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 (i.e., an analytical solution of the basic equations exists), which contains only three or two adjustable parameters, each one with a clear physical meaning. When fitting the parameters to several sets of experimental data obtained at different pressures and temperatures, one of the parameters was shown to be independent of these variables; i.e., the value obtained at one set of conditions can be used to represent data obtained at another set of conditions.

A comparison of the performance of the new models with that of Sovová and VT-II models shows that the first proposed model, with three adjustable parameters, produces 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 and number of parameters of the new model. In addition, the second proposed model, which only has two adjustable parameters, performs well as compared with the rigorous models especially in the first period of the extraction. These results indicate that the proposed models are a useful, simple and quick tool for correlating experimental data on supercritical extraction of natural matter.

Keywords: supercritical extraction, model, adsorption, BET, natural matter.

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 [1-4]. Among them, the Sovová and the VT-II 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.

1.1 Mathematical model

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 [1], we initially consider a packed extractor and write the

material balance for the solute in the supercritical fluid, around a differential element along the axial direction of the extractor:

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

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 assuming that (1) the term that represents the axial dispersion is negligible according to the criteria presented by Carberry and Wendel [5], in which the length of the reactor is at least 50 times the average particle diameter and the Reynolds number is greater than 10; this condition is usually accomplished in the SCF extraction of natural matter, and (2) the term that represents solute accumulation in the SCF is negligible as compared to the amount of solute in the solid material. With these assumptions we get:

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

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.

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

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

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

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:

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

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 Equation 4 as follows:

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

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.

Replacing Equation 4 into 5 we obtain:

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

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

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.

Goto et al. (1998) proposed a BET-type equilibrium relationship for SCF processes in which the solute interacts with the solid matrix [6,7]:

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

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.

Equation 7 can be arranged to obtain a quadratic equation:

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

which can be easily solved by the well-known quadratic formula, as follows:

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

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 $(m_o - 0, x_s \rightarrow \ )$, we obtain an expression for χ as a function of K:

$$\chi = \frac{2 - K \pm K}{2(1 - K)} \tag{10}$$

Because $K \geq 1$ (and $0 \quad \chi \leq 1$), only the root that is obtained with the negative sign in the expression above is possible, and thus in this case $\chi = 1$.

Now, in any case, replacing Equation 9 in 6 we get:

$$\frac{dx_s}{dt} = -\frac{\dot{m}_f}{m_o}y^* \left\{\frac{\left[K\left(1 + \frac{x_m}{x_s}\right) - 2\right] + \sqrt{\left[K\left(1 + \frac{x_m}{x_s}\right) - 2\right]^2 - 4(1 - K)}}{2(K - 1)}\right\} \tag{11}$$

Proposed models. The latter equation can be analytically integrated using the initial condition @ t = 0, $x_{so} = 1$, to obtain, after several arrangements:

$$t = \frac{m_o}{2\,\dot{m}_f y^*}\left\{x_o' - x' + (2 - K)\left[x - x_m ln\left(\frac{\alpha}{\beta}\right)\right] + Kx_m ln\left[\frac{\alpha'}{\beta'(1 - x)^2}\right]\right\} \tag{12}$$

where:

$$x_o' = \sqrt{a + b + c} \tag{13}$$

$$x' = \sqrt{a(1 - x)^2 + b(1 - x) + c} \tag{14}$$

$$a = K^2 \tag{15}$$

$$b = 2(2 - K)Kx_m \tag{16}$$

$$c = (Kx_m)^2 \tag{17}$$

$$\alpha = x' + K(1-x) + (2-K)x_m \tag{18}$$

$$\alpha' = x' + (2-K)(1-x) + Kx_m \tag{19}$$

$$\beta = x_o' + K + (2-K)x_m \tag{20}$$

$$\beta' = x_o' + (2-K) + Kx_m \tag{21}$$

$$y^* = y_{sat}\left[1 - exp\left(-\frac{kL}{u\varepsilon}\right)\right] \tag{22}$$

x is the extraction yield; i.e., the ratio between the mass of the solute extracted at time t, and the mass of solute initially present in the packed bed that can be extracted.

Equation 12 expresses a relationship between time and extraction yield, and has three adjustable parameters, y^*, K, and x_m. The three adjustable parameters have clear physical meaning. y^* is related to the solubility of the solute in the SCF corrected by diffusional limitations, K is the ratio between the adsorption equilibrium constants of the solute in the first monolayer and that in subsequent layers (when the solute-solid interactions are strong $K \to \infty$, and when they are weak, $K \to 0$), and x_m is the ratio between the mass of solute present in the first monolayer and the initial mass of solute that can be extracted.

Notice that according to Equation 22, for situations where diffusional limitations are negligible (i.e., 0 , $L \to \infty$, or $k \to$), $y^* \to y_{sat}$, and in these cases knowing the solubility of the solute in the SCF, the number of adjustable parameters would reduce to two. On the other hand, note that x_m, which is a parameter that represents properties of the solid, might take values greater than 1 for cases where the initial amount of solute is lower than the amount that can conform the first monolayer in the solid.

The argument of the exponential term in Equation 22 is dimensionless and can thus be expressed in terms of dimensionless numbers, to give:

$$y^* = y_{sat}\left[1 - exp\left(-\frac{Bi}{Re\ Sc}\right)\right] \tag{23}$$

where Bi, Re and Sc are the Biot, Reynolds and Schmidt numbers, respectively. These numbers are defined as:

$$Bi = \frac{hL}{D} = \frac{KL}{\varepsilon} \tag{24}$$

$$Re = \frac{u\ d_p}{\nu} \tag{25}$$

$$Sc = \frac{\nu}{D} \tag{26}$$

where D is the diffusion coefficient of the solute, h is a mass transfer coefficient, d_p is the particle size and ν is the kinematic viscosity. Equation 23 allows one to correlate or to estimate the effect of changes in the flow conditions (Re), the mass transfer characteristics due to properties of the solid (Bi) or to properties of the fluid (Sc) from one experimental condition to another, or for scaling up purposes.

In the case when the equilibrium constant for the first monolayer and for subsequent layers are approximately equal, $K \approx 1$, and Equation 12 reduces to a simpler model:

$$t = \frac{m_o}{\dot{m}_f y^*}[x - x_m ln(1-x)] \tag{27}$$

This equation has only two adjustable parameters and can be useful as a first approximation for correlating experimental data.

2. Results and discussion

Some characteristics of the described models were initially explored by applying them to the correlation of the data obtained in our laboratory for the supercritical CO_2 extraction of cocoa butter from cocoa powder, a byproduct of the mechanical expression of cocoa seeds. Extraction yields as a function of time were experimentally determined at five sets of temperature and CO_2 density [8,9]. The model proposed by Sovová [10], and also those proposed in this work were fitted to the data.

Figures 1 and 2 show the correlation of data for the supercritical CO_2 extraction of cocoa butter from cocoa powder. Notice that both proposed models apparently perform similarly, and they represent the data adequately. Proposed model 1 looks like a more convenient choice because it represents adequately the whole set of data by using only one equation, in contrast to the Sovová's model, which uses three equations, one per period of extraction. To compare the performance of the models quantitatively, for each model we computed the average absolute relative deviation (AARD) referred to time (not to extraction yield), because this is the variable that is explic*it i*n the proposed models. Such deviations were obtained using the equation:

$$AARD = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{t_{i,exp} - t_{i,cal}}{t_{i,exp}} \right| \tag{28}$$

where AARD is the Average Absolute Relative Deviation (%), n is the number of data (54), t_i is time for data i, and subscripts exp and cal refer to experimental and calculated, respectively. Notice that the deviation of the proposed model 1 (3.81%) compares well with that of Sovová's (2.54%).

Figure 2 shows that proposed model 2 and Sovova's model perform similarly in the first period of the extraction (i.e., in the linear part of the extraction yield vs. time curve). This is because in this region external mass transfer domains, and both models include the solubility of the solute in the SCF, y_{sat}. In contrast, at higher extraction yields, important deviations occur for the proposed model 2 probably because an internal mass transfer mechanism dominate (e.g. diffusion or desorption of the solute from the solid matrix) and important simplifying assumptions related to this part were done during the derivation of proposed model 2. In fact, the deviation obtained for the proposed model 2 was 5.91%, which is in contrast with 2.54% that obtained for Sovová´s. However, the proposed model 2 might be useful for providing first estimates of parameters y^* and x_m for correlating experimental data with proposed model 1.
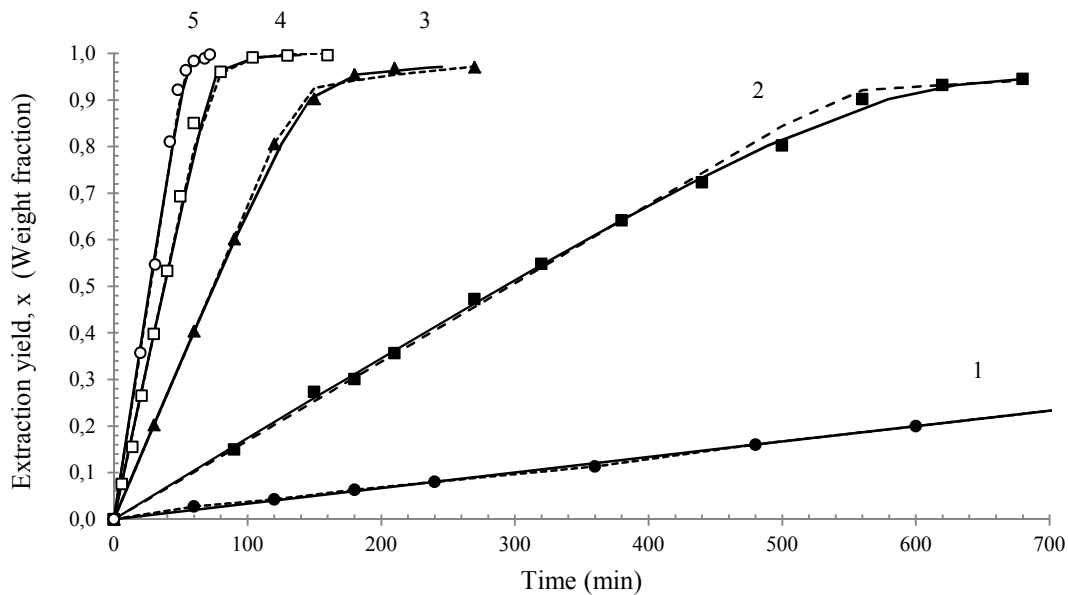

Figure 1. Correlation of data for the supercritical CO_2 extraction of cocoa butter from cocoa powder. The numbers indicate the operating conditions from Table 1. (—) Proposed model 1 (AARD=3.81%), (---) Sovová's model (AARD=2.54%).
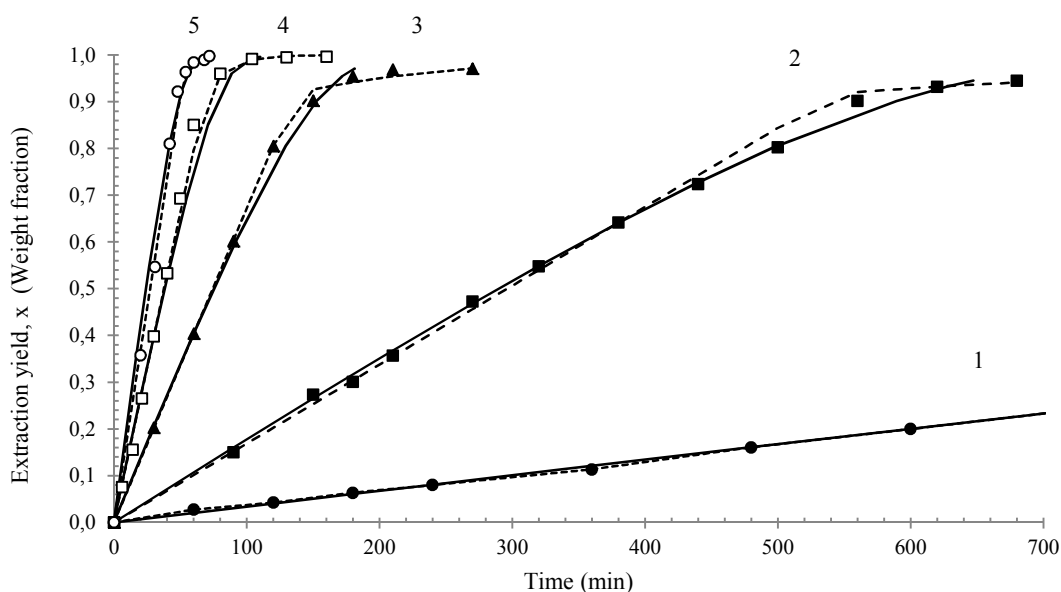
Figure 2. Correlation of data for the supercritical CO_2 extraction of cocoa butter from cocoa powder. The numbers indicate the operating conditions from Table 1. (—) Proposed model 2 (AARD=5.91%), (---) Sovová's model (AARD=2.54%).

Table 1. Adjustable parameters obtained for the proposed models 1 and 2, and for sovová's model

Operating conditions			Adjustable parameters							
			Proposed model 1			Proposed model 2		Sovová's model		
Number	CO_2 density (g/cm^3)	Temperature (°C)	K	y* (x10^5)	x_m	y* (x10^5)	x_m	Z (x10^5)	W(x10^5)	x_k
1	0.7	35.0	79.46	4.15		4.44		104.72	0.18	
2	0.7	50.0	74.51	21.66		23.62		478.09	213.30	
3	0.8	42.5	55.00	84.23	0.044	91.16	0.126	1917.64	673.08	0.082
4	0.9	35.0	30.61	159.67		179.64		3467.79	5088.53	
5	0.9	50.0	4.61	227.16		284.52		4540.28	13859.02	

Table 1 shows the values of the adjustable parameters that were obtained by fitting the models to the 54 experimental data points. For the proposed models, a single value of x_m was obtained to represent the whole set of data because it was observed that this parameter does not strongly depend upon the operating conditions. In fact, this parameter is in essence a property of the solid-solute pair, so we did not expect any effect of the operating conditions on the value of this parameter. In this case the value of x_m was less than one, which indicates that the initial mass of solute that is removable is greater than the mass of solute in the first monolayer. In other cases (i.e., for other systems) the opposite situation might be conceivable, and the values of x_m might be greater than one.

Notice that as the y^* parameter increases, K decreases. Since y^* is directly related to solubility, when solubility of the solute in the SCF increases it is expected that the solid-solute molecular forces become relatively weaker, and thus K decreases.

For the Sovová´s model, the three adjustable parameters were fitted assuming that the values of Z and W depend of the operating conditions and that x_k is independent of such variables. In fact, Z and W are directly related to the mass transfer coefficient, both in the SCF and in the solid matrix, respectively. These coefficients must change with the extraction conditions. On the other hand, the x_k parameter refers to the amount of solute in the solid matrix that is inaccesible to the SCF (i.e., x_k = inaccessible solute/ initial solute), and thus it might be taken as a constant.

As a second example of the performance of the proposed models, we present a comparison of results obtained with the Sovová´s model and the so-called VT-II [11] model for correlating data on supercritical CO_2 extraction of theobromine from cocoa seed shells that were presented by Brunner [11]. The VT-II model is also a rigorous, phenomenological model that uses the Freundlich isotherm to model the change in solute concentration in the solid. If no axial dispersion is taken into account, it has four adjustable parameters. These are: two Freundlich coefficients, the effective diffusivity of the extract in the solid, and a mass transfer coefficient in the fluid.

Figure 3 shows the correlation of data obtained at laboratory scale. Note that the proposed model 1, sovová's and VT-II models perform similarly, while proposed model 2 presents important deviations in the last extraction stage. However, when the parameter x_m takes values greater than one, proposed model 2 fits the experimental data even similarly as all the other models do, as Figure 4 shows.
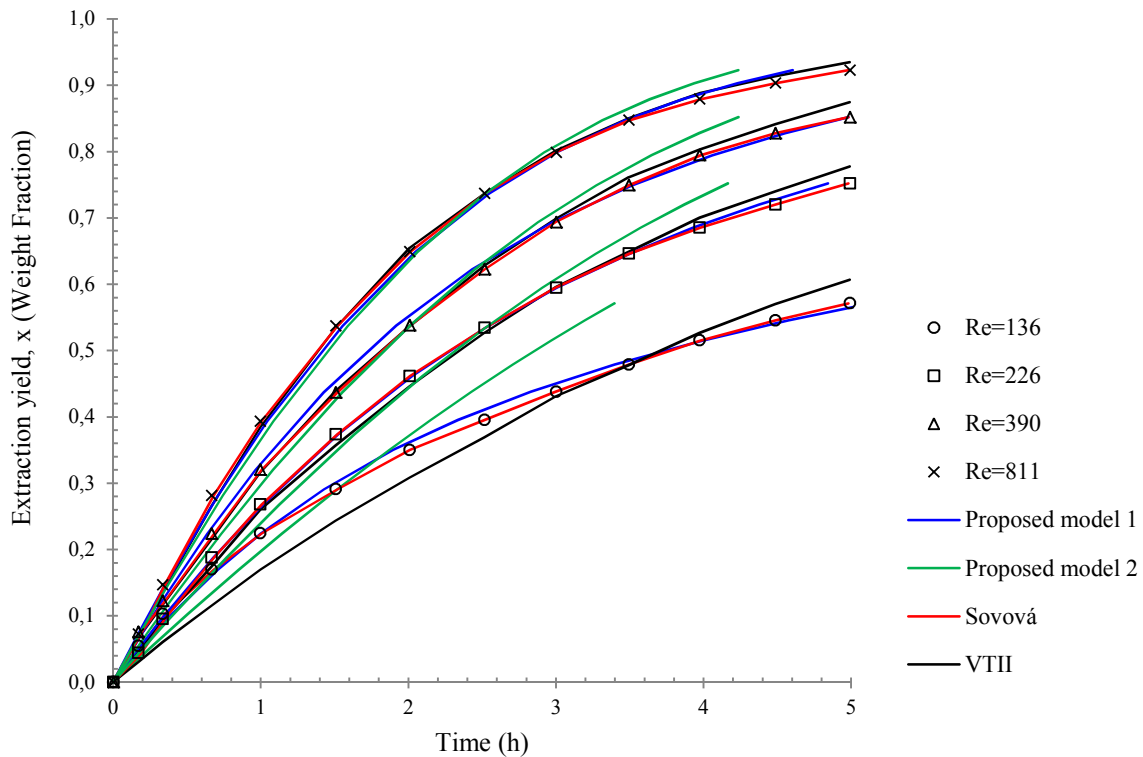

Figure 3. Data correlation for supercritical CO_2 extraction of theobromine from cocoa seed shells at laboratory scale. Experimental data at 30 MPa and 353 K. [11].

In the first case, deviations of the proposed models 1 and 2, sovova's and VT-II models were 3.4, 10.7, 4.3, and 6.0%, respectively. In the second case, the deviation of the proposed model 2 decreases to 6.8 %. These results indicate that the proposed model 1 might be compared favorably with the VT-II and Sovová's models. The proposed model 2 does a remarklably good performance if one takes into account that it only has two adjustable parameters.

Figure 5 shows predictions by the models and data obtained at pilot-plant scale for the supercritical CO_2 extraction of theobromine from cocoa seed shells. The deviations were 10.3% (VT-II), 11.1% (proposed model 1), and 14.3% (proposed model 2). Brunner [11] has shown that for this system the VT-II model can be used with reasonable accuracy for scaling purposes using the parameters obtained at laboratory scale. Although rigorous models such as VT-II take into account parameters that can be affected during scaling, we believe that as long as flow conditions such as Reynolds number are maintained the proposed models should be as good (or bad) as more rigorous models for scaling purposes.
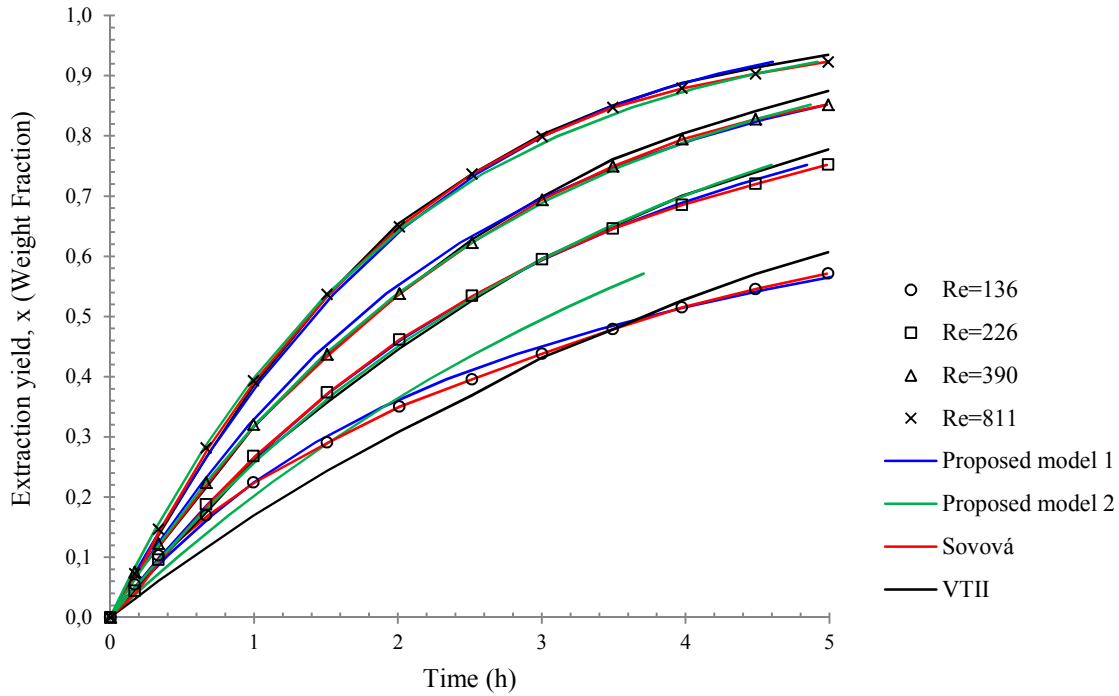
Figure 4. Data correlation for supercritical CO_2 extraction of theobromine from cocoa seed shells at laboratory scale. Experimental data at 30 MPa and 353 K [11]. Proposed model 2 with $x_m > 1$.
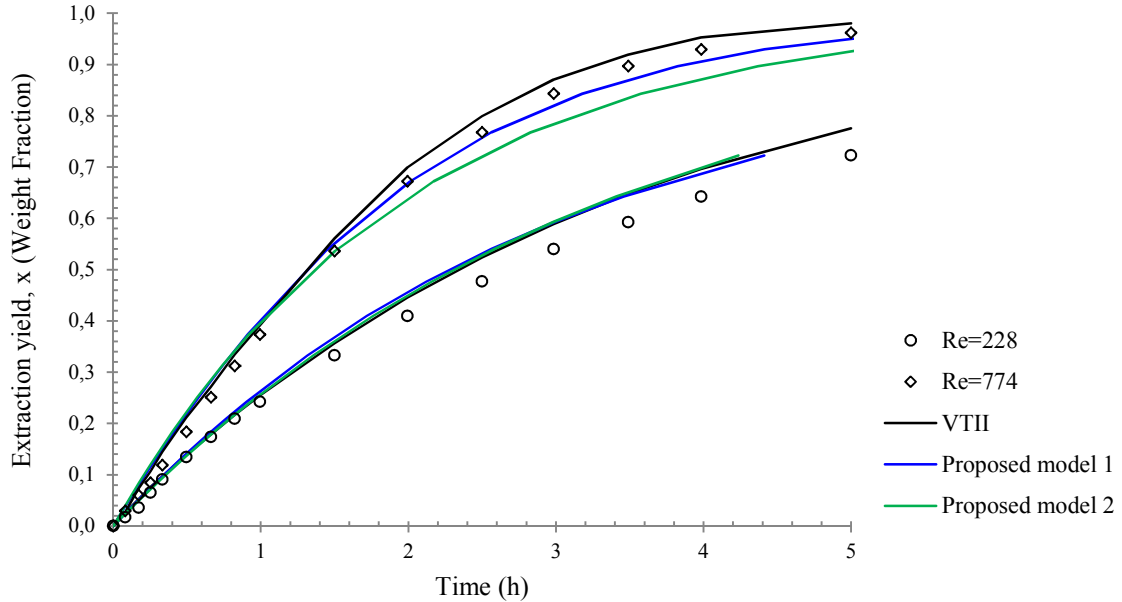

Figure 5. Predictions and data obtained at pilot-plant scale for the supercritical CO_2 extraction of theobromine from cocoa seed shells [11] by the proposed and VT-II models.

Adsorption-based models for supercritical extraction of natural matter have been in the literature for some time. In particular, several models are known that use the BET approach to model adsorption equilibrium together with rigorous balances (see for example references 7 and 12) to take into account diffusion in micropores, mass transfer to the supercritical fluid, and radial and axial dispersion in the extractor. Simple

models such as those presented in this work capture essential elements of the extraction. For example, in addition to the adequate correlation of data that was shown, the models correctly predicts that the apparent solubility (i.e., the slope of the extraction yield vs. time curve) is a function of the amount of solute initially present in the bed, an observation that has been presented in the literature using more elaborated analyses [13]. The models can thus be useful in studies on supercritical extraction of natural matter.

3. Conclusions

Two simple mathematical models that adequately correlate information on the kinetics of supercritical fluid extraction were presented. The models integrate modifications of the BET adsorption equilibrium equation with a simplified material balance of a supercritical extractor. The new models have three and two adjustable parameters, respectively, each one with a clear physical meaning. These models produce an average deviation similar to that obtained with rigorous models such as Sovová and the so-called VT-II models. In particular, the performance of the proposed model 1 is in several cases better than the VT-II and Sovová´s models, a remarkable result given that it is only constituted by one equation compared with the three conditional equations of Sovová's model and the system of differential equations of VT-II. The proposed model 1 is capable of representing the extraction periods as Sovová's model does, in some cases with better accuracy. In addition, the proposed model 2 has a remarkably good performance considering that only has one simple equation and two adjustable parameters. This model might be used as a first approximation for data correlation. These results indicate that the models proposed in this paper are a simple and useful tool for correlating experimental data on supercritical fluid extraction of natural matter.

Acknowledgments

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