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Chemical Engineering Journal 73 (1999) 255–259

Chemical Engineering Journal

Short communication

Solid–liquid extraction from plants — experimental kinetics and modelling

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Received 25 July 1997; received in revised form 28 November 1998; accepted 20 December 1998

Abstract

The kinetics and structural changes in the solid were studied for solid–liquid extraction from plants. Two extraction systems were investigated: tobacco leaves (*Nicotiana tabacum* L.)–water, and oak bark (*Quercus frainetto* Ten)–water. The mathematical model of the process, accounting for variable effective diffusivity and porosity, was stated and solved numerically. The solution was checked with experimental kinetics and porosity data to determine the effective diffusion coefficient. A very good correspondence was found between this value and the results obtained with the regular regime and the standard function methods. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Solid–liquid extraction; Extraction kinetics; Modelling

1. Introduction

The known approaches for the calculation of solid–liquid extraction are based on the experimental kinetics of the process. The use of the characteristic function in the general case of a polydispersed anisotropic solid allows for the integral description of the diffusional resistance and structural changes without the knowledge of the respective kinetic coefficients. In this way, the required retention time and size of the extractor can be determined precisely [1,2]. In a second approach, a mathematical model, together with the experimental information, is used to obtain the values of the kinetic coefficients (D_e and k_l), followed by the sizing up of the extraction unit. In most cases of practical interest, constant values of the kinetic parameters are assumed [3–5]. When the dependence of the effective diffusion coefficient on the concentration is important, the precision of such calculations is no longer satisfactory. When the $D_e(C)$ function is included in the model, a possible relation to structural changes in the solid should also be considered. The variation in porosity with time is supported by experimental observations.

The aim of the present study was to apply a mathematical model of variable internal diffusivity and porosity to experimental kinetic data, and to compare the resulting diffusion coefficient with the values obtained from other methods. Two different extraction systems of interest for industrial practice were chosen, their structural changes being characterized by porosimetry.

2. Experimental

The extraction kinetics of the system tobacco (*Nicotiana tabacum* L.)–water (system I) were studied in a stirred vessel at $t = 20°\mathrm{C}$, liquid-to-solid ratio $\zeta = 0.015\ \mathrm{m^3\ kg^{-1}}$ and constant angular velocity $n = 7\ \mathrm{s^{-1}}$. During the experimental runs, the change with time of the extracted species in the liquid was obtained, the liquid phase concentration being measured by weighting (precision: 10^{-3} g for a total amount of sample ranging from 1 to 1×10^{-2} g). The extracts were evaporated in a drying unit at $t = 70°\mathrm{C}$.

The set of experimental conditions for the system oak bark (*Quercus frainetto* Ten)–water (system II) was: $t = 20°\mathrm{C}$, liquid-to-solid ratio $\zeta = 0.015\ \mathrm{m^3\ kg^{-1}}$ and angular velocity $n = 5\ \mathrm{s^{-1}}$. The initial moisture content in the oak bark was 9.7%.

The internal diffusion was rate limiting for the extraction kinetics in both systems ($\mathrm{Bi} = k_l X/D_0 > 50$). The absence of external mass transfer was proved by varying the angular velocity until constant values for the measured liquid phase concentration were obtained ($n \geq 7\ \mathrm{s^{-1}}$ for system I and $n \geq 5\ \mathrm{s^{-1}}$ for system II).

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PII: S1385-8947(99)00030-3

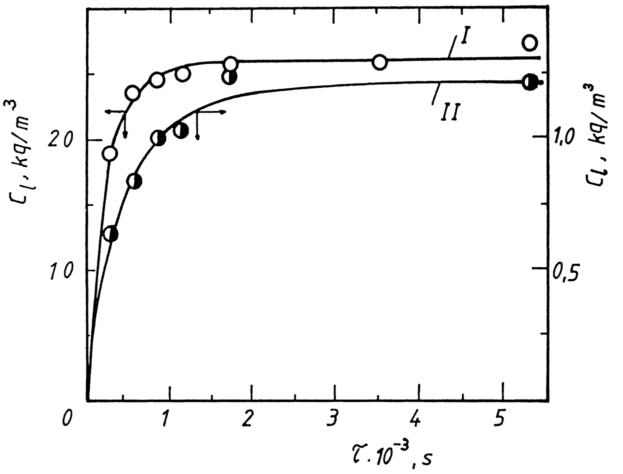

Fig. 1. Extraction kinetic curve: ○, experimental system I; ◐, experimental system II—calculated.

The tannin concentration in the liquid phase was measured by the modified Loewental method [6–8] by titration with $KMnO_4$ in the presence of indigocarmin–sulphonic acid used for regulating the oxidation process. The kinetic curves obtained are shown in Fig. 1. The experimental data can be described accurately by the following relation resulting from the analytical solution [9] and the use of the standard function method [10]:

$$C_l = A - B\exp(-H\tau) \tag{1}$$

where τ is the time, and where the values obtained for the constants are: $A = 25.9$, $B = 25.81$ and $H = 4 \times 10^{-3}$ for the tobacco–water system; $A = 1.21$, $B = 1.20$ and $H = 2.15 \times 10^{-3}$ for the oak bark–water system.

The internal porosity of the solid phase was determined by Hg porosimetry for initial fresh material (totally extracted particles), for extraction times τ equal to 900, 1200 and 3600 s. The values of ε for each extraction time were obtained from the differential pore size distribution curves. A Carlo-Erba 1500 porosimeter was used in which up to 1500 atm pressure was applied, corresponding to a pore size of 0.005 μm. The lower limit is determined by the minimal height of 115 mm Hg, which corresponds to a pore size of 40–50 μm. Five samples of each system were analysed, taken at different times of extraction ($\tau = 0$, 900, 1200, 3600 and 5400 s) to show the increasing internal porosity and anisotropy of the solid compared to the non-extracted raw material. The results for systems I and II are similar and can be seen in Fig. 2 (a) and (b) where the integral curves obtained for system I before and after 5400 s of extraction are presented. Concerning the pore size distribution, the fresh particles are also much more uniform. In the extracted samples, the pore size ranges from 0.007 to 40 μm for system I and 0.001 to 60 μm for system II, thus confirming their anisotropy. The time evolution of the internal porosity is shown Fig. 3. The experimental data are described by the following correlation:

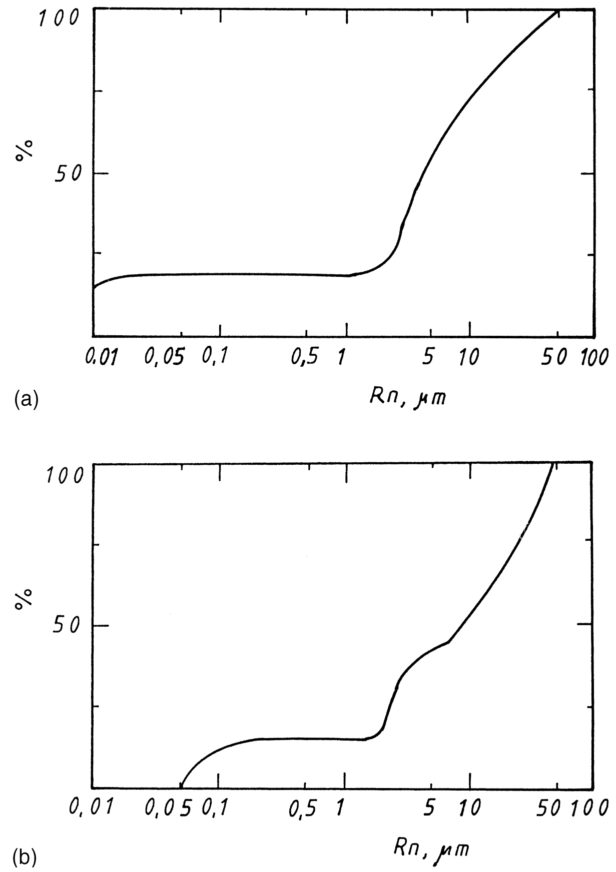

Fig. 2. Integral pore size distribution curve: (a) $\tau = 0$; (b) $\tau = 5400$ s.

$$\varepsilon = a\tau^b + c \tag{2}$$

the constants being $a = 0.053$, $b = 0.194$ and $c = 0.43$ for the tobacco leaves–water system, and $a = 0.0108$, $b = 0.369$ and $c = 0.55$ for the oak bark–water system.

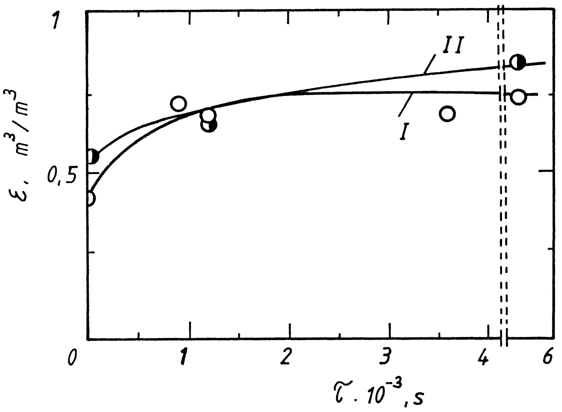

Fig. 3. Internal porosity time evolution curve: ○, experimental system I; ◐, experimental system II—calculated.

3. Numerical results

The basic diffusion model of solid–liquid extraction [9] was used, wherein the simultaneous effect of concentration-dependent diffusivity and variable porosity was included. The resulting set of differential equations is

the balance equation for the particles

$$\frac{\partial(\varepsilon C_s)}{\partial \tau} = \frac{1}{x^{\alpha}}\frac{\partial}{\partial x}\left[x^{\alpha} D_e(C_s)\frac{\partial C_s}{\partial x}\right] \tag{3}$$

with boundary conditions

$$\left.\frac{\partial C_s}{\partial x}\right|_{x=0} = 0 \tag{3a}$$

$$-D_e\left.\frac{\partial C_s}{\partial x}\right|_{x=X} = k^{e}\left(\frac{C_s|_{x=X}}{m} - C_e\right) \tag{3b}$$

and initial condition

$$C_s|_{\tau=0} = C_0 \tag{3c}$$

where C_s and C_l denote the solid and liquid phase concentrations, respectively. Linear equilibrium is assumed at the solid–liquid interface, the distribution coefficient being $m \approx 1$, because of the low concentration range. This fact is known from the literature and was confirmed by our experimental investigations.

The mass balance in the extractor vessel, assuming perfect mixing, is given by Eq. (4):

$$V_l\frac{dC_l}{d\tau} = -V_s\frac{d\overline{\overline{C}}_s}{d\tau} \tag{4}$$

with initial condition

$$C_l|_{\tau=0} = 0 \tag{4a}$$

where $\overline{\overline{C}}_s$ denotes the average solid phase concentration

$$\overline{\overline{C}}_s = \frac{\alpha+1}{X}\int_0^{x} C_s(x)\,dx \tag{5}$$

Eqs. (3) and (4) were solved numerically in dimensionless form using an implicit finite difference technique [11] recommended for heat conduction and diffusional problems with variable coefficients. The curves were obtained as dimensionless liquid phase concentration ($\overline{C}_l = C_l/C_0$) versus time ($\overline{\tau} = \tau D_0/X^2$) and compared with the experimental values. Both systems were modelled as particles of regular form, the form factor being $\alpha = 0$ (plates) for the first, and $\alpha = 2$ (spheres) for the second. The calculations were performed for the following values of the parameters: $X = 0.15 \times 10^{-3}$ m, $C_0 = 679.7$ kg m^{-3} and $V_l/V_s = 18.81$ for system I, and $X = 1.8 \times 10^{-3}$ m, $C_0 = 20.4$ kg m^{-3} and $V_l/V_s = 13.3$ for system II.

The experimentally obtained $\varepsilon(\tau)$ function was used in the solution and the dependence of the diffusion coefficient on concentration was investigated. Thus the effective diffusivity, defined as $D_e = \varepsilon D$, was the adjustable parameter dependent on C_s. In dimensionless form, the effective diffusivity was defined as

$$\overline{D} = \frac{D_e}{\varepsilon_0 D_0} = \frac{\varepsilon D}{\varepsilon_0 D_0} \quad \text{and} \quad \overline{C}_s = \frac{(C_s - C_{se})}{(C_0 - C_{se})}$$

D_0 is defined as the limiting value when $C_s \to 0$, and was found, as a first approximation, as the constant value for which the best coincidence with the experimental data is obtained for the low concentration range (high extraction times). For the tobacco leaves–water system, the value of $D_0 = 4.5 \times 10^{-11}$ m^2 s^{-1} was found. It is in agreement with the values obtained from the regular regime ($D_0 = 3.5 \times 10^{-11}$ m^2 s^{-1}) [12] and the standard function techniques [10] ($D_0 = 4.31 \times 10^{-11}$ m^2 s^{-1}). The comparison between the diffusion coefficients calculated by the different approaches is made for a fixed time of 3600 s chosen for a certain degree of extraction. For the system, oak bark–water, the value of $D_0 = 8.37 \times 10^{-11}$ m^2 s^{-1} was obtained for the same degree of extraction.

Different approaches to obtain the function $\overline{D}(\overline{C}_s)$ are known (parametric as well as non-parametric [13]). We assumed that the latter could be described as

$$\overline{D} = \frac{1}{1+\sigma C_s} \tag{6}$$

Depending on the value of the parameter σ, it can be applied to an increasing as well as a decreasing relation of $\overline{D}$ on $\overline{C}_s$. For both extraction systems, a decreasing $\overline{D}(\overline{C}_s)$ relation was found with $\sigma = 2.5$.

Going back to the diffusion coefficient D, porosity has to be excluded from this relation. As the local porosity evolution $\varepsilon(x)$ was not known, $\overline{D}(\overline{C}_s)$ was integrated to find the volume-averaged diffusivity as a function of time:

$$\overline{\overline{D}}(\tau) = (\alpha+1)\int_0^1 \overline{D}(\overline{C}_s)\,d\overline{x} = (\alpha+1)\int_0^1 \overline{D}(\tau,\overline{x})\,d\overline{x}$$

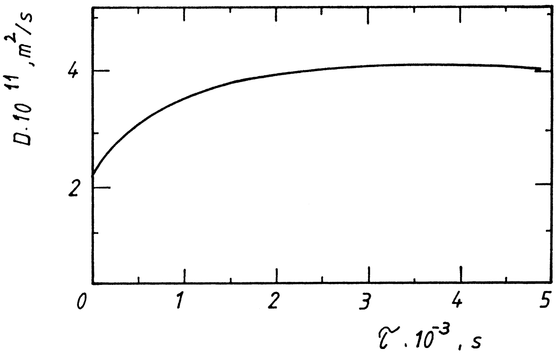

Fig. 4. Diffusion coefficient vs. time.

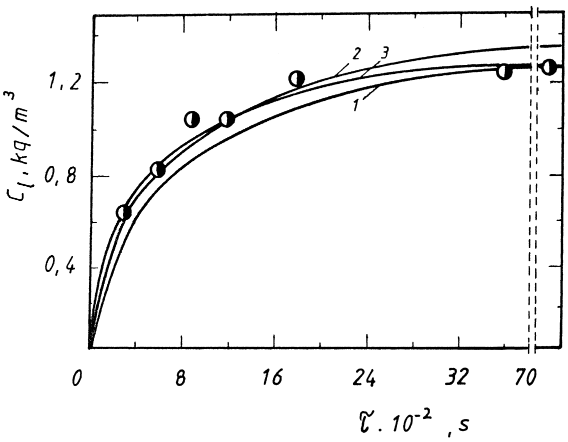

Fig. 5. Calculated kinetic curves for different model hypotheses: 1, $D=\text{const}$, $\varepsilon=\text{const}$; 2, $D\neq\text{const}$, $\varepsilon\neq\text{const}$; 3, $D=\text{const}$, $\varepsilon\neq\text{const}$; ◑, experimental system II.

Here, $\bar{x}$ is a dimensionless coordinate $\bar{x}=(x/X)$. Then, using the known $\varepsilon(\tau)$ relation and the values of D_0 and ε_0, the evolution of the diffusivity (volume averaged over the particle) with the time of extraction can be seen (Fig. 4, system I). The extraction systems I and II are characterized by the same order of values of the diffusion coefficient D_0 (10^{-11} m^2 s^{-1}) and similar functions of change in the porosity Eq. (2) and the diffusion coefficient Eq. (6) with $\sigma=2.5$. So, the results presented in Figs. 4 and 5 can be regarded as representative of both systems. For system II, the comparison between the experimental and the calculated data is illustrated in Fig. 5 (curve 1). In the same figure, the sensibility of the kinetic curve towards the model hypothesis is illustrated. The case of constant diffusivity $D=4.35\times10^{-11}$ (an average value for the $D(C_s)$ relation) and variable porosity $\varepsilon(\tau)$ is presented (curve 2). Curve 3 is calculated with constant parameters $D=\text{const}$ and $\varepsilon=\text{const}$. As can be seen, the consideration of the variable model parameters is significant in the initial part of the curve where faster extraction kinetics are observed, the $\varepsilon(\tau)$ relation having a stronger effect on the calculated results.

4. Conclusions

In the present work, a mathematical model of solid–liquid extraction, accounting for variable effective diffusivity and porosity, was stated and solved numerically. The values of the effective diffusion coefficient for the two extraction systems, tobacco leaves (*N. tabacum* L.)–water (system I) and oak bark (*O. frainetto* Ten)–water (system II), were found. These values were compared with that obtained from the regular regime and the standard function technique, and a very good agreement was observed. The consideration of the variable diffusivity and porosity is of greater importance in the initial steep part of the kinetic curve, and could be used in practice when a greater productivity for a fixed degree of extraction is required.

Acknowledgements

This work was supported by the National Scientific Foundation Grant No. X-492.

Appendix

Nomenclature

Bi	Biot number
C_l	liquid phase concentration (kg m^{-3})
$\overline{C}_l$	dimensionless liquid phase concentration
C_0	initial solid phase concentration (kg m^{-3})
C_s	solid phase concentration (kg m^{-3})
$\overline{C}_s$	dimensionless solid phase concentration
C_{se}	equilibrium solid phase concentration (kg m^{-3})
$\overline{\overline{C}}_s$	volume-averaged solid phase concentration (kg m^{-3})
D	intraparticle diffusion coefficient (m^2 s^{-1})
$D_e=\varepsilon D$	effective diffusion coefficient (m^2 s^{-1})
$\overline{D}$	dimensionless effective diffusion coefficient
D_0	intraparticle diffusion coefficient at $\overline{C}_s\rightarrow0$ (m^2 s^{-1})
$D_{e0}=\varepsilon_0D_0$	effective diffusion coefficient at $C_s\rightarrow0$ (m^2 s^{-1})
k_l	external mass transfer coefficient at (m s^{-1})
m	distribution coefficient
n	angular velocity (s^{-1})
t	temperature (°C)
V_l	liquid phase volume (m^3)
V_s	solid phase volume (m^3)
x	coordinate (m)
X	particle size (m)

Greek letters

α	form factor
ε	internal porosity (m^3 m^{-3})
ε_0	internal porosity at $C_s\rightarrow0$ (m^3 m^{-3})
ρ_s	solid phase density (kg m^{-3})
σ	coefficient in the $D(C_s)$ relation
τ	time (s)
ζ	liquid–solid ratio (m^3 kg^{-1})

References

[1] E. Simeonov, A. Minchev, Mass transfer study of a new construction screw extractor, J. Appl. Chem. 62(4) (1989) 879–882.

[2] E. Simeonov, A. Minchev, A method for calculation of a continuous screw extractor, J. Appl. Chem. 63(10) (1990) 2281–2284.

[3] F. Plachco, J. Krasuk, Co-current solid–liquid extraction with initial concentration profile constant diffusivity, Chem. Eng. Sci. 27 (1972) 221–226.

[4] F. Plachco, M. Lago, Counter-current solid–liquid extraction in a cascade of batch extractors, Can. J. Chem. Eng. 50 (1972) 611–615.
[5] F. Plachco, M. Lago, Successive solid–liquid extraction. Constant diffusivity-spherical geometry, Chem. Eng. Sci. 28 (1973) 897–903.
[6] I. Georgiev et al., Wine technology practicum, in: Chr. Danov (Ed.), Plovdiv, 1964, pp. 147–148.
[7] A. Frolov-Bagreev, G. Agabalyanz, Wine Chemistry, Pistepomizdat, Moscow, 1952, pp. 344–346.
[8] State Pharmacopea X, Medicina I Fizkultura, Sofia, 1970.
[9] G.A. Axelrood, W.M. Lisjanski, Extraction (Solid–Liquid Systems), Chimia, St. Petersburg, 1974, pp. 78–80.
[10] A. Minchev, S. Minkov, A model for determination of the effective diffusion coefficient by the standard function technique, J. Appl. Chem. 57(3) (1984) 717–720.
[11] E.F. Nogotov, B.M. Berkovski, Finite-Difference Methods in Heat Conduction Problems, Minsk, 1976.
[12] A. Minchev, J. Jeliaskova, A. Babinova, Determination of effective diffusion coefficient of extraction of sulphadimezine of granules, Pharmazia 30(2) (1980) 42–47.
[13] A. Brunowska, P. Brunowski, J. Ilavski, Estimation of the diffusion coefficient from sorption measurements, Chem. Eng. Sci. 32 (1977) 717–722.