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МОДЕЛИРАНЕ НА ЕКСТРАКЦИЯ ОТ РАТИТЕЛНИ СУРОВИНИ ЧРЕЗ ПРОМЕНЛИВ КОЕФИЦИЕНТ НА ЕФЕКТИВНА ДИФУЗИЯ

Ч.Чилев, В.Колева, Е.Симеонов
Химикотехнологичен и Металургичен Университет

MODELING OF EXTRACTION PROCESS FROM PLANT MATERIALS WITH VARIABLE COEFFICIENT OF EFFECTIVE DIFFUSION

Ch. Chilev, V. Koleva, E. Simeonov
University of Chemical Technology and Metallurgy - Sofia

Abstract
The kinetic of flavonoids extraction from Cichorium intybus was obtained experimentally. The influence of temperature, liquid-solid ratio and extraction solvent on the extraction rate was investigated. A four parameters model for calculating the values of Deff was found using non-linear regression of the experimental results. The diffusion model was solved using variable Deff. There is a good alignment between the numerical and experimental data.

Keywords: *mathematical modelling; extraction kinetic; Cichorium intybus; flavonoids.*

Introduction

The solid-liquid extraction is a process whose products are widely used in pharmaceutics, cosmetics and food industries. This provokes numerous scientific studies focused on the process kinetics [1-4], the diffusivities, the yield of extraction [5-7]. The modeling is a powerful mean for the optimization of the equipment, simulation, design and control, allowing theoretical description of the process and evaluation of the mass transfer coefficients. The process description is very difficult because of the influence of a large number of parameters: variable in the time solid phase pore structure, irregular particle shape, large particle size distribution. The kinetic coefficients vary during the extraction. To set up an experimental installation we need to be acquainted with the diffusion type and the factors that are of main importance for the process.

The process of extraction of useful components from plant raw material is almost ever limited by the transfer inside the pores of the solid phase. Each experimental kinetic curve (function) includes in a hidden way all factors that influence the diffusion process velocity, like: polydispersion, anisotropy, solid particles form, characteristical change of concentration in the liquid phase. Quantitative these factors are reported by the effective diffusion coefficient. The exact calculation of Deff is of big importance by the engineering decision of the process. In the praxis there are experimental methods and those combining experimental received data and analytical decisions of the process [8,9].

Materials and Methods

The kinetic of periodical extraction from ***Cichorium intybus*** in a stirring vessel was experimentally defined. A series of experiments have been carried out at liquid-solid ratio ξ = 0,02 m^3/kg , ξ = 0,03 m^3/kg at temperature of 20, 40 and 50^0C and at solvent concentration – 50% and 70% ethanol. The experimental results are obtained at stirring velocity of n=5 s^{-1} and it has been proven that the process is limited by internal diffusion (the external diffusion resistance has been eliminated). For defining the content of flavonoids a spectrophotometric analysis has been used, carried out through spectrophotometer BOECO – Germany S-22 UV/Vis.

The concentration of total flavonoids in the extracts is obtained by a colorimetric method with catechin as follows: 4 ml of water are put in a volumetric flask of 10 ml together with 0.3 ml of 5% $NaNO_2$ and 1 ml from the extract, the liquid is well mixed. After 5 min 0.3 ml 10 % $AlCl_3$ are added. On the 6th minute 2 ml 1M NaOH are added and the volume is filled up with water up to 10 ml. The absorption of the solution is measured at 510 nm against a blank probe.

Results and Discussion

The function of total flavonoids concentration of in the liquid phase with the time can be described with the following equation:

$$C_1 = A - B.e^{(-H.\tau)} \qquad (1)$$

where A, B and H are constants numerically obtained from the experimental data shown in Table 1.

Working conditions	A	B	H
t=20°C; ξ=0,02 m³/kg; 70% ethanol	0,363	0,362	0,00166
t=50°C; ξ=0,02 m³/kg; 70% ethanol	0,669	0,665	0,00143
t=40°C; ξ=0,03 m³/kg; 70% ethanol	0,353	0,341	0,00098
t=40°C; ξ=0,02 m³/kg; 50% ethanol	0,394	0,377	0,00121
t=40°C; ξ=0,02 m³/kg; 70% ethanol	0,752	0,761	0,00081

Table. 1. Values of A, B, and H by different working conditions.

Figure 1 presents the extraction kinetic by ζ=0.02 m³/kg and t=20°C, solvent 70% ethanol.

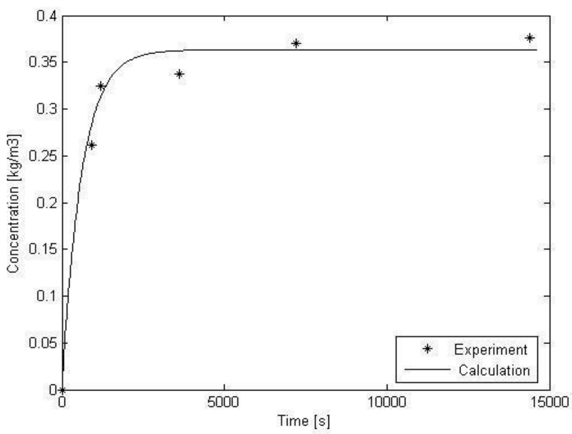

Fig. 1. Flavonoids concentration in the liquid phase as a function of time by ζ= 0.02 m³/kg and t = 20°C, 70% ethanol.

The kinetic curves by other process conditions (from Table 1) are similar.

We obtained the effective diffusion coefficient by the method of the regular regime. This method is based on a comparison between the experimentally obtained data by a non-constant mass transfer from the solid into the liquid phase with the analytical solutions by the same conditions of mass transfer.

$$\frac{\overline{C_2}}{C_0} = \sum_{1}^{\infty} \frac{8}{\pi^2 (2n-1)^2} e^{-\frac{\pi^2}{4}(2n-1)^2 \frac{D_{eff}\tau}{R^2}} \qquad (2)$$

where C_1 – concentration in liquid phase; C_{1i} – initial concentration in liquid phase. For Fo > 0.1 we can narrow (2) to its first term:

$$\frac{\bar{C_2}}{C_0} = B_1 \exp^{-\mu \frac{D_{eff}\tau}{R^2}} \qquad (3)$$

For the investigated system $Bi \to \infty; B_1 = 8/\pi^2; \mu_1 = \pi/2$ equation (3) becomes:

$$\lg \frac{C_2}{C_0} = \lg B_1 - 0{,}434 \mu_1^2 \frac{D_{eff}\tau}{R^2} \qquad (4)$$

Using the method of regular regime, equation (4) for all values of concentration in table 1 we obtained the received values for Deff.

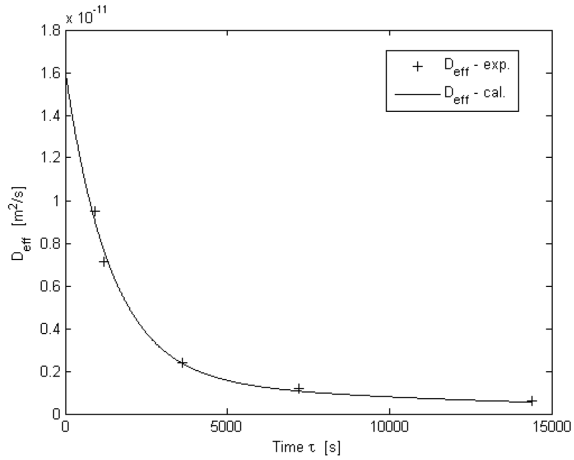

Fig. 2. Experimental values for Deff and their modelling by equation (1).

Figure 2 presents the results for Deff obtained by the method of regular regime by flavonoid extraction from *Cichorium intybus* by 20, 40 and 50°C, liquid-solid ratio ξ = 0,02 and 0,03 *m³/kg* and solvent- 50 and 70% - ethanol/water. Since those values are calculated by the method of regular regime directly from the experimental data they are called experimental $D_{eff} - \exp$. Figure 2 shows the exponential function of D_{eff} with the time. Similar function is obtained by all investigated process conditions. Therefore the change of D_{eff} with the time can be described by an equation like following one:

$$D_{eff} = ae^{-b\tau} + ce^{-d\tau} \tag{5}$$

This is a four parameter model where the parameters can be obtained by a non-linear regression of the experimental data. Table 3 summarises the values for a, b, c and d for modelling D_{eff} by equation (5).

Conditions	Parameters
$T = 20°C$ ξ=0,02 *70% Etanol*	$a = 1.431e\ \ 011$ $b = -0.000726$ $c = 1.801e - 012$ $d = -8.289e - 005$
$T = 40°C$ ξ=0,02 *70% Etanol*	$a = 2.218e - 011$ $b = -0.001206$ $c = 1.801e - 012$ $d = -0.0001625$
$T = 50°C$ ξ=0,02 *70% Etanol*	$a = 1.433e - 011$ $b = -0.0007258$ $c = 1.809e - 012$ $d = -8.293e - 005$
$T = 40°C$ ξ=0,03 *70% Etanol*	$a = 2.301e - 011$ $b = -0.001276$ $c = 3.253e - 012$ $d = -0.000173$
$T = 40°C$ ξ=0,02 *50% Etanol*	$a = 2.304e - 011$ $b = -0.001276$ $c = 3.257e - 012$ $d = -0.0001731$

Table 2. Parameters of equation (5) for the different process conditions.

We are investigated the influence of process parameters on process equilibrium and extraction rate respectively. Figure 3 presents the temperature influence on the flavonoids extraction rate.

Extracted flavonoids amount increases from 20°C to 50°C, and the valuable compounds do not destroy at the higher temperature.

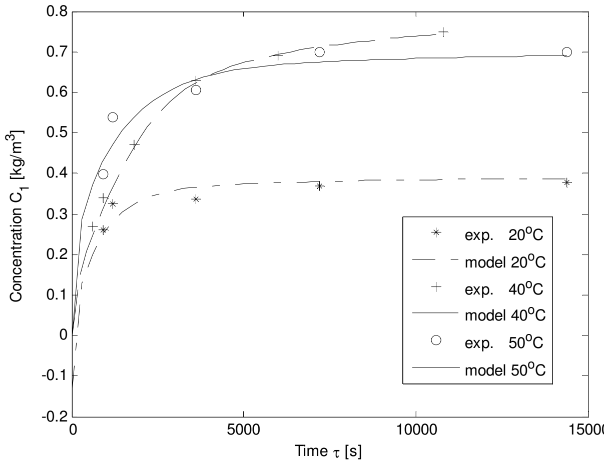

Fig. 3. The influence of temperature on the amount of extracted flavonoids.

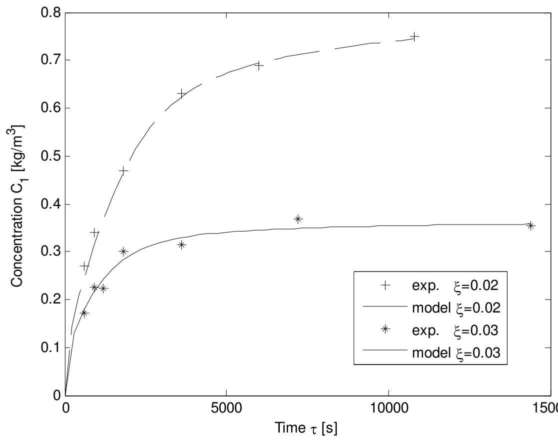

Fig. 4. Liquid-solid ratio influence on flavonoids extraction.

The obtained results are presented on Figure 4. The equilibrium concentration is reached much faster by increased liquid-solid ratio.

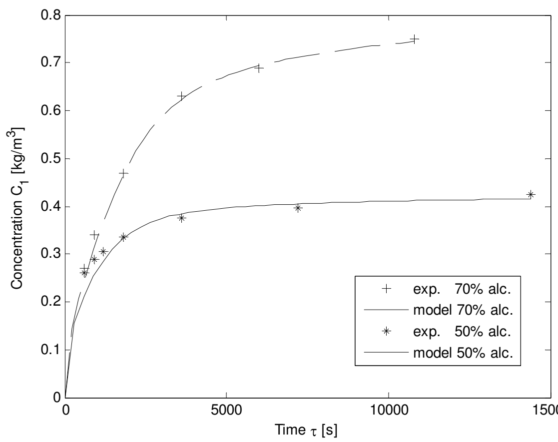

Fig. 5. Solvent influence on flavonoids extraction.

Extraction experiments with 50% and 70% ethanol were carried out. From the data shown on Figure 5 it is clear that the higher extraction rate is achieved by using 70% ethanol.

Conclusion

The extraction kinetic of flavonoids from Cichorium intybus was experimentally obtained. The effective diffusion coefficient was calculated by the method of regular regime. A four parameter model for obtaining Deff by a nonlinear regression of the experimental data was obtained. The influence of the different process parameters on the extraction equilibrium and extraction rate are determined by numerical solution of the diffusion model. There is a very good alignment between the calculated and experimental data.

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