



Simple models for supercritical extraction of natural matter



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ABSTRACT

Based on the Brunauer–Emmett–Teller (BET) theory of adsorption, two mathematical models for correlating supercritical extraction data were developed. Each one of the models expresses the extraction yield as a function of time through one simple equation, which contains only three or two adjustable parameters, respectively, each one with a clear physical meaning. A comparison of the performance of the new models with those of Sovová's and VT-II models shows that the first proposed model, with three adjustable parameters, produces in many cases an average deviation that is similar to that produced by the Sovová's model, and is lower than that by the VT-II model, a remarkable result given the simplicity of the model. In addition, the second proposed model, which only has two adjustable parameters, performs well as compared to the rigorous models especially in the first period of the extraction and can be useful for generating first estimates of the parameters for data correlation with the first model. These results indicate that the proposed models are simple, useful and quick tools for correlating experimental data on supercritical extraction of natural matters.

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1. Introduction

Mathematical models for correlating experimental data on supercritical extraction of natural matter are important tools for scaling laboratory data up to industrial level, in order to make estimates of profitability or to design processing equipment. Many models have thus been proposed, as referenced in comprehensive literature reviews that have been published [1–6]. Among them, that by Sovová [1] and the so-called VT-II [2] are examples of rigorous models. Sovová's model is based on the representation of diffusive and convective transport phenomena that occur during the extraction and has three analytical equations, one for each extraction period. The VT-II model represents the same phenomena through a set of differential equations that has to be numerically integrated. These models have three and four adjustable parameters, respectively, which have to be fitted to each experimental data set measured at constant temperature and pressure. In this work we propose two simple models that have three and two adjustable parameters, respectively, and explicitly express the relation between extraction yield and time; i.e., no differential equations are present in the final expression.

2. Mathematical model

2.1. Material balance in the bulk fluid phase

Based on the general model for the supercritical fluid (SCF) extraction of a solid substrate in a packed bed [5], we initially consider a packed extractor, shown in Fig. 1, and write the material balance for the solute in the supercritical fluid, around a differential element along the axial direction of the extractor:

$$\frac{\partial C_f}{\partial t} + u\varepsilon \frac{\partial C_f}{\partial z} = D_{sf} \frac{\partial^2 C_f}{\partial z^2} + \frac{(1-\varepsilon)}{\varepsilon} a_{sf} k_{sf} (C_f^* - C_f) \quad (1)$$

where C_f is the concentration of the solute in the SCF, u is the interstitial velocity of the solvent, ε is the void fraction of the bed, D_{sf} is the axial dispersion coefficient of the solute in the SCF, a_{sf} is the effective solid–fluid contact area for mass transfer, k_{sf} is the mass transfer coefficient for transport of the solute through the external fluid film around the solid particles, and C_f^* is the concentration of solute in the SCF film that is in equilibrium with the solid surface.

The balance equation is well known, and we use it here assuming that the term that represents the axial dispersion (i.e., the first term on right hand side of Eq. (1)) is negligible. According to Carberry and Wendel [7], this approximation is valid when the length of the extractor is at least 50 times the average particle diameter and the Reynolds number is greater than 10, which are conditions usually accomplished in the SCF extraction of natural matter [8]. We also consider that the term that represents the solute accumulation in

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Nomenclature

a_{sf}	effective solid–fluid contact area for mass transfer
AARD	average absolute relative deviation
Bi	Biot number
cal	refers to calculated
C_f	concentration of the solute in the SCF
C_f^*	concentration of solute in the SCF film that is in equilibrium with the solid surface
d_p	particle size
D	diffusion coefficient of the solute
D_{sf}	axial dispersion coefficient of the solute in the SCF
exp	refers to experimental
h	mass transfer coefficient
K	ratio between the adsorption equilibrium constants of the solute in the first monolayer and that in subsequent layers. Adjustable parameter
k_{sf}	mass transfer coefficient for transport of the solute through the external fluid film around the solid particles
L	length of the extractor
\dot{m}_f	flow rate of the SCF
m_{fl}	mass of solute in the SCF at the exit of the extractor
m_{fT}	mass of solute + SCF
m_o	initial extractable mass of the solute in the packed bed
m_s	mass of the solute in the solid at time t
n	number of data
Re	Reynolds number
Sc	Schmidt number
t	extraction time
t_i	time for data i
u	interstitial velocity of the solvent
W	adjustable parameter of Sovová's model related to diffusion in the solid phase of the extraction bed
x	extraction yield
x_k	adjustable parameter of Sovová's model related to the amount of solute in the solid matrix that is inaccessible to the SCF, relative to initial solute
x_m	solute mass fraction in the first monolayer. Adjustable parameter
x_s	solute mass fraction in the solid at time t
y_f	mass fraction of the solute in the SCF
y_{fl}	solute mass fraction in the bulk fluid phase at the exit of the extractor
y^*	adjustable parameter related to the solubility of the solute in the SCF corrected by diffusional limitations. Defined by Eq. (22).
y_f^*	solute mass fraction in the SCF film that is in equilibrium with the solid surface
y_{sat}	solute mass fraction in a saturated SCF phase
z	axial position along the extractor
Z	adjustable parameter of Sovová's model related to convection in the fluid phase of the extraction bed

Integrating within the usual limits for a packed extractor (at $z=0, y_f=0$ and at $z=L, y_f=y_{fl}$), we obtain:

$$y_{fl} = y_f^* \left[1 - \exp\left(-\frac{kL}{u\varepsilon}\right) \right] \quad (3)$$

where y_{fl} is the solute mass fraction in the bulk fluid phase at the exit of the extractor and L is the length of the extractor.

2.2. Overall material balance in the packed solid

We now use a material balance of the solute in the solid that is packed into the extractor, which is given by:

$$\frac{dm_s}{dt} = -\dot{m}_f \left[\frac{m_{fl}}{m_{fT} - m_{fl}} \right] \quad (4)$$

where m_s is the mass of the solute in the solid at time t , \dot{m}_f is the flow rate of the SCF, m_{fl} is the mass of solute in the SCF at the exit of the extractor, and m_{fT} is the mass of solute + SCF.

Assuming that $m_{fT} \gg m_{fl}$ which is reasonable for low solute concentrations, we can simplify Eq. (4) as follows:

$$\frac{dx_s}{dt} = -\frac{\dot{m}_f}{m_o} y_{fl} \quad (5)$$

where x_s is the solute mass fraction in the solid at time t , and m_o is the initial extractable mass of the solute in the packed bed. We assume that x_s do not change considerably in the axial direction, because the amount of extracted solute from the solid matrix in the differential element is very low, and it is much lower than the solubility of the solute in the SCF.

Replacing Eq. (4) into Eq. (5) we obtain:

$$\frac{dx_s}{dt} = -\frac{\dot{m}_f}{m_o} y_f^* \left[1 - \exp\left(-\frac{kL}{u\varepsilon}\right) \right] \quad (6)$$

The latter equation can be coupled with a BET-type equilibrium relationship, as follows.

2.3. BET-type equilibrium equation

The equilibrium relationship relates the concentration of the solute in a film of SCF located at an infinitesimal distance from the solid substrate surface, y_f^* , with the concentration of the solute in the solid matrix. This relationship depends upon the relative attraction forces exerted by the solid and SCF over the solute.

A BET-type equilibrium relationship for SCF processes was used in order to consider the solute interaction with the solid matrix [9,10]:

$$\frac{x_s}{x_m} = \frac{K\chi}{[1-\chi][1+(K-1)\chi]} \quad (7)$$

where χ is the ratio between the solute mass fraction in equilibrium, y_f^* , and the solute mass fraction in a saturated SCF phase, y_{sat} . x_m is the solute mass fraction in the first monolayer (m_m/m_o) and K is the sorption equilibrium coefficient.

Eq. (7) can be arranged to obtain a quadratic equation:

$$(1-K)\chi^2 + \left[K \left(1 + \frac{x_m}{x_s} \right) - 2 \right] \chi + 1 = 0 \quad (8)$$

which can be solved to give:

$$\chi = \frac{-\left[K \left(1 + \left(\frac{x_m}{x_s} \right) \right) - 2 \right] \pm \sqrt{\left[K \left(1 + \left(\frac{x_m}{x_s} \right) \right) - 2 \right]^2 - 4(1-K)}}{2(1-K)} \quad (9)$$

Taking into consideration the limiting situation when the SCF is saturated with the solute ($y_f \rightarrow y_{sat}$), in which the number of molecules adsorbed on the solid becomes very large

the SCF (the first term on left hand side) is negligible as compared to the amount of solute in the solid material. With these assumptions we obtain:

$$u\varepsilon \frac{\partial y_f}{\partial z} = k(y_f^* - y_f) \quad (2)$$

where $k = (1 - \varepsilon)a_{sf}k_{sf}$, y_f is the mass fraction of the solute in the SCF and y_f^* is the solute mass fraction in the SCF film that is in equilibrium with the solid surface.

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