

# Two-parameter model for mass transfer processes between solid matrixes and supercritical fluids: Analytical solution

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Received 26 May 2006; received in revised form 20 September 2006; accepted 16 October 2006

## Abstract

A simple two-parameter mathematical model with analytical solution applicable for mass transfer processes between solid matrixes and supercritical fluids has been developed. Experimental curves for supercritical extraction of wheat germ (extractors of 10 mL and 100 mL) and supercritical wood impregnation processes (adsorber of 1 L) have been fitted using this model. Moreover, the model has been applied to scale up a supercritical adsorption process onto activate carbon from a laboratory unit (adsorber 10 mL) to pilot plant scale (adsorber of 1 L). The proposed model takes into account the equilibrium step ( $h$ ) and mass transfer from the bulk of the fluid phase to the surface of the solid ( $k_f a$ ). The adjusted results have demonstrated that the model is able to fit all available experimental results with reasonable accuracy. Thus, the fitting average error was 1–6% for extraction process, 3–7% for wood impregnation and 7–10% for adsorption scale-up. The proposed model is versatile and suitable to adjust with only two parameters different supercritical mass transfer processes. The analytical solution based on modified Bessel functions is useful and easily implemented using common computer mathematical programs. Furthermore, a friendly Excel user-interface for the simulation of adsorption/desorption processes is provided within the supporting information; the program runs using MATLAB 7.0 as simulation engine.

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**Keywords:** Analytical solution modelling; Supercritical extraction; Supercritical adsorption; Supercritical impregnation; Scale-up; Simulation package

## 1. Introduction

Supercritical extraction, adsorption, desorption and impregnation are mass transfer processes between solid matrixes and supercritical fluids which, typically, are non-steady state processes where concentration profiles of solute in solvent and solid phases vary along with both time and position in the bed [1–4]. In order to model these processes several simplifications are usually done. Thus, an accepted simplification for this behaviour is to consider only one overall separation curve. This curve represents the variation of the total amount of extract at the end of the separator along with time under given conditions of pressure, temperature, solvent flow-rate and percentage of co-solvent composition used. Important design parameters such as solvent to solid feed ratio and mass transfer coefficients can be inferred from the analysis of experimental extraction data.

Mathematical modelling of processes is a powerful tool to easily describe the behaviour of a process and prepare a subsequent scale-up. Experimental concentration profiles of solute in both solid and fluid phase through the fixed bed cannot be easily obtained during the SFE extraction process. Continuous sampling under high pressures is difficult, expensive, time-consuming and not always possible. Nevertheless, these concentration profiles can be predicted by using SFE models once their parameters have been properly fit to experimental data. Thus, a trained model allows the researcher for predicting the SFE behaviour before doing the experiment, reducing time and targeting the experiments with definitive criteria.

Several authors have fit extraction data using extraction models accurately solved by numerical solutions by discretisation using finite differences and orthogonal collocation [5–7]. Sovová presented a simple model which divides the extraction curve into three main sections [8]. The first part, where extraction rate is constant, is controlled by the thermodynamic equilibrium between solute and solvent and external mass transfer. The last section considers the internal diffusion controls. The mid section is the only non-linear section and represents the period where

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both internal and external mass transfer controls the extraction process. This kind of model is good enough for making predictions within the first section of the extraction curve [9,10].

A simplified generalised extraction model was proposed in a previous work. A semi-analytical solution was given for that model, solving numerically the Laplace-transformed model equations using the fast Fourier transform (FFT). The model was validated by fitting SFE data of sunflower seed oil [6]. Raw material was pre-treated by milling the seeds to smaller particle diameters, minimising considerably the effect of intra-particle diffusion (internal mass transfer). Under such conditions the two model parameters are directly related to physical properties of a desorption process, i.e. mass transfer parameter,  $k_{fa}$ , and thermodynamic surface equilibrium,  $h$ . Added to this, the model was used to describe experimental results for the impregnation of wood with organic compounds using supercritical CO<sub>2</sub> as a solvent [11]. The model parameters were again two, external mass transport,  $k_{fa}$  and the partition coefficient,  $h$ . This model was also used for scaling-up a supercritical adsorption process applied to soil remediation [12].

The main steps involved in a supercritical fluid adsorption process are as follows: firstly, mass transfer from the bulk fluid ( $k_f$ ), secondly, internal diffusion in the solid particle ( $D_e$ ) combined with axial dispersion in the fixed bed ( $D_{az}$ ), thirdly a reversible adsorption or desorption reaction at the solid surface (first-order adsorption/desorption constants,  $k_a$  and  $k_d$ ) and finally a thermodynamic equilibrium distribution between solid and supercritical solvent. Thus, a generalized model would imply five adjustable parameters ( $k_f$ ,  $D_e$ ,  $D_{az}$ ,  $k_a$  and  $k_d$ ) [13]. 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 dimensionless correlation's [14] and  $k_d$  by the determination of Langmuir adsorption isotherm ( $k_d = K/k_a$ ) [15].

Recasens et al. developed two models with analytical solution [16]. Firstly, an equilibrium-desorption model where the rate of desorption was controlled by external and intraparticle mass transfer (the equilibrium is established instantaneously and the equilibrium constant is measured independently). Secondly, a kinetic model where external and intraparticle mass transfer and a first-order irreversible desorption steps controlled the overall process (the analytical solution is presented for mass transfer control). Under these assumptions the model can be solved analytically to obtain the concentration profile of the solute in the fluid phase as a function of position and time ( $c(L,t)$ ).

Currently, PCs computation capacity is enough to solve complex models and to fit a number of experimental data using optimization algorithms. However, the main limitation of the numerical solution relies within the extraction model. The convective flux term of the material balance equations introduces instability in the partial differential equation (PDE) system, so that many of the numerical solutions exhibit a waving-behaviour in the last part of the curve. This is not a desirable situation, especially during the optimisation of the system using experimental data. Some authors cope with this limitation by simplifying the model to the minimum workable and they recommend using the use of simple linear models [8].

In this paper a useful and novel analytical solution for a generalised adsorption/desorption two-parameter model is presented. Mass balance equations for solute in both supercritical and solid phase that consider linear equilibrium on the matrix surface and external mass transfer are considered. These equations can be analytically solved to obtain the concentration profile of the solute in the fluid phase as a function of position and time ( $c(z,t)$ ) and the concentration profile of the solute in the solid as a function of position and time ( $c_s(z,t)$ ), simultaneously. This solution requires evaluations of integrals where the integrand function can be expressed in terms of the modified Bessel function, that it is easily implemented by common mathematical computer programs (e.g. MATLAB). This model is potentially recommended to describe and scale-up supercritical fluid extraction, impregnation and adsorption processes.

## 2. Mathematical modelling

A simple and versatile physicochemical model has been used to get a complete description for supercritical extraction, adsorption and impregnation processes. It is based on a previous one [6] that consider mass balance of solute into the SC phase and linear equilibrium. This model considers only two parameters:

- Convective flow transport between particles and bulk phase (supercritical solvent) modelling with an external mass transfer coefficient ( $k_f$ ).
- Linear equilibrium on the matrix surface ( $h$ ). For the case of supercritical fluid extraction and adsorption processes this parameter considers two mass transfer steps, i.e. internal diffusion and the adsorption/desorption equilibrium. Similarly, for the case of the impregnation process, this parameter represents the partition coefficient, i.e. the maximum amount of solute that can be loaded under conditions of thermodynamic equilibrium.

### 2.1. General hypotheses

Some hypotheses are needed to model the extraction/adsorption curves:

1. The system is considered a “fixed bed” which has two phases:
  - (a) Solid (static phase): wheat germ (for extraction), activated carbon (for adsorption) and wood (for impregnation).
  - (b) Fluid (mobile phase): supercritical solvent + solute (for adsorption and impregnation processes) and supercritical solvent mixture for extraction processes. The solvent was carbon dioxide modified with ethanol for extraction process and carbon dioxide for adsorption and impregnation processes. Solutes were wheat germ oil for extraction (considered as a pseudo-component), ethyl acetate for adsorption and an organic fungicide for impregnation process.
2. A linear relationship between solute concentrations in solid and fluid phases is assumed.

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