MATHEMATICAL MODEL OF SUPERCRITICAL CO$_2$ ADSORPTION ON ACTIVATED CARBON APPLIED TO ADSORPTION SCALE-UP

S. Lucas*[a], M.P. Calvo[b], C. Palencia[b], E. Alonso[a], M.J. Cocero[a]
[a]Departamento de Ingeniería Química
[b]Departamento de Matemática Aplicada y Computación
Universidad de Valladolid, Spain
C/ Mergelina s/n - 47011
e-mail: susana@iq.uva.es   Tfno. 983 42 31 66   Fax: 983 42 30 13

Abstract

A general mathematical model for supercritical CO$_2$ adsorption on activated carbon have been developed. Adsorption curves obtained with a laboratory plant (adsorber of 10 mL) have been adjusted with this model and the results have been extrapolated to adjust the breakthrough curves obtained with a pilot plant (adsorber of 1L).

The proposed model is general and takes into account equilibrium (adsorption isotherm), diffusion in the solid (effective diffusion coefficient), mass transfer from the bulk of the fluid phase (supercritical solvent) to the surface of the solid, axial dispersion (effective dispersion coefficient) and a first order reversible adsorption/desorption reaction at the solid surface site. This model can be considered as *general* due to kinetics of the adsorption-desorption at a site as well as intraparticle diffusion, fluid-particle mass transfer, and axial dispersion are included and the contribution of these parameters (k_a, k_d, D_e, k_f, D_{az}) have demonstrated to be essential for getting a good adjust.

In order to get a suitable adjust, the experimental adsorption curves have been represented by this model by fitting the kinetic coefficients (k_a, D_e and D_{az}) to the experimental curves, obtained from the laboratory installation. The parameters k_f and k_d are calculated, k_f by well-known correlation and k_d by the determination of adsorption isotherm. With the optimised parameters it is possible to model the adsorption curve obtained with the pilot plant with reasonable accuracy. Therefore, the model is *suitable* to determine the kinetic parameters from a laboratory experiment and to *scale-up* the adsorption process.

1. INTRODUCTION

To design an adsorption plant, it is necessary to have reliable mass-transfer models that will allow the determination of optimum operating conditions and the scale-up. Nevertheless, few attempts have been performed to model the supercritical adsorption processes [1,2] and most of the efforts have been centred in supercritical fluid extraction [3] and its scale-up [4].

The most common models are based on differential mass balances along the extraction bed. To integrate the differential equations these models require information on the mass-transfer mechanism that characterizes the extraction process and data on the equilibrium relationship. For this reason, in most cases the authors simplified the system of partial differential equations deriving from the differential mass balances to obtain an analytical solution. Recasens *et al.* developed two practically important models with analytical solution: 1) an equilibrium desorption model where the rate of desorption is controlled by external and intraparticle mass transfer and 2) a kinetic model where external and intraparticle mass

transfer and a first-order irreversible desorption step control the overall process. assumed that mass transfer resistance occurred only in the solvent phase [5]. Madras *et al*. proposed a model to adjust the desorption profiles of various organics from soil [6]. This model takes into account effective diffusion, axial dispersion and external mass transfer, and it is solved using the orthogonal colocation on finite elements. Poletto and Reverchon made an attempt to generalize the simulation mathematical models developing a general dimensionless model for a sensitive analysis of the supercritical extraction process of vegetable oils and essential oils [7].

In spite of the various modelling approaches, the major problem in SFE modeling is the interaction between the equilibrium and mass transfer and kinetics mechanisms implicate in this separation process. For this reason, the first objective of this work is to develop a general model for adsorption on fixed beds of porous particles that includes finite rates for both the adsorption step at a site and mass transfer processes. The proposed model is general and takes into account:

- Mass transfer from the bulk of the fluid phase (supercritical solvent) to the surface of the solid (mass transfer coefficient related to the fluid phase, k_f)
- Diffusion in the solid (effective diffusion coefficient or effective transport coefficient as defined by the transport model, D_e)
- Axial dispersion (effective dispersion coefficient D_{az}, taking into account inhomogeneities of the fixed bed and the solvent distribution)
- Reversible Adsorption/Desorption reaction at the solid surface (first-order adsorption/desorption constants, k_a and k_d)
- Equilibrium distribution between solid and supercritical solvent (adsorption isotherm assumed as non linear Langmuir type with and adsorption constant, K)

The model involves five adjustable parameters (k_f, D_e, D_{az}, k_a and k_d), but in order to get a suitable adjust of the experimental adsorption curves only the kinetics coefficients (D_e, D_{az} and k_a) have been fitted. The parameter k_f can be calculated by well-known Wakao-Kaguei correlation [8] and k_d by the determination of Langmuir adsorption isotherm ($k_d = K/k_a$ [9]). In this conditions the model can be solved numerically to obtain the concentration of the solute in the fluid phase as a function on time (c(L,t)) with great accuracy.

The second objective is to apply the model to scale up of laboratory adsorption results [4]. It is possible because the adsorption data are available at different scales of operation (laboratory adsorber of 10 mL and pilot plant adsorber of 1L) . In this way we are able to check if the laboratory kinetics parameters obtained with the model are able to reproduce the results obtained with a pilot plant.

2. MATHEMATICAL MODELING

2.1. General hypotheses

Some hypotheses are needed to model the adsorption system:

1. The adsorption system is considered as a fixed bed with two phases:
    (a) Solid (static): adsorbent, which adsorbs the solute on
    (b) Fluid (mobile): supercritical solvent + solute

2. For the balance for the supercritical fluid phase some assumptions have been made: gradients of any kind are neglected in radial direction and convection and axial dispersion cause dispersed plug flow

3. The fixed bed was considered as a group of spherical and porous adsorbent particles with an average particle size of 1 mm. Real transport phenomena, like membrane transition, pore diffusion, diffusion in the solid, etc. are summarised in an effective transport coefficient (effective diffusion coefficient). At the solid surface site a first order reversible adsorption/desorption reaction takes places

4. Equilibrium between fluid phase and solid phase is modeled with the non-linear Langmuir isotherm

5. Solvent flowrate, its density and viscosity are constant during adsorption; pressure drop, temperature gradients and heat of adsorption are neglected (it is admitted that adsorption process is isothermal)

6. Superficial velocity is constant and it is calculated with CO_2 flowrate; the concentration of solute in supercritical solvent is very low

7. External and internal porosity remain constant

8. Time from the exit of the bed (packing) to exit of adsorber is negleted

2.2. Mass Balance Equations

Consider a packed bed of spherical adsorbent particles with an initial loading of adsorbate of concentration $c_{so} = 0$. Supercritical solvent loaded with a known quantity of solute (c_o) is introduced to the bed, which operates isothermally. It is first assumed that the adsorption is of the non-linear Langmuir form. Initially the loaded solvent rapidly fills the pores of the adsorbent particles. For these conditions mass conservation equations for the solute in the global supercritical phase, in the pores and on the adsorbent particles, are

$$\varepsilon \frac{\partial c}{\partial t} = -u_z \frac{\partial c}{\partial z} + \varepsilon D_{az} \frac{\partial^2 c}{\partial z^2} - k_f a \, (1-\varepsilon) \, (c - c_i \big|_{r=R_p}) \tag{1}$$

$$\beta \frac{\partial c_i}{\partial t} = D_e \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c_i}{\partial r} \right) - \rho_s \frac{\partial c_s}{\partial t} \tag{2}$$

$$\frac{\partial c_s}{\partial t} = k_a \, c_i - k_d \, c_s \tag{3}$$

with boundary and initial conditions

$CI:$ $t=0$ $c=0$ (4) $t=0$ $c_i = 0$ (5) $t=0$ $c_s = 0$ (6)

$CC:$ $z=0$ $c = c_o + \dfrac{\varepsilon D_{az}}{u_z} \dfrac{\partial c}{\partial z}$ (7) $z=L$ $\dfrac{\partial c}{\partial z} = 0$ (8)

                $r=0$ $\dfrac{\partial c_i}{\partial r} = 0$ (9) $r=R_p$ $D_e \left(\dfrac{\partial c}{\partial r}\right)_{r=Rp} = k_f (c - c_i \big|_{r=R_p})$ (10)

These equations can be solved numerically (*see 2.3. Numerical Solution*) for the effluent concentration c(L,t). The results would be general in that kinetics of adsorption/desorption at a site are included as well as intraparticle diffusion, fluid-particle mass transfer and axial dispersion.

2.3. Numerical Solution

The numerical integration of the model equations has been carried out by using the well-known method of lines. First we have discretized in space and then the time integration of the resulting ordinary differential equations have been done.

For the spatial discretization finite differences are considered and the time integration has been performed using the well-known backward Euler method. Explicit Runge-Kutta methods were also considered but, due to stability requirements, very small step sizes were necessary.

3. EXPERIMENTAL PROCEDURE

In this work ethyl acetate was selected as adsorbate because is a volatile compound responsible for fruity and brandy note of coffee aroma and it is the most common ester present in several kind of fruits (apple, grapes, etc.).

3.1. Materials and Methods

Ethyl acetate (98% purity) was purchased from MERCK and CO_2 (99.95% purity in volume) was supplied by Carburos Metálicos (Valladolid, Spain). The granular activated carbon (CAL) evaluated in this research was obtained from Chemviron Carbon (Barcelona, Spain) The properties of the granular activated carbon used in this work are summarized in **Table 1.**

Table 1: Adsorbent properties.

Type Chemviron	ρ_b (kg/m^3)	V_p (mm^3/g)	β	ε	d_p (mm)	a (m^2/g)
Granular AC (CAL)	450	715	0.588	0.453	0.9-1.1	963

3.2. Apparatus

Two different scale plants have been employed in this work, the small one is a laboratory plant with an adsorber of approximately 10 mL (L/D = 25), and the pilot plant has a pressurized vessel of 1 L (L/D = 12.5). In both cases virgin activated carbon was packed in a stainless steel tube free on either side to confine the carbon in the column. The sample, with a uniform particle size (1 mm), was dried in an oven at about 423 °K. After drying, activated carbon were packed in the column to constitute a fixed bed. Two sections of glass wool were placed above and bellow the packing in order to achieve a uniform flow distribution. A more detailed description of the pilot plant is presented in a previous work [10].

The adsorption column was heated with an insulated constant temperature oven (laboratory adsorber) or by a heat exchanger made of a coil immersed in stirred temperature-controlled bath (pilot jacketed adsorber). Purified CO_2 (99.95%) was sent to the fixed bed by a compressed-air driven, high pressure pump (HASKEL) in the laboratory plant and by a diaphragm pump head type EH1 (LEWA) in the pilot plant. A secondary high pressure pump was used to pump the solute (ethyl acetate) into the fixed bed. The effluent concentration was obtained on-line with a UV-detector connected with an integrator. The micro-metering valves were used to control the flow and to release the pressure of supercritical CO_2 to collect the solute samples under atmospheric pressure. The CO_2 flow rate was measured by a flowmeter. The plot of outlet ethyl acetate concentration versus time, also called breakthrough curve.

4. RESULTS AND DISCUSSION

In order to check the model validity two scale-up experiences of the adsorption of ethyl acetate on carbon activated have been carried out. The experimental adsorption curves obtained with the laboratory installation have been adjusted with the proposed model and the corresponding adjustable parameters (D_e, D_{az} and k_a) have been employed to predict the profile of adsorption with the pilot plant. These parameters remain constant in the scale-up if the operation conditions in both installations are the same.
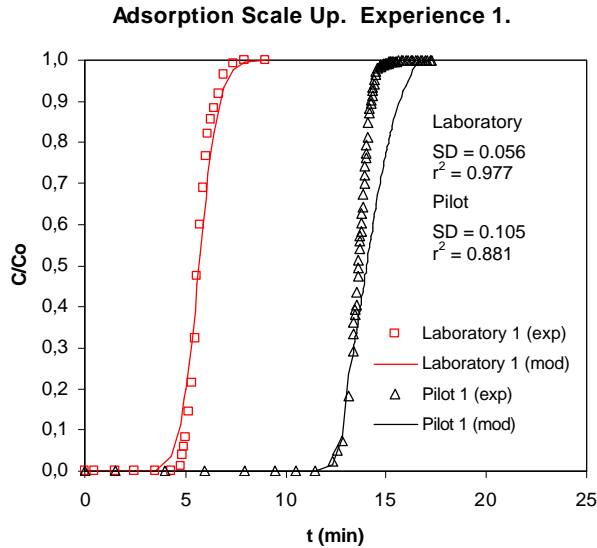

Adsorption Scale Up. Experience 1.

Table 2: Comparison between experimental and calculated (model) values in the operation with the pilot plant. *Experience 1.*

	Exp.	Mod.	$\lvert$Error$\rvert$%
t_b (min)	12.7	12.7	0
t_s (min)	14.8	16.6	12.2
q_b (g_{AE}/g_{CA})	0.259	0.259	0
q_s (g_{AE}/g_{CA})	0.279	0.289	3.6
FLU	92.8	89.6	

Operation conditions: P = 20 MPa; T = 40ºC; u = 0.0012 m/s; C = 4.4 % wt and d_p = 1 mm.

Figure 1: *Experience 1.* Experimental and predicted breakthrough curves obtained with the laboratory and pilot plant experiments.
Model parameters: $D_e = 3.76 \cdot 10^{-9}$ m^2/s; $D_{az} = 9.00 \cdot 10^{-7}$ m^2/s; $k_a = 1.50 \cdot 10^{-9}$ $m^3/Kg \cdot s$.
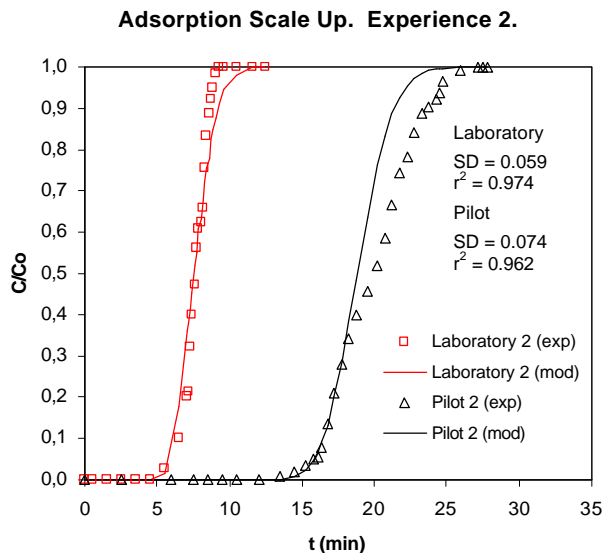

Adsorption Scale Up. Experience 2.

Table 3: Comparison between experimental and calculated (model) values in the operation with the pilot plant. *Experience 2.*

	Exp.	Mod.	$\lvert$Error$\rvert$%
t_b (min)	15.7	15.8	0.6
t_s (min)	26.5	24.3	8.3
q_b (g_{AE}/g_{CA})	0.166	0.167	0.6
q_s (g_{AE}/g_{CA})	0.208	0.197	5.3
FLU	79.7	84.7	-

Operation conditions: P = 17 MPa; T = 40ºC; u = 0.0011 m/s; C = 2.5 % wt and d_p = 1 mm.

Figure 2: *Experience 2.* Experimental and predicted breakthrough curves obtained with the laboratory and pilot plant experiments.
Model parameters: $D_e = 4.41 \cdot 10^{-9}$ m^2/s; $D_{az} = 1.50 \cdot 10^{-6}$ m^2/s; $k_a = 1.50 \cdot 10^{-9}$ $m^3/Kg \cdot s$.

Experimental adsorption curves have been represented by the proposed model by fitting the kinetic coefficients (D_e, D_{az} and k_a) to the experimental curves, obtained from a laboratory installation. Two typical breakthrough are presented in **Figure 1** and **2.** With the optimised parameters is possible to model the pilot plant curve with reasonable accuracy (SD = 7-11%).

From the analysis of model curves, it can be deduced that the shape of the breakthrough remains basically invariable in the scale-up but not it exactly constant. The pilot plant curves are less vertical than the laboratory ones. This phenomena is possible due to the apparition of channelling effect and some problems with the compaction of the bed that are more important in the operation with the pilot plant.

On the other hand the proposed model is able to predict the breakthrough point (time t_b and adsorbed amount q_b) with an error less than 1% as is shown in **Table 2** and **Table 3**. This means that the model is suitable for the scale-up because this point indicate the final of the industrial adsorption operation.

In both cases, the low values of D_e (3-5 10^{-9} m^2/s) show that internal diffusion is the main resistance in the adsorption process. The dispersion term could be neglected in the balance due to the low value of the dispersion coefficient (10^{-6}–10^{-7}), however its contribution have demonstrated to be representative when the linear velocity is lower than $5 \cdot 10^{-4}$ m/s.

5. CONCLUSIONS

The three-parameter proposed model (D_e, D_{az}, k_a) for supercritical CO_2 adsorption on activated carbon have demonstrated be *suitable* to determine the kinetic parameters from a laboratory experiment and to *scale-up* the adsorption process. In all cases the model is able to predict the breakthrough point of pilot plant experiments with an error less than 1%

Notation

a = Specific surface of solid phase (a = 3/R_p) (m^{-1})
c_i = Concentration in the pores (mol/m^3)
c_s = Concentration of solute in the solid phase (mol/kg)
c_{so} = Initial concentration of solute in the solid phase (mol/kg)
D_{az} = Axial dispersion coefficient (m^2/s)
d_p = Particle diameter (m)
k_a = First-order adsorption rate constant (m^3/kg·s)
k_f = Mass transfer coefficient related to the fluid phase (m/s)
r = Radial coordinate from centre of particles (m)
SD = Standard deviation
u = Superficial velocity (m/s)
V_p = Total pore volume (mm^3/g)

c = Concentration of solute in the fluid phase (mol/m^3)
c_o = Initial concentration of solute in the fluid phase (mol/m^3)
c_{sat} = Saturation constant of Langmuir isotherm (mol/kg)
D_m = Molecular diffusivity (m^2/s)
D_e = Effective diffusion coefficient (m^2/s)
K = Adsorption equilibrium constant (K =k_a/k_d) (m^3/kg)
k_d = First-order desorption rate constant (s^{-1})
L = Bed length (m)
R_p = Particle radius (m)
t = Time (min)
u_z = Superficial velocity in the void fraction (m/s)
z = Axial coordinate (m)

Greek Letters

β = Porosity of the particles
ρ = Density of supercritical fluid (kg/m^3)

ε = Bed void fraction
ρ_b = Bed density (kg/m^3)

μ = Viscosity of supercritical fluid (kg/m·s)
ρ_s = Density of particles (kg/m^3)

6. REFERENCES

[1] REVERCHON, E., LAMBERTI, G., SUBRA, P., Chem. Eng. Sci., Vol. 53, **1998**, p. 3537.

[2] KIKIC, I., ALESSI, P., CORTESI, A., Fluid Phase Equilibria, Vol. 117, **1996**, p. 304.

[3] COCERO, M.J., GARCÍA, J., Journal of Supercritical Fluids, Vol. 20, **2001**, p. 229.

[4] ALONSO, E., CANTERO, F.J., GARCÍA, J., COCERO, M.J., Journal of Supercritical Fluids, Vol. 24, **2002**, p. 123.

[5] RECASENS, F., McCOY, B.J., SMITH, J.M., AIChE Journal, Vol. 35, **1989**, p. 951.

[6] MADRAS, g., THIBAUD, C., ERKEY, C., AKGERMAN, A., AIChE Journal, Vol. 40, **1994**, p. 777.

[7] POLETTO, M., REVERCHON, E., Ind. Eng. Chem. Res., Vol. 35, **1996**, p. 3680.

[8] WAKAO, N., KAGUE, S. Heat and Mass Transfer in Packed Beds. Gordon and Breach, New York, **1982**.

[9] YANG, R.T. Gas Separation by Adsorption Processes. Butterworths, Boston, **1987**.

[10] COCERO, M.J., ALONSO, E., LUCAS, S., Ind. Eng. Chem. Res., Vol. 39, **2000**, p. 4597.