



Shorter communication

Mathematical modelling of styrene drying by adsorption onto activated alumina

María J. Rivero, Raquel Ibáñez, M. Inmaculada Ortiz*

Departamento de Ingeniería Química y Química Inorgánica, E.T.S.I.I. y. T., Universidad de Cantabria, Avenida de Los Castros s/n, 39005 Santander, Spain

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Abstract

This work is focused on the analysis and modelling of styrene drying, raw material in the manufacture of synthetic rubber, by means of adsorption onto activated alumina. Equilibrium experiments, carried out under isothermal conditions at 10°C, correlated to the equation q (kg/kg) = $2.659 \times 10^{-4} C$ (mg/kg). Fixed bed column experiments were performed working with different flow rates and using different bed lengths in order to obtain experimental breakthrough curves. A mathematical model that considers the influence of both film and pore mass transfer resistances described satisfactorily well the experimental results. Finally a value of $D_p = 6.101 \times 10^{-9} \text{ m}^2/\text{s}$ was obtained from correlation of experimental data to simulated curves and using the minimum weighted standard deviation as optimisation criterion. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Styrene is produced on a large scale (£ 66 billion p.a.) mainly for production of styrene-butadiene rubber. The anionic polymerization reaction uses *n*-butyl lithium as an initiator and this compound is destroyed by water, a common impurity in commercial styrene (typically 200 ppm wt). The first step in the process therefore involves adsorptive drying of the styrene using a fixed-bed packed with either activated alumina or a zeolite desiccant. Compared with the large literature on gas drying (Rudzinski & Everett, 1992) reported studies of liquid drying are relatively scarce although general information is given in the reviews by Basmadjian (1984) and Ruthven (1984) and some equilibrium data has been tabulated by Valenzuela and Myers (1989).

This study is focused on the modelling of the adsorptive styrene drying using activated alumina and includes the experimental determination of the equilibrium isotherm, the dynamic study of the adsorption process in a fixed bed in order to characterise the breakthrough curves and the development of the mathematical model that predicts the experimental behaviour fairly well.

2. Experimental results and discussion*2.1. Equilibrium isotherm*

Fig. 1 shows the adsorption isotherm of water from styrene onto alumina at 10°C obtained working with alumina/styrene ratios in the range of 1 kg/5 l to 1 kg/200 l in a fixed-bed column.

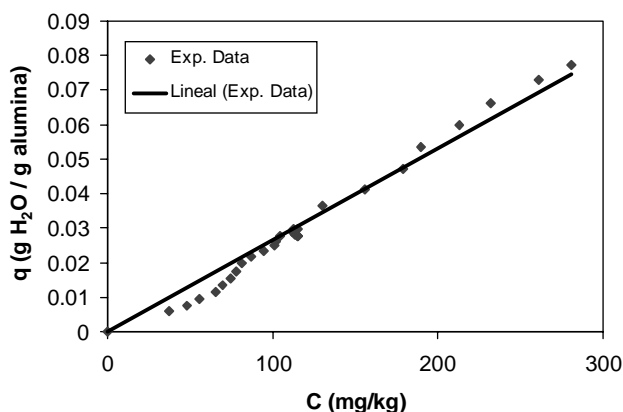


Fig. 1. Adsorption isotherm at 10°C.

* Corresponding author. Tel.: +34-942-20-15-85; fax: +34-942-20-15-91.

E-mail address: ortizi@unican.es (M.I. Ortiz).

Table 1
Summing of experimental conditions

Exp no.	T ($^{\circ}\text{C}$)	Alumina (kg)	Bed length (m)	C_o (mg/kg)	F (l/h)	u_s (m/s)
1	10	0.0625	0.070	100.0	1.02	3.35×10^{-4}
2	10	0.125	0.141	142.0	1.02	3.35×10^{-4}
3	10	0.250	0.282	133.5	1.02	3.35×10^{-4}
4	10	0.125	0.141	163.7	1.98	6.51×10^{-4}
5	10	0.0625	0.070	161.6	1.98	6.51×10^{-4}
6	10	0.0625	0.070	165.2	0.50	1.66×10^{-4}

The solid loading has been calculated through a mass balance to the liquid phase after measurement of the initial and final water concentrations, with the Karl Fisher coulometric titration, according to Eq. (1).

$$q_i = (C_{0,i}V_0\rho_l - C_iV\rho_l)/m. \quad (1)$$

Eq. (2) fits the experimental data obtained,

$$q = 2.659 \times 10^{-4} C \quad (r^2 = 0.98) \quad (2)$$

where q is kg/kg and C is mg/kg.

The linear form is often approximated at very low concentrations (Do, 1998; Goto, Matsumoto, Yang, & Goto, 1986; Prasher & Ma, 1977; Wankat, 1994).

2.2. Dynamic adsorption studies

All the experimental conditions are detailed in Table 1.

The fluid flow was always upwards through the column, in order to achieve better contact between solid and liquid and to avoid channelling.

2.2.1. Mass transfer model development

The differential mass balance for the solute in the packed bed is based on the following hypothesis: (i) there are no radial gradients, (ii) isothermal operation, (iii) constant liquid velocity through the bed, (iv) axially dispersed plug flow, (v) negligible accumulation of adsorbate in the pores, (vi) solid granules modelled as spheres and (vii) linear combination of the mass-transfer resistances corresponding to the external mass transfer from the bulk liquid phase to the particle surface and the internal pore diffusion within the particle itself (Desai, Hussain, & Ruthven, 1992; Joshi, 1987; Ruthven, 1984).

This model is expressed mathematically by Eqs. (3)–(5).

$$\varepsilon_e \frac{\partial C}{\partial t} + u_s \frac{\partial C}{\partial z} + \rho_p(1 - \varepsilon_e) \frac{\partial \bar{q}}{\partial t} = \varepsilon_e E \frac{\partial^2 C}{\partial z^2}, \quad (3)$$

$$\rho_p(1 - \varepsilon_e) \frac{\partial \bar{q}}{\partial t} = k_m a_p (C_i - C_i^*), \quad (4)$$

$$k_m a_p = \frac{1}{1/(k_f a_p) + R_p^2/(15\varepsilon_p D_p)}. \quad (5)$$

With initial conditions:

$$\begin{aligned} C(z, 0) &= C_0, \\ q(z, 0) &= q^*(C_0) \end{aligned} \quad (6)$$

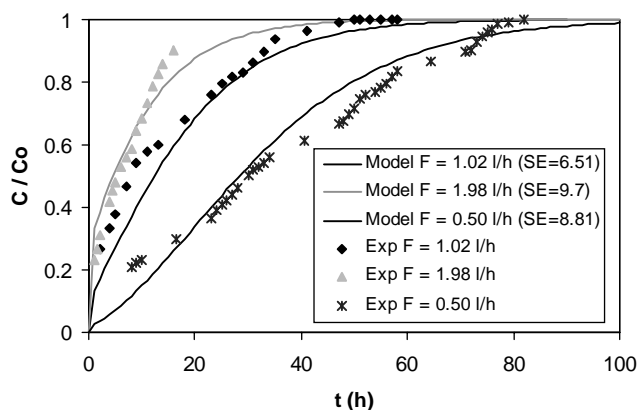


Fig. 2. Breakthrough curves corresponding to different values of styrene flow rate (bed length = 0.070 m).

and boundary conditions for $t > 0$,

$$\begin{aligned} \text{at } z = 0, \quad C &= C_0, \\ \text{at } z = L, \quad \partial C / \partial z &= 0. \end{aligned} \quad (7)$$

The system of coupled partial differential equations plus the adsorption isotherm and the relevant initial and boundary conditions has been solved using gPROMS (general PROCESS Modelling System, version 1.6B) developed by Process Systems Enterprise Ltd. The magnitude of the axial dispersion term was determined from the data reported by Levenspiel (1999). After a literature review of the mass transfer correlations for the prediction of the film mass transfer coefficient, k_f , the best results were obtained with the correlation reported by Wilson and Geankoplis (1966)

$$Sh = (1.09/\varepsilon_e) Sc^{(1/3)} Re^{(1/3)}. \quad (8)$$

2.2.2. Analysis of the experimental breakthrough data

Experimental breakthrough data corresponding to the experiments detailed in Table 1 as well as the predicted curves with the reported model are shown in Figs. 2–4 for different bed lengths and flow rates. In general, it is observed that the predicted breakthrough curves are in reasonable agreement with the experimental data. The first section of the breakthrough curves has not been taken into account because low water concentrations could not be measured properly with the technique employed (Karl Fisher coulometric titration) due to interferences caused by impurities present in the raw styrene such as ketones, aldehydes and oxidising or

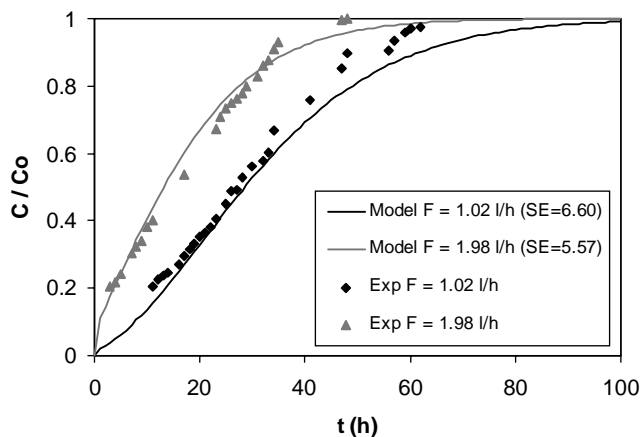


Fig. 3. Breakthrough curves corresponding to different values of styrene flow rate (bed length = 0.141 m).

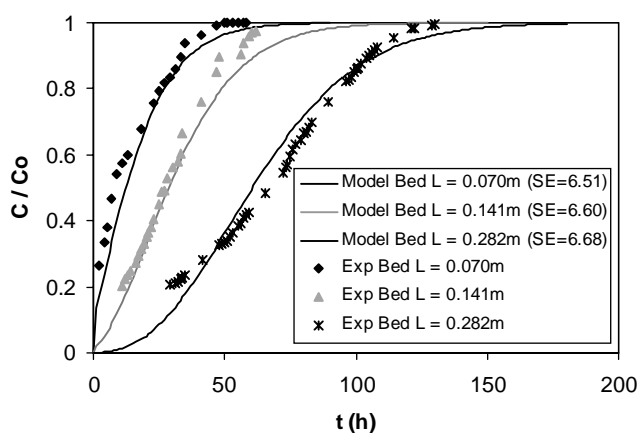


Fig. 4. Breakthrough curves obtained working with different bed lengths (flow rate = 1.02 l/h).

reducing agents (ASTM, 2000). It has also been pointed out that the primary source of uncertainty is the nonuniformity of the adsorbent particles (Joshi, 1987). Smaller than average size particles can produce a delay of the breakthrough while larger than average particles, which approach equilibrium more slowly, can cause the opposite effect to the breakthrough curve (Rasmuson, 1985).

The value of pore diffusivity was determined by the best fitting of the experimental data to the mathematical model based on the minimum value of the standard error (SE) according to Eq. (9). A value of $D_p = 6.101 \times 10^{-9} \text{ m}^2/\text{s}$ (SE = 7.34) was finally obtained.

$$SE = \sqrt{\frac{\sum (C_{exp} - C_{sim})^2}{n - 1}} \quad (9)$$

Joshi (1987) in the analysis of toluene drying with alumina concluded that almost 70–75% of the total resistance to mass transfer resided in the particle, and the best fitting was obtained for a value for D_p of $8.00 \times 10^{-9} \text{ m}^2/\text{s}$, very close to the value reported in this work.

Other authors concluded that in commercial granular alumina pore diffusion is the essential controlling mechanism (Carter & Barrett, 1973; Marcussen, 1982). Teo and Ruthven (1986), drying organic compounds with molecular sieves, found that the process was controlled primarily by intraparticle pore diffusion resistance with some additional contribution from external film resistance, depending on the hydrodynamic conditions. Using activated carbon as desiccant, McKay and Bino (1985) obtained values of D_p in the range of $1 \times 10^{-9} \text{ m}^2/\text{s}$.

Basmadjian (1984) used the data of several authors' references to calculate the value of the pore diffusion coefficient for liquid moisture adsorption concluding that they are spread over the range of $1 \times 10^{-10} \text{ m}^2/\text{s} - 1 \times 10^{-8} \text{ m}^2/\text{s}$.

3. Conclusions

Equilibrium measurements for styrene on activated alumina, carried out at 10°C in fixed-bed column, led to the isotherm equation $q \text{ (kg/kg)} = 2.659 \times 10^{-4} C \text{ (mg/kg)}$ that is in agreement with expressions reported by different authors for drying organic liquids (Goto et al., 1986). Experimental breakthrough curves were determined at different flow rates in the range 0.50–1.98 l/h and for different bed depths (62.5–250 g of alumina). A mathematical model including film and pore resistances to mass transfer has been developed and correlated to the experimental data obtaining the best fitting based on the minimum value of the weighted standard deviation when the design parameters took the values $D_p = 6.101 \times 10^{-9} \text{ m}^2/\text{s}$ and k_f was calculated from the correlation of Wilson–Geankoplis $Sh = 1.09/\epsilon_e Re^{(1/3)} Sc^{(1/3)}$. The parameters obtained for the design of a styrene drying lead to the conclusion that the main controlling resistance to mass transfer lies within the particle, as has also been pointed out in earlier studies, i.e. Ruthven (1984) and Joshi (1987).

Notation

a_p	external surface area/volume, m^2/m^3
C_i	adsorbate concentration, mg/kg
C_i^*	adsorbate equilibrium concentration, mg/kg
$C_{0,i}$	adsorbate initial concentration, mg/kg
C_{exp}	experimental concentration, mg/kg
C_{sim}	simulated concentration, mg/kg
d_p	particle diameter, m
D_m	molecular diffusivity, m^2/s
D_p	diffusivity in pores, m^2/s
F	flow rate, m^3/s
k_f	film diffusion coefficient, m/s
k_m	lumped parameter mass transfer coefficient, m/s
m	amount of alumina, g
n	experimental data number
q_i	amount of solute adsorbed onto the solid/amount of solid, kg/kg

q^*	amount of solute adsorbed onto the solid in the equilibrium, kg/kg
Re	Reynolds number, $\rho_l u_s d_p / \mu$
R_p	particle radius, m
Sc	Schmidt number, $\mu D_m / \rho$
Sh	Sherwood number, $k_f d_p / D_m$
t	time, s
u_s	superficial fluid velocity, m/s
V	styrene volume, l
z	axial distance in column

Greek letters

ε_e	external void fraction
μ	viscosity, kg/ms
ρ_l	liquid density, kg/m ³

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