Evaluation of models for supercritical fluid extraction

Amit Rai [a,*], Kumargaurao D. Punase [b,1], Bikash Mohanty [a,2], Ravindra Bhargava [a,3]

[a] Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India
[b] Department of Chemical Engineering, University of Petroleum and Energy Studies, Deharadoon 248007, Uttarakhand, India

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ABSTRACT

Various models available in the literature for the modeling of supercritical extraction process are studied and validated using published experimental data. The first model considers internal mass transfer coefficient as the controlling parameter for the extraction process. On the other hand, the second model analyzes the dynamic behavior of the extraction process by considering intra-particle diffusion and external mass transfer. These models have also been studied to understand the effects of various model parameters like intra-particle diffusion, mass transfer coefficients & operating parameters on cumulative extraction yield. The model proposed by Reverchon (1996) [13] predicts a cumulative yield within an error limit of +9% in the MATLAB simulation and +4% to −5% in the FEMLAB simulation. Also, the model proposed by Goto et al. (1993) [8] fits the experimental data of Kim et al. (2007) [19], Skerget and Knez (2001) [20], and Tonthubthimthong et al. (2004) [21] within an error band of +10% to −2%.

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1. Introduction

In recent years, the use of supercritical fluid extraction (SFE) process for the removal of organic compounds from different liquid and solid matrices has received much attention. Because, supercritical fluids have several distinctly advantageous properties, such as liquid like density and gas like viscosity and diffusivity, they have high mass-transfer characteristics and their effectiveness can be controlled by small changes in temperature and pressure leading to better fractional separation [1]. The mechanism of supercritical fluid extraction process can be explain by the following steps; (1) Transport of supercritical solvent to the particle surface and then from particle surface to interior of particle by diffusion. (2) Dissolution of the solute with the supercritical solvent. (3) Transport of supercritical solvent with molecules from interior of particle to particle surface. (4) Transport of supercritical solvent and solute molecules from particle surface to bulk solvent. Hence, the possibility of using supercritical solvents at the commercial level has increased in the recent past [2]. To design an extraction plant, it is necessary to have reliable mass-transfer models that will allow the determination of optimum operating conditions [3]. Single stage supercritical extraction and separation produces a quasi-solid extract, which consists of several compound families. However, the yield data and the shape of the extraction curve are influenced by the presence of undesired compounds [4].

Some authors have attempted to describe the evolution of the extraction process by using empirical kinetic equations [5,6]. Heat transfer analogy of a single sphere cooled in a fluid medium was used by Reverchon et al. [7] to describe the extraction process. However, this model describes a highly idealized situation and the performance of the fixed bed of particles used is overestimated.

The extraction process was also modeled by integrating the differential mass balances in the solid and fluid phase. Goto et al. [8] described the extraction of peppermint essential oil as a desorption process characterized by the attainment of an instantaneous equilibrium by breaking the peppermint leaves into differential slab elements.

Sovova [9,10] modeled the vegetable oil extraction process based on the broken and intact cell model by considering the oil contained as either accessible or inaccessible. The same model was also proposed for pepper extraction [11], where the internal and external mass transfer resistances were taken into account. Goto et al. [12] proposed a shrinking core model and explained the ginger rhizomes extraction considering effective diffusivity and solubility as model parameters. However, the model was unable to describe the experimental results obtained for different particle sizes.

Reverchon [13] took into account the shape of the particles (slabs) to obtain a good fit with the experimental data for large particles and found that internal mass transfer controlled the essential

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* Corresponding author. Mobile: +91 75790 75744; fax: +91 1332 276535.
  E-mail addresses: mit.rai123456@gmail.com (A. Rai), kumargaurav04@gmail.com (K.D. Punase), bmohanty@iitr.ernet.in (B. Mohanty), ravibfch@iitr.ernet.in (R. Bhargava).
  [1] Mobile: +91 9917720952.
  [2] Tel.: +91 01332 5710.
  [3] Tel.: +91 01332 285382.

Nomenclature

Reverchon [13]

A_p	total surface of particles (m^2)
c	extract concentration in the fluid phase (kg/m^3)
c_n	fluid-phase concentration in the nth stage (kg/m^3)
h	spatial coordinate along the bed (m)
k_p	volumetric partition coefficient of the extract between the solid and the fluid phase at equilibrium (–)
K	internal mass-transfer coefficient (m/s)
n	number of stages deriving from the bed subdivision (–)
q	extract concentration in the solid phase (kg/m^3)
q_n	solid phase concentration in the nth stage (kg/m^3)
q^*	concentration at the solid–fluid interface (kg/m^3),
t	extraction time (s)
t_i	internal diffusion time (s)
u	superficial velocity (m/s)
V	extractor volume (m^3)
W	CO_2 mass flow rate (kg/s)
ε	bed porosity (–)
ρ	solvent density (kg/m^3)

Goto et al. [8]

a_1, a_2	constants defined by Eq. (3.41) (–)
a_p	specific surface area (1/m)
A	constant defined by Eq. (3.42) (–)
A_b	bed cross section area (m^2)
b, c	constant defined by Eq. (3.43) (–)
C	solute concentration in the solvent (kg/m^3)
C_p	solute concentration within the particle pore (kg/m^3)
C_{p0}	solute concentration in the pore phase at $t = 0$ (kg/m^3)
C_{ps}	solute concentration in the pore space at the particle surface (kg/m^3)
C_s	solute concentration in particle (kg/m^3)

C_{s0}	solute concentration in the solid phase at $t = 0$ (kg/m^3)
C_0	total solute concentration (kg/m^3)
d_p	particle diameter (m)
D_{AB}	binary diffusion coefficient (m^2/s)
D_{ax}	axial dispersion coefficient (m^2/s)
D_e	effective intraparticle diffusion coefficient (m^2/s)
F	cumulative fraction of solute extracted (–)
h	height of the bed (m)
k_a	adsorption rate constant (1/s)
k_p	overall mass transfer coefficient (m/s)
k_f	external mass transfer coefficient (m/s)
K	equilibrium adsorption coefficient (–)
r	radial position in spherical particle (m)
R	radius of spherical particle (m)
t	time (s)
U_s	superficial velocity (m/s)
x	dimensionless solute concentration in effluent (–)
x_0	initial solute mass ratio in the solid phase (–)
x_p	dimensionless solute concentration in pore (–)
x_s	dimensionless solute concentration in solid particle (–)
y	solute mass ratio in the fluid phase (kg/kg)
z	bed height coordinate (m)
α	bed void fraction (–)
β	particle porosity (–)
ϕ	dimensionless mass transfer coefficient (–)
θ	dimensionless time (–)
ρ_s	solid density without void volume of the solid matrix (kg/m^3)
τ	total bed volume/volumetric flow rate (s)
IC	initial condition
BC	boundary condition

oil extraction from sage leaves. Goodarznia and Eikani [14] proposed a model based on differential mass balance on a single particle as well as in the fluid phase and validated the experimental data of Reverchon et al. [7,15] and Sovova [10]. The model also included the effects of internal diffusivity and axial dispersion.

The phase equilibrium depends on solute composition, solvent composition, extraction pressure and temperature. It controls the initial extraction period when the fluid phase leaving the extractor is either in equilibrium or is about to attain equilibrium with the solute in the solid phase. When the solute concentration in solid phase is high, like that of vegetable oil in Canola seed, the fluid-phase equilibrium concentration is independent of the matrix and equal to oil solubility. When the initial solute concentration in the plant is low, which is rare for vegetable oils, the equilibrium is usually controlled by solute–solid interaction and the fluid-phase concentration is much lower than the oil solubility. The equilibrium is expressed as a linear relationship between the solid and fluid phase concentrations and the proportionality constant is called the partition coefficient. Goto et al. [16] used the Brunauer–Emmett–Teller adsorption isotherm to simulate a smooth transition between the equilibrium of free solute at high concentrations and the equilibrium of solute–solid interaction at low concentrations.

Perrut et al. [17] considered a discontinuous equilibrium to model the sunflower oil extraction process. The fluid-phase concentration is equal to the oil solubility above the discontinuity and is determined by partition coefficient below it. The discontinuous equilibrium curve was successfully applied by Wu and Hou [18] in the simulation of egg yolk oil extraction.

It can be concluded that there are various models available in the literature that differ not only from a mathematical point of view, but also in terms of mass transfer mechanisms, which control the supercritical extraction process of different matrices. Hence, a single model cannot describe all the experimental results. In all published models, the initial extraction process is governed by the solubility equilibrium between the solute and the fluid phase, which, in most cases, is assumed to be linear as detailed information is not available for complex matrix systems. From a mathematical point of view, all the proposed models are based on differential mass balance integration with some assumptions. Table 1 shows that the published supercritical fluid extraction models differ in the description of phase equilibrium, flow pattern, and solute diffusion in the solid phase. As the experimental data considered in the present study are related to seeds of sage, black pepper, nimbin and caffeine. Amongst these sages, black pepper and nimbin belong to the category of essential oil. The literature shows that for extraction of essential oil as well as caffeine the model developed by Goto et al. [7] and Reverchon [3,12] are suitable. Therefore, in the present paper these models are considered for extraction of oil from seeds of sage, black pepper, nimbin and caffeine.

2. Mathematical modeling

The initial distribution of the solute within the solid substrate affects the selection of the possible models. The solute may be free on the surface of the solid material, adsorbed on the outer surface, located within pores or evenly distributed within plant cells. In the