EVALUATION OF EQUILIBRIUM MODELS FOR ADSORPTION OF n-BUTYLAMINE ON ALUMINA

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ABSTRACT: *Determining heterogeneity of acid surfaces may be very useful to the kinetic modelling of many industrial processes like catalytic cracking of heavy fractions from petroleum. Previous studies of adsorption and desorption of organic bases on samples of gamma alumina using dynamic microgravimetric method revealed existing strong and weak sites, classified in such manner according to their ability to retain organic bases during the desorption step, conducted at constant temperature. Models assuming homogeneous pores distribution, however, have been widely reported as being also applicable even to media comprehending heterogeneous surface. This work aimed to obtain adsorption parameters through gravimetric-determined isotherms, and through equilibrium models to the particles of adsorber. Samples of alumina were put into a basket exposed to a flow of nitrogen containing n-butylamine. Temperature of saturator has been manipulated to allow different base concentrations through the sample. In each experiment were used about 60 mg of alumina, whose particles had mean diameter equal to 0.105 mm and submitted to a flow of gas about 60 ml/s. Experiments were conducted at atmospheric pressure and 200^oC. Microgravimetric system was composed by a Cahn 200 microbalance*

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connected to a stainless steel wire. Two equilibrium models were tested: the model of homogeneous diffusion in the porous adsorber with a mass transfer resistance in the film covering the particle, and the model of Linear Driving Force (LDF), which estimated the mean adsorbed concentration as a function of time. For the LDF model, analytical solution allows prediction of effective diffusivity by an optimization method when experimental data are provided; for the pore diffusion model the subroutine PDECOL was used to solve the partial differential equation, and to calculate the base concentration inside particles of alumina.

INTRODUCTION

Modelling adsorption processes has lately become widespread, since it may be helpful towards a better understanding of the phenomena involved in such processes. Besides, many economic factors have contributed to the recent developments in this area, inasmuch as tons of catalysts are poisoned and deactivated every year in petrochemical industries.

The study of existing models tends to be exhaustive, although many authors, when comparing experimental data to solutions of differential equations, do not assume a critical position concerning the accuracy of their idealisations, which would be very useful in order to improve the efficiency of simulations.

There are two different manners to face adsorption processes: writing down equations regarding equilibrium, or regarding kinetics. If one decides dealing with equilibrium models, it is implicit the assumption that all catalyst's sites have the same affinity for a given compound. On the other hand, kinetic models consider the coexistence of different sites, where a compound may adsorb more strongly or not. The latter usually give better results, but they do require the determination of more parameters.

It is proposed a comparative study which will focus on equilibrium models, in order to prove their adequacy to the adsorption of n-butylamine, a nitrogenated base very similar to compounds found on petrochemical processes. Once a model is considered to provide a good prediction, its optimum parameters will be determined.

In this first part, there were chosen more simple models, as Linear Driving Force approach, and pore diffusion model, and some conclusions are presented to the usage of both procedures. Concerning the latter, which comprehends two adjustable parameters, the effective diffusivity and the Biot number, some simulations were made to estimate the process limiting step.

EXPERIMENTAL DETAILS

In all the experiments, home-made alumina was used, obtained through precipitation of aluminum hidroxide from a solution of ammonia and

aluminum nitrate. As described by VEDOVA (1996), during the reaction, pH was maintained equal to 9.0 and produced hidroxide was heated to 500°C for five hours.

Graph on Fig. 1 clearly shows alumina could be reasonably described by either a bimodal or a trimodal pore distribution, and should be modelled reaagarding this conformation. Probably each range of pores has its own diffusion coefficient. As the present work is a first step to determine how accurate are equilibrium models, chosen equation assumed just one range of pores and, consequently, just one value for diffusivity inside particles.
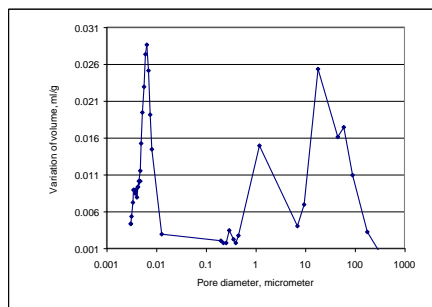

Fig. 1 – Distribution of pores obtained through mercury porosimetry for homemade alumina.

To measure the adsorbed quantity, about 60 mg of alumina were put into a basket exposed to a flow of nitrogen containing n-butylamine. Data acquired by Cahn 200 microbalance were processed by a computer, and experiments finished soon after mass reached a constant value.

MODEL OF LINEAR DRIVING FORCE

For many columns, the usage of Linear Driving Force approximation reduces the problem's complexity, since it assumes the mean variation of surface adsorbate concentration as a function of the concentration on the external surface, given by an equilibrium isotherm, and its own value. So, one could write down:

$$\frac{\partial \langle q \rangle}{\partial t} = K_p \left[q^* - \langle q \rangle \right] \qquad (1)$$

where <q> is the mean adsorbed concentration, K_p is a mass transfer coefficient, t represents time, in min, and q^*, expressed in mg/m^2, is given by a Langmuir isotherm:

$$q^* = \frac{K_1 \cdot p}{1 + K_2 \cdot p} \qquad (2)$$

where K_1 and K_2 are the isotherm constants and p is the n-butylamine partial pressure. The constants of the isotherm were determined gravime-trically, and their values are:

$K_1 = 0.0102885$ mg / (kPa.m^2)

$K_2 = 0.057$ kPa^{-1}

For more accurate predictions, however, more complex isotherms should be used, since the hypothesis supporting Langmuir model is the occurrence of just monolayer adsorption, and does not take into account phenomena like capillary condensation, for example.

According to Glueckauf (1955), the mass transfer coefficient may be written as:

$$K_p = 15 \frac{D_{eff}}{R_p^2} \tag{3}$$

where R_p is the particle's radius and D_{eff}, the effective diffusion coefficient, the parameter which was manipulated by the optimization routine.

For the studied system, as the concentration of n-butylamine in the gas phase does not vary much along the sample of alumina, it is assumed to have a constant value. Therefore, the equation (1) has analytical solution:

$$\langle q \rangle = q^* \left(1 - e^{-K_p t} \right) \tag{4}$$

To compare simulations with experimental data, it was necessary calculating the total mass adsorbed. It was done by multiplying the mean adsorbed amount by the specific area and by the mass of alumina.

As the equation is very simple, a FORTRAN optimization routine was used to obtain the effective diffusivity. Some results can be seen on the next graph, figure (2). The fits show an interesting behaviour. The results show a good prediction once reached the equilibrium, but not for the transient step. Some hypotheses can be formulated, concerning the fact that adsorption is not an instantaneous process, and there would be a small period, not observed in the equation, for n-butylamine to adsorb.

As LDF model was formulated almost half a century ago, there could be a historical reason for this approach being adequate just to the equilibrium. Data acquisition systems improved a lot last years, and it was probably too difficult to take samples in the very beginning of experiment. So, experimental data, obtained even minutes after t_0, did not reveal very accurately the transient step. With on line acquisition data, one may study more carefully such region.
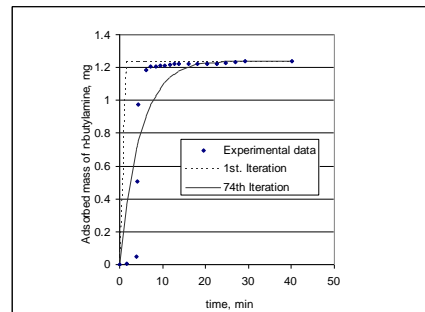

Fig.2 – Optimization of LDF approach. Experimental data obtained using 57.557 g of alumina and base partial pressure equal to 40.1 kPa.

On the other hand, Linear Driving Force is widely used while modelling adsorption and chromatographic columns since space time is much bigger than the time for a compound to adsorb. So, this effect is less significative than convection or axial dispersion. The optimisation method consists of minimisation of an objective function which is the cumulative total of the square deviations between experimental and simulated data:

$$v = \sum (y - \hat{y})^2 \tag{5}$$

where y represents simulated data and $\hat{y}$, experimental points.

As one may realise by looking at the last picture, this algorithm, however, may provide unreal approaches, when a model does not describe accurately a process. To avoid such mistakes, it is suggested the minimisation of an alternative objective function, namely w, involving the deviations of derivatives:

$$w = \sum \left(\frac{\partial y}{\partial x} - \frac{\partial \hat{y}}{\partial x} \right)^2 \qquad (6)$$

The association of both v and w functions in a program could provide more adequate optimum data, or, if the model does not represent the process behaviour, indicate how far is proposed equation from reality.

PORE DIFFUSION MODEL

Writing down equations for the pore diffusion model means doing a mass balance inside the particles of alumina. Although there are pores bigger than 1000 Å, intraparticle convection is not considered since process is not conducted at high pressures.
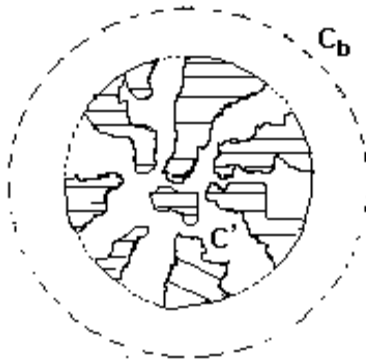

Fig. 3 – A porous spherical particle.

Considering diffusion in the pores and spherical particles, one will obtain:

$$\varepsilon_p \frac{\partial C'}{\partial t} + (1 - \varepsilon_p) \frac{\partial q}{\partial t} = \frac{D_{eff}}{R_p^2} \left(\frac{\partial^2 C'}{\partial \eta^2} + \frac{2}{\eta} \frac{\partial C'}{\partial \eta} \right)$$

$$(7)$$

where C' is the concentration of n-butylamine in the fluid phase inside the particle; q, the adsorbed quantity; ε_p, the particle's porosity; and η is the non-dimensional particle's radius, defined as follows:

$$\eta = \frac{r}{R_p} \qquad (8)$$

As initial condition is set that, at t = 0, there is no solute in the fluid phase. Boundary conditions take into account the assumption that particles are symmetric, and resistance to film mass transfer:

$$\eta = 0, \frac{\partial C'}{\partial \eta} = 0 \qquad (9)$$

$$\eta = 1, \frac{D_{eff}}{R_p} \frac{\partial C'}{\partial \eta} = h(C_b - C') \qquad (10)$$

where h represents convective mass transfer coefficient and C_b is the concentration of solute in the flow of N_2.

The variation of adsorbed amount may be derived from the equilibrium isotherm, then the system is reduced to one partial differential equation.

Using the Biot number, defined as follows:

$$Bi = \frac{h.R_p}{D_{eff}} \qquad (11)$$

So, equation (10) may be rewritten as:

$$\eta = 1, \frac{\partial C'}{\partial \eta} = Bi(C_b - C')$$ (12)

It was used a program based on PDECOL, a public domain FORTRAN's subroutine, to solve the problem by the method of orthogonal collocation applied to finite elements.

It was necessary again evaluating total adsorbed mass, but first mean adsorbed amount was calculated by integration in the whole particle:

$$\langle q \rangle = \frac{1}{V} \int_0^V q \, dV$$ (13)

To determine limiting step of pore diffusion model, simulations were made using different values for effective diffusivity and Biot number, and results were compared to experimental data.

As it is seen on Fig. 4, simulations were done by varying diffusivity while Biot remained fixed. The less significative the diffusivity, the more divergent the graph's behaviour.
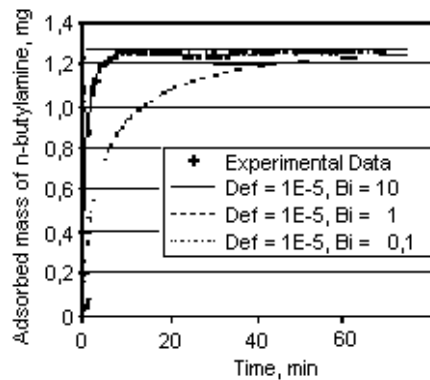

Fig. 4 – Comparative graph for experimental and simulated data

Fig. 5 and Fig. 6 show that, for high diffusivities, the effect of variations in Biot number is less significative than for systems with minor inner diffusion. So, limiting step is diffusion inside pores, and its value will be searched between 10^{-3} and 10^{-5} cm^2/ min, by associating an optimization routine to the PDECOL in a further work.
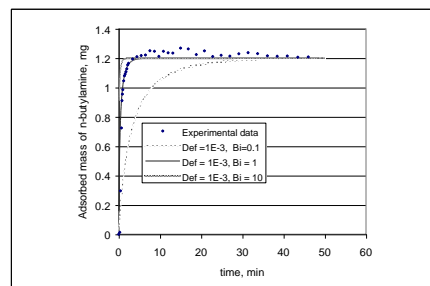

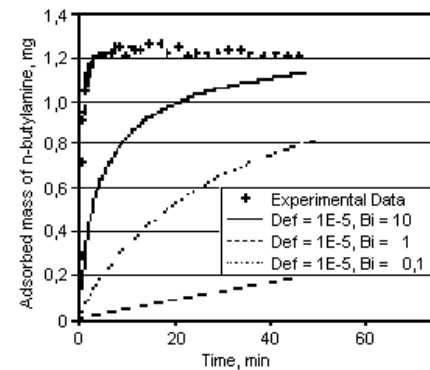Fig. 5 – Graph showing effect of Biot's variation when $D_{eff} = 10^{-3}$ cm^2/ min

Fig. 6 – Graph showing effect of Biot's variation when $D_{eff} = 10^{-5}$ cm^2/ min.

CONCLUSIONS

Linear Driving Force does not allow further studying of phenomena involved in adsorption processes,

although it is useful while solving more complex problems
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Both models predict well the equilibrium, but they are not adequate to the transient step. To improve pore diffusion model, alumina's inner structure must be taken into account, by writing mass balances including transport in both macropores and micropores.

Graphs of pore diffusion results indicate that process is governed by diffusion inside particles, since variations in Biot number do not show significative changes if diffusivity is considered to be high.

Next step of this work will include studying of other equilibrium models, such as shrinking core model, and the usage of porosimetry data to determine tortuosity and to derive models considering diffusion in different ranges of pores. Besides, transient step will be investigated, because it may indicate either non-instantaneous adsorption or resistance to inner diffusion, effects that are not easily realised on adsorption columns. The routine of optimisation will also be improved and associated to the PDECOL routine, in order to evaluate optimum parameters.

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