric and positive-definite linear systems with multiple right-hand sides. The paper by Rüppel et al. presents a constructive proof of the complete nonholonomy of the rolling ellipsoid. The two articles by Lopes and collaborators deal with important theoretical aspects of dynamical systems (such as the fat attractor) and quantum mechanics.

Summing up, the present volume displays a variety of works by leading researchers in a broad range of subjects where mathematical models have a substantial role and impact in society.

Rio de Janeiro, Brasil
March 2017

Jorge P. Zubelli

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Contents

Dynamics of a Fixed Bed Adsorption Column in the Kinetic Separation of Hexane Isomers in MOF ZIF-8

Patrícia A. P. Mendes, Alírio E. Rodrigues, João P. Almeida and José A. C. Silva

Abstract A fixed bed adsorption mathematical model has been developed to describe the kinetic separation of hexane isomers when they flow through a packed bed containing the microporous Metal-Organic Framework (MOF) ZIF-8 adsorbent. The flow of inert and adsorbable species through the fixed bed is modeled with fundamental differential equations according to the mass and heat conservation laws, a general isotherm to describe adsorption equilibrium and a lumped kinetic mass transfer mechanism between bulk gas phase and the porous solid. It is shown that a proper combination of two characteristic times (the residence time of the gas in the fixed bed, τ_{fb} and the characteristic time of diffusion of solutes into the pores τ_{dif}) can lead to very different dynamics of fixed bed adsorbers where in a limiting case can gives rise to a spontaneous breakthrough curves of solutes. The numerical simulations of an experimental breakthrough curve with the developed mathematical model clearly explain the complete separation between linear n-Hexane (nHEX) and the respective branched isomers: 3-Methyl-Pentane (3MP) and 2, 2-Dimethyl-Butane (22DMB). The separation is due to significant differences in the diffusivity parameters τ_{dif} between 3MP and 22DMB and the residence time of the gas mixture τ_{fb} within the fixed bed. This work shows the importance of mathematical modelling for the comprehension and design of adsorption separation processes.

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1 Introduction

The gasoline used by automotive cars has a high Research-Octane Number (RON above 95) and is mainly obtained from a stream fraction of the crude distillation column called Light Naphtha which in turn has a very low RON content (average RON of 63). To be upgraded the Light Naphtha mainly composed by n-pentane (RON 61.7) and n-hexane (RON 24.8) is treated in processes such as: Hysomer, TIP or IPsorb [1-5] where a catalytic reactor isomerize the linear compounds into branched ones with a much higher RON content. The final output stream of TIP processes (RON around 88) needs to be further upgraded with additives. Some of these additives were forbidden due to their toxicity (the case of lead) to make it usable by cars. Also they increase significantly the final price of gasoline (MTBE and ETBE). Since this final TIP output stream still contains compounds such as the linear nHEX (RON 24.8), mono-branched 3MP (RON 74.5) and di-branched 22DMB (RON 94.0), there is nowadays a significant effort to discover new adsorbents to separate in a clean way the low from the high RON paraffins of the final TIP output stream (the separation by distillation is very energy consuming due to the close boiling point of the isomers) to reduce the use of additives.

Among the several adsorbents being discovered for the separation of close boiling point compounds, the zinc methyl-imidazolate ZIF-8 [6] with the sodalite (SOD) topology, which possesses a significant porosity ($S_{BET} \sim 1800$ m^{2}g^{-1}; $V_p \sim$ 0.66 cm^{3}g^{-1}) involving large spherical cavities (11.4 Å) connected by a flexible six members rings of free aperture of 3.4 Å, is of particular interest due to its chemical and thermal robustness. Regarding the separation of pentane/hexane isomers in ZIF-8, the study of Luebbers et al. [13] showed a complete separation between the linear n-pentane and the branched isopentane. More recently, a screening study of Peralta et al. [17] proved that ZIF-8 is an interesting material for the separation of linear nHEXand branched hexane isomers. However, under static conditions, Ferreira et al. [7] showed that the linear and mono-branched hexane isomers were adsorbed well, but 22DMB was totally excluded. A similar study was performed by Zhang et al. [23] obtaining completely different results. All hexane isomers were adsorbed in ZIF-8 especially the branched ones. However, they estimated diffusional parameters from the uptakes and found that the diffusion selectivities for nHEX/3MP, nHEX/23DMB and 3MP/23DMB were of 20, 54, and 3, respectively. They concluded that the separation linear/mono/di-branched hexane isomers could also be attained by a kinetic selectivity.

Mathematical modelling is a valuable tool in the design and optimization of industrial processes. Most of the industrial adsorption processes occur in fixed beds and it is the overall dynamics of this packed bed system, rather than the adsorption equilibrium or the adsorption kinetics in a single particle, that determine the efficiency of such process [11]. Fundamentals of mathematical modelling of fixed bed adsorbers are presented by Ruthven [19] and Yang [22].

The aim of this work is the formulation of a mathematical model to simulate the transient adsorption behavior of a mixture of hexane isomers (nHEX, 3MP, 22DM-

B) flowing through a packed bed containing the microporous adsorbent ZIF-8. The physical parameters of the model are determined on the basis of results of equilibrium and kinetics of adsorption and from correlations available in the literature. The numerical solution of the coupled mass and heat balances partial differential equations is obtained by orthogonal collocation. Application of the model is illustrated by a typical example, a so called breakthrough curve, which shows how the different hexane isomers are separated from one another.

2 Simulation of Fixed Bed Adsorption Dynamics

2.1 Mathematical Model

Consider a fixed bed adsorption column of length L, void fraction ε_b, packed with an adsorbent through which a fluid mixture of hexane isomers flows at a molar flow rate F. Let C represent the total gas concentration of all species in the fluid mixture and $\bar{q}_i$ the average adsorbed concentration of absorbable species i in the solid phase. The total material balance in a section between axial planes z and $z + \Delta Z$ from the entrance of the bed over a period of time t to $t + \Delta t$ yields, in the limit, the following first order partial differential equation,

$$\frac{\partial F}{\partial z} + \varepsilon_b \frac{\partial C}{\partial t} + (1 - \varepsilon_b) \sum_{i=1}^{ncp} \frac{\partial \bar{q}_i}{\partial t} = 0. \tag{1}$$

The initial and boundary conditions for a clean column subjected to a step change of adsorbable species at the inlet and at time zero are,

Boundary condition

$$z = 0; \quad t > 0; \quad F = F_f. \tag{2}$$

Initial condition

$$t = 0, \forall z; \quad \bar{q}_i = 0; \quad F = F_f; \quad C = C_f, \tag{3}$$

where the subscript f represents the feed conditions.

The differential fluid phase mass balance for a solute species i represented by an axially dispersed plug flow pattern is the second order partial differential equation,

$$-\varepsilon_b D_{ax} \frac{\partial}{\partial z}\left(C \frac{\partial y_i}{\partial z}\right) + \frac{\partial (F y_i)}{\partial z} + \varepsilon_b \frac{\partial (C y_i)}{\partial t} + (1 - \varepsilon_b) \frac{\partial \bar{q}_i}{\partial t} = 0. \tag{4}$$

where y_i is the molar gas fraction of solute i and D_{ax} is the coefficient of axial dispersion. The initial and boundary conditions (known as Danckwerts boundary conditions [5]) are,

Initial condition

$$t = 0, \forall z; \quad y_i = \bar{q}_i = 0. \tag{5}$$

Boundary conditions

$$z = 0; \quad t > 0; \quad Fy_{if} = Fy_i - \varepsilon_b D_{ax} C \frac{\partial y_i}{\partial z} \tag{6}$$

$$z = L; \quad t > 0; \quad \frac{\partial y_i}{\partial z} = 0, \tag{7}$$

where L is the length of the column.

Due to axial diffusion, the molar fraction of the adsorbable entering the bed is different from the one in the entrance. Accordingly, Eq. (5) ensures that the mass fed to the column is equal to the one that crosses the plane at $z = 0$. At the outlet of the bed ($z = L$), Eq. (6) simply assumes that the concentration gradient ends and the molar fraction of the absorbable just at the end of the bed is not affected by counter-diffusion.

The mass transfer rate from bulk fluid phase to solid particles is mainly governed by: (i) external fluid film resistance around the particles, and (ii) intraparticle diffusion of solutes. A rigorous treatment of intraparticle diffusion of solutes leads to a diffusion model with partial differential equations that incorporates several mechanisms and a new radial coordinate (if adsorbents particles are spherical or cylindrical). To simplify the solution, a linear rate model is generally used,

$$\frac{\partial \bar{q}_i}{\partial t} = k_{LDF}(q^* - \bar{q}_i), \tag{8}$$

where q^* is the adsorbed phase concentration of species i in equilibrium with gas phase concentration, $\bar{q}_i$ is the average adsorbed phase concentration of species i within the particle and k_{LDF} is called the Linear Driving Force (LDF) mass transfer coefficient. Glueckauf [9] showed that the parameter k_{LDF} for spherical particles is equal to $15D_c/r_c^2$ where D_c is the diffusivity constant and r_c the particle radius.

Adsorption is an exothermic *phenomenum* and the importance of heat effects should also be considered in the modelling of an adsorption column. Consider a non-isothermal, non-adiabatic column with axial heat dispersion. Let T be the temperature in bulk gas phase, T_s the temperature of solid phase, T_w the temperature of the surroundings, c_{pg} the heat capacity per unit mol of gas, K_{ax} the axial heat dispersion coefficient, h_p the heat transfer coefficient between gas and solid phase, h_w the overall heat transfer coefficient at the wall of the column, a_c the specific area of the column and a_p the specific area of the particle. Then, the following differential energy balance may be formulated to give the equation

$$-K_{ax}\frac{\partial^2 T}{\partial z^2}+Fc_{pg}\frac{\partial T}{\partial z}+\varepsilon Cc_{pg}\frac{\partial T}{\partial t}+(1-\varepsilon_b)a_p h_p(T-T_s)+a_c h_w(T-T_w)=0. \quad (9)$$

Boundary conditions

$$z=0;\quad t>0;\quad Fc_{pg}T_f=Fc_{pg}T-K_{ax}\frac{\partial T}{\partial z} \quad (10)$$

$$z=L;\quad t>0;\quad \frac{\partial T}{\partial z}=0. \quad (11)$$

Initial condition

$$t=0,\forall z;\quad T=T_s=T_f. \quad (12)$$

Since mass and heat transfer are similar mechanisms, the previous boundary conditions are applied by analogy with the Danckwerts boundary conditions.

The existence of an interphase heat transfer mechanism within the column implies that in certain cases the temperature of bulk fluid phase T is different from the solid phase temperature T_s, under transient conditions. The energy balance for the solid phase neglecting radial temperature gradients is

$$c_{ps}\frac{\partial T_s}{\partial t}=a_p h_p(T-T_s)+\sum_{i=1}^{ncp}(-\Delta H_i)\frac{\partial \bar{q}_i}{\partial t}, \quad (13)$$

where, c_{ps} is the heat capacity per unit volume of solid and $(-\Delta H_i)$ the heat of adsorption per mole of solute species i or, in other words, the amount of heat that is generated by adsorption within the particle.

2.2 Adsorption Isotherm

The equilibrium thermodynamic relation between adsorbed phase concentration of solutes q_i and the respective gas phase concentration c_i can be represented by the ideal localized model introduced by Langmuir [12]

$$q_i=\frac{q_m K_i c_i}{1+\sum_{j=1}^{ncp}K_j c_j}, \quad (14)$$

where q_m is supposed to be constant and independent of temperature, in order to give thermodynamic consistency to the model, and K_i a Langmuir isotherm constant. The Langmuir isotherm constant K_i is strongly dependent upon temperature obeying the Van’t Hoff dependence

$$K_i = K_i^0 e^{-\Delta H_i/RT}, \tag{15}$$

where K_i^0 is the frequency factor of the Langmuir constant, R is the universal gas constant and T is the temperature.

2.3 Numerical Solution of Model Equations

The fluid flow problem formulated above consist in a set of partial differential equations (PDES) subjected to boundary and initial value conditions that lead to parabolic equations which are time dependent. Several numerical techniques have been developed to solve PDEs where the most widely used are the: (i) finite-difference (FD); (ii) the method of lines (MOL) [20] and (iii) orthogonal collocation (OC) [8]. The choice between the methods depends on the complexity, simplicity in setting-up the numerical solution, accuracy, stability and computational effort [2, 18].

The classical finite difference method consists in replacing the derivatives in the PDE by finite difference approximations using a uniform mesh. The method of lines is similar to the finite-difference except we do not discretize the time variable. In the orthogonal collocation technique trial functions are chosen as sets of orthogonal polynomials and collocation points are the roots of these polynomials.

The numerical methods convert the PDES into a set of non-linear equations (FD) or in set of ordinary's differential equations (ODES) that must be solved by a proper numerical technique. The diffusion-adsorption problem formulated above can give rise to profiles very steep with the necessity to increase the mesh if we use the FD or MOL methods or the roots of the polynomials in the OC method, to obtain stability and accuracy. Consequently the numerical computation effort increase significantly to obtain accuracy in such cases. The most widely used methods to handle the diffusion-adsorption problems are the MOL and OC techniques. The flexibility of the OC technique in handle such problems, for example using orthogonal polynomials [21], means that the solution error decreases faster as the polynomial order increases. However, the selection of a method to handle the solution of a PDE problem is in most cases a matter of experimentation since many factor have to be considered [2].

Based on such experimentation (during past years) and given the collection of subroutines by Villdasen and Michelsen [21] to help readers handle the solution of PDE problems by using the accurate computation of collocation points obtained by the zeros of an orthogonal polynomial, $P_{N^{(\alpha,\beta)}}(x)$, called Jacobi polynomial, are the base to select the OC technique to obtain a solution for the problem formulated above.

In this work, the set of coupled partial differential equations was reduced firstly to a set of ordinary differential/algebraic equations (DAE's) applying orthogonal collocation technique to the spatial coordinate [16]. In this reduction, the first and second order differential terms were replaced by collocation matrices $A(i, j)$ and $B(i, j)$, respectively. The collocation points were given by the zeros of Jacobi polynomials $P_{N^{(\alpha,\beta)}}(x)$, with $\alpha = \beta = 0$, calculated by subroutine JCOBI. The collocation matrices $A(i, j)$ and $B(i, j)$ were found by using subroutine DFOPR. A FORTRAN code of both subroutines can be found in Villadsen and Michelsen's book [21]. The number of interior interpolation points N was chosen to give stability to the numerical solution of discretized equations. The resulting system was solved using a fifth order Runge-Kutta code (ODE's) together with Gauss elimination for the algebraic equations. Sixteen collocation points appeared to give satisfactory accuracy for all calculations performed. For two adsorbable species, this results in 128 (64×2) ODEs being integrated at the same time: 32 (16×2) from the Mass balance to adsorbable species; 32 (16×2) from the equation representing the Mass transfer rate, 32 (16×2) from the energy balance in the gas phase and 32 (16×2) from the energy balance for the solid phase. At the same time there are 32 (16×2) equations being solved by Gaussian elimination from the equation representing the overall mass balance.

3 Experimental Framework

3.1 Adsorbent and Sorbates

ZIF-8 crystals were synthesized for the adsorption studies of hexane isomers. For that, a solution of 5 g of 2-methylimidazole (H-MeIM; 60.9 mmol; Alfa Aesar, 97%) in 25 mL of methanol (6.15 mmol; VWR, 99.9%) was poured into a solution of 2.305 g zinc nitrate hexahydrate, ($Zn(NO_3)_2.6H_2O$; 7.5 mmol; Aldrich, 99%) in 25 mL methanol (6.15 mmol, VWR, 99.9%). The mixture was then putted into a metallic PAAR digestion bomb at 100 C during 16 h. The resulting white powder was filtered and washed with ethanol. This procedure was repeated five times to finally obtain the enough ZIF-8 amount for the fixed bed experiments (∼2 g). The crystallinity of each batch was checked by XRPD before mixing all of them. Thereafter the powder was characterized by X-ray powder diffraction patterns were collected in a SIEMENS D5000 diffractometer (θ–2θ), Thermogravimetric analysis using a Perkin Elmer Diamond TGA/DTA STA 6000. The BET surface area was 1950 $m^2.g^{-1}$ with a total pore volume around 0.66 $cm^3.g^{-1}$. The hexane isomers used in the experimental study were obtained from Merck (Germany) and are all above 99% purity.

3.2 Single and Multicomponent Fixed Bed Experiments

The experimental data were obtained in an apparatus developed for the measurement of single and multicomponent breakthrough curves consisting of three main sections. The preparation section includes a syringe pump used to introduce the adsorbable species in the carrier gas followed by a heating chamber where this stream is completely vaporized. The adsorption section consists in a 4.6 mm *i.d.* stainless steel column with 80 mm in length containing the adsorbent and placed in a ventilated chromatographic oven, as well as a heated collector to collect samples at the outlet of the column. The third part is an analytical section composed by a chromatographic column and a flame ionization detector (FID). Complete information about the experimental setup is reported in, for example, [1].

4 Results and Discussion

The mathematical model developed contains important time dependent group parameters that influence the overall dynamics of the fixed bed namely: (i) the residence time (contact time or space time) measured by a characteristic time L/v_i; and (ii) the Linear Driving Force (LDF) mass transfer coefficient k_{LDF} equal to $15D_c/r_c^2$. Here, L/v_i has units of time and the group $15D_c/r_c^2$ has units of the reciprocal of time. The term L/v_i can be viewed as the residence time τ_{fb} of the gas in the column, that is, the time that gas and the adsorbent within the fixed bed are in contact and the reciprocal of $15D_c/r_c^2$ as the time τ_{dif} that the adsorbable species spent needs to diffuse into the pores of the adsorbent. The importance of these parameters in the overall dynamics of the fixed bed will be analyzed.

Figure 1 shows the effect of changing τ_{dif} for a constant value of $\tau_{fb} = 1$ min under isothermal conditions. The parameters of the model used in simulations are shown in Table 1. When τ_{dif} is 10 times lower ($\tau_{dif} = 0.1$ min) the diffusion limitations are insignificant when compared to the residence time of the gas in the bed and the breakthrough curve is a pure “shock wave”. When τ_{dif} is ten times higher (that is, the time that solutes need to diffuse into the pores is much higher than the residence time in the bed) the breakthrough curves become dispersive (e.g. $\tau_{dif} = 10$ min) indicating strong mass transfer resistance. In the worst case presented ($\tau_{dif} = 100$ min), the solute breakthroughs spontaneously at the residence time of the bed because the time it spends in the bed is shorter than the time it needs to diffuse into the pores. These results mean that a proper combination of τ_{dif} and τ_{fb} can lead to very different dynamics and consequently breakthrough curves of fixed bed adsorbers.

Previous studies of hexane isomers adsorption in the microporous ZIF-8 are controversial. Peralta et al. [17] show in a breakthrough apparatus that 3MP was kinetically separated from 22DMB. In contrast, Chang et al. [3] and Luebbers et al. [13] proved that branched alkanes can be totally sieved from the linear ones. Moreover, results of Ferreira et al. [7], who studied the same system but in static conditions (manometric system coupled with a micro calorimeter), are different from both of the previously mentioned ones. They noticed that the linear and mono-branched isomers were well adsorbed, but the di-branched 22DMB was totally excluded. Moreover, the recent work of Zhang et al. [23] that studied the same system in static conditions (uptake system), shows completely different results relatively to the results obtained in the experiments of Ferreira et al. [7]. In this case [23], all isomers can enter into the pores of ZIF-8 and the amounts adsorbed of the branched isomers are even

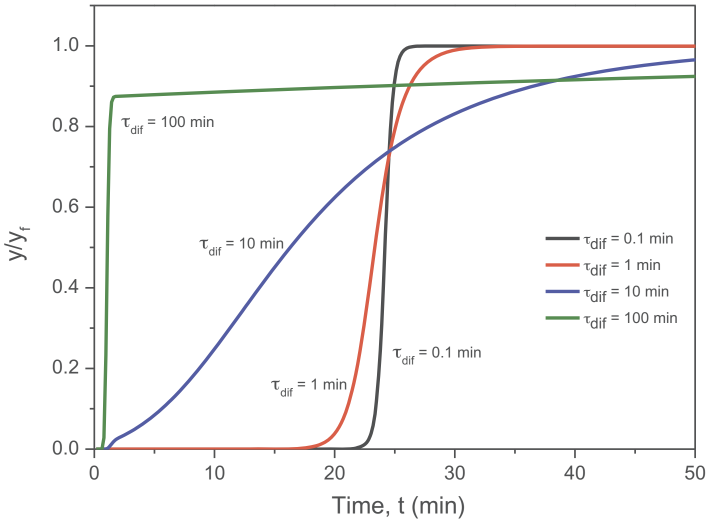

Fig. 1 Effect of changing the characteristic time of diffusion τ_{dif} in the overall dynamics of an isothermal fixed bed adsorber for a constant value of the residence time of the gas τ_{fb} equal to 1 min

Table 1 Model parameters for the simulation of breakthrough curves shown in Fig. 1

Isotherm parameters (nHEX)	
q_m	1 mmol/g
K_i	0.01 kPa^{-1} at 313 K
Experimental conditions	
C_f	40 mol/m^3
Q	20 mL/min
P_c	101.3 kPa
V_c	40 cm^3
y_{if}	0.5
Model parameters	
Pe	100
Greek letters	
ε_b	0.5
ρ_b	0.7 g/cm^3

higher than the linear ones. However, they estimated diffusional parameters from the uptakes and found that the diffusion selectivities for nHEX/3MP, nHEX/23DMB and 3MP/23DMB were of 20, 54, and 3 respectively in ZIF-8. This means that the separation linear/ branched can be kinetically driven.

A convenient way to evaluate the performance of an adsorbent for a certain separation is to perform a set of experimental breakthrough curves in a packed column. These response curves to a step change in solute concentration at inlet contain the

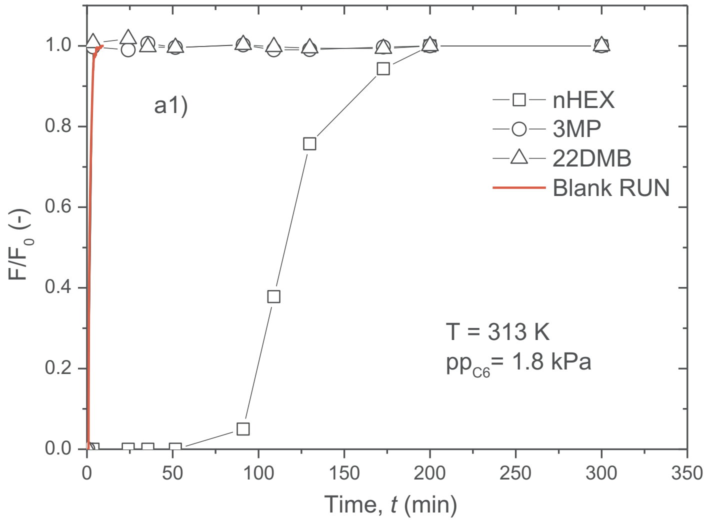

Fig. 2 Typical experimental breakthrough curve for sorption of an equimolar ternary mixture nHEX/3MP/22DMB in ZIF-8. Experimental conditions: a1) pp = 1.8 kPa, T = 313 K; Red lines represent blank runs at the same experimental conditions with the column filled with glass spheres

basic information of the underlying phenomena that governs the system. With such data is it possible using a convenient mathematical model to identify which are the controlling mechanisms of the process and thereafter to proceed to a convenient design of an industrial process. Moreover, it is generally the dynamics of the fixed bed system, rather than the equilibrium conditions, and then kinetic mechanism in single particles that control the adsorption separation process.

To clarify the discrepancies previously observed by several authors, we have performed several breakthrough experiments with the mixture nHEX/3MP/22DMB in commercial and home-made ZIF-8 [14]. Figure 2 shows a typical breakthrough curve where it can be seen that branched isomers 22DMB and 3MP practically elute the column at the beginning of the experiment with no separation between them, but they are completely separated from linear nHEX that elute much later. This result indicates that 3MP and 22DMB leave the column practically with no adsorption in ZIF-8 in contrast with nHEX that adsorbs significantly in the column. These results are controversial since Zhang et al. [23] observed in a static system that all hexane isomers adsorb on ZIF-8. However, they are in agreement with the ones found by Chang et al. [3] and Luebers et al. [13] who studied the same system in a chromatographic column. A possible explanation could be the different methods used to study the adsorption of hexane isomers in ZIF-8. Some studies were performed in flow conditions and others in static conditions. However, that justification is not totally satisfactory since Peralta et al. [17] performed also the study in a breakthrough apparatus and found a certain degree of separation between 3MP and 22DMB. A possibility concerning this discrepancy could be related to differences in residence time of the gas mixture in the fixed bed column. In Peralta et al. experiments, the

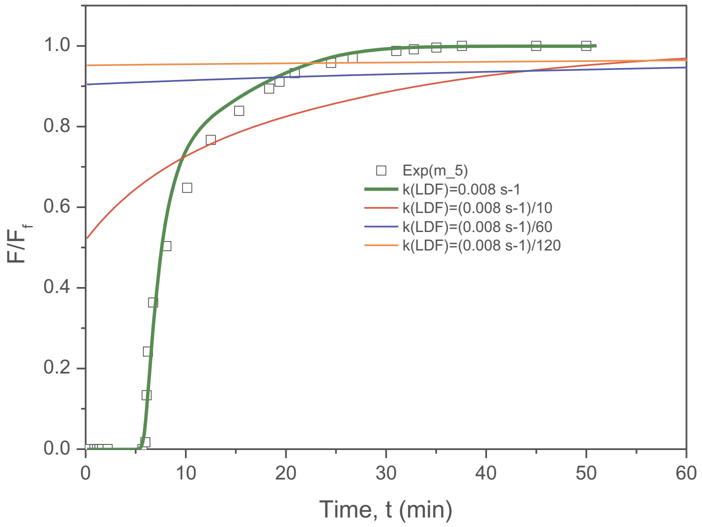

Fig. 3 Single component nHEX breakthrough at 313 K. The green line represents the simulation of the experiment with a K_{LDF} of 0.008 s^{-1}. The other lines (red, blue and orange) show the effect of decreasing the K_{LDF} by 10, 50 and 100 times, respectively, in the breakthrough curve (or increasing τ_{dif}). Points are experimental data and lines are model predictions

contact time (residence time) measured by $\tau_{fb} = L/v_i$ is around 20 s, where v_i is the interstitial velocity. In our experiments, it ranges from 1 to 4 s. Since 3MP and 22DMB are slow diffusing species [23], this could explain why 3MP enters partially in the adsorbent in the case of Peralta's experiments due to at least 5 times higher residence time of the gas mixture if the fixed bed column. Apart from being slow diffusion species, the ratio of diffusivities 3MP/23DMB is 3 which combined with the ratio of diffusivities and residence time of the gas in the column could support the separation observed in the breakthrough curves.

To prove that the separation between nHEX and the branched isomers 3MP and 22DMB observed in our experiments is kinetically driven, we use the mathematical model previously described to simulate a single component breakthrough. For the study, we select an experimental single component breakthrough curve of n-HEX since we do not have isotherm data for 3MP and 22DMB because they do not adsorb in the packed column. Figure 3 shows the experiment together with the simulations performed by the mathematical model. The experimental conditions and model parameters used for the simulation are shown in Table 2. For the simulation we use the corrected diffusivity D_0 for nHEX reported by Zhang et al. [23] which is 3.4×10^{-19} m^2/s at 313 K. Since this value is a corrected diffusivity we transform it to the Fickian diffusivity using the correction factor for the Langmuir isotherm $D_c = D_0/(1 - q/q_{max})$ (see [19]). Since the amount adsorbed in the experiment is 2.94 mmol/g and the total loading taken from the Langmuir isotherm is 3.13 mmol/g (see [14]) we estimate a Fickian diffusivity D_c of 5.4×10^{-18} m^2/s for nHEX. If we use the LDF model for the mass transfer in the bed, the characteristic

Table 2 Experimental conditions and model parameters for the simulation of the single component (nHEX) breakthrough experiment shown in Fig. 3

Isotherm parameters (nHEX)	
q_m	3.13 mmol/g
K_i	1.73 kPa^{-1} at 313 K
Experimental conditions	
C_f	57.6 mol/m^3
F_f	1.33 $\text{mol/m}^2\text{.s}$
m_a	0.318 g
P_c	150 kPa
T_f	313 K
y_{if}	0.0656
Model parameters	
c_{pg}	20 J/mol.K
c_{ps}	1.6 J/g.K
d_p	0.2×10^{-6} m
d_c	4.6×10^{-3} m
D_{ax}	2.59×10^{-5} m^2/s (see *Note 1*)
h_p	42500 W/m^2.K (see *Note 2*)
h_w	0.38 W/m^2.K (see *Note 3*)
k_{LDF}	0.008 s^2 (see *Note 4*)
K_{ax}	0.030 W/m.K
L	0.08 m
Greek letters	
ε_b	0.5

Note 1 Calculated by the correlation $D_{ax} = 0.7D_m + 0.5d_p v$, taken from Ruthven [19]. The axial mass Peclet number is 179

Note 2 This value was estimated from the limit of $Nu = 2$ and it can be considered a very high value, which means that the temperature between solid and bulk gas phase is in equilibrium

Note 3 This parameter was obtained through the fitting of the experimental breakthrough curve

Note 4 The LDF parameter was calculated by $k_{LDF} = 150D_c/r_c^2$, with D_c calculated from the data of Zhang et al. [23]

mass transfer coefficient will be $K_{LDF} = 15 \times 5.4 \times 10^{-18}/(0.1 \times 10^{-6})^2 = 0.008$ s^{-1} (we assume that the size of the crystals is similar to size of the commercial ones, that is 0.2 μm [17]). The mean residence time or contact time $\tau_{fb} = L/v_i$ for the experiment is around 1.3 s. Figure 3 shows the simulation of the breakthrough of nHEX (green line) using the mass transfer parameter $k_{LDF} = 0.008$ s^{-1}. The experimental conditions and model parameters are specified in Table 2. To fit the curvature of the breakthrough curve we also need to use a non-isothermal model due to the slow approach of concentration to equilibrium. It is clear from Fig. 3 that it is possible to fit the profile of the nHEX curve with the diffusivity data reported by Zhang et al. [23] and using an LDF model. To see what happens in the fixed bed by decreasing the diffusivity (or increasing τ_{dif}) we simulate the same experiment using a value of k_{LDF} 10, 60 and 120 times lower (we note that Zhang et al. [23] report a diffusivity 20 times lower for 3MP and 147 times lower for 23 DMB at 313 K). Figure 3 clearly shows that if we decrease at least 10 times the diffusivity of the adsorbable species in the bed the compound will come out of the column immediately at the residence time τ_{fb}. This simulation clearly explains that the separation between normal and branched paraffins is indeed kinetically driven and can be predicted with diffusivity data already published using a convenient mathematical model.

These results also prove that the discrepancy between experiments in flow and static systems are due to kinetic considerations proper of fixed bed adsorbers. In a static system, the gas mixture of hexane isomers contact with the adsorbent ZIF-8 in a completely different time scale compared to experiments that could occur for few seconds. This means that an appropriate selection of the residence time of the gas mixture τ_{fb} in the fixed bed could give rise to a separation of hexane isomers due to their different diffusivities apart for being all adsorbed with identical amounts.

Figure 3 also shows that to capture the profile of the breakthrough curve it is necessary to use a non-isothermal model. Figure 4 shows the simulation results for the concentration and temperature profiles of the breakthrough curves in isothermal and adiabatic cases. The experimental conditions and model parameters are specified in Table 2. It is clear that only using a non-isothermal model it is possible to capture the profile of the experimental breakthrough curve. Moreover, the gas temperature

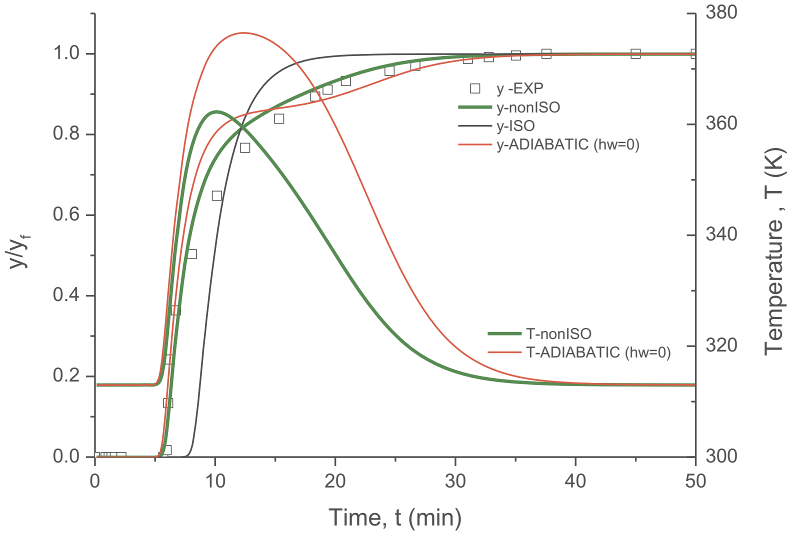

Fig. 4 Simulation of the breakthrough curve shown in Fig. 3 with a non-isothermal, isothermal and adiabatic models. The green lines represent the simulation with the non-isothermal model, the red the adiabatic model, and the black the isothermal model. Points are experimental data and lines are model predictions

of nHEX can increase 50 C at the outlet of the bed due to the large amount of adsorbed nHEX. Figure 4 also shows, for comparison, the profile of composition and temperature in the bed for the limiting isothermal and adiabatic cases. In the adiabatic case the temperature can increase around 70 °C.

5 Conclusions

A mathematical model has been developed to study the hexane isomers adsorption in a fixed bed packed with the microporous adsorbent ZIF-8. Simulations of isothermal breakthroughs show that a proper combination of residence time in the bed measured by τ_{fb} and characteristic time of diffusion of the solutes into the pores of the adsorbent measured by τ_{dif} can lead to very different dynamics of fixed bed adsorbers. It was shown that a τ_{dif} 100 times higher than τ_{fb} leads to spontaneous breakthrough curves of solutes in the fixed bed.

Ternary breakthrough experiments with mixtures of nHEX/3MP/22DMB flowing through the packed bed show a complete separation of linear nHEX from the branched paraffins 3MP/22DMB which spontaneously come out of the bed at the beginning of the experiment. These results contradict previously published works [7, 17, 23] but are similar to other results obtained in chromatographic columns [3, 13].

To explain the uncommon experimental sorption behavior observed, the mathematical model developed in this work was used to simulate an experimental breakthrough curve. The parameters of the mathematical model were obtained from different sources. In particular, the diffusivity values of the hexane isomers were taken from the work of Zhang et al. [13].

The simulations results show that the spontaneous breakthrough curves of the branched hexane isomers 3MP and 22DMB are due to the very low diffusivity of these compounds in ZIF-8 when compared to the one in the linear nHEX. Moreover, a proper combination of the residence time in the bed $\tau_{fb} = L/v_i$ and the characteristic time of diffusion $\tau_{dif} = 1/k_{LDF} = r_c^2/15D_c$ of the hexane isomers in ZIF-8 can give rise to a complete separation between normal and branched paraffins.

It can also be retained from this work that experimental results of hexane isomers sorption in ZIF-8 measured under batch equilibrium conditions or flow systems can be completely different. Indeed, it is noteworthy that it is possible to completely separate linear from branched alkanes while equilibrium isotherms show similar amounts adsorbed for all the compounds.

Finally, this work shows the importance of mathematical modelling in the analysis and interpretation of experimental data and the design of adsorption processes.

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