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SOLID-LIQUID EXTRACTION PROCESS OF ACTIVE INGREDIENTS FROM MEDICINAL PLANTS- MATHEMATICAL MODELS

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ABSTRACT:

Mathematical modelling of solid-liquid extraction process of active ingredients from medicinal plants plays a crucial role in basic research of herbal extraction. It is very important to select the best fitted mathematical model with experimental data for estimation of diffusion/mass transfer coefficient. In this paper, efforts have been made to explain the various mathematical models (unsteady state diffusion model, extraction kinetics model, and mass transfer model) for solid-liquid extraction process are explained with experimental data.

Keywords: Mathematical Modelling; Solid-Liquid Extraction; Unsteady State Diffusion Model; Kinetics Model; Mass Transfer Model

Introduction

The important aspects for performance evaluation of solid-liquid extraction process are mainly based on the experimental kinetics of the extraction process. In most of the cases, estimation of effective diffusivity plays an important role in extraction kinetics. For estimation of effective diffusivity mathematical models can be used, which are based on basic fundamental laws of kinetics and mass transfer. Steady state mass transfer model [1 & 2], kinetic model [3], and unsteady diffusion models [3, 4 & 5] are reported to represent solid-liquid extraction of different ingredients from plants. The efforts have been taken to explain these mathematical models and comparison with experimental data.

Mathematical Models

Steady State Mass Transfer Model:

Handayani et al. (2008) proposed steady state mass transfer model to study the solid-liquid extraction process of astaxanthin from giant tiger (Panaeus monodon). In this model they assumed that main mechanism that controls the rate of astaxanthin extraction is mass transfer of astaxanthin from solid to bulk liquid palm oil. Rate of mass transfer of astaxanthin from solid to bulk liquid can be written as

$$\frac{dN_A}{dt} = k_L A[C_{Ae} - C_A] \qquad (1)$$

where dN_A/dt is the rate of astaxanthin mass transfer (μg/s), C_A and C_{Ae} are concentration of astaxanthin in bulk liquid and at equilibrium (μg/L), respectively. Here kL is mass transfer coefficient and A is surface area for mass transfer process. Since the extraction process was carried out in batch mode, and the volume of solution (V) was kept constant during the process, therefore

$$dN_A = VdC_A \qquad (2)$$

Substitution of Eq. (2) into Eq. (1) yields

$$\frac{VdC_A}{dt} = k_L A[C_{Ae} - C_A]$$

$$\frac{dC_A}{dt} = k_L \frac{A}{V}[C_{Ae} - C_A]$$

$$\frac{dC_A}{dt} = k_L.a[C_{Ae} - C_A] \qquad (3)$$

Where, (k_L.a) is volumetric mass transfer coefficient. To solve Eq. (3), we used the initial conditions as follow

At beginning of extraction process (t = 0), the concentration of astaxanthin in bulk liquid is zero, $C_A = 0$.

• At any time the concentration of astaxanthin in bulk liquid is $C_A = C_A$

With those initial conditions, integration of Eq. (3) gives the following result

$$C_A = C_{Ae}\left[1 - \exp\left(-k_L.a.t\right)\right] \quad (4)$$

Eq. (4) can be written in term of yield per mass of shrimp waste

$$Y = Y_e\left[1 - \exp\left(-k_L.a.t\right)\right] \quad (5)$$

where Y and Ye are yield of astaxanthin in bulk liquid and at equilibrium per mass of shrimp waste, respectively.

Figure 1 depicts the experimental kinetic data of extraction of astaxanthin in palm oil at various temperatures, and the fits of mass transfer kinetic model. In this figure, the experimental data are represented as symbols and kinetic model as solid lines. For the kinetic model, the parameters Ye and (k_L.a) were estimated by nonlinear least squares fit of Eq. (5) to experimental kinetic data.

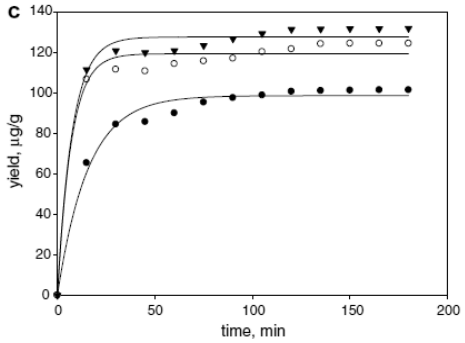

Figure 1: Yield of astaxanthin at 50 °C, 60 °C, and 70 °C and mass transfer kinetic model fit.

Kinetic Model:

Adamou Harouna-Oumarou et al. (2006) shows, in the study of the mechanisms and kinetics in the extraction process of water soluble compounds from *tilia* sapwood, that a model based on a second-order extraction process was the most suitable model for a solid–liquid extraction process. It was then possible to build the kinetic models of a solid–liquid extraction and the extraction order and rate constant remained to be determined by experiments. According to a second-order rate law [6, 7], Rakotondramasy-Rabesiaka, *et. al.* (2008) described the rate of dissolution for the protopine contained in the solid from plant cells to solution by Eq. (6):

$$\frac{dC_t}{dt} = k\left[C_s - Ct\right]^2 \quad (6)$$

where *k* is the second-order extraction rate constant (L g^{-1} min^{-1}), C_s the extraction capacity (concentration of protopine at saturation in mg L^{-1}) and C_t is the concentration of *F. officinalis* protopine in the suspension at any time *t* (min).

By considering the initial and boundary conditions, t=0 to t and C_t =0 to C_t, the integrated rate law for a second-order extraction was obtained:

$$C_t = \frac{C_s^{\,2}kt}{1 + C_s kt} \quad (7)$$

By transforming Eq. (7), a linear form shown in Eq. (8) can be obtained and the extraction rate can be written as Eq. (9):

$$\frac{t}{C_t} = \frac{1}{kC_s^2} + \frac{t}{C_s} \quad (8)$$

$$\frac{C_t}{t} = \frac{1}{\left(1/kC_s^2\right) + \left(t/C_s\right)} \quad (9)$$

The initial extraction rate, *h*, as *Ct*/*t* when *t* approaches 0, can be defined as:

$$h = kC_s^2 \quad (10)$$

and, the concentration of protopine at any time can be expressed after rearrangement as:

$$C_t = \frac{t}{\left(1/h\right) + \left(t/C_s\right)} \quad (11)$$

The initial extraction rate, *h*, the extraction capacity, *C*s, and the second-order extraction rate constant, *k*, can be determined experimentally from the slope and intercept by plotting *t*/*Ct* versus *t* as shown in Figure 2.

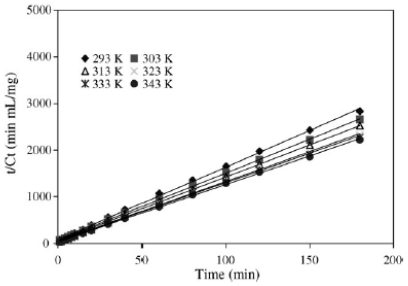

Figure 2: Second-order extraction kinetics of protopine in ethanol 44% (w/w) from *Fumaria officinalis* at various temperatures (ratio of solid/solvent of 0.04, particle size of 0.4–0.5mm and stirring speed of 200 rpm) [8]

Unsteady State Diffusion Model:

Wongkittipong, *et. al.* (2004); Simeonov *et. al.* (1999); Rakotondramasy-Rabesiaka, *et. al.* (2008) and Taralkar (2009) was used unsteady state diffusion model for estimation of diffusivity for solid-liquid extraction of active ingredients from medicinal plants.

Wongkittipong, *et. al.* (2004) described the andrographolide transfer from plant with following hypotheses:

1. The solid particle has two shapes: plane shape corresponding to leaves and cylindrical shape corresponding to stems. The solute diffusion takes place in the transverse direction and is monodirectional.
2. Every particle is symmetrical and homogeneous.
3. The diffusion coefficient is constant in all experiment. The andrographolide concentration in a particle, $C1$, depends only on position and time.
4. The solvent in the batch reactor is perfectly mixed. The transfer resistance in the liquid phase is negligible and the andrographolide concentration in the solvent depends only on time.
5. The transport of the andrographolide particles is a diffusion phenomenon. It is described by a diffusion coefficient that relates to $D1$ (or D) and independent of the time.
6. At the interface, the concentrations of every species in solution between the internal liquid (in pores) and external to particles are supposed to be equal.
7. Initial concentration in each experiment is calculated using the experiment at 150 min because the ability of extraction for each solvent is different.
8. The mass percentage of leaves in all samples is supposed to be about 80%.

The general diffusion model of solid–liquid extraction

$$\frac{\partial C(t,x)}{\partial t} = D\frac{1}{x^{\varphi-1}}\frac{\partial}{\partial x}\left(x^{\varphi-1}\frac{\partial C(t,x)}{\partial x}\right) \quad (12)$$

where t is the time, x the radial distance in the direction of material transfer (the thickness of plate is equal to $2e$). ϕ the geometric shape factor values for the shapes involved in the experiment.

For the leaves:

$$\frac{\partial C_1}{\partial t} = D\frac{\partial^2 C_1(t,x)}{\partial x^2} \quad (13)$$

For the stems:

$$\frac{\partial C_2(t,x)}{\partial t} = D\left(\frac{1}{x}\frac{\partial C_2(t,x)}{\partial x} + \frac{\partial^2 C_2(t,x)}{\partial x^2}\right) \quad (14)$$

The mass balance is

$$C_L(t)V_L + \int_0^e C_1(x,t)\,dV_1(x) + \int_0^e C_2(x,t)\,dV_2(x) = C_{10}V_1 + C_{20}V_2 \quad \forall t \quad (15)$$

Initial conditions (t = 0)

- For the continuous phase: $Cs = 0$ (concentration of solution in the solvent),
- For the dispersed phase: $C1 = C10$ and $C2 = C20$ $\forall x$.
- At the center of a particle ($x = 0$)

$$\left(x^{\varphi-1}\frac{\partial C(t,x)}{\partial x}\right)_{x=0} = 0 \quad \forall t \quad (16)$$

At the interfacing ($x = e$), equality of flux of andrographolides (in mass):

The retiring flux of the solid (which has to be integrated for the entire solid) is:

$$F = -DA\left(\frac{\partial C(t,x)}{\partial x}\right)_{x=e} \quad (17)$$

The incoming flux in the liquid is:

$$F = V_L \frac{dC_L(t)}{dt} \quad (18)$$

where V_L is the solvent volume and A the specific area.

Figure 3 shows the comparison of experimental data with model data for the extraction of andrographolides from plant matrix.

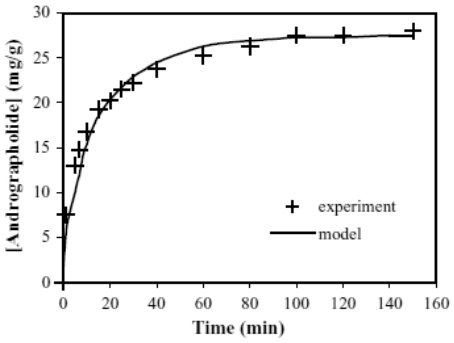

Figure 3: Comparison between experimental data and the final model 60% ethanol at 22°C and diameter of solid 0.6–0.8 mm [4].

Conclusions:

In this paper, mathematical models (Unsteady state diffusion model, steady state mass transfer model and mass transfer kinetics model) for solid-liquid extraction of active ingredients from medicinal plants are discussed and comparison has been given with experimental data. Steady state mass transfer model and mass transfer kinetics model are the approximate models which gives approximate values of mass transfer coefficient which is not the actual case. Unsteady state diffusion model helps to estimation of diffusion coefficient for solid-liquid extraction process. This model is some what accurate than the earlier models as it considers the shape and size of particle, actual transfer mechanism of compound from cellulose matrix (plant material) to solvent.

References:

1. Handayani A. D., Sutrisno, Indraswati N., Ismadji S., (2008) Extraction of astaxanthin from giant tiger (Panaeus monodon) shrimp waste using palm oil: Studies of extraction kinetics and thermodyanmic, Biore. Tech. 99, 4414-4419.
2. Hau K., Zheng Q., Li Y., Shen J., Hu S., Shen J., Hu S., (2000) Modeling and optimization of herb leaching processes, Comp. and Chem. Engg. 24, 1343-1348.
3. Rakotondramasy-Rabesiaka L., Havet J., Porte C., Fauduet H., (2008) Solid-liquid extraction of protopine from Fumaria officinalis L.-experimental study and process optimization, Sep. and Puri. Tech. 59, 253-261.
4. Wongkittipong R., Prat L., Damronglerd S., Gourdon C., (2004) Solid-liquid extraction of andrographolide from plants-experimental study, kinetic reaction and model, Sep. and Puri. Tech. 40, 147-152.
5. Simeonov E., Tsibranska I., Minchev A., (1999) Solid-liquid extraction from plants-experimental kinetics and modelling, Chem. Engg. Jr. 73, 255-259.
6. Adamou Harouna-Oumarou H., Fauduet H., Porte C., Ho Y.-S., (2005) Kinetics and model building of leaching of water-soluble compounds of *Tilia* sapwood, Sep. Purif. Technol. 45, 169.
7. Adamou Harouna-Oumarou H., (2006) Extraction solide-liquide aqueuse de l'aubier de tilleul en r´egimes discontinu et continu: caract´erisation, cin´etique, mod´elisation, d´eveloppement pilote, PhD thesis, Universit´e Pierre et Marie Curie, Paris.
8. Rakotondramasy-Rabesiaka L., Havet J.-L., Porte C., Fauduet H., (2007) Solid-liquid extraction of protopine from Fumaria officinalis L.-Analysis determination, kinetic reaction and model building, Sep. and Puri. Tech. 54, 253-261.
9. Taralkar S. V., (2009) Engineering principles of extraction of active ingredients from medicinal plants, PhD thesis, Dr. B. A. Technological University, Lonere, India.